Investigation of the Nonlinear Properties of Plasmonic Gold Nanocrescents for Surface-Enhanced Spectroscopies

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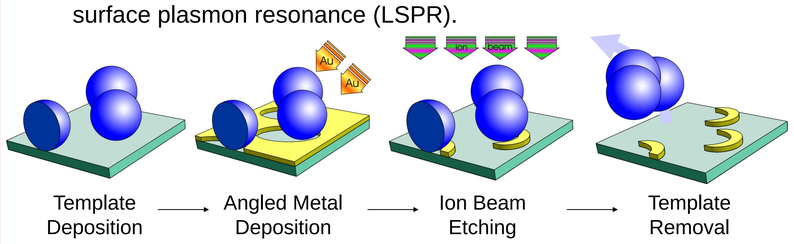
I. Introduction

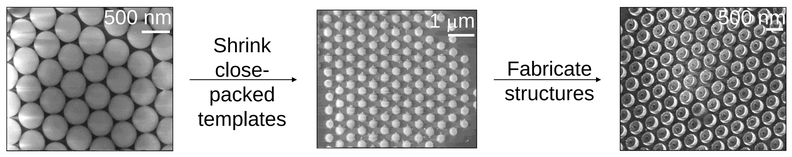
Plasmonic nanocrescents are of interest as substrates for surface-enhanced spectroscopies due to their tunable resonance in the visible to mid-IR region and high optical near-fields.[1,2] Due to the asymmetric nature of the nanocrescent structure multiple resonance modes arise, and can be selectively excited by the polarization of the incident light.[3] In order to obtain maximum signal enhancement from a nanostructure in any surface enhanced spectroscopy, the molecule of interest must spatially overlap with the localized near fields of the structure, which simulations have shown to be spatially inhomogeneous.[4] For surface enhanced spectroscopy applications, this leads to an ensemble measurement of non-uniform signal enhancement from the nanostructure. Maximized signal enhancement, and thus better sensitivity, could be achieved by understanding the near field distribution and subsequently localizing molecules of interest in the regions of highest field enhancement. Enhanced second harmonic generation and two photon absorption of photopolymers are used to experimentally probe the near field distribution of nanocrescents.

II. Nanosphere Template Lithography

Nanosphere Template Lithography[3,5] allows for control in the fabrication process which leads to tunability of the localized surface plasmon resonance (LSPR).

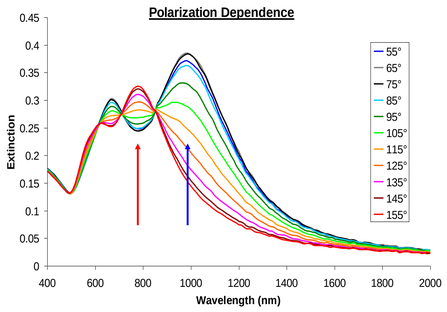


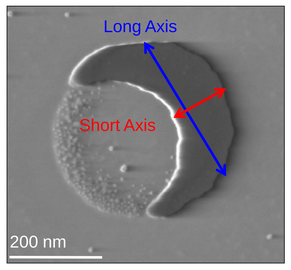
- Polystyrene beads are used as a mask to fabricate individual structures
- Angled metal deposition leads to a shadow on one side of the bead
- Ion beam etching normal to surface removes metal except the metal protected by bead
- Template beads removed with tape



III. Polarization Dependence

Due to the asymmetry of the structure, multiple plasmon resonance modes arise and can be selectively excited by the polarization of incident light.



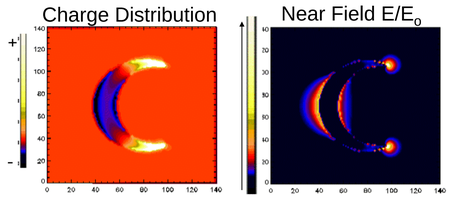


- Polarization of incident light:
  - Along the short axis of crescent leads to a higher energy LSPR (shown in red)
  - Along the long axis of crescent leads to lower energy LSPR (shown in blue)
  - At angles between short and long axes lead to excitation of both resonances

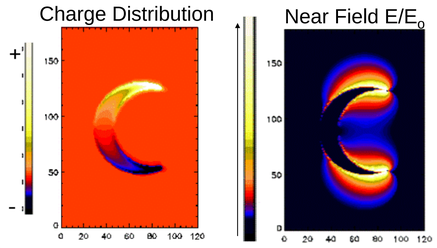
IV. Near Field Enhancement

Finite difference time domain simulations of nanocrescent structures show different near field distributions for short and long axis polarizations.

For light polarized along the short axis, electrons oscillate between the backbone and tips of the crescent which leads to enhanced near fields localized to these same regions.



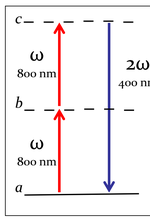
For light polarized along the long axis, electrons oscillate between the tips of the crescent which leads to enhanced near fields localized to these same regions.



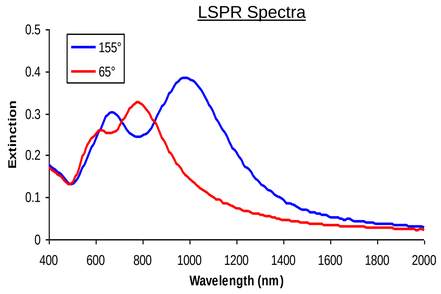
Tamer Ali and Peter Nordlander, Rice University, unpublished

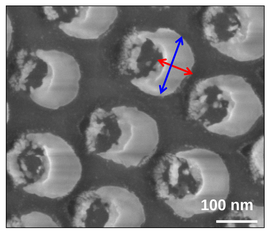
V. Second Harmonic Generation

We probed enhanced second harmonic generation (SHG) of nanocrescent arrays to understand the near field distribution and nonlinear properties of the nanostructures.

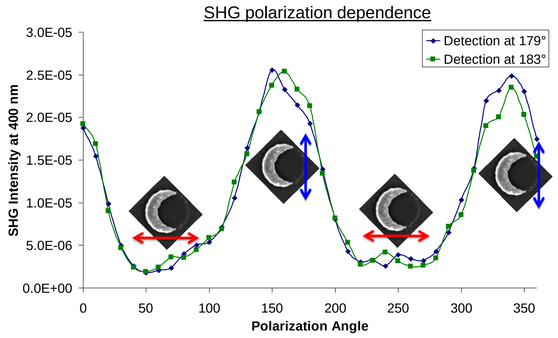


- SHG is a second order nonlinear process where two photons combine to produce a photon of twice the frequency of the input photons
- Inefficient process that requires high light intensity, but can be enhanced by near fields of nanostructures





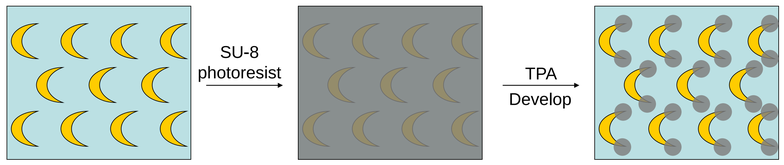
- Nanocrescents engineered so that LSPR of both long axis and short axis overlap with 800 nm output of Ti:Sapphire laser
- LSPR spectra show short axis at 65°, long axis at 155°



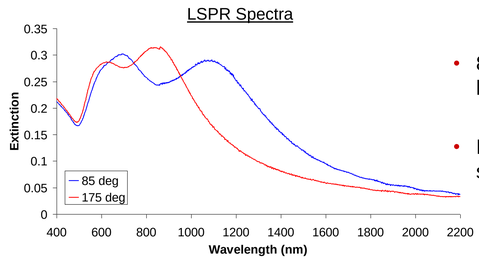
- SHG intensity was monitored as a function of polarization angle of incident light
- Minima in signal occur at 65°, corresponds to short axis
- Maxima in signal occur at 155°, corresponds to long axis
- Signal enhancement from both polarizations, but order of magnitude difference, indicating different field distributions and intensities
- Enhancement of nonlinear process

VI. Near Field Mapping

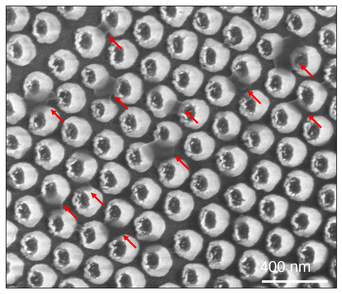
Since nanocrescents enhance nonlinear processes, the near field distribution of the structures can be mapped through two photon absorption (TPA) of a photopolymer.

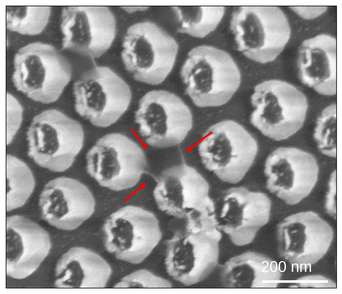


- TPA is the simultaneous absorption of two low energy photons to excite a higher energy transition
- It is an inherently weak process that requires high light intensity, but can be enhanced by near fields of nanostructures
- Exposure with low light intensity leads to spatially selective polymerization in or near regions of near field enhancement



- 800 nm output of Ti:Sapphire laser used to expose SU-8 film
- Incident light polarized along short axis of nanocrescents





- Photoresist localized between multiple crescents (tips and backbone)
- Possibly due to coupling of near fields in nanocrescent arrays

- Future work:
  - AFM to understand topology of resist and crescents
  - Probe near field distribution of better defined, isolated nanocrescents

VII. References

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5. Aizpurua, J.; Hanarp, P.; Sutherland, D.S.; Kall, M.; Bryant, G.W.; Garcia de Abajo, F.J. *Phys. Rev. Lett.* **2003**, *90*, 1-4.

Acknowledgments

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