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14. ABSTRACT The goals of this MURI were to develop the next generation suite of instruments for sensitively probe biomolecules of interest. We have very successfully pursued plasmon based nanostructures as substrates to enhance various optical spectroscopies such as surface enhanced Raman spectroscopy, surface enhanced infra red absorption, metal enhanced fluorescence, surface enhanced Raman optical activity and LSPR sensing. We have developed a complete theoretical understanding of the electromagnetic field enhancement using Plasmon				
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Report Title

MURI Final Report

ABSTRACT

The goals of this MURI were to develop the next generation suite of instruments for sensitively probe biomolecules of interest. We have very successfully pursued plasmon based nanostructures as substrates to enhance various optical spectroscopies such as surface enhanced Raman spectroscopy, surface enhanced infra red absorption, metal enhanced fluorescence, surface enhanced Raman optical activity and LSPR sensing.

We have developed a complete theoretical understanding of the electromagnetic field enhancement using Plasmon Hybridization, FDTD, FEM, along with rigorous analytical and quantum mechanical calculations. This has been applied to rationally design and optimize the substrates. The Plasmon Hybridization theory is now a well accepted approach to understanding plasmons in complex and coupled systems. We have developed the first near infra red ROA spectrometer and used it to obtain the first NIR excited ROA spectra. This has also lead to the funding of two STTRs and collaborations with Biotools, the only company selling a commercial ROA spectrometer.

Finally we have developed the plasmonic equivalent of coherent phenomenon: electromagnetically induced transparency, sub- and super-radiant modes, and Fano resonances, previously observed only in atomic systems. Nanostructures that have a Fano resonance have been demonstrated to have some of the highest LSPR sensitivity reported.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

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

1. D. R. Ward, N. J. Halas, and D. Natelson, "Localized heating in nanoscale Pt constrictions measured using blackbody radiation emission", *Applied Physics Letters* 93, 213108 (2008).
2. Bruce Brinson, J. Britt Lassiter, Carly S. Levin, Rizia Bardhan, Nikolay Mirin and Naomi J. Halas, "Nanoshells made easy: improving Au layer growth on nanoparticle surfaces", *Langmuir* 24, 14166-14171 (2008).
3. F. Hao, S. Maier, N. J. Halas, and P. J. Nordlander, "Symmetry breaking in plasmonic nanocavities: subradiant LSPR sensing and a tunable Fano resonance", *Nano Letters* 8, 3983-3988 (2008).
4. K. Heck, B. Janesko, G. Scuseria, M. S. Wong, and N. J. Halas, "Observing Metal-catalyzed Chemical Reactions in situ using Surface enhanced Raman Spectroscopy on Pd-Au Nanoshells", *JACS* 130, 16592-16600 (2008).
5. S. Lal, S. E. Clare and Naomi J. Halas, "Nanoshell-enabled Photothermal cancer therapy: Impending Clinical Impact", *Accounts of Chemical Research* 41, 1842-1851 (2008).
6. Dongmao Zhang, Hui Wang, Oara Neumann, Aoune Barhoumi, Michael Perham, Jeffrey Hartgerink, Pernilla Wittung-Stafshede and Naomi J. Halas, "Gold nanoparticles can induce the formation of protein-based aggregates at physiological pH", *Nano Letters* 9, 666-671 (2009).
7. Rizia Bardhan, Oara Neumann, N. Mirin, H. Wang, and N. J. Halas, "Au nanorice assemble electrolytically into mesostars", *ACS Nano* 3, 266-272 (2009).
8. N. J. Halas, "Connecting the dots: reinventing optics for nanoscale dimensions", *Proceedings of the National Academy of Sciences*, Vol 106, 3643-3644 (2009).
9. R. Bardhan, N. K. Grady, J. Cole, A. Joshi and N. J. Halas, "Fluorescence Enhancement by Au nanostructures: nanorods and nanoshells", *ACS Nano* 3, 744-752 (2009).
10. Nikolay Mirin and N. J. Halas, "Light-bending Nanoparticles", *Nano Letters* 9, 1255-1259 (2009).
11. M. W. Knight, Yanpeng Wu, J. B. Lassiter, Peter J. Nordlander, and N. J. Halas, "Substrates matter: Influence of an adjacent dielectric on the plasmon modes of an individual nanoparticle", *Nano Letters* 9, 2188-2192 (2009).
12. Carly S. Levin, Cristina Hofmann, Tamer A. Ali, Anna T. Kelly, Emilia Morosan, Peter Nordlander, Kenton H. Whitmire, and Naomi J. Halas, "Magnetic-Plasmonic core-shell nanoparticles", *ACS Nano* 3, 1379-1388 (2009).
13. R. Acevedo, R. Lombardini, N. J. Halas, B. R. Johnson, "Plasmonic enhancement of Raman optical activity in molecules near metal nanoshells", *The Journal of Physical Chemistry A*, 13173-13183 (2009).
14. J. Kundu, O. Neumann, A. Barhoumi, B. Janesko, G. Scuseria, and N. J. Halas, "Adenine and Adenosine Monophosphate (AMP)-Gold Binding Interactions Studied by Surface-Enhanced Raman and Infrared Spectroscopies," *Journal of Physical Chemistry C*, 113, 14390-14397 (2009).
15. J. Kundu, C. S. Levin, and N. J. Halas, "Real-time monitoring of lipid transfer between vesicles and hybrid bilayers on Au nanoshells using surface enhanced Raman scattering (SERS)", *Nanoscale* 1, 114-117 (2009).
16. J. B. Lassiter, M. W. Knight, Nikolay A. Mirin and N. J. Halas, "Reshaping the plasmonic properties of an Individual Nanoparticle", *Nano Letters*, 9, 4326-4332 (2009).
17. Rizia Bardhan, Wenxue Chen, Carlos Perez-Torres, Marc Bartels, Ryan M. Huschka, Liang Zhao, Emilia Morosan, Robia Pautler, Amit Joshi, and Naomi J. Halas, "Nanoshells with targeted simultaneous enhancement of magnetic and optical imaging and photothermal therapeutic response", *Advanced Functional Materials*, 19, 3901-3909 (2009).
18. Oara Neumann, Dongmao Zhang, Felicia Tam, Surbhi Lal, Pernilla Wittung-Stafshede, and Naomi J. Halas, "Direct Optical Detection of Aptamer Conformational Changes Induced by Target Molecules", *Analytical Chemistry* 2009, 81, 10002-10006.
19. R. Bardhan, S. Mukherjee, N. A. Mirin, S. Levit, P. Nordlander, and N. J. Halas, "Nanosphere in a nanoshell: a simple nanomatryushka", *Journal of Physical Chemistry C*, articles ASAP.
20. Chizuko M. Dutta, Tamer A. Ali, Daniel W. Brandl, Tae-Ho Park, and Peter Nordlander, "Plasmonic properties of a metallic torus", *The Journal of Chemical Physics* 129, 084706, 2008.
21. N. Fofang, Tae-Ho Park, P. Nordlander, and N. J. Halas, "Plexcitonic Nanoparticles: Plasmon-exciton hybridization in a nanoshell-J-aggregate complex", *Nano Letters* 8, 3481-3487 (2008).
22. Mark W. Knight and Naomi J. Halas, "Nanoshells to nanoeggs to nanocups: optical properties of reduced symmetry core-shell nanoparticles beyond the quasistatic limit", *New Journal of Physics* 10 (2008) 105006-105016
23. N. J. Halas, "Connecting the dots: reinventing optics for nanoscale dimensions", *Proceedings of the National Academy of Sciences*, Vol 106, 3643-3644 (2009).
24. Z.P. Li, F. Hao, Y. Huang, Y. Fang, P. Nordlander, and H.X. Xu, "Directional light emission from propagating surface plasmons of silver nanowires", *Nano Lett.* 9(2009)4383-4386
25. F. Le and P. Nordlander, "Optical properties of nanoparticle arrays for oblique excitation using the Multiple Unit Cell Method", *J. Comput. Theor. Nanosci.* 6(2009)2031-2039
26. Y. Fang, H. Wei, F. Hao, P. Nordlander, and H.X. Xu, "Remote-excitation surface-enhanced Raman scattering using propagating Ag nanowire plasmons", *Nano Lett.* 9(2009)2049-2053

27. N.A. Mirin, K. Bao, and P. Nordlander, "Fano resonances in plasmonic nanoparticle aggregates, *J. Phys. Chem. A* 113(2009)4028-4038
28. N. Verellen, Y. Sonnefraud, H. Sobhani, F. Hao, V.V. Moshchalkov, P.V. Dorpe, P. Nordlander, and S.A. Maier, "Fano resonances in individual coherent plasmonic nanocavities", *Nano Lett.* 9(2009)1663-1667
29. T.-H. Park and P. Nordlander, "On the nature of the bonding and antibonding metallic film and nanoshell plasmons", *Chem. Phys. Lett.* 472(2009)228-231
30. F. Hao, P. Nordlander, Y. Sonnefraud, P.V. Dorpe and S.A. Maier, "Tunability of subradiant dipolar and Fano-type plasmon resonances in metallic ring/disk cavities: Implications for nanoscale optical sensing, *ACS Nano* 3(2009)643-652
31. J. Zuloaga, E. Prodan, and P. Nordlander, "Quantum description of the plasmon resonances of a nanoparticle dimmer", *Nano Lett.* 9(2009)887-891
32. E.M. Larsson, F. Hao, L. Eurenus, E. Olsson, P. Nordlander, and D.S. Sutherland, "Plasmon hybridization in stacked double gold nanorings with reduced symmetry, *Small* 4(2008)1630-1634
33. B. Willingham, D.W. Brandl, and P. Nordlander, "Plasmon hybridization in nanorod dimmers", *Appl. Phys. B* 93(2008)209-216
34. H. Wei, F. Hao, Y. Huang, P. Nordlander, and H.X. Xu, "Polarization dependence of surface-enhanced Raman scattering in the gold nanoparticle-nanowire system *Nano Lett.* 8(2008)2497-2502
35. F. Hao, E.M. Larsson, T.A. Ali, D.S. Sutherland, and P. Nordlander, "Shedding light on dark plasmons in gold nanorings, *Chem. Phys. Lett.* 458(2008)262-266
36. Seunghyun Lee, Kathryn M. Mayer, and Jason H. Hafner, "Improved Localized Surface Plasmon Resonance Immunoassay with Gold Bipyramid Substrates", *Anal. Chem.*, 81 (4450–4455) 2009
37. Yaroslav A. Urzhumov, Gennady Shvets, "Optical magnetism and negative refraction in plasmonic metamaterials", *Solid State Communications* 146 (208–220) 2008
38. Richard Lombardini, Ramiro Acevedo, Naomi J. Halas, and Bruce R. Johnson, "Plasmonic Enhancement of Raman Optical Activity in Molecules near Metal Nanoshells: Theoretical Comparison of Circular Polarization Methods", *J. Phys. Chem. C, ASAP*

Number of Papers published in peer-reviewed journals: 38.00

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

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Number of Presentations: 0.00

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

Peter Nordlander

1. "Plasmonic nanostructures: Artificial molecules", ChinaNano 2009, Beijing, 9/2/09
2. "Plasmons in strongly coupled nanostructures", Zhong-Guan-Cun Forum, CAS, Beijing 8/31/09
3. "Plasmonic nanostructures: Artificial molecules", KNOS2009, Seoul, Korea 8/27/09
4. "Plasmons in strongly coupled nanostructures", Korea University, Seoul, Korea 8/26/09
5. "Modeling plasmonic nanostructures", LANL, Los Alamos, 8/7/09
6. "Symmetry breaking in plasmonic nanostructures", SPIE San Diego, 8/5/09
7. "Plasmons in strongly coupled nanostructures", SPIE San Diego, 8/4/09
8. "Symmetry breaking in plasmonic nanostructures", ICMAT 2009, Singapore 6/30/09
9. "Symmetry breaking in plasmonic nanostructures: Subradiant LSPR sensing and tunable Fano resonances", SPP4, Amsterdam, 6/25/09
10. "Coherence phenomena in plasmonic nanostructures", Taiyuan, China 6/11/09
11. "Plasmonic properties of narrow nanoparticle junctions", IOP-CAS, Beijing 6/10/09
12. "Quantum description of plasmons in strongly coupled metallic nanostructures", ICQS Beijing, China 6/9/09
13. "Coherence phenomena in plasmonic nanostructures", MURI meeting, ARL Adelphi, MD, 5/27/09
14. "Plasmon hybridization in plasmonic nanostructures", MURI meeting, ARL Adelphi, MD, 5/27/09
15. "Coherence phenomena in plasmonic nanostructures", MRS Spring meeting, San Francisco, CA, 4/14/09
16. "Plasmonic Nanostructures: Artificial Molecules", Tutorial APS Meeting, Pittsburg, PA 3/15/09
17. "Plasmonic Nanostructures: Artificial Molecules", U. Washington, Seattle, WA 3/10/09
18. "Symmetry breaking in plasmonic nanostructures", NANOMETAS2009, Seefeld, Austria, 1/7/09
19. "Plasmonic Nanostructures: Artificial Atoms", Kansas State University, Manhattan, KS 10/9/08
20. "Plasmonic Nanostructures: Artificial Molecules", 10th International Conference on Near Field Optics, Buenos Aires, Argentina, 9/1/08
21. "Metallic nanoparticle arrays: A common substrate for both SERS and SEIRA", SPIE conference on "Plasmonics: Nanoimaging, nanofabrication and their applications", San Diego, CA, 8/12/08
22. "Plasmonic nanostructures: Artificial Atoms", SPIE conference on "Plasmonics: Metallic nanostructures and their optical properties", San Diego, CA 8/13/08

Naomi Halas

1. "Plasmonics for SERS, SEIRA, and SERS-SEIRA: Substrate design and applications", keynote talk, SPIE Plasmonics, San Diego, CA, August 2008.
2. "Plasmonics: expanding the capabilities of near field optics to molecular dimensions", Frontiers of Near-Field Optics, Buenos Aires, Argentina, September 2-5, 2008.
3. "Plasmonic Nanoparticles: artificial molecules with real applications", ISSPIC XIV, Valladolid, Spain, September 14-19, 2008.
4. "Plasmonic Nanoparticles: artificial molecules with real applications", MESA+ Annual Symposium, Plenary Speaker, Enschede, Netherlands, September 2008.
5. "Combining SERS and SEIRA", Invited talk, Federation of Analytical Chemistry and Spectroscopy Societies Meeting, Reno, Nevada, September 28-October 2, 2008.
6. "Plasmonics: Merging Nanoparticles with Light", Invited talk, NanoTX, Dallas, TX, October 2008
7. "Optics at the Nanoscale: Merging Nanoparticles with Light", Keynote Speaker, COMSOL Conference, Boston, MA, October 9-11, 2008.
8. "Plasmonic Sensing", Invited talk, Plasmonics and Metamaterials, (held in conjunction with Frontiers in Optics), Rochester, NY, October 2008.
9. "Plasmonics: merging nanoparticles with light", Physics Colloquium, Drexel University, Philadelphia, PA October 30, 2008.
10. "Plasmonics: Sensing, actuating and responding at the nanoscale- by design", Invited talk, AFRL workshop, Washington, DC, November 2008.
11. "Oriented Au Nanocups: 3D nanoantennas with Electric, magnetic, and coupled magnetic-magnetic plasmon resonances", Invited talk, Nano-Meta Conference, Seefeldt, Austria, January 2009.
12. "When plasmons interact, worlds collide: the emerging field of Nanophotonics", NSF Distinguished Lecture Series, National Science Foundation, February 23rd 2009.
13. "Nanocups: light-manipulating plasmonic nanostructures and nanosystems", Invited talk, Spring MRS Meeting, San Francisco, CA, March 2009.
14. "Plexcitonics: Plasmon enhanced fluorescence spectroscopy and coherent effects", Invited talk, Special seminar in Nano-Optics, Center for Molecular and Nanoscience, UT Austin, April 2009.
15. "Light-manipulating properties of reduced symmetry plasmonic nanostructures and nanosystems", Nanophotonics Workshop, Chinese

Academy of Sciences, Beijing, China, June 2009.

16. "Plasmonics at the Nanoscale: taking light in new directions", Keynote talk, Plasmonics Symposium, ICMAT, Singapore, June 2009.
17. "When plasmons interact, worlds collide: the emerging field of Nanophotonics", Institute for Microelectronics (IME) Singapore, July 2009.
18. "New routes to reduced-symmetry plasmonics", SPIE Annual Meeting, San Diego, CA, August, 2009.
19. DOE LANL Energy Frontiers Research Center Kickoff Meeting, Los Alamos, NM, August 2009.
20. "Direct optical detection of aptamer conformational changes induced by target analytes", ACS Meeting, Washington, DC, August 2009.
21. "Symmetry Breaking in plasmonic nanostructures: new properties driving new synthetic opportunities", ACS Meeting, Washington, DC, August 2009.
22. "Plasmonic nanoparticles: artificial molecules, real applications", Seoul National University, August 2009.
23. "Plasmonics: merging nanoparticles with light", KNOS2009, Seoul, Korea, August 2009.
24. "Plasmonics: artificial molecules, real applications", University of Korea, Seoul, Korea, August 2009.
25. "When plasmons interact, worlds collide: the emerging field of nanophotonics", Nanophysics and Device division lecture series, inaugural lecture, Institute of Physics, Chinese Academy of Sciences, Beijing, China, September 2009.

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 47

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

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Ramiro Acevedo	0.83
Kui Bao	0.71
Bruce Brinson	0.53
Lisa Brown	0.08
Albert Chang	0.79
Jared Day	0.08
Nathaniel Grady	0.13
Feng Hao	0.83
Ryan Huschka	0.41
Cyre Kalu	0.79
Janardan Kundu	0.75
James Lassiter	0.04
Carly Levin	0.80
Kathryn Mayer	0.42
Nikolay Mirin	0.67
Tae Ho Park	0.79
Heidar Sobhani	0.42
Britain Willingham	0.71
Yanpeng Wu	0.79
Joseph Young	0.04
Chris Feitz	0.13
James Mchargey	0.13
FTE Equivalent:	10.87
Total Number:	22

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Surbhi Lal	0.42
Yoav Avitzour	0.29
Alexander Khanikaev	0.29
FTE Equivalent:	1.00
Total Number:	3

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Naomi J. Halas	0.10	No
Jason Hafner	0.06	No
Jeffrey Hartgerink	0.06	No
Bruce Johnson	0.26	No
Gennady Shvets	0.03	No
Simeon Trendafilov	0.08	No
FTE Equivalent:	0.59	
Total Number:	6	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
William Frierson	0.17
Jon Snyder	0.17
FTE Equivalent:	0.34
Total Number:	2

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

<u>NAME</u> Britain Willingham	
Total Number:	1

Names of personnel receiving PHDs

<u>NAME</u> Carly Levin Bruce Brinson Tae Ho Park	
Total Number:	3

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

1. Foreword

This MURI grant has funded the development of a suite of next generation instruments designed to sensitively image and characterize large biomolecules. The approach taken by the team at Rice University and The University of Texas at Austin researchers is to exploit plasmon based surface enhanced spectroscopy to enhance the sensitivity of various optical spectroscopies for biomolecules.

Gold nanoshells, spherical silica nanoparticles coated with a thin shell of gold form the basic substrate for the enhanced spectroscopy. The plasmon resonance of gold nanoshells is tunable across the visible and near infrared regimes by changing the ratio of the size of the core to the thickness of the shell. This tunability allows for optimization of the substrate for the selected spectroscopy. Based on the gold nanoshell structure various other nanoparticle substrates have been developed as part of the project and nanoshell based substrates have been optimized for combining different spectroscopic techniques on the same substrate. These nanostructures form a suite of optimized substrates with some of the best reported sensitivities for each of the spectroscopic methods studied. In addition to the high sensitivity, this MURI has established a number of firsts: The first near IR excited ROA spectrometer, and the first NIR ROA spectrum with mirror image enantiomer spectrum, and the first superlens structure in the infra red regime.

Along with the extensive experimental investigations we have developed a comprehensive suite of theoretical techniques to understand the underlying science for each nanostructured substrate. These techniques have allowed us to model and often quantitatively simulate the experimental results. This synergy has been a major strength of the research conducted as it has allowed the theorists to model realistic systems and the experimentalists to gain insights into the system and rationally optimize the substrates. A large number of applications of the enhanced spectroscopic platforms have resulted from this and the development of new sensing modalities such as exploiting the Fano resonances in plasmonic nanostructures for LSPR sensing.

2. Statement of problem studied

The specifically stated goals of this project were:

In this MURI project we will design and fabricate optical probe instruments that utilize tunable plasmonic nanostructures as substrates to enhance the optical spectroscopies uniquely suited for the characterization of peptides, proteins and viruses. The focus of our efforts is on three spectroscopies where the plasmon response is known to enhance the molecular response:

- Raman Spectroscopy and its circularly polarized light analog Raman Optical Activity;
- Infrared Spectroscopy and its circularly polarized light analog Vibrational Circular Dichroism; and
- Fluorescence Spectroscopy.

Three instrument platforms that utilize these three spectroscopies will be designed fabricated and characterized:

- Platform I: a multimodality sensing substrate where the spectroscopies can be optimized in the simplest and most straight forward optical geometries;
- Platform II: a multimodality scanning local probe that optimizes all three spectroscopies within a composite probe tip, for ultrahigh spatial resolution and for simultaneously topographically and spectroscopically mapping cellular or viral surfaces;
- Platform III: a superlens microscope, with integrated spectroscopies, where the superlens focusing provides both near field enhancement for spectroscopies and subwavelength imaging, as an integrated local probe of cellular or viral structure and composition.

We can state that we have achieved success in developing all three platforms and demonstrating the surface enhanced spectroscopies in each platform.

3. Summary of most important results:

Design of Tunable Plasmonic Substrates:

One of the major advances in this MURI has been in the area of substrate development for surface enhanced spectroscopies, establishing both a strong theoretical foundation, and a direct connection between theoretical design and actual experimentally developed substrates.

A basic requirement for enhancing the spectroscopic signature of the various optical spectroscopies is a plasmonic substrate. At the start of the project the basic substrate was the silica core, gold nanoshells. As part of this MURI project we have developed an improved method for the growth of continuous Au shell layers on dielectric oxide nanoparticles. The reduction of Au³⁺ by CO(gas) results in the formation of thin, uniform shell layers on these nanoparticles at lower Au³⁺ concentrations, where continuous shell layers are not achievable with current liquid phase reduction methods. This approach relies only on the introduction of CO(g) into the solution of prepared precursor nanoparticles and Au³⁺, and is not susceptible to variations in shell layer morphology influenced by preparation of reductant or precursor solutions, a limitation of current shell layer growth methods. The use of CO as a reductant also has the potential to transform the manufacturing of nanoshells from a batch to a continuous flow process.

The tunability of nanoshells is a powerful tool in optimizing substrates for enhancing various surface enhanced spectroscopies. We have synthesized and investigated the size dependant tunability of solid gold nanoparticles, and nanoshells by making sub 100 nm diameter nanoshells to mesoscopic sized nanoparticles (gold meatballs) and micron sized nanoshells. In addition to gold nanoshells, we have investigated the effects of dielectric properties of the core and shell material on the tunability and field enhancement of nanoshells. We have developed silver, copper and nickel nanoshells, nanoshells with magnetic iron oxide cores and copper oxide cores to study these properties.

In addition to the nanoshell substrates we have developed a number of nanoparticle substrates that allow for surface enhanced spectroscopy. Techniques to synthesize nanoshell/nanoparticle dimers, nanorice (core-shell nanoparticles with the tunability of nanoshells and the field enhancements of nanorods), nanoeggs (reduced symmetry core-shell particles with enhanced fields), nanocups, and nanostars (star shaped nanoparticles with intense fields at the tips) have been investigated. The plasmonic properties of these nanoparticles show excellent quantitative agreement with theoretical models developed to understand these properties and their origins.

The junction between two plasmonic substrates shows intense enhanced fields. The plasmonic properties of the junction between nanoshell dimers, trimers, quadrumers etc. nanorods, a nanoparticle on film geometry, a concentric ring disk system have been studied. These investigations have lead to the development of an entirely new direction in plasmonics - coherent phenomenon previously only observed in atomic systems.

The development of various nanostructures and the investigation of their optical properties have been in concert with theoretical modeling of these systems with excellent quantitative agreement in many systems. The theoretical Plasmon Hybridization (PH) model developed to gain intuitive understanding of coupled plasmonic systems has been expanded from spherical systems to a generalized curvilinear system and maybe applied to any particles of geometrical structures that can be described using separable curvilinear coordinates. The PH model is now a widely accepted theoretical model for understanding the hybridized plasmons in any coupled plasmonic system that maybe deconvolved into simpler plasmonic structures.

A second theoretical development to investigate the optical properties of nanostructures fabricated is the Finite Difference Time Domain (FDTD) technique. The completely generalized, fully parallelized code including retardation effects has been developed and implemented at Rice University.

Surface Enhanced Raman Spectroscopy (SERS)

One of the major achievements of this MURI has been the development of the basic understanding of SERS, optimizing substrates for SERS, designing substrates that combine SERS and Surface Enhanced Infra Red Absorption (SEIRA) and the numerous applications developed using SERS. As Raman scattering and infra red absorption are complementary techniques combining the two provides a powerful tool for identification of analytes.

We have developed a reliable technique to assemble spherical gold nanoparticles and gold nanoshells into a well ordered array with sub 10 nm gaps between the nanoparticles. The nanoshell array substrates reported provide a new, multifunctional platform for chemical sensing applications by enhancing both Raman spectroscopy and infrared spectroscopy. Integrating SERS and SEIRA on a single substrate will enable the identification of unknown molecules by combining both surface-enhanced vibrational spectroscopies, allowing more detailed investigations of molecular structure, orientation, and conformation, as well as adsorbate–substrate and adsorbate–adsorbate interactions. This substrate geometry also provides a system for detailed and highly reproducible correlations between surface-field properties and spectroscopic enhancements, which enhances our ability to unravel the complex mechanisms involved in surface enhanced spectroscopic processes.

We have developed a standalone, all-optical nanoscale pH meter that monitors its local environment through the pH-dependent surface-enhanced Raman scattering (SERS) spectra of the adsorbate molecules. We show that an Au nanoshell with a pH-sensitive molecular adsorbate functions as a sensitive nano pH meter. By using a statistical learning theory analysis of the SERS spectra, a quantitative pH sensor has been developed. The average accuracy of the nano pH-meter was found to be ± 0.10 pH units across its operating range. This is possibly the first nanosensor. The analysis method demonstrated here may also be broadly applicable across a family of chemically functional, SERS-based nanodevices that, in principle, could be fabricated on an ever-increasing variety of plasmon-resonant nanoparticle substrates with large local field enhancements at their surfaces.

Another success has been in developing methods to determine the reproducibility of SERS spectra of large biomolecules such as DNA and dipeptides. For obtaining highly reproducible surface-enhanced Raman spectroscopy (SERS) of single and double-stranded thiolated DNA oligomers, a thermal uncoiling protocol relaxes the DNA into an extended conformation, before they are attached to nanoshells. SERS spectra of DNA oligonucleotides are found to be extremely similar, strongly dominated by the Stokes modes of adenine, regardless of the DNA composition, sequence, and hybridization state. A spectral correlation function analysis useful for assessing reproducibility and for quantifying the highly complex changes corresponding to modifications in molecular conformation of the adsorbate molecules is introduced. This approach has been used to monitor the change in conformation of aptamers with specific and non specific analyte molecules.

SERS spectra obtained for three cysteine-containing aromatic peptides, phenylalanine-cysteine, tyrosine-cysteine, and tryptophan-cysteine, conjugated to Au nanoshell substrates show excellent reproducibility and close similarity to their respective solution-phase Raman spectra. The relative Raman and SERS cross-sections of the characteristic Stokes modes of the three aromatic amino acids were obtained. The Raman and SERS spectra of penetratin, a 19 amino acid cell-penetrating peptide, can be reproduced very well, except in the backbone spectral region, by using the appropriate Raman and SERS spectra of these aromatic peptides as an empirical “basis set”. This study reveals that the spectral features of aromatic amino acid residues, when present, along with the protein backbone, are dominant in the Raman and SERS spectra of peptides/proteins, greatly simplifying spectral interpretation.

Many biomolecules of interest lack a facile moiety to attach to a gold surface. We have demonstrated a technique using a hybrid lipid bilayers to attach molecules close to the nanoshell surface to enhance the SERS and SEIRA spectra. Using ibuprofen as a molecule of interest, the spectroscopic results combined from SERS and SEIRA studies provide chemical insight into the nature of ibuprofen-lipid interactions and have clinical importance in understanding the effects of NSAIDs on the integrity and permeability of the gastric mucosal membrane. The plasmonic nanostructures utilized in these studies are applicable for spectroscopic investigation of other biologically relevant phenomena in membrane mimics. This technique also provides a general method to investigate the SERS/SEIRA spectra of small molecules that may not be conveniently attached to a nanoshell substrate.

Another application of nanoshell based SERS has been in the area of studying catalysis. Pd islands grown on nanoshells have been used to investigate directly the reaction pathways and intermediates formed during the catalytic hydrodechlorination of 1,1-dichloroethene in H₂O using surface-enhanced Raman spectroscopy (SERS). More broadly, the results highlight the exciting prospects of studying catalytic processes in water in situ.

We have applied SERS techniques to map the profile of the enhanced near field of a nanoshell. This defines a characteristic length associated with a plasmonic nanostructure L_{SERS} that is useful to define a sensing volume around the nanostructure. SERS techniques to determine the packing density of analyte molecules have been developed. These rely on a SERS active moiety attached to the analyte molecule of interest.

Surface Enhanced Infra Red Absorption (SEIRA):

We have developed nanoshell based substrates for SEIRA. Aggregates of nanoshells with “hot spots” in the junctions act as effective SEIRA substrates. By increasing the refractive index of the substrate (silicon instead of glass), the IR plasmons of the nanoshell aggregate can be further redshifted, increasing the mid-IR plasmon response and the overall spectral range for SEIRA enhancement. By detailed modeling and statistical analysis of the infrared ‘hot spots’ formed within nanoshell aggregates, we have shown that large SEIRA enhancement factors, of the order of 10^2 - 10^3 , are achievable using these substrates.

Combined SERS and SEIRA spectroscopic investigations and quantum mechanical calculations have been used to elucidate the binding of adenine, and adenosine monophosphate to gold surfaces.

Metal Enhanced Fluorescence:

Fluorescence of dye molecules in the vicinity of metal nanostructures is modified. We have examined the role of the nanoparticle plasmon resonance energy and nanoparticle scattering cross section on the fluorescence enhancement of adjacent indocyanine green (ICG) dye molecules. We find that enhancement of the molecular fluorescence by more than a factor of 50 can be achieved for ICG next to a nanoparticle with a large scattering cross section and a plasmon resonance frequency corresponding to the emission frequency of the molecule. Both experimental observations and theoretical analysis involving nanoparticles of different plasmon

resonance energies and scattering properties show that fluorescence enhancement is optimized by increasing particle scattering efficiency while tuning the plasmon resonance to the emission wavelength of the fluorophore.

We have investigated both nanoshells and nanorods as substrates for enhancing fluorescence of weak dyes. Silica epilayers of controlled thickness for spacing the dye molecules at controlled distances from the nanoparticle surfaces have been developed. Nanoshells prove to be more versatile substrates as the scattering cross section of nanoshells is larger. These nanoparticles have found use in enhancing contrast agents for imaging.

Surface Enhanced Raman Optical Activity:

We have designed and built the first near IR Raman Optical Activity spectrometer. For investigating the ROA spectra from peptides fluorescence in the visible regime is a competing phenomenon to the ROA. By designing and building the first near IR ROA spectrometer the potential fluorescence is reduced. We have presented the first examples of ROA spectra collected with NIR laser excitation. These are also the first ROA spectra recorded with laser excitation outside the blue-green spectral region between 488 and 532 nm. Comparisons of the Raman and ROA spectra of neat S-(-)- α -pinene and L-alanyl-L-alanine in H₂O demonstrate that the major differences in normalized intensities for these two excitation regions can be attributed to the expected frequency-to-the-fourth power dependence for the Raman spectra and a frequency-to-the-fifth power dependence for the ROA spectra. Further nanoshell and gold colloid based substrates have been developed and the first surface enhanced NIR ROA spectra have been demonstrated.

We have developed models for the electromagnetic enhancements in surface enhanced Raman optical activity (SEROA) spectroscopy. The model extends previous treatments of SEROA to substrates, such as metal nanoparticles in solution that are orientationally averaged with respect to the laboratory frame. Our theoretical treatment combines analytical expressions for unenhanced Raman optical activity with molecular polarizability tensors that are dressed by the substrate's electromagnetic enhancements. We evaluate enhancements from model substrates to determine preliminary scaling laws and selection rules for SEROA. The results of the model are illustrated via numerical calculations of surface enhanced Raman and ROA spectra from (R)-(-)-bromochlorofluoromethane on various model substrates.

Localised Surface Plasmon Resonance Sensing:

We have developed a single particle spectrometer to investigate the optical properties of a single nanoparticle. Single nanoparticle spectroscopy measurements on specific isolated nanoshells, and a comparison of this response to theory quantitatively was carried out.. The optical properties were correlated with the nanoscale structure of the particle as determined by scanning electron microscopy. This study constituted the first time that single nanoparticle structural measurements and optical measurements have ever been performed on the exact same particle. This led to better design of nanoshell substrates for LSPR sensing. Next we performed LSPR measurements on nanoshells of various sizes and resonances to investigate the range of LSPR tuning with dielectric media for nanoshells.

We have also investigated LSPR sensing with the various nanoparticle substrates developed: nanoshells, nanorods, nanorice, mesoscopic gold ‘meatballs’, gold bipyrimids etc. In addition nanoparticles such as the nanostar demonstrate some of the highest LSPR sensitivity but the shape of the stars varies from one sample to another. Plasmon Hybridization theory has been successfully applied to even irregularly shaped nanostar particles.

Recently we have discovered the plasmonic equivalent of coherent phenomenon in nanoparticle clusters ranging from dimmers, trimers and higher aggregates. The Fano resonance supported by these structures shows some of the highest LSPR sensitivity reported. These nanoclusters are still under investigation.

Metamaterials:

One of the platforms to be developed under this MURI was a superlens for both enhanced spectroscopy and imaging capability. Materials that show negative permittivity and permeability can be used to overcome the diffraction focusing limit of traditional lenses and form super lenses. We have investigated numerous structures and geometries both theoretically using Finite Element Methods (FEM, COMSOL) and experimentally for imaging and spectroscopy in the infra red regime. The most successful geometry consists of sandwich geometry of SiC between SiO₂ layers.

We have demonstrated superlens based near field microscopy using a SiC superlens in the infra-red region. This allows for sub wavelength scale resolved imaging of buried objects. In our experiments, a superlens consists of a thin (440 nm) SiC layer which show negative permittivity between 10.3 μm and 12.5 μm is sandwiched between 2 layers of SiO₂ (220 nm thick) which serve as the object and image planes. Holes milled in a 60 nm gold layer deposited on the object plane are imaged in reflection mode using a scattering mode SNOM. This geometry exhibits sufficient optical contrast to observe $\lambda/20$ sized objects 880 nm away from the SNOM tip.

We also introduce the concept of metafluids—liquid metamaterials based on clusters of metallic nanoparticles which we term Artificial Plasmonic Molecules (APMs). APMs comprising four nanoparticles in a tetrahedral arrangement have isotropic electric and magnetic responses and are analyzed using the plasmon hybridization (PH) method, an electrostatic eigenvalue equation, and vectorial finite element frequency domain (FEFD) electromagnetic simulations. With the aid of group theory, we identify the resonances that provide the strongest electric and magnetic response and study them as a function of separation between spherical nanoparticles. We demonstrate that a colloidal solution of plasmonic tetrahedral nanoclusters can act as an optical medium with very large, small, or even negative effective permittivity, ϵ_{eff} , and substantial effective magnetic susceptibility, $\chi_{\text{eff}} = \mu_{\text{eff}} - 1$, in the visible or near infrared bands. We suggest paths for increasing the magnetic response, decreasing the damping, and developing a metafluid with simultaneously negative ϵ_{eff} and μ_{eff} .

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