Polarization Anisotropy of Multiple Localized Plasmon Resonance Modes in Noble Metal Nanocrescents

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ABSTRACT: Multiple localized surface plasmon resonance (LSPR) modes induced in gold and silver nanocrescents exhibit anisotropic behavior with respect to polarization of incident light. Extinction spectroscopy with polarization control was used to characterize the optical properties of asymmetric nanocrescents with diameters ranging from 100 to 500 nm. The analysis shows that selective induction of distinct dipole and quadrupole LSPR modes can be accomplished through polarization of incident light. Finite-difference timedomain calculations of the LSPR responses of the nanocrescent corroborate the polarization-dependent optical behavior. Simulations reveal optical near field enhancements with unique spatial patterns associated with the individual resonance modes depending on the polarization and wavelength of incident light. Quantitative analysis of the anisotropic LSPR behavior supports the potential for controlling the near field through selective induction of specific resonance modes with particular near field distributions.

INTRODUCTION

Manipulating light in a controlled manner has led to advances in spatial resolution beyond the diffraction limit for imaging and spectroscopy techniques. One approach to this “nano-focusing” is to use localized surface plasmon resonances (LSPR) in noble metal nanostructures which confine local fields to nanoscale probe volumes. This reduction in probe volume has been used to push the limits of the spatial resolution of characterization techniques like surface or tip enhanced Raman spectroscopy (SERS and TERS, respectively) and nonlinear laser-induced scanning tunneling microscopy (NLL-STM) and the high electron confinement intensifies local fields which enhance vibrational spectroscopy signals to obtain local chemical information.

A key factor in pushing the limits of spatial resolution and maximizing signal enhancements is the architecture of the plasmonic nanostructures. Great efforts have been made in designing, optimizing, and characterizing a wide variety of metallic nanoparticles through both synthetic (bottom-up) and fabrication (top-down) techniques. Some of the more common shapes of plasmonic nanostructures include colloidal spheres, rods, and cubes as well as fabricated disks and triangles. As the shapes of these structures become more complex, the resulting plasmon resonance modes and electromagnetic field distributions increase in complexity as well.

Recent studies have utilized the dependence of the optical response of asymmetric plasmonic nanostructures on the polarization of incident light to better understand the correlation between induced plasmon modes and optical near field distributions as well as how to exploit and control surface enhancement effects. Previous investigations have used polarization controlled illumination to map the location and distribution of enhanced near fields via photopolymerization, correlate SERS signal intensity with theoretically predicted regions of high electric field enhancement or “hot spots”, determine the orientation of particles or ligand molecules, and better understand the electromagnetic effect of signal enhancement.

The anisotropic characteristic of asymmetric nanostructures has another advantage that has not been fully explored, namely the opportunity to control the spatial distribution of optical near field enhancements through polarization of incident light. Hot spots are formed by the spatial confinement of electrons to small structural regions, effectively focusing incident energy from a far field source to nanoscale probe volumes. Manipulation of the near field through incident light polarization could improve spatial resolution by predictably limiting probe volumes and controlling their physical locations as well as make it possible to determine analyte positions with respect to plasmonic structures, control light–matter interactions, and initiate photochemical reactions at specific sites.

Here, we present investigations of the polarization anisotropy of noble metal nanocrescents. Simulations of the LSPR behavior of plasmonic gold and silver nanocrescent structures (AuNC and AgNC, respectively) predict unique field enhancement distributions based on the induced plasmon resonance.
mode.24,25 We demonstrate the controlled induction of several plasmon resonance modes and their optical responses to polarized light. These modes are well resolved spectrally and occur within distinct wavelength ranges. The anisotropy of the structure allows us to turn modes on or off, or, in the case of broadband excitation, independently excite a single mode at a specific wavelength based on polarization controlled illumination. Calculations predict the generation of hot spots at unique locations on the nanocrescent corresponding to each plasmon mode, indicating the potential for near field control through manipulation of incident light polarization.

EXPERIMENTAL AND THEORETICAL METHODS

Materials. BK7 glass microscope slides and soda lime staining jars were purchased from Ted Pella Inc. (Redding, CA). Concentrated H$_2$SO$_4$ and NH$_4$OH (30 wt%) were purchased from EMD Chemicals. Concentrated HCl and H$_2$O$_2$ (30 wt%) were purchased from Sigma-Aldrich. Absolute ethanol (200 proof) was obtained from Pharmco-Aaper, NaHCO$_3$ from Macron Chemicals, and RBS-35 concentrated detergent from Thermo-Scientific. Polystyrene template nanospheres (~2.6% w/v in water) were purchased from Polysciences, Inc. (Warrington, PA). Gold and silver pellets (99.999%) were obtained from K.J. Lesker (Clairton, PA). All water used was purified to 18 MΩ using a NANOpureDiamond system from Barnstead.

Substrate Preparation. Glass slides were cut into one square inch substrates using a diamond-tipped pen and cleaned using one of two procedures. The first procedure involved immersing the glass squares in piranha solution (3:1 volume ratio of H$_2$SO$_4$ and 30% H$_2$O$_2$) in a staining jar for 30 min. (Warning: piranha solution is very corrosive as well as exothermic and must be handled with extreme caution. It reacts violently with organic materials and should not be stored in closed containers.) Following decantation, the substrates were rinsed repeatedly with nanopure water and then sonicated for 1 h at 50 °C in a solution of 5:1:1 volume ratio H$_2$O:NH$_4$OH:HO$_2$. After sonication, the substrates were again rinsed copiously with nanopure water and either used immediately or stored in nanopure water.

The second procedure is simpler and uses less harmful chemicals. After cutting, substrates were immersed in 20% v/v RBS-35 detergent solution and sonicated at 50 °C for 5 min. The detergent solution was then removed by suction as well as multiple subsequent rinsings with nanopure water. A 1:1 volume ratio of ethanol:HCl was added and allowed to react for 30 min. The substrates were then rinsed repeatedly with water, the solution was removed by suction, and the slides were dried overnight in a 60 °C oven. Substrates were used immediately after cooling to room temperature in a closed container or stored under nitrogen in sealed, airtight containers. A comparison of the wettability of surfaces cleaned using both procedures and measured using a goniometer yielded similar results. A template nanostructure was fabricated by using one of two procedures. The first procedure involved placing a 5 μm thick glass substrate. However, electric fields localized at the nanocrescent surface are expected to decay rapidly, and the substrate thickness was consequently reduced to approximately 1.5 μm by perfectly matched layer (PML) boundaries which act to absorb and prevent reflection of incident fields. The refractive indices used for gold, silver, and glass were fitted material properties to Palik values and a mesh resolution of 2 nm was used in each direction of a three-dimensional simulation setup. The nanocrescent model was enclosed by six two-dimensional power flow monitors to determine absorption cross section with six additional power flow monitors enclosing the source to ascertain the scattering cross section. The extinction spectra were then calculated as the

dx.doi.org/10.1021/jp4107876
sum of the absorption and scattering cross sections using a wideband source from 800 to 2600 nm and MATLAB was used to generate the near field images.

**RESULTS AND DISCUSSION**

The modified nanosphere template lithography (NTL) procedure used to fabricate nanocrescents utilizes each nanosphere as an individual template to produce nanostructures with controllable and uniform size, shape, and orientation (Figure 1).\(^{26,27}\) Several parameters of the fabrication technique can be systematically changed to control nanocrescent thickness, tip sharpness, tip gap angle, orientation, and other structural characteristics. This uniformity allows the optical properties, including multiple polarization-dependent LSPR modes, of the nanocrescent to be probed in ensemble measurements. For this study, we focus on open-structure nanocrescents with relatively large tip gap angles (\(\alpha \approx 90^\circ\), Figure 1B) and diameters over a range of 100–500 nm. The

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**Figure 1.** SEM images of 356 nm template AuNCs: (A) dispersed structures show uniformity of size, shape, and orientation from NTL fabrication and (B) illustration of the direction of electric field polarization with respect to nanocrescent axes for distinct resonance modes.

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**Figure 2.** Calculated (A, C) and experimental (B, D) extinction spectra of 356 nm diameter template AuNC (A, B) and AgNC (C, D) samples. The varying polarization angles (\(P\)) demonstrate selective excitation, coexcitation, or nonexcitation of resonances at specific angles. Peak labels correspond to unique resonance modes described in text: 1, long axis dipole; 2, short axis dipole; 3, long axis quadrupole; 4, out-of-plane dipole. Long and short axis resonance modes are selectively excited at 0° and 90° (red and purple spectra), respectively.
asymmetry of these open nanocrescents gives rise to multiple distinct LSPR modes which can be induced in the same structure.24,25 The wavelengths of these resonance modes were determined using simple extinction spectroscopy and studied for polarization-dependent behavior.

Typical extinction spectra for open-tip gold or silver nanocrescents illuminated with unpolarized light exhibit multiple distinct plasmon resonance modes as four unique peaks (Figure 2B,D). Each of these peaks represents a resonance mode corresponding to a distinct directional oscillation of electrons associated with the polarization of the electric field of the incident light with respect to the orientation of the nanostructure. The plasmon resonance modes occur over a specific range of wavelengths which can be tuned by altering physical aspects of the nanostructure.27 Polarizing the incident light along specific axes of the nanocrescent (defined in Figure 1B) allows for selective excitation of particular resonance modes. Spectral peaks corresponding to the individual modes, termed the long axis dipole (LA-D), short axis dipole (SA-D), long axis quadrupole (LA-Q), and out-of-plane dipole (OOP-D), are labeled in the spectra of Figure 2. Simulations of the near field enhancement resulting from the unique electron oscillations for the three former resonance modes (LA-D, SA-D, and LA-Q) are shown in Figure 3.

The two long axis (LA) resonance modes can be selectively induced when light is polarized along the long axis of the nanocrescent (0°, Figure 1B). Incident light polarized in this manner induces either a dipole or quadrupole plasmon resonance depending on the wavelength. Excitation of the LA-D occurs in the near-infrared to mid-infrared wavelength range (1000–3000 nm) and results in an oscillation of electrons between the two symmetric halves of the nanocrescent structure. This resonance occurs at the lowest energy wavelength for any of the nanocrescent resonance modes but has the highest calculated electric field enhancement (I/I₀), localized at the tips, resulting from the high spatial confinement of electrons to the smallest region of the nanocrescent (Figure 3A). The LA-Q couples less strongly with incident light than the dipolar mode, resulting in a much weaker spectral peak and lower calculated field enhancement. This higher order resonance mode involves four distinct regions of charge separation, the oscillation of which results in four spatially localized regions of near field enhancement (Figure 3B). The LA-Q mode is present as a distinct peak in all LA polarized spectra for gold and silver nanocrescents within a spectral range of approximately 600–1200 nm.

When the electric field polarization is orthogonal to LA excitation (90°, Figure 1B), the short axis (SA) dipole resonance mode is induced. Oscillations of electrons in this mode alternate between the nanocrescent tips and backbone (Figure 3C). This direction of oscillation leads to a more delocalized near field distribution for SA polarization and a lower calculated field enhancement factor than the stronger LA-D. This is attributed to the decreased spatial confinement of electrons for this mode leading to a lower local electric potential difference. The resulting SA-D spectral peak observed between the wavelengths of 700 and 2200 nm is also lower in amplitude than the LA-D at respective maximum excitation angles, indicating relatively strong, but not the most efficient, coupling with incident light. We do not observe any higher order resonances for this polarization in the open-tip nanocrescents.

The out-of-plane resonance mode, a weak dipole that oscillates perpendicular to the plane of the nanocrescent, is observed for both LA and SA polarization in the visible range (Figure 2B,D). Experimental data indicate that this mode is largely independent of incident polarization. The method used for fitting the dielectric data in the simulations is less accurate in the visible range near the interband transitions of the metals; therefore, this mode is not included in the simulations. The presence of this peak in all spectra is attributed to the noncollimated light source. With light incident from many angles, the dipole for this resonance mode is weakly induced, coupling less strongly with incident light than the in-plane dipole modes.

The selective excitation of the three LA and SA modes is demonstrated in Figure 2 for both Au and Ag nanocrescents. The changes in peak amplitude indicate the transition from distinct excitation to simultaneous excitation to nonexcitation of the individual resonance modes as the incident polarization angle is rotated with respect to the structure. The polarization dependence is observed in both calculated and experimental spectra. Here, AuNCs fabricated from 356 nm diameter templates serve as a representative example (Figure 2A,B). At 0°, the LA resonance mode was selectively induced, and the corresponding spectra (red) have two distinct peaks. The high amplitude peaks at 2275 nm (theoretical, Figure 2A) and 2278 nm (experimental, Figure 2B) correspond to the LA-D and are in excellent agreement for the wavelength of this plasmon mode (Table 1). The smaller peaks at 950 and 962 nm (theoretical and experimental, respectively) represent the quadrupole and again show excellent agreement between calculated and measured resonance wavelength values for the plasmon mode. Both of these peaks diminish in amplitude as the polarization angle of the incident light is increased from 0° to 90°. It can be seen that at 50°, approximately halfway

Figure 3. Calculated near field enhancement (I/I₀) map of 356 nm diameter template AuNC for (A) long axis dipole, (B) long axis quadrupole, and (C) short axis dipole resonance modes. Electric field polarization (E) indicated by arrows. Intensity scale is logarithmic.
between the maximum excitation angles, both the LA and SA resonance modes were simultaneously induced and all three distinct plasmon mode peaks are present in the spectra, although at decreased amplitudes. At 90°, perpendicular to LA excitation, the SA resonance mode was selectively excited (purple spectra). The peaks at 2275 and 950 nm previously observed in the LA polarized spectra are not observed at this polarization angle, and the new peaks at 1295 nm (theoretical, Figure 2A) and 1284 nm (experimental, Figure 2B) correspond to a dipolar oscillation across the short axis of the nanocrescent.

A similar, polarization-based selective induction of distinct plasmon resonance modes was observed for the AgNCs (Figure 2C,D). The calculated values for resonance wavelengths at the LA-D, LA-Q, and SA-D have slightly greater differences from the experimental values than the AuNC sample due to less perfect fitting of the refractive index of silver across the wavelength range of interest, but all values are within 100 nm of the measured values (Table 1). The optical response pattern described was observed in additional gold and silver nanocrescent samples over a broad size range. Extinction spectra for AuNCs fabricated from 130, 243, and 456 nm diameter templates show the polarization-controlled induction of the LA and SA plasmon resonance modes in both smaller and larger diameter nanocrescents (Figure 4A–C). The polarization-dependent peak at 1500 nm observed for the 130 nm template diameter AuNCs is due to a small number of nanocrescent dimer structures which are physically connected and effectively elongate the long axis of the nanocrescents. Further experimental data and insight into this additional peak are forthcoming.

A plot of the average wavelength for the three dipolar plasmon resonance modes (LA-D, SA-D, and OOP-D) demonstrates the persistence of the anisotropic behavior of the long and short axis modes over a visible to near-infrared spectral range, polarization independence of the out-of-plane mode, and a linear trend in resonance wavelength with respect to template diameter (Figure 4D). The three separate plasmon modes (LA-D, LA-Q, and SA-D) observed at different resonance wavelengths in a single nanocrescent structure can be selectively induced by controlling the polarization of incident light.

A polar plot of the normalized extinction intensities of the long and short axis dipole resonance modes quantitatively illustrates the polarization dependence of the plasmonic nanocrescent (Figure 5A). Extinction spectra were obtained for 356 nm template diameter AuNCs at incident polarization angles from 0 to 360° and constant wavelength. For 2278 nm,

### Table 1. Theoretical and Experimental Values (in nm) for Wavelengths of Distinct Plasmon Resonance Modes

<table>
<thead>
<tr>
<th>Resonance Mode</th>
<th>Theoretical (AuNC)</th>
<th>Experimental (AuNC)</th>
<th>Δ (theor-expt)</th>
<th>Theoretical (AgNC)</th>
<th>Experimental (AgNC)</th>
<th>Δ (theor-expt)</th>
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<tr>
<td>Long axis dipole</td>
<td>2275</td>
<td>2278</td>
<td>3</td>
<td>2427</td>
<td>2330</td>
<td>97</td>
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<tr>
<td>Long axis quadrupole</td>
<td>950</td>
<td>962</td>
<td>12</td>
<td>988</td>
<td>950</td>
<td>38</td>
</tr>
<tr>
<td>Short axis dipole</td>
<td>1295</td>
<td>1284</td>
<td>11</td>
<td>1333</td>
<td>1250</td>
<td>83</td>
</tr>
</tbody>
</table>

*Δ* Difference between theoretical (theor) and experimental (expt) resonance wavelengths (absolute values).

Figure 4. Extinction spectra of AuNCs with template diameters of (A) 130, (B) 243, and (C) 456 nm showing selective excitation of long and short axis resonance modes at 0° (red) and 90° (purple), respectively. (D) Dependence of average resonance wavelength of AuNCs on nanosphere template diameter.
the resonance wavelength of the LA-D mode, the plot shows 
maxima at 0° and 180°, indicating that selective induction of 
this mode should occur at either of the two directionally 
equivalent angles. The polar plot for 1284 nm, the maximum 
resonance wavelength of the SA-D mode, shows maxima at 90° and 270°. 
These are the angles of maximum excitation for the SA-D mode 
and are orthogonal to those for the LA-D resonance mode. 
This plot demonstrates the selective induction of two distinct 
plasmon resonance modes with different resonance 
lengths by controlling the polarization angle of incident light, a 
mapping of near field behavior through far field control.

We analyzed the relative optical response of the LA and SA 
dipole modes for 356 nm template diameter AuNCs (Figure 1) 
in order to provide further quantitative assessment of the 
polarization anisotropy of the NC structure. For this analysis 
we modified the equations described by Wang,28 Ha,29 and 
colleagues which compare calculated and experimental 
anisotropy values. Wang and co-workers showed that the 
polarization anisotropy, $A$, is proportional to the fourth power 
of the cosine (for LA polarization) or sine (for SA polarization) 
of any angle, $\theta$, using the equation28

$$A_{LA} = \frac{\cos^4(\theta) - \sin^4(\theta)}{\cos^4(\theta) + \sin^4(\theta)}$$

(1)

To calculate theoretical $A_{SA}$ values, the functions of sine and 
cosine are transposed. For true polarization dependence, $A = 1$. 
This equation gives the polarization angles at which selective 
excitation of a specific resonance mode should occur. 
To calculate polarization anisotropy using experimental data for the 
nanocrescent structure, eq 1 is modified to29

$$A_{LA} = \frac{I_{LA} - I_{SA}}{I_{LA} + I_{SA}}$$

(2)

where $A_{LA}$ is the anisotropy of the long axis mode and $I_{LA}$ and 
$I_{SA}$ are the normalized intensities of the LA-D and SA-D 
resonance extinction values, respectively, at a common angle. 
The values are transposed to calculate the anisotropy of the 
short axis mode, $A_{SA}$. Again, for selective excitation of a specific 
resonance mode, $A$ should be equal to 1 at the maximum 
excitation angle for that mode.

We used only the LA-D and SA-D resonance mode 
extension values, remaining consistent with the axes defined 
in Figure 1B, to demonstrate the anticorrelation of these two 
modes at orthogonal polarization angles. Results for eq 1 show 
that selective induction should occur at 0° for the LA-D 
resonance mode and 90° for the SA-D resonance mode, 
corroborating what was predicted by simulation. Calculations 
using measured and normalized extinction values at 2278 nm 
(LA-D) and 1284 nm (SA-D) in eq 2 do, in fact, yield values of 
1 at 0° and 90° for $A_{LA}$ and $A_{SA}$, respectively (Figure 5B). 
These calculated values support what was observed in the polar 
plot; that when incident light at the appropriate wavelength is 
polarized along the long axis of the nanocrescent, the LA-D is 
selectively excited while the SA-D is not. Rotation of the 
polarization of the electric field across the short axis will not 
induce the SA-D because the incident wavelength does not 
match the wavelength of that resonance mode. The anisotropy 
of the structure has been exploited to independently excite a 
single mode at a specific wavelength based on polarization 
controlled illumination.

**CONCLUSION**

Multiple, polarization-dependent resonance modes can be 
excited in nanocrescents that are well-defined, reproducible, 
occur over a visible to near-infrared spectral range, and 
demonstrate polarization control over near field behavior. 
Selective induction of these distinct modes can be achieved 
using specific wavelengths and electric field polarization of 
incident light, leading to unique patterns of near field 
enhancement resulting from the electron oscillations. We are 
currently applying this research of polarization-dependent 
control to photochemically map areas of polarization-depend- 
ent field enhancement corresponding to simulation-based 
predictions. Identifying and controlling the locations of hot 
spots could increase the effectiveness of plasmonic substrates in 
surface enhanced spectroscopy and microscopy techniques by 
directing analyte molecules to areas of highest field enhance- 
ment. This control could also be used to initiate chemical 
reactions at precise surface locations or follow hot spot-bound 
reaction mechanisms as they occur.

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**Notes**

The authors declare no competing financial interest.
ACKNOWLEDGMENTS

The experimental portion of this work was supported by NSF Grants #CHE 0844764 and #0802913. The simulations were supported by NSF, #MRSEC DMR 1121252. M.K. gratefully acknowledges an NSF IGERT Award (DGE0903715).

REFERENCES