REPORT DOCUMENTATION PAGE	Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY) 28-06-2018	2. REPORT TYPE Final Report	3. DATES COVERED (From - To) 1-Aug-2015 - 31-Jul-2016

4. TITLE AND SUBTITLE
Final Report: In-situ integrating sphere apparatus for quantitative analysis of heterogeneous surfaces interacting with photons under controlled environments

5a. CONTRACT NUMBER
W911NF-15-1-0321

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611103

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

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

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
66834-CH-RIP.1

12. DISTRIBUTION AVAILIBILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

This DURIP grant was use to purchase the necessary components to build a unique spectroscopy facility that allows for quantitative measurements of the influence of adsorbates on photon absorption and scattering by metallic nanostructures. The equipment has been successfully acquired and assembled and data collection is beginning soon.

15. SUBJECT TERMS
Spectroscopy, DURIP, Equipment

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Phillip Christopher
UU	UU	UU	UU		19b. TELEPHONE NUMBER 805-893-2610

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

RPPR Final Report
as of 06-Jul-2018

Agency Code:

Proposal Number: 66834CHRIP **Agreement Number: W911NF-15-1-0321**

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DUNS Number: 627797426 EIN: 956006142
Report Date: 31-Oct-2016 Date Received: 28-Jun-2018
Final Report for Period Beginning 01-Aug-2015 and Ending 31-Jul-2016
Title: In-situ integrating sphere apparatus for quantitative analysis of heterogeneous surfaces interacting with photons under controlled environments
Begin Performance Period: 01-Aug-2015 **End Performance Period:** 31-Jul-2016
Report Term: 0-Other
Submitted By: Phillip Christopher Email: pchristopher@ucsb.edu
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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 1 **STEM Participants:** 1

Major Goals: It was proposed to purchase necessary components for construction of a one-of-a-kind apparatus that enables quantitative measurements of extinction, absorption and scattering coefficients for nanoparticles under controlled environmental conditions and electronic transitions localized at adsorbate-nanoparticle interfaces. The equipment is expected to enable detailed and quantitative analysis of photon driven reactions on metal nanoparticles mediated by photoexcitation of identified electronic transitions localized at adsorbate-nanoparticle interfaces. The system was designed to enable measurements as a function of adsorbate molecular structure, coverage, nanoparticle composition, size and shape. It was hypothesized that characterization of quantitative light extinction coefficients and photo-induced reaction efficiencies will provide fundamental information enabling rational control of the outcome of catalytic processes through targeted activation of desired adsorbate- catalyst bonds. Generally, the proposed equipment allows quantification of light-matter interactions in nanoparticle and nanostructured materials of interest in DoD applications.
The unique feature of the proposed system is coupling an integrating sphere to a vacuum chamber where photon-induced reactions can be executed in well-controlled environments from nanoparticle samples that can be concurrently characterized by quantitative UV-vis spectrophotometry. The proposed equipment will improve on our current methodology of using diffuse reflectance UV-Vis spectrophotometry to characterize interactions of nanoparticles with adsorbates, which allows measurement of qualitative spectral response, but no quantitative information on the efficiency of photon extinction through various mechanisms.
The proposed equipment will educate students in fundamental principles of chemical engineering, materials science and physical chemistry. The deeper understanding of experimental systems allowed by acquisition of this equipment, compared to how we currently make measurements, will provide students atomistic insights into the processes they are studying.

Accomplishments: See uploaded document.

Training Opportunities: The primary training opportunities associated with this grant were the training of an involved PhD student, Matthew Kale, in the construction of the vacuum chamber, the operation of a quantitative UV-Vis spectrometer and the associated insights required to design this system. Matthew Kale was supported through a now completed YIP grant from ARO and was solely responsible, with the help of the PI, for designing, outsourcing, constructing and validating the equipment. This provided invaluable insights into spectroscopy, the optical properties of small metal nanoparticles and vacuum technology.

Results Dissemination: The dissemination of data collected on this uniquely constructed equipment has not yet been executed. We expect in the near future to report on the use of this equipment to make careful measurements of the influence of adsorbates on the optical properties of small metal nanoparticles and relationships between interfacial electron transitions and photocatalytic processes.

Honors and Awards: PI Phillip Christopher received NSF CAREER Award.

Matthew Kale, who worked on the construction of this equipment received the Dissertation Year Fellowship (2015-2016) from UC Riverside.

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Faculty
Participant: Phillip Christopher
Person Months Worked: **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member:
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Matthew Kale
Person Months Worked: **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member:
Other Collaborators:

Project Summary - Grant # W911NF-15-1-0321

(Reporting Period: August 2015 – July 2016)

Title: In-situ Integrating Sphere Apparatus

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Objectives

It was proposed to purchase necessary components for construction of a one-of-a-kind apparatus that enables quantitative measurements of extinction, absorption and scattering coefficients for nanoparticles under controlled environmental conditions and electronic transitions localized at adsorbate-nanoparticle interfaces. The equipment is expected to enable detailed and quantitative analysis of photon driven reactions on metal nanoparticles mediated by photoexcitation of identified electronic transitions localized at adsorbate-nanoparticle interfaces. The system was designed to enable measurements as a function of adsorbate molecular structure, coverage, nanoparticle composition, size and shape. It was hypothesized that characterization of quantitative light extinction coefficients and photo-induced reaction efficiencies will provide fundamental information enabling rational control of the outcome of catalytic processes through targeted activation of desired adsorbate-catalyst bonds. Generally, the proposed equipment allows quantification of light-matter interactions in nanoparticle and nanostructured materials of interest in DoD applications.

The unique feature of the proposed system is coupling an integrating sphere to a vacuum chamber where photon-induced reactions can be executed in well-controlled environments from nanoparticle samples that can be concurrently characterized by quantitative UV-vis spectrophotometry. The proposed equipment will improve on our current methodology of using diffuse reflectance UV-Vis spectrophotometry to characterize interactions of nanoparticles with adsorbates, which allows measurement of qualitative spectral response, but no quantitative information on the efficiency of photon extinction through various mechanisms.

The proposed equipment will educate students in fundamental principles of chemical engineering, materials science and physical chemistry. The deeper understanding of experimental systems allowed by acquisition of this equipment, compared to how we currently make measurements, will provide students atomistic insights into the processes they are studying.

Accomplishments

Because this is a DURIP grant, funds were solely provided to purchase equipment. In this case, the equipment was designed based on multiple vendors to allow the construction of equipment with unique capabilities. We worked with Kurt J Lesker Inc on the design of the Vacuum chamber, sample holder and sample manipulator. We worked with Hiden Inc on the design of the mass spectrometer for photo-induced desorption measurements. We worked with Lab Sphere for the design of the integrating sphere for UV Vis measurements. We worked with Avantes for the design of the spectrometer for UV-Vis measurements. All components were assembled into a single functioning apparatus.

We tested and validated the primary function of the apparatus: making quantitative UV-Vis measurements of metallic nanostructures under controlled environments. It is important to note that there are no previous reports of making quantitative extinction, scattering and absorption measurements in a single reflective device geometry, thus a measurement methodology had to be developed. To achieve this, well-defined lithographically patterned Ag nanodisc arrays were produced using a hole-mask lithography approach. Using this approach, arrays of 49.5, 71.5 and 87.9 nm diameter Ag nanodiscs were fabricated with a constant thickness of 35 nm, Figure 1(A). The lithographic approach allows for the production of nanostructures with reasonably tight particle size distributions, ~10-15% standard deviation, which is important for making quantitative UV-Vis measurements, Figure 1(B). The lithographically produced Ag nanodisc array sizes were specifically produced to generate a range of relative extinction, absorption and scattering cross sections in order to validate our measurement approach, as will be shown below.

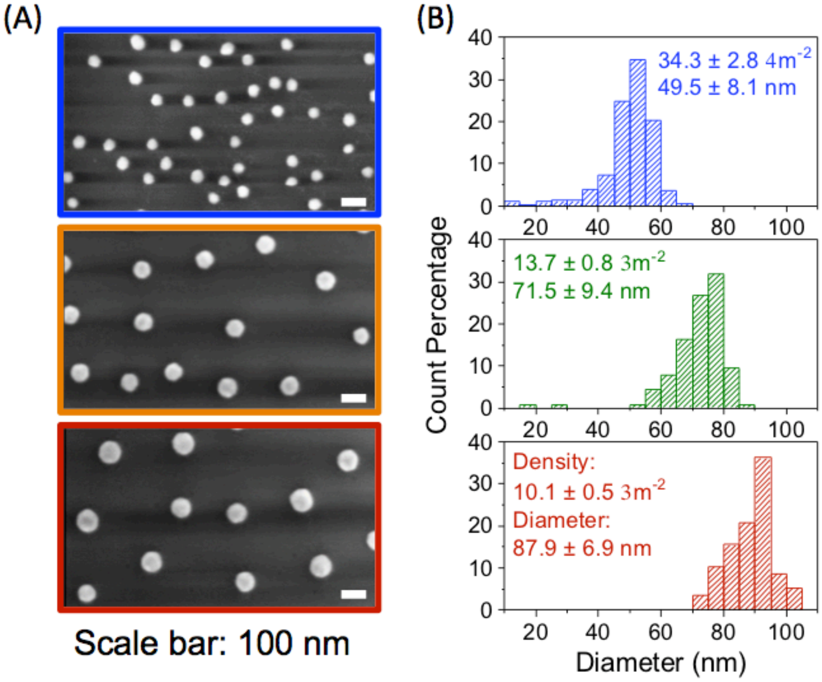

Figure 1. (A) Scanning electron micrographs of Ag nanodisc arrays produced using hole-mask lithography. **(B)** Particle size distributions measured for the samples shown in (A) with quantified average size, standard deviation and particle density (which is required to calculate extinction, absorption and scattering cross sections).

To initially compare the optical properties of the plasamonic Ag nanodisc arrays we performed extinction measurements on each sample using a traditional transmission extinction measurement, Figure 2(A). These measurements were compared to reflection extinction measurements made in the vacuum chamber using the integrating sphere apparatus, Figure 2(B) and calculated optical properties using electromagnetic simulations in Lumerical, Figure 2(C). The transmission extinction measurements were enabled by the use of glass substrates for the Ag nanodisc arrays and a mirrored back was deposited on the same substrates to allow the reflection measurements in the vacuum chamber. As shown in Figure 2, the transmission (A) and reflection (B) measurements of light extinction agree almost quantitatively. Furthermore, both measurements agree quite well with the simulated spectra, with the primary difference stemming from the thin Ag oxide shell in the experimental measurements that was not captured in the simulations. Regardless, this provides evidence that extinction measurements of metal nanoparticles could be made in the vacuum chamber with a coupled integrating sphere and that the approach matches well results from traditional transition measurements.

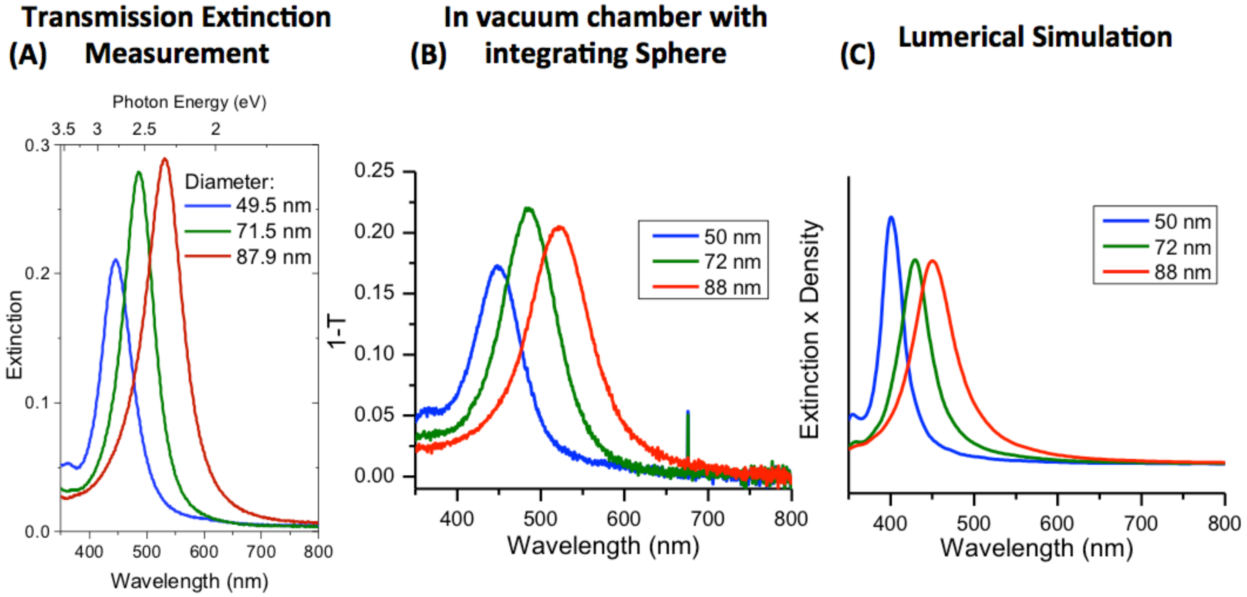

Figure 2. UV-Vis extinction spectra of the nanodisc arrays shown in Figure 1 measured by (A) transmission extinction measurements, (B) reflection measurements in the vacuum chamber and (C) simulated using the Lumerical software.

The next challenge was to develop an approach to separate the extinction measurement into absorption (photon conversion to electron hole pairs in the nanoparticle) and scattering (radiative re-emission of photons) components for UV-Vis measurements made in using the integrating sphere on the vacuum chamber. Figure 3 shows the measurement setup, where it is seen that light enters the vacuum chamber through the integrating sphere and a reflective port. Light can then by specularly reflected from the sample and directed back into the integrating sphere, scattered from the plasmonic structures in an isotropic (all directions) manner where only a portion of this light will make it back into the integrating sphere, or the light can be absorbed by the plasmonic structures. A measurement made using the geometry and light pathways shown in Figure 3 would detect a loss of light from absorbance by the particles and a loss of light from isotropic light scattering by the particles, although this would only be a fraction of the scattered light. To calibrate the amount of scattered light by the sample that makes it back into the integrating sphere we performed a series of measurements where the sample was moved away from the entrance of the light port such that we varied the amount of scattered light that made it back into the integrating sphere, see Figure 4. This was done for all 3 nanodisc arrays, which were then fit to consistent model that described a relationship between the sample position and fraction of scattered light collected in the integrating sphere. With this calibration the extinction measurements could be separated into absorption and scattering components.

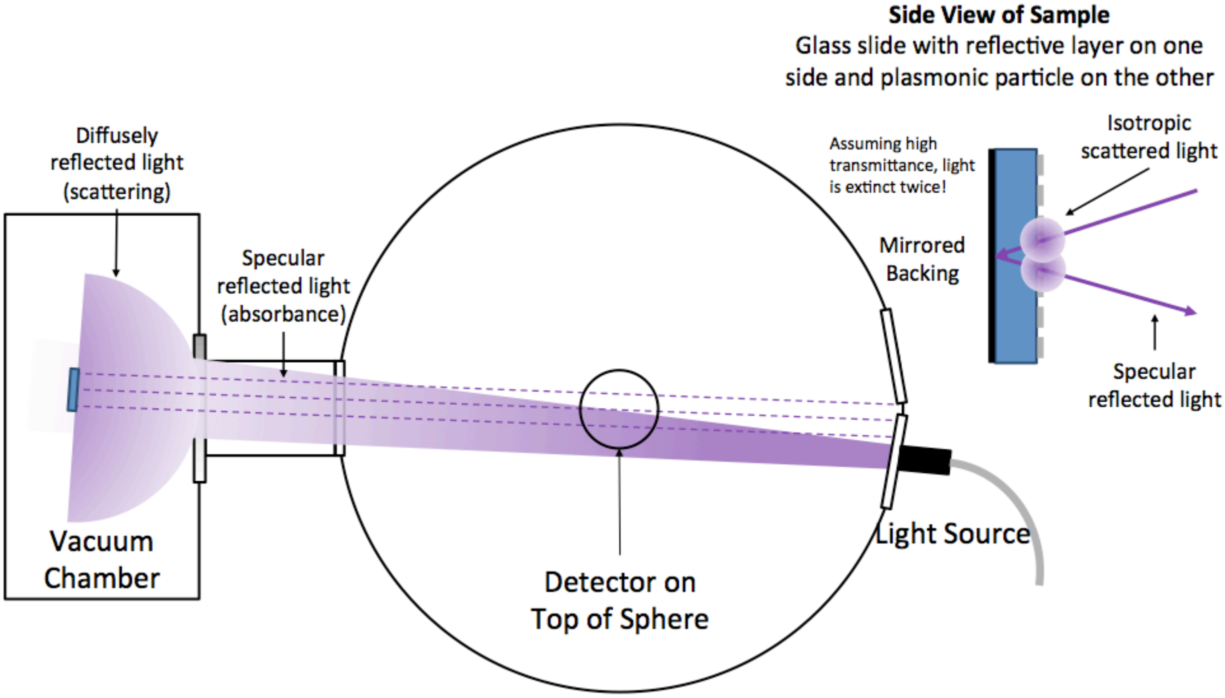

Figure 3. Schematic of the measurement approach and light pathways for extinction measurements in the vacuum chamber-integrating sphere apparatus.

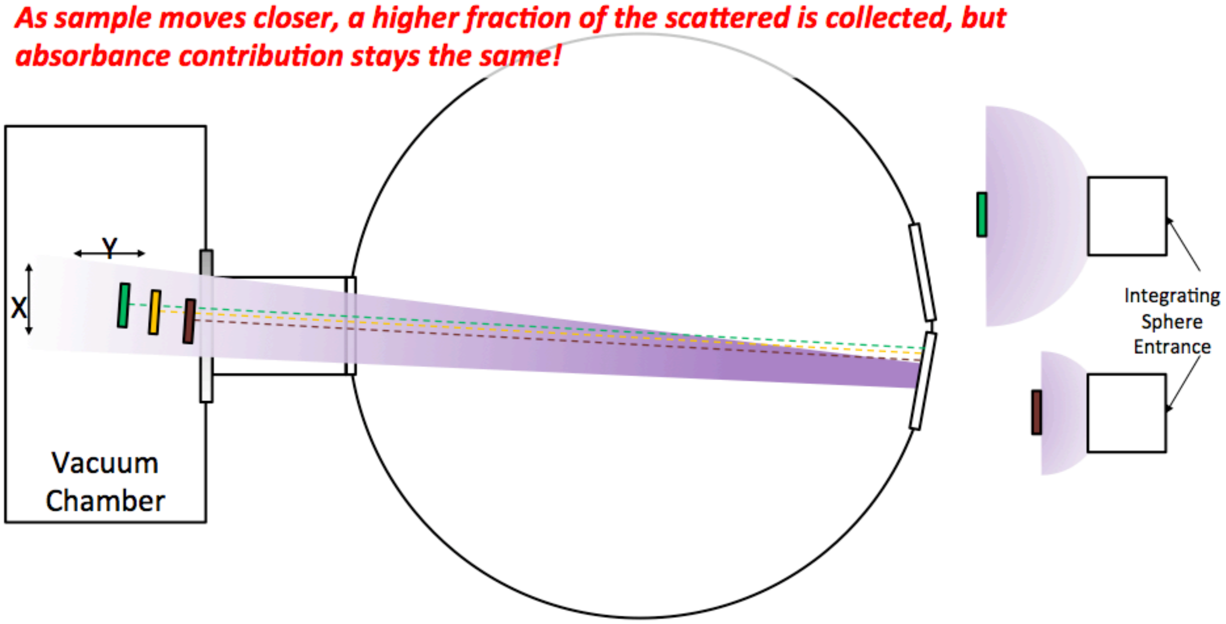
As sample moves closer, a higher fraction of the scattered is collected, but absorbance contribution stays the same!

Figure 4. Schematic of the approach used to quantify the scattering contribution to extinction by varying the sample distance from the light port and thus varying the amount of isotropically scattered light by the particles that makes it back into the integrating sphere.

Using this approach the extinction, absorption and scattering spectra for the 3 nanodisc array samples were measured and compared to the calculated spectra, Figure 5. The spectra in Figure 5 show that the experimental measurements nicely captured the broad trends of the absorption and scattering contributions to extinction for the three samples, with absorption being dominant for the smaller discs and scattering being dominant for the larger discs. The relative contribution of absorption and scattering to extinction as a function of plasmonic particle size is a well-known phenomenon in the field and an important attribute to validate the measurement approach. Importantly, finer scale details of the simulated spectra were also captured in the measurements, for example the dominant contribution of absorption to the high energy (low wavelength) mode seen in the spectra. This gives good confidence that both broad trends and finer details can be elucidated from the *in-situ* integrating sphere vacuum chamber measurement approach.

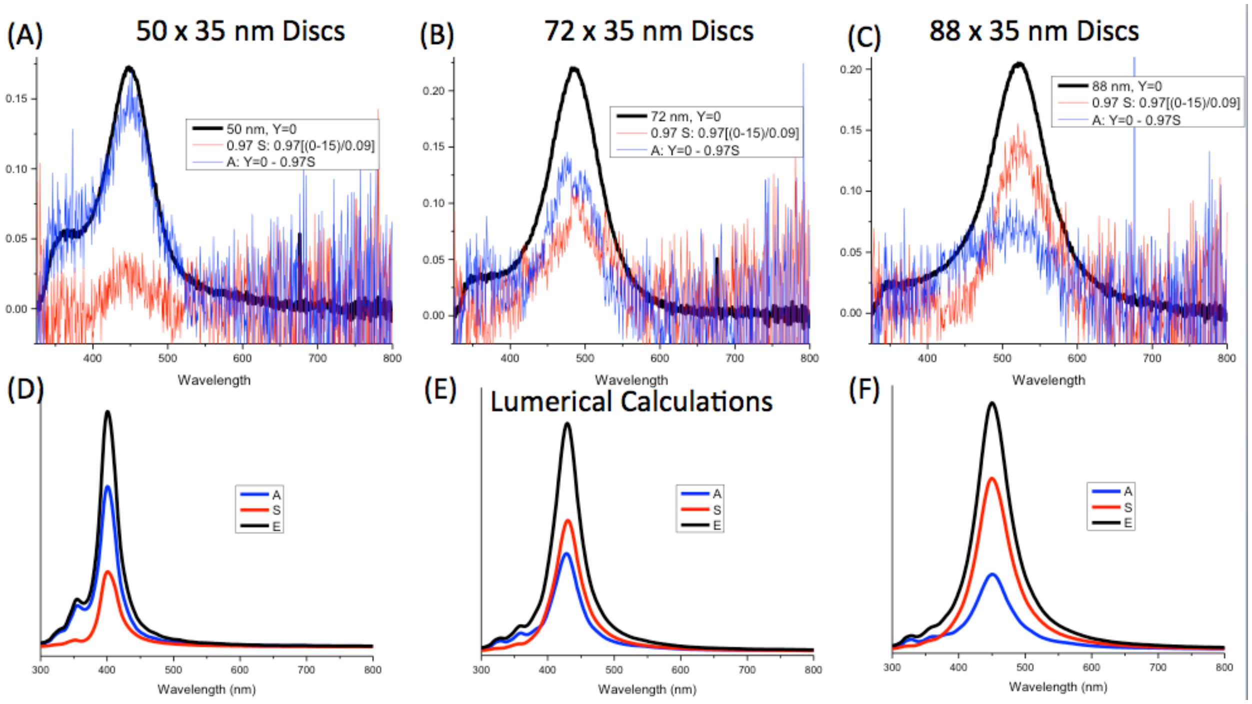

Figure 5. (A)-(C) Extinction (black), absorption (blue) and scattering (red) spectra for the 3 Ag nanodisc array samples. **(D)-(F)** show the corresponding simulations of the nanodisc arrays shown in experimental measurements.

With the validated approach for measuring extinction, absorption and scattering of plasmonic nanostructures in the controlled vacuum environment using the integrating sphere apparatus we then examined the influence of adsorbates on the optical properties of Ag nanoparticles. Rather than using the nanodisc arrays, we used Ag nanostructures deposited *in-situ* in the vacuum chamber to remove requirements of sample cleaning in our initial analysis of adsorbate influence on plasmonic properties. We choose to start our focus on thiol compounds that have very similar structure and packing density on Ag surfaces, but different electronic properties. We hypothesized that this would provide initial indication of the importance of the bond formed between the metal and adsorbate on the induced optical properties. Phenylthiol and pentalfluorothiol were dosed into the vacuum chamber following purification by freeze pump thaw cycles. Both molecules were dosed in 1 Langmuir (10^{-6} Torr over 1 second) at a time and it was observed that the UV-Vis extinction spectra of the Ag nanostructures damped in intensity, redshifted in energy and broadened. In both cases changes in the UV-Vis spectra were quenched after 30 Langmuir dosing, suggesting that similar adsorbate coverage existed in both cases. The spectra of the clean Ag and adsorbate covered Ag nanostructures are shown in Figure 6. It is clearly seen that the phenylthiol more strongly damped the Ag plasmon resonance that the pentafluorophenylthiol. New measurements with a single fluorinated phenylthiol at the para position show Ag plasmon damping intermediary to the two limiting cases shown here. This provides direct evidence that the nature of the Ag-S bond, which is mediated by the level of fluorination of the phenyl ring, controls the damping of the plasmon. It is expected that the amount of damping of the plasmon will be directly related to the efficiency of plasmon-mediated photochemistry.

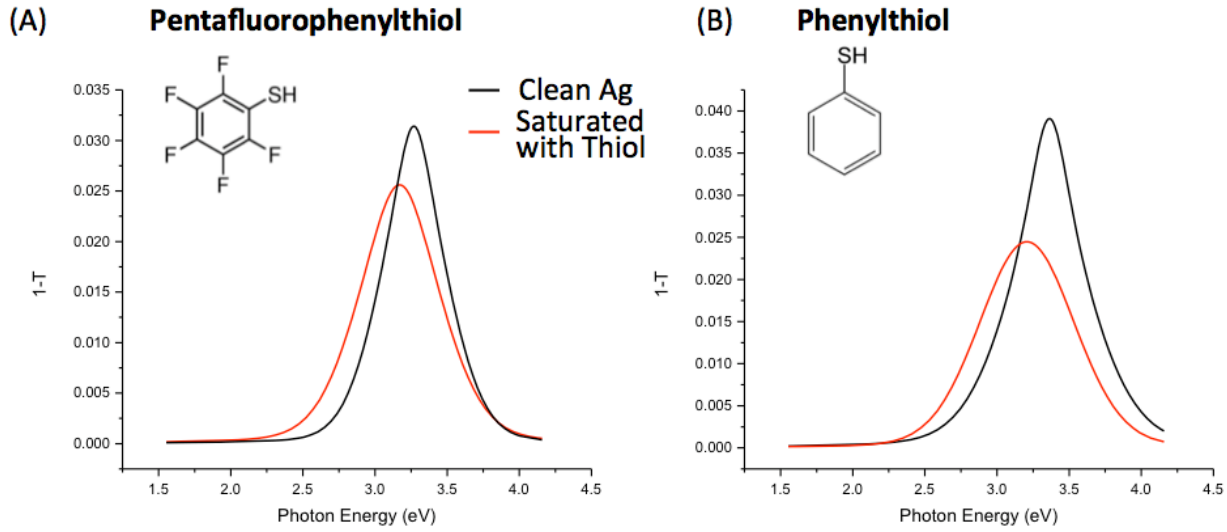

Figure 6. UV-Vis extinction (here shown as 1-T(transmission)) spectra obtained from Ag nanostructures via the *in-situ* integrating sphere apparatus when the surface is clean and saturated with (A) pentafluorophynelthiol and (B) phenylthiol.

In future experiments we will analyze the influence of molecular adsorption on the damping of the absorbance and scattering properties (rather than extinction as highlighted here) to provide more fundamental insights into the influence of interfacial bonds on plasmon dephasing properties. Furthermore, we will transition to the examination of more catalytically relevant molecules such as CO, NO and HCN to provide insights into the role of interfacial electronic transitions on photon and electron stimulated chemical conversion processes. Finally, insights gained from these studies will be related to parallel studies being performed in non-thermal plasmas in the context of grant W911NF1710340.

Summary

In summary, the *in-situ* integrating sphere apparatus was successfully constructed. Using well-defined lithographically patterned Ag nanodisc substrates it was demonstrated that *in-situ* UV-Vis measurements in the vacuum chamber associated with extinction, absorbance and scattering of these substrates well reproduced more traditional experimental measurements and theoretical predictions. This allows the direct measurement of the influence of molecular adsorption on the optical properties of plasmonic nanoparticles, which provides insights into the nature and strength of interfacial electronic transitions that are hypothesized to mediate photocatalytic processes. Initial measurements of adsorbate induced optical effects in this apparatus highlight that subtle changes in molecules can induce highly different optical effects on plasmonic nanostructures. It is expected that further studies relating molecular properties to their induced optical effects and further to catalytic processes will provide detailed insights into the governing phenomena associated with plasmon mediated photon and electron stimulated catalysis.