NRC Publications Archive Archives des publications du CNRC

Surface-enhanced Raman and optical scattering in coupled plasmonic nanoclusters

Tay, Li-Lin; Hulse, John

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1080/09500340.2013.821535>

Journal of Modern Optics, 60, 14, pp. 1107-1114, 2013-08-15

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=d1324025-bad7-4b28-934e-5818a12163a3>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=d1324025-bad7-4b28-934e-5818a12163a3>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Surface Enhanced Raman and Optical Scattering in Coupled Plasmonic Nanoclusters

Li-Lin Tay and John Hulse

*Measurement Science and Standards, National Research Council Canada, Ottawa
Ontario, Canada*

Li-Lin Tay
Building M-50, 1200 Montreal Road, Ottawa Ontario Canada K1A0R6
Email: lilin.tay@nrc-cnrc.gc.ca
TEL: 613-993-3919

John Hulse
Building M-50, 1200 Montreal Road, Ottawa Ontario Canada K1A0R6
Email: john.hulse@nrc-cnrc.gc.ca
TEL: 613-993-3919

Surface Enhanced Raman and Optical Scattering in Coupled Plasmonic Nanoclusters

Optical excitation of small Au nanoparticle (NP) clusters of appropriate wavelength is known to generate intense electromagnetic fields localized uniquely at nanoparticle junction sites within the nanoclusters. These intense and localized field hot-sites can induce intense surface enhanced Raman scattering (SERS) of molecules residing at the junction hot-sites. In this paper, we present a series of electromagnetic simulations, experimental SERS and extinction data obtained from small self-assembled Au NP clusters coated to saturation with a Raman reporter molecule. Our experimental data show that the SERS enhancement factor remains relatively constant despite the heterogeneity of the nanocluster and this is supported by the simulation results. Furthermore, our simulation results show significant variations in the localized electric field intensities of the junction hot-sites in different nanocluster geometries. This explains the observation that increasing the number of hot-sites does not necessarily result in a higher SERS enhancement factor.

Keywords: Plasmonics; surface enhanced Raman scattering; Gold nanoparticles, nanocluster structure

1. Introduction

Plasmonic nanoparticles exhibit extraordinary optical properties that have found many practical applications in sensing,^{1, 2} imaging,^{3, 4} therapeutics,^{5, 6} photovoltaic devices⁷ and a host of surface enhanced spectroscopies;^{8, 9} with the best known example being surface enhanced Raman spectroscopy (SERS).¹⁰ With its unprecedented sensitivity, SERS has become an extremely valuable analytical tool in trace chemical detection and identification. Resonant excitation of localized surface plasmon resonances (LSPR) in metal nanostructures results in highly confined regions of strong electromagnetic field intensity responsible for SERS. The LSPR of a nanoparticle is particularly sensitive to the size, shape, composition and geometry of the particle but it can also be modified through coupling with any near-by plasmonic nanostructures.¹¹ The ability to engineer a specific LSPR response of a plasmonic nanostructure can be crucial in enabling many unique plasmonic phenomena to be observed, but a direct correlation with SERS activity remains somewhat elusive. Many earlier studies have found an unexpected lack of correlation between the SERS and LSPR responses of plasmonic Nanoclusters.^{12,13,14} In a recent paper, Kleinman et al. presented a set of elegant studies that

established a correspondence between the SERS enhancement factor and a nanocluster's LSPR behavior using surface-enhanced Raman excitation spectroscopy.¹⁵ The authors concluded that discrepancies between SERS and LSPR response are due to the contribution of molecular dipole re-radiation through the excitation of normally “dark” plasmon modes. While there have been some studies aimed at fine-tuning the LSPR behavior of well-defined individual plasmonic nanostructures,^{16, 17, 18} few studies have examined correlations between LSPR, structural geometry and their SERS activities in self-assembled plasmonic nanoclusters.^{14,15,18} Moreover, although it is well recognized that the formation of the electromagnetic “hot-sites” in strongly coupled plasmonic nanoclusters is key in generating strong SERS activities,^{9, 11} the variability of SERS strength or different geometric assemblies of spherical NPs has not been quantified systematically. This is important as the synthesis of controllably aggregated SERS active plasmonic nanoclusters (e.g. SERS nanotags,¹⁹ encapsulated plasmonic nanobeads,^{20, 21, 22}) becomes increasingly common in developing labeling agents for bioanalytical and imaging applications.^{23, 24} In this paper, we will discuss the ways in which the structural geometry of self-assembled plasmonic nanoclusters affect their LSPR and SERS responses. Experimental measurements of LSPR and SERS were obtained through light scattering (dark-field illumination) and Raman spectroscopy, respectively; while structural geometry of the NP aggregates was elucidated with scanning electron microscopy (SEM). We also carried out comprehensive electromagnetic field calculations using the discrete dipole approximation (DDA) to provide insights and guide our interpretations of experimental results. Similar to earlier studies of structural correlation and with SERS activities, we found that all nanoclusters sustain broad LSPR and strong SERS responses with the dimer nanoclusters showing the broadest SERS enhancement factor (EF) distribution. We also observed that the measured average SERS EF remains relatively constant and even drops slightly for the larger nanoclusters. We will explain this trend with the insights provided by the DDA calculations.

2. Experimental

The Raman reporter molecule of choice, 4-mercaptobenzonitrile (4-MBN), was purchased from Synchem and used as received. The molecule contains thiol and nitrile functional groups para-substituted on the phenyl ring. The thiol functional group facilitates conjugation with Au NPs while the C≡N stretching vibration from the nitrile functional group provides a strong, sharp and easily identifiable Raman signature for SERS intensity characterization. The nitrile vibration occurs in a relatively quiet part of the spectral window so that no other organic constituent of the colloidal NP suspension will mask the reporter.

Colloidal Au sol containing nominally 80 nm Au NPs was purchased from Ted Pella.

The Au sol was citrate stabilized with a concentration of 1.1×10^{10} particles/ml as specified by the manufacturer. A 25 μ l aliquot of NP was diluted four fold by adding 75 μ l of deionized (DI)

water. To this solution, 4 μ l of 0.1 mM 4-MBN was added. The solution was allowed to incubate overnight. The final sample was prepared by drop casting 1 μ l of the incubated sol onto a cleaned ITO substrate (Delta Technologies Ltd.) and allowed to dry in a N₂ purged box. This experimental condition ensures a sufficient number of 4-MBN molecules to fully saturate the surface of the NPs.

Saturation coverage is important in this study. Formation of the nanoclusters is likely driven by the reduction of electrostatic charge repulsion between the Au NPs due to the chemisorption of the charge neutral 4-MBN molecules. As only the molecules situated in the junction hot-sites will benefit from the intense field enhancement, saturation of the Au NP surfaces with 4-MBN molecules will ensure that every junction hot-sites will be sampled.

Raman spectra were acquired with a commercial microRaman system (LabRAM HR, Horiba Jobin Yvon) equipped with a software controlled XYZ stage and a thermoelectrically cooled CCD detector. SERS spectra of NP samples were excited with 632.8 nm radiation at a power density of $\sim 10^2$ W/cm². Incident radiation was coupled into an Olympus BX51 optical microscope and focused to ~ 1 μ m diameter spot through a 100X objective. The same objective also collects the retro-reflected radiation and guides it to a notch filter that removes the Rayleigh scattered radiation. A half-wave plate was inserted in the beam path of the incident radiation for polarization selection. Raman spectra in figure 1d are collected in 2 seconds integration time.

Resonance Rayleigh Scattering (RRS) images and optical spectra of nanoparticles and their aggregates were obtained using a purpose built microscope system constructed from an Olympus BX51 component microscope with coarse motion manual stage and fine motion piezoelectric nanopositioner (Mad City Labs) operable in bright field or dark field mode using Olympus BD objectives. Samples were illuminated with a quartz halogen lamp and collected light was imaged either onto a digital camera or onto the end of a fiber connected to the input of an Ocean Optics spectrograph fitted with a thermoelectrically cooled CCD detector (OE65000). Integration times were typically 2.5s. Significant signal throughput was limited by the microscope optics to the wavelength range of 400-800 nm. All nanoparticle scattering spectra were referenced to a halogen lamp spectrum obtained by measuring the scattering from a white reference.

Discrete Dipole Approximation (DDA) calculations were performed using the DDSCAT codes developed by Draine and Flatau.^{25, 26} The codes were used without modification. Briefly, the method involves solving for the scattering of an incident electromagnetic wave by a target represented by a suitable array of dipoles arranged on a simple cubic lattice. The method has been applied with great success to many problems in astrophysics and atmospheric physics and of particular interest for this study it has been successfully applied to light scattering of metallic NPs as outlined in references 25-27. All nanoclusters were calculated with an interstitial gap of 1 nm and grid resolution of 0.5 nm.

Scanning electron micrographs were measured using a Hitachi 4700S field-emission microscope. Images were typically acquired with 10 KV acceleration voltage at a working distance of 13.3 mm.

3. Results and Discussion

The surfaces of isolated gold NPs, and nanoclusters (dimers, trimers and multimers) were saturated with 4-MBN, a non-resonant Raman reporter molecule, to ensure that SERS activities of all hot-sites are reported. Dark-field microscopy was employed to aid in the selection of isolated NPs and measurements of their LSPR in the form of resonance Rayleigh scattering spectra. SERS spectra of well isolated nanoclusters were acquired with a confocal microRaman spectrometer. Figure 1 shows the SERS responses from two distinct nanoclusters excited with 632.8 nm radiations. Nanocluster I is a pentamer and II a dimer. Their SEM images are shown in Fig. 1a and b, respectively. Fig. 1d shows the SERS responses for 632.8 nm excitations with incident radiation polarized horizontally in the plane of the SEM image (parallel to the Y axis). Excitation of dimer nanoclusters with light polarized parallel to the interparticle axis will produce the most intense localized electric field strength at the interparticle junction hot-sites. Fig. 1c shows the SERS polarization responses of the Fig. 1b dimer (solid red circle) and Fig. 1a pentamer (blue open squares) in a polar plot. The dimer SERS polarization intensity plot (solid red circles in Fig. 1c) shows the characteristic dumbbell shape tracing out the orientation of the dimer nanoclusters. Interrogated with horizontally polarized radiation, SERS spectrum of dimer nanocluster (II) is 6-fold stronger SERS than that of the pentamer, estimated by comparing the area under the CN stretching band (2220 cm^{-1}) as shown in Fig. 1d. This may seem surprising since the pentamer would have contained many interparticle junction hot-sites compared to just one in the case of the dimer. One should also take into consideration that there is a significant intensity variation in the polarization intensity plot of the dimer with strongest SERS intensity observed from incident light polarized parallel to the interparticle axis. The SERS spectrum acquired from the dimer nanocluster with incident light polarized nearly perpendicular to the dimer's interparticle axis is 50-times less intense than the spectrum excited with light polarized nearly parallel to the interparticle axis. The dimer SERS spectrum in Fig. 1d is excited with radiation nearly parallel to interparticle axis thus approaching the maximum SERS response for this nanocluster. By contrast, the pentamer exhibits much less polarization anisotropy with less than 3-fold differences in its polarization SERS intensity plot as depicted in Fig. 1c (blue open squares). The SERS polarization intensity plot (Fig. 1c) clearly shows that pentamer intensities lie nicely between the strongest and weakest response of the dimer nanocluster. Excitation of a dimer under nearly optimal polarization conditions generates more intense SERS than a pentamer. This is particularly true when the pentamer is assembled in a close-packed geometry

as in the case of the pentamer in Fig. 1a. We will discuss this in further detail with the results of the DDA simulations below.

Figure 1. SERS responses of two different Au nanoclusters on ITO surface. (a) and (b) SEM images of a pentamer (I) and a dimer (II) nanocluster. The scale bar is 100 nm. (c) Polarization response of the CN stretches of the dimer (solid red circle) and pentamer (blue open square). (d) SERS signals for the pentamer (I) and dimer (II) excited with 632.8 nm radiation polarized in the Y direction. Spectra are offset for clarity

Figure 2a shows the SERS EF of all of the measured nanoclusters. SERS EF was estimated by normalizing the SERS intensity per molecule to the unenhanced Raman intensity per molecule for the CN stretch at 2220 cm⁻¹.²⁸ Among all of the probed NPs, all aggregates, including dimers, trimers and other multimers showed a strong SERS response with dimers showing the largest intensity variability as shown in figure 2a. Higher aggregates, nanoclusters containing three or more Au NPs, showed a relatively narrow intensity variation despite the heterogeneity of the geometric assembly of the nanoclusters. Figure 2b shows the SEM images of a subset of the higher aggregates that were measured. Although most of the gold monomers overwhelmingly exhibited no detectable SERS activity, we did observe a few that were able to sustain weak but detectable SERS. These were all triangular prism-shaped NPs. The generation of a hot-spot through coupling of the LSPR from two individual NPs (e.g. a dimer) represents the simplest NP aggregate that is able to sustain local field strength many orders of magnitudes larger than the field strength for a typical spherical NP. However, generating additional hot sites

through formation of larger aggregates does not significantly improve the signal intensities as shown in figures 1c and 2a. One factor that contributes to this observation is the difference in the variations of local electric field intensity at the various interparticle hot-sites. Dimer nanoclusters assembled on the planar substrates will inherently exhibit a high degree of polarization anisotropy. Excitation radiation that is polarized parallel to the interparticle axis of the dimer generates the strongest SERS response while polarization perpendicular to the interparticle axis results in very weak SERS signal as shown in Fig. 1c as well as many reports in the SERS literature.^{29, 30, 31} In fact, such strong polarization anisotropy exists for all linearly assembled nanoclusters, such as linear trimers, tetramers, etc. Our DDA calculation showed that SERS intensity from linear aggregates tends to sustain the largest SERS EF under optimal excitation condition (with incident excitation polarization parallel to the interparticle axis). In the case of a dimer, SERS intensity can differ by orders of magnitude depending on the excitation polarizations. Since the probed dimers are randomly oriented on the ITO substrate, we observed large intensity variation anywhere between the optimal and minimal excitation condition (electric field vector parallel or perpendicular to the interparticle axis, respectively).

Figure 2. (a). Experimentally measured SERS enhancement factors for nanoclusters containing upto 9 Au NPs (b). SEM images of a subset of the sampled nanoclusters (Scale bar shown is 500 nm.)

Although the strongest SERS intensities are expected from linear forms of larger nanoparticle aggregates, we have not observed that truly linear aggregates form through the assembly process operating in this study. Linear aggregates are not known to be favoured in the assembly process. And if the aggregation process were stochastic, they would be unlikely. Of the nearly linear nanocluster geometries observed (see Fig. 2b and Fig. 4), almost all exhibited

some degree of bending. The slight deviation from the fully linear chain will cause the overall SERS EF to drop as shown in the DDA simulation outlined in the next paragraph. Most commonly, nanoclusters consisting of three or more AuNPs assemble in a closed-packed geometry as shown in figures 1a, 2b and 4. Although the close-packed geometry generally exhibits lower polarization anisotropy, it usually has the lowest overall SERS EF compared to nanoclusters with higher degrees of anisotropy. This manifests itself in a much narrower SERS EF distribution for the multimers observed in Fig. 2a. In addition to the narrower SERS intensity (hence SERS EF) dispersion for the multimers, it is also worth noting that the overall SERS EF (Fig. 2a) did not increase significantly with increasing nanocluster size. In fact, a very slight decrease as the nanoclusters size increases was noted. This is surprising as one might expect that creation of more junction hot-sites would result in higher SERS response.⁹ To help us understand this trend, we carried out a set of DDA simulations of various nanocluster geometries from monomers up to heptamers.

Figure 3 shows the DDA simulation of the local electric field strength of trimers and a subset of tetramers. In each image, the red circles indicate the most intense junction hot-sites with the normalized local electric field intensity value specified in red. Orange, green and blue circles indicates local electric field in decreasing order of strength with their values specified in the corresponding colour. All clusters are excited with incident radiation polarized in the vertical direction (parallel to the interparticle axis of the two linear nanoclusters in Fig 3a and 3c). From these two sets of calculations, we observe some general trends for the local electric field distribution with the geometrical arrangement of the nanoclusters. Figures 3(a-d) show the field strength of a set of trimers arranged from a linear geometry that benefits most from the vertically polarized incident excitation to the close packed geometry that benefits least. In the linear position, both junction hot-sites have equal value of 121.4. As the top NP begins to bend and deviate from the perfectly linear position, the value of both junction hot-sites decreases. In Fig. 3b, the top NP is deviated by 45° from vertical interparticle axis as defined by the linear trimer in Fig. 3a. It is expected that only a component of the dipole from the top NP will now contribute to the junction hot site created between the top and middle NPs under the vertically excited incident radiation. This causes the local electric field of the upper interparticle junction hot-site to drop from 121.4 to 72.2. In addition, the value of the lower interparticle junction hot-sites in Fig. 3b also decreased from 121.4 to 104.6. Moving the top NP 90° from the vertical interparticle axis established in the linear molecule, results in even further decrease in the values of the junction hot-sites (Fig. 3c). As SERS EF is proportional to the fourth power of local electric field, the drop in local field strength will be observed as a significant decline in the SERS EF. In the close-packed geometry as shown in Fig. 3d, even with the addition of an extra interparticle hot-site, the overall SERS EF is an order of magnitude lower than for the linear trimer geometry in Fig. 3a. The SERS EF of the four trimer geometries in Fig. 3(a-d), taking the

summed field strengths to the fourth power, are 4.34×10^8 , 1.47×10^8 , 6.1×10^7 and 3.2×10^7 , respectively. The linear geometry (Fig. 3a) with all the dipoles lined up with the vertically polarized incident field sustains the highest SERS EF while the close-packed geometry (Fig. 3d) has the lowest SERS EF. In most cases, we found that the hottest junction hot-sites (encircled in red) tend to dominate the nanocluster's overall activity. In the case of the trimer, creation of an additional hot-site in the close-packed arrangement (Fig. 3d) did not off-set the drop in local electric field strength at the most intense hot-sites (from 88.2 to 74). Of course, one should also take the polarization anisotropy into consideration as well. In typical experimental conditions, few linear clusters will assemble into perfectly linear geometry and not all will be excited in the most optimal condition. Other conditions such as the gap-separation between the coupled NPs will also affect the overall SERS activities. The DDA simulations, nevertheless, provide an informative guide in our understanding of our experimentally observed variations in the SERS intensities of nanoclusters of various sizes.

Figure 3. Discrete dipole approximation (DDA) of local electric field intensity (normalized to incident electric field) of trimers (a-d) and tetramers (e-h). All nanocluster calculations are for 20 nm spherical Au NPs separated by a 1 nm gap, with a grid resolution of 0.5 nm and with the incident electric field vector polarized in the vertical direction. In each image, red circles indicate the most intense junction hot-site. Orange, green and blue circles indicate successively lower intensity hot-sites. The electric field strength values are indicated in corresponding colours.

Similar trends are observed in the tetramers as shown in figures 3(e-h). The linear tetramer (Fig. 3e) again sustains the highest local electric field strength in all three of its junction hot-sites with the central hot-site being the most intense. Re-arrangement of the NP from linear assembly into the close-packed arrangement (Fig. 3f) adds an additional hot-site, but reduces the field strength in all of the interparticle junctions. Again, the drop in field strength is not fully compensated by the creation of the extra hot-site. The SERS EF of the linear tetramer (Fig. 3e)

is more than triple that of the tetramer in Fig. 3f. Because of the E^4 dependency in the SERS response, the overall all SERS EF is dominated by the most intense spot. Thus, in the case of Fig. 3e and f, creation of an additional weaker “hot-sites” contributes very little to the overall SERS EF. The SERS EF drops further as nanoclusters assemble into geometries with higher degrees of symmetry as in the case of Fig. 3g and h. The SERS EF of the four tetramer geometries shown in figures 3(e-h) are 1.38×10^9 , 3.94×10^8 , 7.82×10^7 and 5.93×10^7 , respectively.

It is interesting to compare two geometrically very similar structures, linear and close-packed geometries, between the trimer and tetramer. Local field strengths in the linear tetramer are significantly higher than in the linear trimer. In terms of SERS EF, the linear tetramer ($EF = 1.4 \times 10^9$) is enhanced by nearly an order of magnitude more than the linear trimer ($EF = 1.5 \times 10^8$). This is likely the result of the well-coupled dipole units in all four contributing nanospheres. Curiously, in the close-packed trimer (Fig. 3d) and tetramer (Fig. 3g), the SERS EF only differ by two. This is likely due to the less concerted coupling of their dipole contributions. In other words, only the vertical components of the electric dipole contribute importantly to the local electric field at the junction hot-sites thus resulting in a less substantial increase in EF for the close-packed larger clusters. These trends are also observed in the simulations of larger aggregates. As examples, the linear pentamer, hexamer and heptamer all showed the highest SERS EF compared to other geometrical arrangements of nanoclusters made of the same number of NPs. Also, in most multimers, geometries with the highest degree of symmetry developed much lower overall local electric field strengths as compared to their less symmetric counterparts. These simulations have provided important insights into the experimental observations. That is, not all hot-sites are created equal and the geometric arrangement of each nanocluster does influence its overall SERS activity.

Figure 4. Resonance Rayleigh scattering spectra of nanoclusters with various geometries as identified by SEM. The scale bar is 100 nm.

We have also measured the LSPR of individual nanoclusters in the form of resonance Rayleigh scattering spectroscopy. Figure 4 above shows a series of LSPR spectra obtained from the corresponding nanoclusters as shown in the SEM images just to the right of each spectrum. Figures 4 (a-c) and (d-f) show the LSPR of dimers and trimers in different orientation and geometry. The dimer LSPR spectra generally are made up of two very broad peaks with the higher energy peak centred at ~ 550 nm and the lower energy dipole peak at 700 to 800 nm. Trimer LSPR spectra are more complex with the highest energy peak centred between 500 to 600 nm with a weak peak located between 600 to 750 nm and the low energy dipole band shifted in the NIR spectral range beyond the optically available range. In the larger aggregates such as tetramer (fig. 4g) and pentamer (Fig. 4h), LSPR spectra are dominated by broad dipolar resonances beyond 700 nm and extending into the NIR spectral region. The LSPR spectra of individual nanoclusters are extremely sensitive to such details of the nanostructures as shape, size, morphology, assembly geometry and coupling of the NPs. The excitation and coupling of LSPR is key for the generation of an intense SERS response in nanoclusters.^{32, 33} In lithographically produced nanostructured systems that are not dominated by hot-spots, it has been shown through ensemble-averaged studies that SERS enhancement is largest when the LSPR peak lies in between the excitation wavelength and the wavelength of the stoke Raman shift.³⁴ This seemed reasonable as excitation energy situated in this window will benefit both incident and Raman scattered photon. However, it is important to point out that the LSPR measured using the dark-field microscopy setup is a far-field response. Near-field scattering behaviour especially at the junction hot-sites cannot be deduced from the far-field scattering measurements. At 632.8 nm excitation, it may seem that we are probing near the LSPR minimum of some dimer and trimer structures. Yet, we observe very strong SERS response from dimers as seen in figures 1d and 2a. Other earlier studies have all noticed a rather relaxed (or lack of) relationship between the LSPR and the SERS excitation energy.¹² A recent surface enhanced Raman excitation spectroscopy study has addressed this discrepancy.¹⁵ In reference 15, the authors found that in the hot-site dominant systems (such as aggregated nanoclusters), the enhancing properties will differ from the LSPR. It is speculated that “dark” plasmon modes contribute to the excitation and re-radiation of the molecular dipole near the nanocluster surface. Hence, there exists a general lack of correlation between the observed far-field LSPR spectral response and the SERS excitation energy, and it is important to realize that measured far-field LSPR spectra are not replicas of the near-field spectral response at the junction hot-sites in the nanoclusters. So even though the excitation energy of 632.8 nm seems to be situated near the LSPR minima of some dimer nanoclusters, we do observe significant SERS responses from all dimers with this excitation wavelength.

4. Conclusion

We have performed SERS and light scattering measurements and a DDA simulation of the local electric field strength of various geometric arrangements of Au nanoclusters. The hot-spots exhibited by these geometries vary widely in local electric field strength. The strongest local field strength was observed for a linear geometry while the least enhancement is typically observed and predicted for geometries with a high degree of symmetry as found, for example, in close-packed structures. The simulations also show us that not every hot spot contributes equally within a NP aggregate. As the number of NP increases, this trend becomes more pronounced. However, random assembly of nanoclusters and reduction of surface charges tends to favor the close-packed nanoclusters especially in larger nanoclusters. Thus, the experimentally observed SERS EF does not show large intensity changes for nanoclusters containing more than 3 NPs.

We have also measured the LSPR of nanoclusters of various geometry and sizes in the form of resonance Rayleigh spectroscopy. LSPR spectra of the nanoclusters are extremely sensitive to the shape, size, geometry and coupling of the constituent NPs. We find that while excitation near the LSPR minima can generate significant SERS response it need not in all cases since the far-field LSPR measurement is not indicative of the near-field behavior near the junction hot-sites.

References:

- ¹ Willets, K. A., Van Duyne R. P., *Annu. Rev. Phys. Chem.*, **2007**, 58, 267-297
- ² Gordon, R., Sinton, D., Kavanagh, K. L., Brolo, A. G. *Acc. Chem. Res.*, **2008**, 41(8), 1049-1057
- ³ Hu, Q., Tay, L.-L., Noestheden, M., Pezacki, J. P., *J. Am. Chem. Soc.*, **2007**, 129 (1), 14-15
- ⁴ Kennedy, D. C., Tay, L.-L., Lyn, R. K., Rouleau, Y., Hulse, J., Pezacki, J. P., *ACS Nano*, **2009**, 3 (8), 2329-2339
- ⁵ Bardhan, R., Lal, S., Joshi, A., Halas, N. J., *Acc. Chem. Res.*, **2011**, 44, 936-946
- ⁶ Jain, P.K., Huang, X., El-Sayed, I.H., El-Sayed, M. A., *Acc. Chem. Res.*, **2008**, 41, 1578-1586
- ⁷ Atwater, H. A., Polman, A. *Nature Materials*, **2010**, 9(3), 205-213
- ⁸ Moskovits, M., *Rev. Mod. Phys.*, **1985**, 57, 783-826
- ⁹ Moskovits, M., *J. Raman Spectrosc.* **2005**, 36, 485-496
- ¹⁰ Stiles, P.L., Dieringer, J.A., Shah, N.C., Van Duyne, R.P., *Annu. Rev. Anal. Chem.*, **2008**, 1, 601-626
- ¹¹ Halas, N.J., Lal, S., Chang, W.-S., Link, S., Nordlander, P., *Chem. Rev.*, **2011**, 3913-3961
- ¹² Michaels, A.M., Nirmal, M., Brus, L.E., *J. Am. Chem. Soc.*, **1999**, 121, 9932-9939
- ¹³ Tay, L.-L., Hulse, J., Kennedy, D., Pezacki, J.P., *J. Phys. Chem. C*, **2010**, 114, 7356-7363
- ¹⁴ Wustholz, K. L., Henry, A.-I., McMahon, J. M., Freeman, R.G., Valley, N., Piotti, M. E., Natan, M. J., Schatz, G. C., Van Duyne R. P., *J. Am. Chem. Soc.*, **2010**, 132, 10903-10910
- ¹⁵ Kleinman, L. S., Sharma, B. Blaber, M. G., Henry, A.-I., Valley, N., Freeman, R. G., Natan, M. J., Schatz, G. C., Van Duyne, R. P., *J. Am. Chem. Soc.*, **2013**, 135, 301-308

- ¹⁶ Ye, J., Wen, F., Sobhani, H., Lassiter, B., Van Dorpe, P., Nordlander, P., Halas, N. J., *Nano Lett.* **2012**, 12, 1660-1667
- ¹⁷ Rahmani, M., Lei, D. Y., Giannini, V., Lukiyanchuk, B., Ranjbar, M., Liew, T. Y. F., Hong, M., Maier S. A. *Nano Lett.* **2012**, 12, 2101-2106
- ¹⁸ Ou, F. S., Hu, M., Naumov, I., Kim, A., Wu, W., Bratkovsky, A. M., Li, X., Williams, R. S., Li, Z., *Nano Lett.*, **2011**, 11, 2538-2542
- ¹⁹ Mulvaney, S.P., Musick, M.D., Keating, C.D., Natan, M. J., *Langmuir*, **2003**, 19, 4784-4790
- ²⁰ (a). Tay, L.-L., Huang, P.-J., Tanha, J., Ryan, S., Wu, X., Hulse, J., Chau, L.-K., *Chem. Comm.*, **2012**, 48, 1024-1026 (b). Huang, P.-J., Tay, L.-L., Tanha, J., Ryan, S., Chau, L.-K., **2009**, *Chem. Eur. J.*, 15, 9330-9334 (c). Huang, P.-J., Chau L.-K., Yang, T.-S., Tay, L.-L., Lin, T.-T., *Adv. Func. Mater.*, **2009**, 19, 242-248
- ²¹ Moskovits, M., Braun, G. B., Lee, S. J., Laurence, t., Fera, N., Fabris, L., Bazan, G. C., Reich, N. O., *J. Phys. Chem. C*, **2009**, 113-13622-13629
- ²² Chen, G., Wang, Y., Tan, L. H., Yang, M., Tan, L.S., Chen, Y., Chen, H., *J. Am. Chem. Soc.*, **2009**, 131, 4218-4219
- ²³ Zavaleta, C.L., Smith, B. R., Walton, II, Doering, W., Davis, G., Shojaei, B., Natan, M. J., Gambhir, S. S., *Proc. Natl. Acad. Sci. U.S.A.*, **2009**, 106, 13511 - 13516
- ²⁴ Xie, H.-N., Stevenson, R., Stone, N., Hernandez-Santana, A., Faulds, K., Graham, D., *Angew. Chem. Int. Ed.*, **2012**, 51, 8509-8511
- ²⁵ Draine, B. T., Flatou, P. J., *J. Opt. Soc. Am. A*, **1994**, 11, 1941
- ²⁶ Draine, B. T., Flatou, P. J., **2009** <http://arxiv.org/abs/0809.0337>.
- ²⁷ Kelly, K. L., Coronado, E., Zhao, L. L., Schatz, G. C., *J. Phys. Chem. B*, **2003**, 107, 668
- ²⁸ Haynes, C. L., Van Duyne, R. P., *J. Phys. Chem. B*, **2003**, 107, 7426-7433
- ²⁹ Xu, H.-X., Kall M., *ChemPhysChem*, **2003**, 4, 1001-1005
- ³⁰ Lee, S. Y., Hung, L., Lang G. S., Cornett, J. E., Mayergoyz, I. D., Rabin O., *ACS Nano*, **2010**, 4, 5763-5772
- ³¹ Lee, S. J., Baik, J. M., Moskovits, M., *Nano Lett.*, **2008**, 8, 3244-3247
- ³² Aravind, P. K., Nitzan, A., Metiu, H., *Surf. Sci.*, **1981**, 110, 189-204
- ³³ Garcia-Vidal, F. J., Pendry, J. B., *Phys. Rev. Lett.*, **1996**, 77, 1163
- ³⁴ McFarland, A. D., Young, M. A., Dieringer, J. A., Van Duyne, R. P., *J. Phys. Chem. B*, **2005**, 109, 11279