Beamed Raman: directional excitation and emission enhancement in a plasmonic crystal double resonance SERS substrate

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Abstract: The angular dependencies of the local field enhancement and the Raman emission enhancement are investigated, numerically and experimentally, for a plasmonic crystal double resonance SERS substrate consisting of a periodic array of gold disks above a gold film. We find that the local field enhancement is very sensitive to the incident angle. The Raman emission enhancement has a strong angular dependence on the detection direction, with the substrate “beaming” the Raman emission so that different Raman lines have different far-field patterns. We demonstrate that a stronger SERS signal results when the plasmonic substrate is illuminated with a collimated, rather than focused, laser beam.

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References and links
1. Introduction

Metallic nanostructures can sustain surface plasmon modes which couple strongly with electromagnetic radiation \[1–3\]. This interaction can be used to generate highly enhanced near-fields at the surfaces of the nanostructures \[1\]. Reciprocally, the same mechanism leads to enhanced Raman scattering from molecules placed in these near-fields \[4\]. Surface enhanced Raman scattering (SERS) is an important application of surface plasmons \[5–14\]. Some SERS substrates have been shown to exhibit single molecule sensitivity \[15,16\]. SERS takes advantage of the fact that the plasmonic structure enhances both the excitation and scattering processes. This is termed the electromagnetic (EM) enhancement mechanism, and is believed to provide most of the enhancement of SERS signals \[17\]. The EM mechanism consists of three steps \[4\]. 1) The excitation field \(E_x\) with frequency \(\omega_L\) excites localized surface plasmons (LSPs) on the metallic nanostructures and the intensity of the electric field \(E_{loc}\) on the nanostructure surface is enhanced by a factor \(M_{loc}(\omega_L) = |E_{loc}|^2 / |E_0|^2\). This factor varies with the direction of the field illuminating the nanostructures. 2) The enhanced near field induces Raman scattering from the molecules on the nanostructures. For an isotropic Raman tensor, each molecule may be modeled by a dipole with \(d = \alpha E_{loc}\) that radiates at the Raman frequency \(\omega_R\). 3) The fields generated by the Raman dipole excite surface plasmons in the metallic nanostructure, resulting in an enhancement by a factor \(M_{Raman}(\omega_R)\) of the radiated power, compared to the hypothetical case of the dipole \(d\) being situated in free space. Here, \(M_{Raman}\) is defined as the ratio between the power radiated, per unit solid angle, by a Raman dipole near the metallic nanostructure in a particular direction to the power radiated, per unit solid angle, by the same Raman dipole in free space, in the direction normal to the dipole axis \[4\]. This factor varies with direction. Therefore, for given illumination and detection directions, the EM enhancement factor is proportional to the product of the local field enhancement factor \(M_{loc}(\omega_L)\) with the Raman emission enhancement factor \(M_{Raman}(\omega_R)\). Usually, in a SERS measurement, the total EM SERS enhancement is averaged over all possible collection directions. A previous study showed that the local field enhancement factor \(M_{loc}\) for a given illumination angle and the Raman emission enhancement factor \(M_{Raman}\) for the same angle are related by reciprocity theorem. Both have the same physical origin, i.e. coupling with surface plasmon phenomena \[4\].

In addition to the magnitudes of the local excitation field and the scattered power being altered, substantial modification of the angular dependence of the excitation and the scattering can occur in SERS substrates. Here, we investigate these phenomena, experimentally and theoretically. We consider a plasmonic crystal double resonance SERS substrate that we recently introduced, consisting of a periodic gold nanoparticle array, an SiO$_2$ spacer and a continuous gold film [8,18,19]. Here, we term it a “plasmonic crystal” to emphasize its periodicity, which is central to its directionality properties. The substrate is termed “double resonance” as it exhibits two hybridized resonances. These result from the coupling between localized surface plasmons (LSPs) on the particles and surface plasmon polaritons (SPPs) on the film, and enable a large local field enhancement factor $M_{\text{Loc}}(\omega_L)$ and a large Raman emission enhancement factor $M_{\text{Raman}}(\omega_R)$ to be simultaneously achieved. We demonstrated that this structure can provide average SERS enhancement factors of nearly $10^9$ [8]. These are the enhancement factors averaged over all the molecules that bind to the nanostructure surfaces; still larger enhancement is expected for those molecules in the hot spots. Measured at normal incidence, the plasmon extinction spectrum exhibited relatively sharp resonances [8,18,19]. One therefore might conclude that the SERS substrate exhibits narrow enhancement bandwidth. Here, we show that this is not the case. We show that the plasmon resonance frequencies vary with k-vector. Rather than being narrow, the SERS enhancement bandwidth is angle dependent. This leads to the interesting property that the Raman emission is “beamed” by the substrate so that different Raman lines have different far-field profiles. We show that a consequence of the local near field enhancement being sensitive to the incident angle is that stronger SERS signals are observed when the incident illumination is a collimated, rather than focused, laser beam.

It has been demonstrated that the emission patterns of molecules placed near a single metallic nanoparticle have approximately dipolar angular dependencies [20]. There has been recently considerable interest in optical antennas, e.g. Yagi-Uda, with improved directionality [21,22], especially for modifying the angular distribution of the fluorescent emission from single molecules and single quantum dots. The importance of directionality to SERS has also been recognized, since it facilitates efficient excitation and efficient collection [23–26]. It has been shown that ring structures can boost the measured Raman signal because they concentrate the excitation light and realize directional Raman emission [24–26]. Like the substrates we study in this paper, these have the advantage that the main beam is emitted surface-normal, rather than being directed into the substrate as in the case of Refs 21 and 22.

2. Methods

The plasmonic crystal double resonance structure consists of a gold nanoparticle array on top of an SiO$_2$ spacer and a continuous gold film (Fig. 1(a)). The gold film is 100 nm thick, deposited by e-beam evaporation onto an indium tin oxide (ITO) coated glass substrate. The SiO$_2$ spacer is 26.5 nm, deposited by plasma-enhanced chemical vapor deposition (PECVD). The thickness of the SiO$_2$ is measured by ellipsometry. Finally, a gold nanoparticle array is fabricated by e-beam lithography and lift-off on top of the SiO$_2$ spacer. A scanning electron micrograph (SEM) of a fabricated device is shown in Fig. 1(b). The gold nanoparticle array is a square lattice with a period of 780 nm. The diameter of the gold nanoparticle is 128 nm and the thickness of the gold nanoparticles is 40 nm.

The finite-difference time-domain (FDTD) method (FDTD Solutions package, developed by Lumerical Solutions, Inc.) is used to calculate the near fields of the double resonance structures. The side view of the modeled structure is shown in Fig. 1(c). The refractive indices of the glass substrate and the SiO$_2$ spacer are 1.517 and 1.46, respectively. The dielectric permittivity of gold is taken from Johnson and Christy’s experimental data [27]. The structure is illuminated by a linearly-polarized plane wave. To simulate an infinite periodic array, Bloch boundary conditions are used at the boundaries perpendicular to the substrate surface, i.e. the x-y plane. To simulate a single nanoparticle on top of the SiO$_2$ spacer and gold film, perfectly matched layer (PML) boundary conditions are used at the boundaries perpendicular to the substrate surface. In both cases, PML boundary conditions are used at the top and
bottom boundaries. In the simulations, the thicknesses of the gold film and the SiO$_2$ are taken as 100 nm and 25 nm, respectively. The gold nanoparticles are 40 nm thick and 135 nm in diameter. The period of the gold nanoparticle array is 780 nm. A monitor is placed at a quarter period (195 nm) away from the center of the gold nanoparticle at the interface between the SiO$_2$ and the gold film (position 1 in Fig. 1(c)). Recording the amplitude of $E_z$ at this point enables the excitation of SPPs on the gold film to be observed. Another monitor is placed at the edge of the gold nanoparticle at the interface between the gold nanoparticle and the SiO$_2$ spacer (position 2 in Fig. 1(c)). Recording the near field intensity at this position enables the excitation of LSPs excited on the nanoparticles to be monitored. A broad band plane wave source is used for all the simulations. When using Bloch boundary conditions, for each simulation with a fixed in-plane wavevector, the incident angle varies as a function of wavelength. To calculate the spectra for a single incident angle, we therefore perform multiple simulations with different in-plane wavevectors, and interpolate the results [28].

The extinction spectra of the fabricated plasmonic crystal double resonance structures are measured using the setup shown as Fig. 1(d). The sample is illuminated by collimated and polarized white light through a beam splitter. The reflected light is collected by a long working distance microscope objective and a tube lens, and coupled into a spectrometer. An iris placed at the image plane of the objective ensures that only the light reflected by the array, and not the surrounding regions, is detected. The reflection spectra are normalized by the
spectrum of a region without the nanoparticle pattern, i.e. consisting of the SiO$_2$ spacer on the gold film. As shown in Fig. 1(d), the sample can be rotated with respect to the x and y axes in a range from $-8^\circ$ to $8^\circ$. The extinction cross section per gold nanoparticle is calculated by the relation $C_{ext} = (1-R) \times \Lambda^2 \times \cos \theta$, where $R$ is reflectance, $\Lambda$ is the period of the nanoparticle array and $\theta$ is the angle between the incident wave vector and z axis.

The SERS spectra of monolayers of benzenethiol molecules on the plasmonic crystal double resonance SERS substrates are measured by a Horiba Jobin Yvon HR800 Raman microscope. These monolayers are formed as follows: the SERS substrates are immersed in a 3 mM solution of benzenethiol in ethanol for 1 hour, rinsed with neat ethanol and then blown dry with nitrogen.

3. Angular dependence of the local field enhancement

3.1 Focused illumination

In SERS measurements, to maximize the intensity at the sample, focused illumination is usually employed. As shown in Fig. 2(a), the incident rays are collimated and polarized before a microscope objective. These rays are refracted by the objective, and come to focus on the sample. We employ a Cartesian coordinate system, with the origin at the focal point. The direction of an incident ray is defined by $(\theta, \phi)$, as shown in Fig. 2(b). $\theta$ denotes the angle between the wave vector $k_0$ of the incident ray and the z axis. $\phi$ denotes the angle between the projection of $k_0$ on the x-y plane and the x axis. The incident rays are assumed to be polarized along the x axis before the objective. The polarization of an incident ray propagating along the direction $(\theta, \phi)$ after the objective can therefore be calculated by [29]:

$$E(\theta, \phi) = E_{in}(\theta, \phi) \left[ \begin{array}{c} (1 + \cos \theta) - (1 - \cos \theta) \cos 2\phi \\ -(1 - \cos \theta) \sin 2\phi \\ -2 \cos \phi \sin \theta \end{array} \right] (\cos \theta)^{1/2} \quad (1)$$

$E(\theta, \phi)$ is the electric field of the incident ray after the objective and $E_{in}(\theta, \phi)$ is the amplitude of electric field of the incident ray before the objective. The vector in the square bracket in Eq. (1) determines the polarization direction of the incident ray in the direction $(\theta, \phi)$. It can be seen that the polarization direction changes with both $\theta$ and $\phi$. However, for a small $\theta$, e.g. $\theta < 10^\circ$, we have

$$(1 + \cos \theta) - (1 - \cos \theta) \cos 2\phi = 2[\cos \theta + \sin^2 \phi (1 - \cos \theta)] \approx 2 \cos \theta \quad (2)$$

and

$$-(1 - \cos \theta) \sin 2\phi \approx 0 \quad (3)$$

To calculate the spectra for a given incident angle by the method described above, we approximate the electric field of an incident ray propagating along direction $(\theta, \phi)$ to be:

$$E(\theta, \phi) = E_{in}(\theta, \phi) \left[ \begin{array}{c} 2 \cos \theta \\ 0 \\ -2 \cos \phi \sin \theta \end{array} \right] (\cos \theta)^{1/2} \quad (4)$$

The polarization of the electric field expressed by Eq. (4) is in the x-z plane.
3.2 SPP modes: angular dependence

In this section we investigate the angular dependence of the SPP modes numerically. To exclude the effect of LSPs on the gold nanoparticles, we replace the gold nanoparticle array with an SiO$_2$ nanoparticle square array with a period of 780 nm. The SiO$_2$ nanoparticles are 100 nm thick and 290 nm in diameter. Figure 3(a) shows the side view of the structure, which consists of an SiO$_2$ nanoparticle array on top of the SiO$_2$ spacer (25 nm thick) and gold film. The direction of the incident plane wave is defined by $(\theta, \phi)$, as shown in Fig. 2(b). As discussed in Section 3.1, for each incident direction $(\theta, \phi)$, we choose the polarization direction to be parallel to the x-z plane, as given by Eq. (4).

$E_z$ is recorded at position 1 to monitor the SPP on the gold film. The incident wave vector can be decomposed to $k_x = -k_0 \sin \theta \cos \phi$, $k_y = -k_0 \sin \theta \sin \phi$, and $k_z = -k_0 \cos \theta$. The Bragg vector provided by the periodic array can be decomposed to $k_{\text{grating}, x} = p \times 2 \pi / \Lambda$ and $k_{\text{grating}, y} = q \times 2 \pi / \Lambda$, where $\Lambda$ is the period of the array and $p$ and $q$ are integers. The SPP modes on the gold film can be excited when two requirements are satisfied. One is that the wave vectors satisfy the equation:

$$k_{\text{spp}} = \sqrt{(k_x \pm p \times 2 \pi / \Lambda)^2 + (k_y \pm q \times 2 \pi / \Lambda)^2}$$

(5)

where $k_{\text{spp}}$ is the wave vector of the SPP and the integer pair $(p, q)$ denotes the order of the SPP mode. The other one is that the incident field has a non-zero overlap with that of the SPP modes. Here, we only consider the first order SPP modes, i.e. the $(+1, 0)$, $(-1, 0)$, $(0, +1)$ and $(0, -1)$ SPP modes. At normal incidence, i.e. $\phi = 0^\circ$ and $\theta = 0^\circ$, the $(+1, 0)$ and $(-1, 0)$ SPP modes can be coupled to, when $k_{\text{spp}} = 2 \pi / \Lambda$. The resonance wavelengths of these two SPP modes are the same. For a nonzero $\theta$, when $\phi = 0^\circ$, four first order SPP modes exist. They are the $(+1, 0)$ and $(-1, 0)$ modes satisfying the equation $k'_{\text{spp}} = \sqrt{(-k_y \sin \theta \pm 2 \pi / \Lambda)^2}$ and the $(0, +1)$ and $(0, -1)$ modes satisfying the equation $k'_{\text{spp}} = \sqrt{(-k_y \sin \theta)^2 + (\pm 2 \pi / \Lambda)^2}$. It can be seen that the resonance wavelengths of the $(0, +1)$ and $(0, -1)$ modes are the same. Figure 3(b) plots the simulated intensity of $E_z$, i.e. $|E_z|^2$, at position 1, as a function of $\theta$ and illumination wavelength when $\phi = 0^\circ$ and $0^\circ \leq \theta \leq 10^\circ$. The intensity of $E_z$ is normalized by the illumination intensity. When $\phi = 90^\circ$, the incident wave is purely x-polarized for all values of $\theta$. The $(0, \pm 1)$ SPP modes, therefore, cannot be excited, as their electric fields are in the y-z plane. Only the $(\pm 1, 0)$ SPP modes are coupled to, and this occurs when $k_{\text{spp}} = \sqrt{(\pm 2 \pi / \Lambda)^2 + (-k_0 \sin \theta)^2}$. In Fig. 3(c), the simulated intensity of $E_z$, at position 1, plotted as a function of $\theta$ and illumination wavelength when $\phi = 90^\circ$ and $0^\circ \leq \theta \leq 10^\circ$, is shown.
When we have $0^\circ \leq \phi \leq 90^\circ$ and $\theta > 0^\circ$, four first order SPP modes, i.e. the $(+1,0)$, $(-1,0)$, $(0,+1)$ and $(0,-1)$ SPP modes, can be excited. The resonance wavelengths of these four first order SPP modes follow Eq. (5). Figure 3(d) plots the simulated intensity of $E_z$, when $\theta = 4^\circ$. The $(\pm 1,0)$ SPP modes are excited by both the $x$ and $z$ components of the incident electric field. The $(0,\pm 1)$ SPP modes are excited by the $z$ component of the incident electric field [1]. As shown in Eq. (4), for small $\theta$, the $z$ component of the incident electric field is much smaller than the $x$ component. As a result, coupling efficiencies to the $(0,\pm 1)$ SPP modes are much smaller than those of the $(\pm 1,0)$ SPP modes. In Fig. 3(d), when $\phi < 20^\circ$ and $\phi > 60^\circ$, the $(0,\pm 1)$ SPP modes are too small to be seen. Anti-crossing behaviors can be seen between the $(+1,0)$ and $(0,+1)$ SPP modes at around $\phi \approx 45^\circ$, as well as between the $(-1,0)$ and $(0,-1)$ SPP modes.

Fig. 3. (a) Simulated structure, consisting of an SiO$_2$ nanoparticle array, an SiO$_2$ spacer and gold film. The thickness of the SiO$_2$ spacer is 25 nm. The SiO$_2$ nanoparticles are 100 nm thick and 290 nm in diameter. The period of the square array is 780 nm. (b) Simulated intensity of $E_z$, at position 1, plotted as a function of $\theta$ and illumination wavelength, when $\phi = 0^\circ$ and $0^\circ \leq \theta \leq 10^\circ$. (c) Simulated intensity of $E_z$, at position 1, plotted as a function of $\theta$ and illumination wavelength, when $\phi = 90^\circ$ and $0^\circ \leq \theta \leq 10^\circ$. (d) Simulated intensity of $E_z$, at position 1, plotted as a function of $\phi$ and illumination wavelength, when $0^\circ \leq \phi \leq 90^\circ$ and $\theta = 4^\circ$.

3.3 Coupling between LSPs and SPPs: angular dependence

We now add the LSP to the system. The structure modeled in simulations consists of a gold nanoparticle array on top of the SiO$_2$ spacer and gold film, as shown in Fig. 1(c). The SiO$_2$ thickness is 25 nm. The period of the array is 780 nm. The gold nanoparticle diameter is chosen to be 135 nm. For these geometric parameters, were the LSPs and SPPs not coupled, the LSP resonance and first order SPP mode wavelength would be identical at normal incidence. We simulate the near field spectra with different incident angles. The polarization direction of the incident plane wave is parallel to the $x$-$z$ plane. The monitor placed at the
edge of the gold nanoparticle at position 2 in Fig. 1(c) records the near field intensity $|\mathbf{E}_{loc}|^2$. The local field enhancement spectra are obtained by normalizing the near field intensity spectra with the intensity of the incident plane wave, $|\mathbf{E}_0|^2$. The left column of Fig. 4 shows the simulated local field enhancement spectra for six incident angles. The black curves are the spectra of the periodic array and the red curves are the spectra of a single gold nanoparticle on top of the SiO$_2$ spacer and gold film. The spectra of single nanoparticle cases indicate the resonance wavelength of the uncoupled LSP mode under different incident angles. It can be seen that the uncoupled LSP resonance does not change with the incident angle. For the periodic array, the spectra present very different profiles for different incident angles. In the normal incidence spectrum ($\phi=0^\circ$, $\theta=0^\circ$) of the periodic array (black curve), two hybridized resonances with similar line width can be seen, indicating the strong coupling between the LSP and the first order SPP. Figure 4 also plots the local field enhancement spectra for the incident angles with $\phi=0^\circ$, $\theta=1^\circ,2^\circ,4^\circ,8^\circ$ and $\phi=90^\circ$, $\theta=8^\circ$. When $\phi=0^\circ$, $\theta=1^\circ$, two additional features appear between the two primary hybridized resonances. As discussed in Section 3.2, for incidence at $\phi=0^\circ$, $\theta=1^\circ$, three first order SPP modes can be excited. One can see that, when the LSP resonance wavelength matches that of the SPP modes, the LSP strongly couples with one of these SPP modes, resulting in two hybridized resonances. The small features between these two hybridized resonances arise from the other two SPP modes. As $\theta$ increases to $2^\circ$, the $(\pm 1,0)$ SPP modes shift away from the uncoupled LSP resonance. The features between the two hybridized resonances become larger. When $\theta$ is larger than $2^\circ$, the difference between the wavelengths of the $(\pm 1,0)$ SPP modes and the wavelength of the uncoupled LSP mode is even larger. In the local field enhancement spectrum for the incidence with $\phi=0^\circ$, $\theta=4^\circ$, the two small resonances around 760 nm and 890 nm correspond to the $(-1,0)$ and $(+1,0)$ SPP modes, respectively. The broad feature around 830 nm corresponds to the LSP mode. On the other hand, the resonance wavelength of the uncoupled $(0, \pm 1)$ SPP mode doesn’t change much with $\theta$, when $\phi=0^\circ$, as shown in Fig. 3(b). A small dip on the broad feature can be seen. This line shape is a typical electromagnetically-induced-transparency-like (EIT) line shape [30], due to the coupling between the LSP mode and the $(0, \pm 1)$ SPP mode. The small depth of the dip in the broad resonance and the small separation of the two peaks indicate the small coupling strength between the $(0, \pm 1)$ SPP mode and the LSP mode. The bottom graph in the left column in Fig. 4 plots the local field enhancement spectrum for the incidence with $\phi=90^\circ$, $\theta=8^\circ$. In this case, only one $(\pm 1,0)$ SPP mode is excited, as discussed in Section 3.2. Two hybridized resonances arising from the strong coupling between the $(\pm 1,0)$ SPP mode and the LSP mode can be seen.

To observe these angular effects experimentally, we carry out extinction measurements on a fabricated structure with different incident angles using the setup shown in Fig. 1(d). The SiO$_2$ thickness is measured to be 26.5 nm. The gold nanoparticles are 40 nm thick and 128 nm in diameter. The right column in Fig. 4 shows the extinction spectra measured for incident angles of $\phi=0^\circ$, $\theta=0^\circ,1^\circ,2^\circ,4^\circ,8^\circ$ and $\phi=90^\circ$, $\theta=8^\circ$. The results can be seen to be in very reasonable agreement with the predictions of simulations.
We also calculate the local field enhancement spectra for three other arbitrary incident angles, as shown in Fig. 5(a). As we have discussed above, for an arbitrary incident angle, four first order SPP modes can generally be excited. For the incident plane wave with polarization parallel to the x-z plane, the amplitude of the \((+1,0)\) and \((-1,0)\) SPP modes is
larger than that of the \((0, +1)\) and \((0, -1)\) SPP modes. Also the coupling strength between the \((\pm 1, 0)\) SPP modes and the LSP mode will be larger than that between the \((0, \pm 1)\) SPP modes and the LSP mode. This is due to the fact that the electric field generated by \((\pm 1, 0)\) SPP modes is almost parallel to the LSP field, while the electric field generated by \((0, \pm 1)\) SPP modes is perpendicular to the LSP. As shown in Fig. 5(a), when the incident angle is \(\phi = 10^\circ\), \(\theta = 4^\circ\), the features at 760 nm and 890 nm correspond to the \((-1, 0)\) and \((+1, 0)\) SPP modes, respectively. The broad resonance around 830 nm corresponds to the LSP mode. In this case, the uncoupled \((0, +1)\) SPP mode occurs at 840 nm (shown in Fig. 3(d)), which is close to the wavelength of the LSP mode. The coupling between the LSP and the \((0, +1)\) SPP results in the EIT-like dip at 825 nm. For the case of incidence at \(\phi = 40^\circ\), \(\theta = 4^\circ\), the features at 770 nm and 880 nm correspond to the \((-1, 0)\) and \((+1, 0)\) SPP modes. As shown in Fig. 3(d), in this case, the \((0, \pm 1)\) SPP modes shift away from the LSP. In the local field enhancement spectrum, the \((0, \pm 1)\) SPP modes cannot be observed. For incidence at \(\phi = 80^\circ\), \(\theta = 4^\circ\), the uncoupled \((\pm 1, 0)\) SPP modes occur at 825 nm and 845 nm (Fig. 3(d)). The LSP strongly interacts with one of them, resulting in the two hybridized resonances. The small feature at 823 nm between the two hybridized resonances is due to the other SPP mode.

One can see that, for a given structure, the uncoupled LSP mode resonance is largely unaffected by the incident angle. On the contrary, the uncoupled SPP modes are very sensitive to the incident angle. The local field enhancement spectrum profile of the double resonance structure is determined by the interaction of the LSP and the first order SPP modes and exhibits complex behaviors.

We next measure the extinction spectra with focused illumination (Fig. 2(a)) using three objectives with different numerical apertures (NAs). The extinction spectrum under focused illumination can be considered as the weighted superposition of the extinction spectra over all the incident angles provided by the objective. As shown in Fig. 5(b), for the objective with NA=0.15, the reflection spectrum consists of two primary resonances, arising from strong coupling between the LSP and one of the \((\pm 1, 0)\) SPP modes, and small features due to the additional SPP modes. For the objectives with NA=0.25 and NA=0.5, the features between the two primary resonances mainly arise from the LSP mode under large incident angles. A previous work observed similar extinction spectra on a structure consisting of a gold nanoparticle array, an SiO\(_2\) spacer and a gold film with focused illumination [31]. However, in that work, the variation of the extinction profile for different incident angles in the focused illumination was not considered.

In the SERS measurements, an excitation laser with wavelength \(\lambda = 783\) nm is focused by an objective. As discussed in Section 3.1, the incident laser beam can be considered to comprise of rays at different incident angles. The blue dashed lines in Fig. 4 and 5(a) indicate the position of the excitation wavelength. It can be seen that, for different incident angles, the local field enhancement factors are very different. For example, for normal incidence with \(\phi = 0^\circ\) and \(\theta = 0^\circ\), the intensity enhancement factor \(|E_{\text{Loc}}/E_0|^2\) at \(\lambda = 783\) nm is about \(1.5\times10^7\). However, for the incidence with \(\phi = 0^\circ\), \(\theta = 4^\circ\), the enhancement factor at \(\lambda = 783\) nm is very close to zero. To find the total local field enhancement factor at a given position on the SERS substrate, one would need to average the local field enhancement factors over the incident angles comprising the illumination.
Fig. 5. (a) Local field enhancement spectra for incident angles with \( \phi = 10^\circ, 40^\circ, 80^\circ \), \( \theta = 4^\circ \). Black curves: spectra of gold nanoparticle array. Red curves: spectra of single nanoparticle cases. Blue dashed line: wavelength of the excitation laser, \( \lambda = 783 \text{nm} \). (b) Extinction spectra for focused incidence using three objectives. Black: 5x magnification, with NA=0.15. Red: 10x with NA=0.25. Green: 20x with NA=0.5.

4. Raman emission enhancement: angular dependence

We now investigate the angular dependence of the Raman emission enhancement. Molecules are placed on the gold nanoparticle surface and excited by the local electric field. The hot spot, at which the field enhancement is greatest, is at position 2 of Fig. 2(b) [8]. In modeling the angular dependence of the emission, therefore, we consider the molecule to be located there. In Ref. 4 the reciprocity theorem was used to relate the radiated far field of a dipole in the presence of an arbitrary nanostructure to the local near fields produced by plane wave illumination of that nanostructure. It was shown that the radiation in a given direction from a dipole in a complex environment, i.e. the arbitrary nanostructure, can be found from simulations of the local field at the position of the dipole under plane wave illumination [4]. Two plane wave illumination simulations need to be performed. As depicted in Fig. 6(a), the plane waves propagate along the same direction, but have orthogonal polarizations. Here, we use this method to calculate the far field angular distribution of the Raman emission of a molecule placed at the hot spot (position 2 in Fig. 6(a)) of the double resonance SERS substrate. We assume that the Raman tensor of the molecules is isotropic. Thus, the molecule is approximated as a point dipole with dipole moment proportional to the local electric field which is generated in response to illumination by the excitation laser. When the excitation laser is at normal incidence and the polarization of the excitation laser is along x axis at the hot spot, the y component of the local electric field is zero and the z component of the local electric field is about 10 times larger than x component. For this case, the Raman dipole can be described as \( \mathbf{d} = \alpha \mathbf{E}_{\text{loc}} \mathbf{e}_x + \alpha \mathbf{E}_{\text{loc}} \mathbf{e}_z \), where \( \mathbf{E}_{\text{loc}} \) and \( \mathbf{E}_{\text{loc}} \) are the x and z components of the local field, respectively, and \( \mathbf{e}_x \) and \( \mathbf{e}_z \) are the unit vector along x and z axes, respectively. To calculate the Raman emission enhancement in a given direction (\( \theta, \phi \)), we need to...
calculate the near field at the position of the Raman dipole under each of two types of plane wave illumination. The polarization of plane wave 1 is chosen to parallel the x-z plane. \( \mathbf{E}_1 \) denotes the local electric field excited by this plane wave at the dipole position. The polarization of plane wave 2 is orthogonal to the first polarization. \( \mathbf{E}_2 \) denotes the local electric field excited by the second plane wave. The Raman emission enhancement factor of the molecule at the given direction \((\theta, \phi)\) can be calculated by [4]:

\[
M_{\text{Raman}}(\theta, \phi) = \frac{|\mathbf{e}_d \cdot \mathbf{E}_1|^2 + |\mathbf{e}_d \cdot \mathbf{E}_2|^2}{|\mathbf{E}_0|^2}
\]

(6)

In Eq. (6), \( \mathbf{e}_d \) is the unit vector along the direction of the Raman dipole modeling the molecule, and \( \mathbf{E}_0 \) is the electric field of the incident plane wave. \( M_{\text{Raman}}(\theta, \phi) \) is the ratio between the power radiated, in direction \((\theta, \phi)\), by a Raman dipole placed near a structure and the power radiated by the same Raman dipole in free space in the direction normal to the dipole moment. The power radiated per unit solid angle of a dipole in free space in the direction normal to the dipole moment can be calculated by [32]:

\[
\frac{dP}{d\Omega} = \frac{|d^2d / dt^2|^2}{32\pi^2 \varepsilon_0 c^2}
\]

(7)

where \( \Omega \) is the solid angle and \( d \) is the dipole moment. Therefore, for a given Raman line, the power radiated per unit solid angle of a Raman dipole at a given direction \((\theta, \phi)\) is \( M_{\text{Raman}}(\theta, \phi) \times dP/d\Omega \). The variation with direction of the power radiated by a Raman dipole near a structure therefore follows the variation of \( M_{\text{Raman}} \) with direction. Simulations we perform, however, show that the local electric field at position 2 excited by plane wave 2, i.e. \( \mathbf{E}_2 \), is much smaller than that of plane wave 1 (\( \mathbf{E}_1 \)). This is due to the fact that the polarization of plane wave 2 is almost entirely along the y axis, while the dipole is oriented in the x-z plane. Thus, \( M_{\text{Raman}}(\theta, \phi) \approx |\mathbf{e}_d \cdot \mathbf{E}_1|^2 / |\mathbf{E}_0|^2 \), i.e. only one set of plane wave simulations (plane wave 1) is needed. These simulations are performed, yielding Fig. 6(b) and 6(c). These show \( M_{\text{Raman}} \) as a function of \( \theta \) and \( \phi \), for two Raman lines, at frequency shifts of 421 cm\(^{-1}\) (at \( \lambda = 809 \) nm) and 1074 cm\(^{-1}\) (at \( \lambda = 855 \) nm). These two images, thus, correspond to the power distribution that would be measured at the back apertures of the collection objective for these two Raman lines. One can see that, in the presence of the plasmonic crystal SERS substrate, the Raman line at 421 cm\(^{-1}\) mainly emits to the direction with \( \theta \gtrsim 3^\circ \) and \( \phi = 0^\circ \) or \( 180^\circ \). On the other hand, in the presence of the plasmonic crystal SERS substrate, the Raman line 1074 cm\(^{-1}\) mainly emits to the direction with \( \phi \) close to 90° or 270°.

5. SERS measurements

We have shown above that, for the double resonance SERS substrate, angular effects play an important role in both the local field enhancement factor and the Raman emission enhancement factor. The local field enhancement factor at a certain wavelength is very sensitive to the incident angle. To investigate this effect experimentally, we carry out SERS measurements using focused and collimated illumination. The experimental setups of Fig. 7(a) are employed. For the focused illumination, the Raman microscope (Horiba Jobin Yvon HR800) is used without modification, and the collimated laser beam input to the objective lens is focused onto the SERS substrate. The Raman emission of the benzenethiol molecules on the SERS substrate is collected by the same objective, focused by a lens at the confocal pinhole and input to the spectrometer. For the collimated illumination case, two additional lenses are added to the Raman microscope. These bring the laser beam to a focus at the back focal plane of the objective, meaning that the beam at the other end of the objective, where the SERS substrate sits, is almost collimated. We compare the SERS spectra measured under focused and collimated illumination with an NA=0.15 objective (5× magnification) and an NA=0.5 objective (20× magnification). The spread angle for a particular configuration is
defined as the largest angle ($\theta$) measured from the illumination. For the focused and collimated cases with the low NA objective (NA=0.15), the spread angles are measured to be 2° and 0.2°, respectively. For the focused and collimated cases with the high NA objective (NA=0.5), the spread angles are measured to be 9° and 1.1°, respectively. Figure 7(b) and 7(c) show the SERS spectra of the plasmonic crystal double resonance substrate measured by the NA=0.15 and NA=0.5 objectives. The SERS spectra are normalized by the power of the excitation laser at sample. For the low NA objective, there is not much difference between the SERS spectra measured by the focused and collimated illumination setups. This is because the spread angle for the focused illumination case is less than 2 degrees. For all the angles provided by the objective, the local electric field has large enhancement at the excitation wavelength. Therefore, the focused and collimated illumination cases provide similar local field enhancement factors. However, for the larger NA objective, the spread angle is much larger under focused incidence. As we have shown in Section 3.3, for incident angles with $\theta > 4^\circ$, the local field enhancement is smaller than the local field enhancement at normal incidence. In the Fig. 6(c), the SERS signal measured under collimated illumination is about twice as large as the SERS signal measured under focused illumination. These results indicate that, the collimated incidence setup provides larger total local field enhancement due to the smaller angular spread of the illumination.

![Diagram](image)

Fig. 6. (a) Schematic diagram of unit cell of simulation. Plane waves 1 and 2 propagate along the same direction ($k_0$), but have orthogonal electric fields ($E_{PW1}$ and $E_{PW2}$). (b) Angular distribution of Raman emission enhancement factor for Raman line $421\text{ cm}^{-1}$, in the presence of the plasmonic crystal SERS substrate. (c) Angular distribution of Raman emission enhancement factor for Raman line $1074\text{ cm}^{-1}$, in the presence of the SERS substrate.
Fig. 7. (a) Experimental setups for SERS measurements with focused and collimated illumination. Inset: shape of the mask which is placed at the back focal plane of the objective when SERS measurements with varied collection angles are made. (b) SERS spectra of benzenethiol on a plasmonic crystal double resonance SERS substrate measured with NA=0.15 objective (5× magnification). Black: focused illumination. Red: collimated illumination. The spectra are normalized by the power at the sample. (c) SERS spectra of benzenethiol on a plasmonic crystal double resonance SERS substrate measured with NA=0.5 objective (20× magnification). Black: focused illumination. Red: collimated illumination. The spectra are normalized by the power at the sample. (d) SERS spectra of benzenethiol on a plasmonic crystal double resonance SERS substrate measured with different diameters of the open window of the mask.

We now measure Raman spectra with fixed illumination, but with different collection angles. The collimated illumination setup equipped with the NA=0.15 (5× magnification) objective is used. A mask, as shown in the inset of Fig. 7(a), is placed at the back focal plane of the objective. The mask has a ring shape with an open window in the center. The collection angle is defined as the largest angle θ for which the Raman emission is collected by the objective and the mask. By choosing the diameter of the open window, the collection angle can be selected. We denote the size and position of the excitation laser beam by the red dot in the inset of Fig. 7(a). This beam is about 1 mm in diameter at the back focal plane of the objective. Figure 7(d) plots the SERS spectra of a single SERS substrate measured with different diameters for the open window of the mask, i.e. with different collection angles. It can be seen that the relative intensities of the different Raman lines change with collection angle. When the diameter of the open window is 2 mm (black curve in Fig. 7(b)), the Raman signal at 421 cm$^{-1}$ is extremely weak. As the size of the open window is enlarged, the rate of increase of the 421 cm$^{-1}$ line is larger than that of the 1074 cm$^{-1}$ line. This behavior indicates that, in the presence of the plasmonic crystal double resonance substrate, the 421 cm$^{-1}$ Raman line mainly emits to large collection angles. On the other hand, in the presence of the plasmonic crystal double resonance SERS substrate, the Raman signal at 1074 cm$^{-1}$ is...
appreciable even at the smallest size of the open window, implying that this line emits in the normal direction. To compare the experimental and simulation results, the emission power for different collection angles is plotted in Fig. 8 for the 421 cm$^{-1}$ and 1074 cm$^{-1}$ Raman lines. The red curves show the simulation data which are calculated by integrating the Raman emission enhancement factor over the appropriate range of collection angles. The black curves plot the intensities of the Raman lines in the measured SERS spectra as a function of the mask’s open window diameter. It can be seen that, to within a constant factor, the simulations are in very reasonable agreement with the experiments.

![Fig. 8. Comparison between the experimental and simulation results for (a) Raman line 421 cm$^{-1}$ and (b) Raman line 1074 cm$^{-1}$. Red: simulations of Raman emission enhancement factor over ranges of angles corresponding to circular masks of different diameters used in the experiments. Black: Raman line intensity in the experimental SERS spectra for different sizes of the open window of the mask.](image)

6. Conclusions

We have shown that angular effects have significant influence on the performance of the double resonance plasmonic crystal SERS substrates. The local field enhancement has a large variation with the incident angle and the Raman emission enhancement has a strong angular dependence on the detection direction. We demonstrate that by modifying the SERS measurement setups, larger SERS signal can be detected. We anticipate that the directional properties of the substrate we study could have advantages for applications beyond SERS. Its ability to direct radiation could have significant impact on guiding emission from single photon sources, on sensing, and on optical microscopy, where efficient excitation and collection are critical.

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