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ADVANCES IN UV-PLASMONICS: A DETAILED ANALYSIS OF METALLIC MATERIALS AS CANDIDATES FOR NEW APPLICATIONS IN NANOTECHNOLOGY

Abstract: *An exhaustive numerical analysis of different metallic materials that may offer new plasmonic applications in the UV range has been performed. In particular, we have studied the plasmonic response of metallic nanoparticles deposited on substrates through numerical procedures based either on the discrete dipole approximation (DDA) or on finite elements methods (COMSOL). Both Far and Near-field configurations have been considered. In particular, the latter for localization and spectral analysis of hot-spots where spatial concentration of intense electromagnetic fields can be found. Also, a polarimetric spectral study of the scattered radiation has been done through polar decomposition methods of the Mueller matrix. The effects of nanoparticle geometry (shape (in particular, the nano-star geometry) and size), scattering configuration (polarization, incidence, etc.) and single or multiple particle contribution (size/shape polydispersity) have been considered. This analysis is relevant for the construction of spectroscopic tools in the UV range based on plasmonic effects for applications of surface enhanced techniques or equivalent. The project has finished with the publication of 2 papers in high impact journals, another in preparation (specifically for NPs made of Rhodium), and the presentation of two contributions to two conferences (one national and one international sponsored by OSA).*

1) Statement of the problem

Plasmonics is a very active branch of Nanophotonics. When the electronic plasma of metals is confined in small structures at the nanometric scale, its interaction with electromagnetic radiation in the UV-VIS-NIR frequency range can generate interesting resonance effects known as Localized Surface Plasmons (LSP's). This has opened the world of Plasmonics with many applications in nanotechnological fields like those related to health, communications, information storage, surface enhanced spectroscopy for matter analysis, etc.

The last decade has seen an explosion in the development and exploitation of nanometer scale metallic structures so that their LSP's can be tuned *à la carte* by playing with their geometry (shape), size and optical properties since these nanostructure characteristics are determinant in fixing the spectral position of LSP resonances. Most of this research work has been done for metals in the VIS, NIR and even THz (in general, $\lambda > 400\text{nm}$) ranges because of some necessities imposed mainly by applications in microscopy, spectroscopy, medicine, biology, antenna communications, etc. Gold (Au) is an example because of some of its physical properties like biocompatibility, easy to functionalize, low tendency to oxidation, etc. However, there is an increasing demand to extend Plasmonics to higher frequencies ($\lambda < 300\text{nm}$) where biological material has strong absorption and therefore enhancing biological imaging. Also, other technological areas like device engineering demands this kind of research since Plasmonics in the UV is crucial to characterize semiconductor devices at the nanometric scale. The UV range is challenging not only in handling this radiation and detecting it but also in the process itself of interaction with matter. Metals like Silver (Ag), but especially Aluminum (Al), are good candidates for developing plasmonic nano-tools in the UV. Both present plasma frequencies well above 7eV but their high tendency to oxidation introduces some difficulties for implementing effective stable nano-devices for direct use. Very recently, metallic nanoparticles made of Gallium deposited on low refractive index substrates have overcome this difficulty while keeping a good response in the UV range. A study of the shape effect and polarization of the incident radiation have demonstrated Gallium to be a suitable alternative against Aluminum and Silver for working at LSP's resonances above 4eV. Following with the aim of analyzing more possibilities

for developing an effective UV-Plasmonics, the purpose of this project is to make a comparative analysis of the plasmonic behaviour of metallic nanoparticles made of different metals like Indium, Rhodium, Ruthenium, Tungsten, Titanium, Chromium, Palladium, Copper, Platinum and Magnesium. These have been chosen because all of them present a plasma frequencies, ω_p , high enough to be UV plasmonic candidates.

In general and for calculation purposes, the basic system has been constituted by a metallic nanoparticle located on a substrate and excited by a linearly polarized plane wave. This electromagnetic problem was numerically analyzed by using the Discrete Dipole Approximation (DDA) and COMSOL methods; in particular, the plasmonic absorption efficiency, the near field distribution and related near field electromagnetic parameters were considered and compared with more commonly used materials like Gold, Silver and Aluminium and more recently, Gallium. Polarimetric calculations have also been carried out in order to help experimentalists (ACS Photonics doi:10.1021/ph500042v)

2) Summary of the most important results

- a. A graduate student in Physics, Mrs. Ángela Barreda, was selected for the research assistant position included in this award.
- b. During the first three months we started new collaborative lines. One, directly with Dr. Everitt and his team in Duke University, about their recent investigation of the ultraviolet-visible plasmonic properties of gallium nanoparticles by spectroscopic ellipsometry and the other, with Rice University group led by Prof. Naomi Halas concerning experimental results through cathode-luminescence techniques applied to dense samples of Ga NP's. In both cases, they are interested in applying our numerical techniques to analyze multiple scattering effects on the plasmonic response of the samples analyzed.
- c. During the second three-months period, we focus our research on self-assembled, irregular ensembles of hemispherical Ga NPs deposited on sapphire by molecular beam epitaxy. These samples, whose constituent unimodal or bi-modal distribution of NP sizes was controlled by deposition time, exhibited a wide range of localized surface plasmon resonances tunable from the ultraviolet to the visible spectral range. The optical response of each sample was characterized using a variable angle spectroscopic ellipsometer, and the dielectric response of the ensemble of NPs on each sample was parameterized using Lorentz oscillators. From this, a relationship was found between NP size and the deduced Lorentzian parameters (resonant frequency, damping, oscillator strength) for most uni-modal and bi-modal samples at most frequencies and angles of incidence. However, for samples with a bi-modal size distribution, Mueller matrix ellipsometry revealed non-Lorentzian behavior and nonspecular scattering at particular frequencies and angles, suggesting a resonant interparticle coupling effect consistent with recently observed strong local field enhancements in the ultraviolet.
- d. Visit to Duke University (17th to the 21st of February): Discussion of Rhodium (Rh) NPs project with Drs. Liu (Chemistry Dept.) and Finkelstein (Physics Dept.) of Duke University. NPs made of Rhodium show interesting properties to develop new plasmonic tools for the UV range. Duke groups have been able to fabricate Rh NPs with interesting

geometries. Our purpose was to provide physical interpretation of recent experimental results performed in Drs. Liu and Finkelstein laboratories.

e. During the third three-months period, the manuscript entitled *Ultraviolet-visible plasmonic properties of gallium nanoparticles investigated by variable angle spectroscopic and Mueller matrix ellipsometry*, by Y. Yang, N. Akozbek, Tong-Ho Kim, J. M. Sanz, F. Moreno, M. Losurdo, A. S. Brown & H. O. Everitt, was finally accepted for publication in ACS Photonics. The main conclusions of this research can be summarized as follows:

- i. A series of UV/Vis VASE and VAMM measurements on self-assembled irregular ensembles of truncated spherical gallium NPs grown by MBE on sapphire substrates have been reported.
- ii. The samples, whose constituent uni-modal or bi-modal distribution of NP sizes was controlled by deposition time, exhibited tunable localized surface plasmon resonances.
- iii. Using a Lorentz oscillator model to parameterize the dielectric response of the ensemble, relationships were found between NP size and the deduced Lorentzian parameters (resonant frequency, damping, oscillator strength) for most uni-modal and bi-modal samples at most frequencies and angles of incidence.
- iv. The Lorentz model also accurately predicts the frequency- and angle-dependence of the critical terms in the measured Mueller matrix characterizing the polarimetric scattering by these samples.
- v. Our findings indicate that the plasmonic behavior of self-assembled gallium NP ensembles with a uni-modal size distribution <100 nm in diameter is dominated by the isolated, single particle response of the numerous NPs of average diameter.
- vi. For samples exhibiting a bi-modal distribution of larger NPs surrounded by a halo of smaller NPs, deviations from this Lorentzian behavior are observed, but only at certain combinations of incidence angle and frequency. Non-specular scattering and depolarizing features observed in the Mueller

matrix spectra for these same conditions suggest that electromagnetic coupling between NPs alters the plasmonic performance.

- vii. Considering that the observed behaviors occur precisely where UV surface-enhanced Raman spectra indicated strong local field enhancements, we conclude that VAMM analyses may be used to characterize heterogeneous arrays of metal NPs to ascertain the spectral regions and optical geometries that produce the strongest local field enhancements.
- f. During the last three months and following the main purposes of this project, our research objective was centered on the UV plasmonic properties of Rh NPs by means of surface-enhanced Raman spectroscopy, surface-enhanced fluorescence, and photo-induced degradation. In particular, Rh tripod nano-structures with 8 nm-long arms were chemically synthesized, and surface-enhanced spectroscopy was performed on 4-aminothiophenol (PATP) attached to the surface of the Rh nanostructures. Comparing the response for laser excitation at UV and visible wavelengths resonant and not resonant with the Rh NP LSP resonance respectively, we found that Raman and fluorescence spectra were enhanced and photo-degradation was accelerated in the presence of Rh under resonant UV excitation. Although Raman spectra rapidly deteriorated upon UV exposure, fluorescence spectra often increased for many minutes, an indication that photo-excited hot electrons efficiently transfer from the Rh nanostructure to the PATP before photo-damage ultimately quenched the fluorescence. These findings confirm the exciting potential of these particular Rh nanostructures for UV plasmonics and photocatalytic applications. This research has been done in collaboration with Prof. Jie Liu (Department of Chemistry), Dr. Gleb Finkelstein (Department of Physics) and their students, Anne Watson and Xiao Zhang, all of them from Duke University. Our contribution in this research part was the numerical assistance of the experimental group by calculating the plasmonic response of n-pods nano-structures made of Rh for different experimental configurations.

3) List of all publications and technical reports published

- a. Sanz, J. M., Ortiz, D., Saiz, J. M., Brown, A. S., Losurdo, M., Everitt, H. O., & Moreno, F. *UV Plasmonic Behavior of Various Metal Nanoparticles in the Near- and Far-Field Regimes: Geometry and Substrate Effects*. The Journal of Physical Chemistry C, 117, 19606–19615, 2013
- b. We have presented to the Workshop on Optical Plasmonic Materials, sponsored by the Optical Society of America (19 March 2014, Messe Berlin, Berlin, Germany) the contribution entitled *Metals for UV Plasmonics*. It was accepted as an oral contribution.
- c. We have presented to the Spanish Nanophotonics Conference, (May 14-16, 2014, Santander, Spain, <http://www.phantomsnet.net/cen2014/index.php?p=1>) the contribution entitled *UV Plasmonic behavior of various metals* by D. Ortiz, J. M. Sanz, R. Alcaraz de la Osa, J. M. Saiz, F. González, A. S. Brown, M. Losurdo, H. O. Everitt & F. Moreno. It was accepted as a poster contribution.
- d. Yang, Y., Akozbek, N., Kim, T., Sanz, J. M., Moreno, F., Losurdo, M., ... Everitt, H. O. (2014). *Ultraviolet – Visible Plasmonic Properties of Gallium Nanoparticles Investigated by Variable-Angle Spectroscopic and Mueller Matrix Ellipsometry*. ACS Photonics. doi:10.1021/ph500042v
- e. Anne Watson, Xiao Zhang, R. Alcaraz de la Osa, J. M. Sanz, F. González, F. Moreno, G. Finkelstein, Jie Liu, and H. O. Everitt, *UV Surface Enhanced Spectroscopy Mediated by Plasmonic Rhodium Nanoparticles* (in preparation)

4) List of all participating scientific personnel (Spanish part)

- a. Prof. Francisco González. Member of the project team.
- b. Dr. José M. Saiz. Member of the project team.
- c. Dr. Juan M. Sanz. External collaboration for DDA calculations.
- d. Dr. Rodrigo Alcaraz. External collaboration for COMSOL calculations.
- e. Dr. Dolores Ortiz. External collaboration for DDA calculations.
- f. Mrs. Ángela Barreda. During the project development, Mrs. Barreda got her Master Degree in Physics with the maximum academic qualification.