

nanocylinder array. The bulk refractive index sensitivities represent upper bounds to sensitivities of plasmonic particles to local refractive index changes, such as those associated with chemical and biomolecule sensing. The bulk RIS which is measured in terms of change of a far-field property, it is found, shows some dependence on near-field coupling properties in particle arrays.

### **3.1.1 Background**

The plasmonic properties of a nanoparticle can be either measured by its far-field properties such as absorption, scattering, and extinction spectra or the near-field properties such as the intensity and spatial variation of the enhanced electromagnetic field. Both the far-field and near-field properties depend on the size, shape and dielectric environment of the nanoparticle. The change in the plasmon resonance peak position, width or intensity with change in dielectric environment is used in refractive index sensing while the enhanced electromagnetic field can be exploited for the various forms of surface enhanced spectroscopies such as SERS. As modern lithography and bottom-up fabrication techniques have advanced and can now be used to reproducibly manipulate the plasmonic properties of nanostructured systems, the relationship between the far-field and near-field properties along with the implication of this relationship for physical applications such as sensing and SERS for complex systems needs to be better understood.

### **Surface Enhanced Raman and Electromagnetic Enhancement**

As mentioned already, excitation of the LSPR in a nanoparticle is characterized by strong, wavelength-selective extinction and enhanced electromagnetic fields at the nanoparticle surface. This enhancement is responsible for the observation of all surface-enhanced spectroscopies, and it is the basis for the electromagnetic (EM)

enhancement mechanism, which is used to account for the large enhancement in Raman scattering intensity relative to what it would be in the absence of a surface.

The far-field power radiated ( $P_{rad}$ ) by an oscillating dipole (Raman scatterer) oscillating at a frequency of  $\omega$  is proportional to the square of the dipole moment  $|\bar{\mathbf{p}}|^2$ .

$$\frac{dP_{rad}}{d\Omega} = \frac{\omega^4}{32\pi^2\epsilon_o c^3} |\bar{\mathbf{p}}|^2 \sin^2 \theta \quad (3.1)$$

$$P_{rad} = \frac{\omega^4 |\bar{\mathbf{p}}|^2}{12\pi\epsilon_o c^3} \quad (3.2)$$

In Raman scattering, the applied field induces an oscillating dipole in the Raman-active molecule. This dipole then radiates, and there is a small probability that the radiated light is Stokes shifted by the vibrational frequency of the molecule. Consider Stokes Raman scattering from a specific vibrational mode of energy  $\hbar\omega_\nu$ . The inelastically scattered radiation is at a frequency  $\omega_R = \omega_L - \omega_\nu$ , and the induced dipole (Raman dipole) oscillates at the radiated frequency  $\omega_R$ . The induced dipole moment is given by;

$$\bar{\mathbf{p}} = \hat{\alpha}_{\mathbf{R}}(\omega_{\mathbf{L}}, \omega_\nu) \bar{\mathbf{E}}_{\text{inc}}(\omega_{\mathbf{L}}) \quad (3.3)$$

Where  $\hat{\alpha}_{\mathbf{R}}$  is the Raman polarizability tensor, and  $\bar{\mathbf{E}}_{\text{inc}}(\omega_{\mathbf{L}})$  is the incident laser electric field at frequency  $\omega_L$ . This induced dipole will radiate power proportional to  $|\bar{\mathbf{p}}|^2$  at a frequency of  $\omega_R$  as shown in equation 3.2.

In the presence of a plasmonic particle adjacent to the Raman-active molecule, the local field is greatly enhanced and the local field  $\bar{\mathbf{E}}_{\text{loc}}$  now determines the magnitude of the induced Raman dipole moment. So the power radiated which is proportional to  $|\bar{\mathbf{p}}|^2$  is enhanced compared to in absence of the plasmonic particle and the enhancement factor (*local field intensity enhancement factor*) is

$$M_{loc}(\omega_L) = \frac{|\bar{\mathbf{E}}_{\text{loc}}|^2}{|\bar{\mathbf{E}}_{\text{inc}}|^2} \quad (3.4)$$

Along with the local field enhancement the radiation of the Raman dipole is also enhanced/altered by the presence of a plasmonic particle resulting in an additional *radiation enhancement factor*,  $M_{rad}$ . The treatment for the enhanced emission intensity is more complex and depends on several factors that include the substrate geometry and optical properties, the dipole position, orientation, and its emission frequency  $\omega_R$ . Overall,

$$EF = M_{loc}(\omega_L)M_{rad}(\omega_R) \approx M_{loc}(\omega_L)M_{loc}(\omega_R) \quad (3.5)$$

Thus,

$$EF = \frac{|\bar{\mathbf{E}}_{loc}|^2(\omega_L)}{|\bar{\mathbf{E}}_{inc}|^2} \frac{|\bar{\mathbf{E}}_{loc}|^2(\omega_R)}{|\bar{\mathbf{E}}_{inc}|^2} \quad (3.6)$$

In most cases the Raman shift is small enough that one can assume  $\omega_R \approx \omega_L$  and,

$$EF = \frac{|\bar{\mathbf{E}}_{loc}|^4(\omega_L)}{|\bar{\mathbf{E}}_{inc}|^4} \quad (3.7)$$

which is the famous  $|E|^4$  approximation by which calculating the locally enhanced electric field at the excitation frequency of the incident laser using numerical simulations provides a direct insight into the expected SERS enhancement factor [4, 91, 55, 138, 16, 168].

Despite the apparent simplicity of the above approximation, the spectral relationship between the far-field scattering properties and the near-field Raman-enhancing properties are far from well-understood for complex nanostructured systems. This makes the predictive comparison of the effectiveness of different particle morphologies and array geometries impossible [74, 43, 198, 94, 134]. Ensemble measurements on lithographically fabricated substrates studies have tried to relate the far-field extinction to the measured SERS intensities and have successfully demonstrated that the peak SERS enhancement is obtained when the laser frequency is higher in en-

ergy than or approximately equal to the plasmon resonance, a condition at which the optimum plasmonic enhancement of both the incoming (exciting) and outgoing (Raman scattered) photons was achieved [109, 51, 74]. However, this relationship is not universal and the conditions essential for maximum SERS intensity vary depending on particle shape, aspect ratio, as well as the laser excitation wavelength [43].

These empirical relationships have also been found to be invalid in structures with closely interacting plasmonic systems where “hot spots” form in the inter-particle junctions or gaps. In such systems, single molecule SERS (SMSERS) measurements have shown that the SMSERS intensity is not correlated with the spectral position of the LSPR peak [74, 94]. In a recent study by Kleinman et al. a combination of wavelength-scanned SERS, LSPR spectroscopy, and high-resolution transmission electron microscopy (HRTEM) along with computation modeling for Au nanoparticle aggregates coated in a reporter Raman probe molecule and encased in a protective silica shell was used to show that the wavelength of maximum enhancement observed for individual nanoantennas is sometimes unrelated to the plasmon maximum associated with the single nanoantenna as well as the ensemble LSPR spectrum. It is dominated by the hot spots created by the interaction of the gold cores in the aggregates as well as the excitation of plasmon resonances by the Raman emitter in close proximity to the hot spot [74]. These results show the importance of dipole re-radiation effects in the SERS enhancement expression the nuances of which are ignored in the  $|E|^4$  rule.

In addition, the wavelength of maximum near-field enhancements appear to be red-shifted from the far-field LSPR maximum in many systems [74, 134, 198]. This phenomenon has been physically rationalized invoking damped harmonic oscillator models for the plasmon [198]. Based on quasi-static models of single spherical Ag and Au particles with added radiative damping it has been shown that no single wavelength is optimum for the individual far-field measures (absorption, scattering, and extinction) and near-field properties (average and maximum electric field en-

hancement). Phenomenological relationships have been derived for each individual measure for these nanospheres to assist rational optimization [198]. However, a understanding of the relationship between the near field enhancement and far field spectrum is missing in the case of complex nanoparticle arrays.

### Refractive Index Sensitivity

The remarkably high sensitivity of the plasmonic properties of nanoplasmonic systems to the immediate dielectric environment makes them invaluable as label-free chemical sensors [168, 2, 107, 54]. The sensitivity to local changes in the interfacial refractive index is typically manifested in shifts in LSPR peak wavelength when molecules are in close contact or adsorbed on the nanoplasmonic particle surface. The refractive index sensitivity is defined as

$$S = \frac{d\lambda_{LSPR}}{dn} \quad (3.8)$$

where  $n$  is the refractive index of the dielectric environment [110, 111, 135].

Using quasi-static approximations Miller et al. developed an analytical model to describe the dependence of the refractive index sensitivity of nanoparticles embedded in a homogeneous matrix on the LSPR peak position [citemiller2005sensitivity](#), [miller2006sensitivity](#). More specifically, electrodynamic simulations (Discrete Dipole Approximation and Mie theory) were used to calculate the sensitivity of the plasmon resonance maximum on the refractive index  $n$  of the surrounding dielectric medium. It was demonstrated that the refractive index sensitivity of the resonance is determined by the same two relations that determine the wavelength of the plasmon peak  $\lambda_{LSPR}$ , which include the resonance condition that determines the real part of the metal dielectric function at resonance,  $\varepsilon'_{LSPR}$ , given a particular particle structure and medium refractive index  $n$ , and the way the real part of the metal dielectric function,

$\varepsilon'$ , evolves with the wavelength [110, 111].

$$S = \frac{d\lambda_{LSPR}}{dn} = \frac{\frac{d\varepsilon'}{dn}}{\left. \frac{d\varepsilon'(\lambda)}{d\lambda} \right|_{\lambda_{LSPR}}} \quad (3.9)$$

Applying a Drude-like model for the wavelength-dependent dielectric function of the metal where  $\varepsilon'(\lambda) = m\lambda + q$  and the quasi-static approximation for the polarizability tensor of the particle, they showed that the refractive index sensitivity was independent of the nanoparticle shape and linearly dependent on the LSPR peak position.

$$S = \frac{2(m\lambda_{LSPR} + q)}{nm} \quad (3.10)$$

where  $m$  and  $q$  are constants obtained from linear fit of the real part of the gold dielectric function.

Saison et al. modified this expression for a wider range of wavelengths (500-2200 nm) using a quadratic fit of the metal dielectric function and found that the FDTD results for refractive index sensitivity for nanowire arrays embedded in a homogeneous matrix vary quadratically independent of nanoparticle shape and inter-particle distance( coupling strength)[110, 111].

$$S = \frac{2(A\lambda_{LSPR}^2 + B\lambda_{LSPR} + C)}{n(2A\lambda_{LSPR} + B)} \quad (3.11)$$

However, they also found that for a given type of nanoparticle shape, plasmonic systems organized in arrays have better refractive index sensitivities because their LSPR wavelengths are increased due to the inter-particle coupling [135].

Particle arrays supported on substrates, such as the cylinder arrays which are the subject of this chapter, constitute one of the most versatile and tunable substrates for refractive index sensing but suffer from the drawback of decreased refractive index sensitivity due to the presence of the dielectric substrate compared to particles in

spectroscopy ) with decrease of the inter-particle separation distance in gold and silver nanosphere pairs [191]. However, this effect could be attributed to the increase in plasmon resonance wavelength with increased coupling. In fact, for experimental measurements on 2D ensembles of small Ag nanoparticles deposited on glass slides, it has been found that changing the medium from air to hexane always manifests a 0.14 eV shift (as for the individual nanoparticle) independent of inter-particle coupling and distance. When the LSPR is positioned at longer wavelengths due to coupling the same energy shift manifests as an increased shift in wavelength and hence, an increased sensitivity  $S$  [161]. It is surprising that the change in the near-field properties such as electric field enhancement due to coupling have no direct effect on the refractive index sensitivity as measured by the shift in far-field absorbance response.

### 3.1.2 Contributions

In this chapter, the near-field enhancement of the electric field at an excitation wavelength of 532nm for square lattice arrays of nanocylinders on silica are determined using FDTD simulations. The effect of nanocylinder morphology and inter-particle distance (array pitch) on the near-field properties is investigated and the relationship to the far-field LSPR peak position is examined. An optimum SERS nanocylinder and array geometry is proposed. Secondly, the variation in refractive index sensitivity (RIS) of square lattice arrays of gold nanocylinders due to change in the inter-particle distance is investigated using FDTD simulations and the relationship between RIS and the electric field enhancement is analyzed.

maximum occurs at the resonance frequency of the oscillator. On the other hand, the plasmon-induced electric field enhancements are proportional to the plasmon-induced surface charges. These charges are proportional to the plasmon amplitudes. In a damped harmonic oscillator the maximum displacement amplitudes occur at a lower energy than the resonance frequency by an amount determined by the damping  $\beta$ .

$$f_{NF} = \sqrt{f_0^2 - \frac{\beta^2}{2}} \quad (3.16)$$

Hence, the intensity of the plasmon induced near-field, which is proportional to the plasmon amplitude, should peak at a lower energy  $f_{NF}$  than the maximum absorption, which occurs at the plasmon energy  $f_0$ . The structure for which there is maximum field enhancement at 532nm should have  $\omega_{NF} \approx c/532$ . Thus the plasmon far-field peak should be at a higher energy or blue shifted from  $\lambda = 532\text{nm}$ .

However, this condition seems to be violated in the nanocylinder arrays and in fact, for a particle height of 160nm where the plasmon peak is blue shifted from 532nm the field enhancement is lower. Additionally, no dependence is apparent between the far-field absorbance peak and the field enhancement of the cylinder arrays as shown in Figure 3.5. This independence of the near and far-field properties has been observed in systems with closely-interacting or coupled nanoparticles where the presence of hot spots dominates the near-field properties of the plasmon [74, 94].

The effect of inter-particle coupling on the near-field enhancement can be observed by varying the pitch of the array as shown in Figure 3.6 for a nanocylinder with diameter of 80 nm and height of 35nm. Again, there is no apparent dependence of the field enhancement of the array on the far-field absorbance peak position (Figure 3.7, The peak field enhancement occurs when the plasmon peak is red-shifted by 59-60nm from the excitation wavelength. For different particle sizes the value of this shift seems to vary randomly (Figure 3.8). Thus, it is most likely that the near field enhancement for a system of coupled cylinders is dominated by near field coupling.



disagrees with the damped harmonic oscillator model of plasmon resonance found in literature [198]. The most probable reason for the lack of correlation is that the near-field properties are dominated by inter-particle coupling effects. A similar lack of correlation has been observed for particle systems with hot spots [74, 94]. The importance of near-field coupling is indicated by the fact that the optimum inter-particle distance for maximum field enhancement is the same for cylinder arrays with the same diameter irrespective of height, indicating the importance of in-plane coupling of the transverse resonances of the cylinders which will be analyzed further in Chapter 4. The variation of the optimum inter-particle distance needs to be further analyzed for different in-plane diameters of the cylinder as well as for a longitudinal polarization of the incident plane wave, in order to elucidate the role played by plasmon coupling.

The refractive index sensitivity (RIS) of the nanocylinder arrays also show a deviation from the expected linear/quadratic dependence on the far-field LSPR peak [135] which can be explained by change in the bulk refractive index sensitivity due to inter-particle coupling. Although the RIS is measured by a shift in a far-field optical property, its variation shows an apparent relation with the near-field enhancement properties of the array as evidenced by the fact that only in the distance range where inter-particle coupling increases field enhancement compared to the non-coupled cylinder is there a linear variation with plasmon peak position. In this range, as the plasmon peak red shifts with increased array pitch, the RIS increases. However, at distances where the field enhancement is lower than the non-coupled cylinder there is a deviation from linearity. To the best of our knowledge, this effect has not been reported previously in literature due to the fact that the RIS has not been measured previously over sufficiently wide range of inter-particle distances. The nature of the near field effect on bulk RIS needs to be further analyzed by analyzing the spatial variation of the field and charge density around the nanoparticle at different coupling

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