Double resonance surface enhanced Raman scattering substrates: an intuitive coupled oscillator model

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Abstract: The strong coupling between localized surface plasmons and surface plasmon polaritons in a double resonance surface enhanced Raman scattering (SERS) substrate is described by a classical coupled oscillator model. The effects of the particle density, the particle size and the SiO₂ spacer thickness on the coupling strength are experimentally investigated. We demonstrate that by tuning the geometrical parameters of the double resonance substrate, we can readily control the resonance frequencies and tailor the SERS enhancement spectrum.

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References and links

1. Introduction

Noble metal nanostructures exhibit unique optical properties due to the excitation of localized surface plasmons (LSPs) and/or surface plasmon polaritons (SPPs) [1–5]. These phenomena can lead to strong electromagnetic field enhancement near the nanostructure surfaces, and this has been employed for enhanced fluorescence, surface-enhanced Raman scattering (SERS), and biosensing [6–17]. The coupling between plasmonic phenomena provides additional interesting properties such as resonance shift, hybridized modes and Fano line shape [18–25]. The effects of coupling are attracting considerable interest across a variety of systems, ranging from coupled microresonators to coupled quantum wells [26,27]. It has been shown that the strong coupling between a broad radiative mode and a narrow dark mode results in a pronounced Fano line shape [20–22, 26–29]. Analogies can be drawn between these phenomena and electromagnetically induced transparency (EIT) in an atomic system [30]. This phenomenon can be modeled by a system with two classical oscillators coupled by a weak spring [28, 29]. EIT-like properties have been demonstrated using plasmonic nanoparticles in which the broad radiative mode is represented by the dipole plasmon mode and the narrow dark mode is represented by quadrupole plasmon mode [20–22].

We recently investigated strong coupling between LSPs and SPPs in a double resonance plasmonic structure consisting of a gold nanoparticle array, a SiO$_2$ spacer and a continuous gold film [11, 18]. Two hybridized modes were observed and the structure was employed for SERS [11]. We demonstrated that the double resonance structure can provide SERS enhancement factor of nearly 10$^7$, which was more than two orders of magnitude larger than the largest enhancement we measured for gold nanoparticles on glass substrates [11]. In that work [11], however, we did not develop a model. The plasmon resonance frequencies of the structure are critical for its performance as a SERS substrate, but an intuitive model for how they follow from the structure parameters was lacking. They therefore had to be predicted by finite difference time domain (FDTD) simulations. Similarly, an unusual extinction cross section line shape was observed, but could not be physically interpreted. Here, we address this by studying the use of a classical coupled oscillator model to describe the coupling between LSPs and SPPs. We investigate the influence of the geometrical parameters on the coupling strength. We find that changes on the nanoparticle density, the nanoparticle size and the SiO$_2$ spacer thickness lead to the change on the coupling strength, therefore lead to the shift of the hybridized resonance frequencies. For the application of SERS, we demonstrate that by
choosing the geometrical parameters of the device appropriately, different portions of the Raman spectrum can be selectively enhanced.

2. Method

A schematic diagram of the double resonance SERS substrate is shown in Fig. 1(a). It consists of a gold nanoparticle array, an SiO$_2$ spacer and a continuous gold film. The fabrication method is described in Ref. 18. Fig. 1(b) shows a SEM image of a fabricated device. The gold nanoparticles are cylinders with thickness of 40 nm. The nanoparticle array is a rectangular lattice with overall extent of about 100 μm × 100 μm. We fabricate devices with different periods in the range from 400 nm to 900 nm. The gold film is 100 nm thick. The thickness of the SiO$_2$ spacer is varied from 20 nm to 60 nm. The extinction cross sections are determined using the method described in Ref. 18. The fabricated devices are illuminated with collimated and polarized white light from a Xe lamp at normal incidence. The polarization is parallel to one of the axes of the rectangular lattice, i.e. the x axis in Fig. 1(a). The reflection is collected by a long working distance objective. The reflection spectra are normalized by the spectra of the area without the gold nanoparticle pattern, i.e. just the SiO$_2$ spacer and underlying gold film. The gold film is sufficiently thick to make the transmission negligible. The extinction cross section associated with each gold nanoparticle can be calculated by the relation $C_{\text{ext}} = (1-R) \times \Lambda_x \times \Lambda_y$, where $R$ is reflectance, and $\Lambda_x$ and $\Lambda_y$ are the periods along x and y axes, respectively.

![Fig. 1](image)

As shown in Fig. 1(a), the double resonance substrate is illuminated at normal incidence. The LSPs on the gold nanoparticles can be directly excited by the illumination. The reciprocal lattice vector provided by the gold nanoparticle array enables coupling to the SPP, which exists at the interface between the SiO$_2$ spacer and the gold film. Our previous work showed that the LSP and SPP resonances exhibit an anti-crossing behavior, with a splitting between resonances due to strong coupling [11,18]. The black curve in Fig. 1(c) shows the measured extinction spectrum of a typical device. The gold nanoparticle diameter is 120 nm. The periods $A_x$ and $A_y$ are both 780 nm. The thickness of the SiO$_2$ is 24 nm, as measured by ellipsometry. Two hybridized resonances with similar line width can be seen. Here, we utilize the classic coupled oscillator model to describe the coupling between the LSP and SPP. The LSP in our structure is represented by oscillator 1, which is driven by an external source $E(t) = E_0 e^{i \omega t}$, where $E_0$ and $\omega$ are the amplitude and the frequency of the electric field, respectively. The SPP mode is represented by oscillator 2, and can be excited only through the coupling between the two oscillators. The coupling between the two oscillators is provided by scattering by the gold nanoparticle array. The motion of the charges of oscillators 1 and 2 are given as follows:
\[
\frac{d^2 r_1(t)}{dt^2} + \gamma_1 \frac{dr_1(t)}{dt} + \omega_1^2 r_1(t) - gr_1(t) = \frac{eE_0 e^{-ia}}{m_e} \tag{1}
\]

\[
\frac{d^2 r_2(t)}{dt^2} + \gamma_2 \frac{dr_2(t)}{dt} + \omega_2^2 r_2(t) - gr_2(t) = 0 \tag{2}
\]

where \(\omega_1\) and \(\omega_2\) are the resonance frequencies of the uncoupled LSP mode and the uncoupled SPP mode, respectively. \(r_1\) and \(r_2\) are the displacements of an electron from its equilibrium position. \(m_e\) is the effective mass of the electrons. The anti-crossing occurs when \(\omega_1 = \omega_2\). \(r_1\) and \(r_2\) are the damping coefficients, and related to the loss of the oscillators. Since the LSP is a radiative mode and the SPP is a dark mode, we have \(\gamma_2 \ll \gamma_1\). Both \(\gamma_1\) and \(\gamma_2\) are \(\ll \omega_1\). \(g\) is defined as the coupling coefficient, and we have \(g \ll \omega_1^2\). As we discuss below in detail, the strength of the coupling between the two oscillators determines the splitting between the hybridized resonances. The energy dissipation can be written as:

\[
P(\omega) = \frac{-2\pi i e^2 E_0^2 \omega (\omega_1^2 - \omega^2 - i\gamma_1 \omega)(\omega_2^2 - \omega^2 - i\gamma_2 \omega) - g^2}{m_e^2[(\omega_1^2 - \omega^2 - i\gamma_1 \omega)(\omega_2^2 - \omega^2 - i\gamma_2 \omega) - g^2]} \tag{3}
\]

To find the parameters \(\{\omega_1, \omega_2, \gamma_1, \gamma_2, g\}\), we fit the experimental data (black curve in Fig. 1(c)) to Eq. (3). The result is shown as the curve comprising red circles in Fig. 1(c). Good agreement between the experimental spectrum and the fitting curve can be seen.

3. Experimental results

3.1 Effects of geometrical parameters on the coupling strength

We first investigate the influence of the nanoparticle density on the coupling strength. A series of structures is fabricated. The SiO\(_2\) thickness is 24 nm. For all the structures, the diameter of the gold nanoparticles is 120 nm. The period \(\Lambda\), along the x axis, i.e. parallel to the direction of the polarization of the incidence is fixed at 780 nm. To change the particle density, we vary the period \(\Lambda\), along the y axis of the array from 400 nm to 900 nm. For normal incidence, for a particular frequency, the first order SPP mode occurs when the wave vector satisfies the equation \(k_{spp} = 2\pi /\Lambda\), where \(k_{spp}\) is the wave vector of the SPP for that frequency. Thus, for a given SiO\(_2\) thickness, the first order SPP resonance frequency is only determined by the period along the x axis. Therefore the frequency of the uncoupled SPP mode is fixed for all the structures, though the period along the y axis changes. The measured extinction spectra of three structures are shown in Fig. 2(a). It can be seen that the splitting between the two resonances is larger when the period along the y axis is smaller. The parameters of the coupled oscillator model are fitted to the experimental data, with the results also shown Fig. 2(a) as black, red and green circles. The coupling coefficients \(g\) are calculated and plotted in Fig. 2(b) as a function of \(\Lambda\). It can be seen that the coupling coefficient decreases with decrease in particle density, i.e. with increase in the y period \(\Lambda\). This is due to the fact that, for the structure with larger particle density, there are more scattering centers. For larger particle densities, more energy from the incident illumination is coupled into the SPP and more of the SPP’s energy is radiated by scattering by the nanoparticles. The resonance frequencies of uncoupled LSP and SPP, the damping coefficients and the coupling coefficient are listed in Table 1. It can be seen that, for the fabricated structures, \(\omega_1\) is slightly larger than \(\omega_2\), indicating that the uncoupled resonance frequency of the LSP is slightly larger than that of the SPP mode. The damping coefficient \(\gamma_1\) is about one order of magnitude larger than \(\gamma_2\), indicating that oscillator 1 is bright radiative mode.
Fig. 2. (a) Extinction cross section spectra of three devices with different periods along y axis ($\Lambda_y$). Experimental measurements: solid curves. Coupled oscillator model: circles. For all the devices, the SiO$_2$ spacer is 24 nm thick, the diameter of the gold nanoparticles is 120 nm and the period $\Lambda_x$ of the array along the x axis is 780 nm. Black curve: $\Lambda_y = 400$ nm. Red curve: $\Lambda_y = 600$ nm. Green curve: $\Lambda_y = 900$ nm. (b) Coupling coefficient $g$ as a function of array period $\Lambda_y$.

Table 1. Fitting Parameters for the Devices with Different Periods Along y Axis

<table>
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<tr>
<th>$\Lambda_y$ (nm)</th>
<th>$\omega_1 (\times 10^{15})$</th>
<th>$\gamma_1 (\times 10^{14})$</th>
<th>$\omega_2 (\times 10^{15})$</th>
<th>$\gamma_2 (\times 10^{13})$</th>
<th>$g (\times 10^{29})$</th>
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<td>1.794</td>
<td>2.311</td>
<td>1.604</td>
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We next investigate the influence of the particle size. A series of structures is fabricated. The periods along x and y axes are fixed at 780 nm. The LSP resonance position mainly depends on the particle’s dimension along the same direction of the polarization, i.e. the x axis. As shown in Fig. 3(a), the nanoparticles are chosen to have a rod-shaped cross section in the xy plane, comprising a rectangle with a semicircle at each of its two ends along the x axis. The diameter of each semicircle matches the side length of the rectangle along the y axis. The total length of the nanorod along the x axis, including the semicircular ends, is fixed at 120 nm. The width $dy$ of nanorod, i.e. its dimension along the y axis, is varied from 40 nm to 100 nm. Figure 3(b) shows the extinction spectra of three structures for which the nanorod widths $dy$ are 50, 80, and 100 nm. A SEM image of a fabricated device with nanorod array is shown in Fig. 3(c). One can see that the splitting of the two resonance increases as the nanoparticle width increases, indicating that larger particles provide greater coupling. The coupling coefficients calculated by fitting the experimental spectra according to the coupled oscillator model are plotted in Fig. 3(d). The resonance frequencies of uncoupled LSP and SPP, the damping coefficients and the coupling coefficient are listed in Table 2.
Finally, we investigate the influence of the SiO$_2$ spacer thickness. A series of structures with different SiO$_2$ thicknesses is fabricated. The periods along the x and y axes are fixed at 780 nm. With increasing SiO$_2$ spacer thickness, the frequencies of both the uncoupled LSP mode and the uncoupled SPP mode change. For the LSP mode, the interaction of the excited dipole on the nanoparticle and its image dipole becomes weaker for a thicker SiO$_2$ spacer, resulting in a blueshift of the LSP resonance [31]. On the other hand, the resonance of the uncoupled SPP mode has a slight redshift due to the increase of the effective index of the space above the gold film. To match the frequencies of the uncoupled LSP and SPP modes,
with the period of the array fixed, the nanoparticle length along the x axis has to be increased as the SiO$_2$ spacer thickness is increased. The extinction spectra of two structures with different SiO$_2$ thicknesses are shown in Fig. 4(a). For the structure with SiO$_2$ thickness of 21 nm, the nanoparticle length $dx$ along the x-axis is 120 nm. For the structure with SiO$_2$ thickness of 56 nm, the nanoparticle length $dx$ is 155 nm. It is obvious that the splitting of the two resonances for the device with the 56 nm SiO$_2$ spacer is larger than that for the device with the 21 nm SiO$_2$ spacer, indicating that the coupling strength for the structure with the thicker SiO$_2$ spacer is larger. However, as discussed above, the increasing coupling strength could come from the nanoparticles being larger. To understand the influence of the SiO$_2$ thickness on the coupling strength, we make another series of structures. For these structures, the periods along x and y axes are fixed at 780 nm, and the nanoparticle length $dx$ along the x axis is fixed at 150 nm, so that the effect of the nanoparticle size can be eliminated. Here, we assume that the coupling between the two oscillators is independent of the resonance frequencies of the uncoupled oscillators. The extinction spectra of the devices with SiO$_2$ thicknesses of 21 nm and 56 nm are shown in Fig. 4(b) and 4(c). By fitting the extinction spectra to the coupled oscillator model, the coupling coefficient is found and plotted in Fig. 4(d). The fitting curves are shown as circles in Fig. 4(b) and 4(c). The features around 600 nm in Fig. 4(b) and around 650 nm in Fig. 4(c) are the second order SPP modes. They are not considered in the coupled oscillator model, and therefore contribute to differences between the coupled oscillator model fit and the experimental data. The fitting parameters are listed in Table 3. It can be seen that with an increasing thickness of SiO$_2$, the coupling coefficient decreases when the SiO$_2$ thickness is smaller than 30 nm. On the other hand, when the SiO$_2$ thickness is larger than 30 nm, the coupling coefficient increases with thickness. To explain this phenomenon, we investigate the coupling efficiency of a dielectric grating coupler on top of a continuous gold film numerically, using the FDTD method [32]. The dielectric grating is a 2D square array. The diameters of the dielectric nanoparticles are 150 nm and the x- and y-periods of the array are 780 nm. The spacer between the dielectric particle layer and the gold film is either air or SiO$_2$. The structures are illuminated by a polarized plane wave at normal incidence. The electric field component in the direction perpendicular to the surface of the structure, $E_z$, is recoded by a time monitor (indicated by black dot in Fig. 5) placed on the surface of the gold film at the 1/4 of period away from the center of the dielectric particle to measure amplitude of the first SPP mode on the top surface of the gold film. The first order SPP mode occurs around 800 nm. When the thickness of the spacer changes, the resonance wavelength of the first order SPP mode undergoes a slight shift due to the change of the local refractive index. For each structure, we find $E_z$ over a range of illumination wavelengths. Its peak value is denoted as $E_{zpp}$ and plotted in Fig. 5 as a function of the spacer thickness. The amplitude of the SPP decreases with thickness when the thickness is smaller than 20 nm. When the thickness is between 20 nm and 120 nm, the amplitude increases with thickness. When the thickness is greater than 120 nm, the amplitude of the SPP decreases with thickness. It can be seen that the coupling coefficient of the double resonance structure (Fig. 4(d)) also follows this pattern. We conclude that the variation in coupling coefficient vs spacer thickness for the double resonance structure arises from the dependence of the efficiency with which SPPs on a gold film are excited by an array of scatterers on the distance from the scatterers to the film.
Fig. 4. (a) Measured extinction cross section spectra of double resonance devices. $h$ denotes the thickness of the SiO$_2$ spacer, $dx$ denotes the length of the gold nanoparticles along x axis. For all devices, the periods of the array along the x and y axes are 780 nm. Black curve: $h = 21$nm, $dx = 120$nm. Red curve: $h = 56$nm, $dx = 155$nm. (b) Extinction cross section spectra for device with 21 nm thick SiO$_2$ spacer. Black line: experimental results. Red circles: coupled oscillator model fit. Nanoparticles have $dx = 150$nm. (c) Extinction cross section spectra for device with 56 nm thick SiO$_2$ spacer. Black line: experimental results. Red circles: coupled oscillator model fit. Nanoparticles have $dx = 150$nm. (d) Coupling coefficient of double resonance structures as a function of SiO$_2$ thickness.

Table 3. Fitting Parameters for the Devices with Different Thicknesses of SiO$_2$

<table>
<thead>
<tr>
<th>thickness (nm)</th>
<th>$\omega_1 (\times 10^{15})$</th>
<th>$\gamma_1 (\times 10^{14})$</th>
<th>$\omega_2 (\times 10^{15})$</th>
<th>$\gamma_2 (\times 10^{15})$</th>
<th>$g (\times 10^{29})$</th>
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<td>1.457</td>
<td>2.204</td>
<td>1.549</td>
<td>5.403</td>
</tr>
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</table>
Fig. 5. Perpendicular component of electric field $E_{zspp}$ on the surface of gold film as a function of spacer thickness. Position at which electric field $E_{zspp}$ is monitored is indicated by black dot and arrow. Dielectric grating has period of 780 nm along x and y axes. Structure is illuminated at normal incidence with a plane wave. Each structure consists of a 2D SiO$_2$ grating on top of a spacer and a continuous gold film. Black dots: the spacer is air. Red dots: the spacer is SiO$_2$.

### 3.2 SERS enhancement spectra

We have shown above that the double resonance substrate can be modeled by coupled oscillators, and that the splitting between the resonances can be modified by appropriate choice of the substrate’s geometric parameters. We now show that this enables portions of the SERS spectrum to be selectively enhanced. SERS measurements are performed on benzenthiol monolayers formed on two double resonance substrates. The first has an SiO$_2$ spacer thickness of 23 nm, gold nanoparticle diameter of 133 nm and x- and y-axis periods of 780 nm. The second has an SiO$_2$ spacer thickness of 60 nm, gold nanoparticle diameter of 150 nm and x- and y-axis periods of 760 nm. For both structures, the geometrical parameters are chosen so ensure that the LSP and SPP are strongly coupled. The extinction spectra are found by measuring the reflection from the samples using an optical microscope equipped with a spectrometer [11]. The objective lens has a numerical aperture of 0.12. The illumination, therefore, does not comprise the normally incidence plane waves depicted in Fig. 1(a), but the range of angular spread is relatively small due to the modest numerical aperture. The extinction spectra measured for the two substrates are shown in Fig. 6(a) and 6(b) as red curves. For both substrates, two hybridized resonances with approximate equal intensity and line width can be seen. The small features located between the two primary resonances are due to the angular spread of the illumination [11]. Benzenthiol molecules are coated on the two structures and form monolayers on the surfaces of the gold nanoparticles. This is performed by immersing the devices in a 3mM solution of benzenethiol in ethanol for 1 hour, rinsing with neat ethanol and then blow drying with nitrogen. SERS measurements are carried out using a confocal Raman microscope equipped with a 5 × objective (NA = 0.12), with excitation at $\lambda = 783$nm. The incident laser power at sample is ~20 mW and the acquisition time for each spectrum is 5 seconds. The black curves in Fig. 6(a) and 6(b) show the SERS spectra obtained from the two structures. The excitation laser wavelength is indicated with a dashed line in each spectrum, and is located near the high energy resonance peak for both structures. It can be seen, however, that the low energy resonance of the substrate with the 60 nm thick SiO$_2$ spacer is red shifted from that of the substrate with the 23nm SiO$_2$ spacer. This phenomenon is due to the fact that the coupling strength is larger for the 60 nm SiO$_2$ structure than that for the 23 nm SiO$_2$ structure, as discussed above. The SERS spectrum of the substrate with 23 nm thick SiO$_2$ has a distinctly strong signal around 1100cm$^{-1}$ corresponding to the low energy resonance at 855 nm, while the SERS spectrum of the substrate with 60 nm thick SiO$_2$ has a strong signal around 1500 cm$^{-1}$ corresponding to the low energy resonance at 890 nm. The background around 1350cm$^{-1}$ (at 875nm) is from the SiO$_2$ layer. One can see
that with different designs of the double resonance SERS substrate, the different portions of SERS spectrum can be selectively enhanced.

Fig. 6. Measured extinction (left hand axes) and SERS (right hand axes) spectra of double resonance structures on which monolayers of benzenthiol are formed. (a) Double resonance structure with 23 nm thick SiO$_2$ spacer, gold nanoparticles with diameters of 133 nm and x- and y-axis periods of 780 nm. (b) Double resonance structure with 60 nm thick SiO$_2$ spacer, gold nanoparticles with diameters of 150 nm and x- and y-axis periods of 760 nm. Dashed line: wavelength of the excitation laser ($\lambda = 783$ nm).

4. Conclusions

Strong coupling between LSPs and SPPs in double resonance SERS substrates has been explained by a classical coupled oscillator model. We investigated the influence of the geometrical parameters of the substrate on the coupling strength between LSPs and SPPs. We found that by increasing the particle density and the particle size, the coupling between the LSPs and SPPs becomes larger, leading to enhanced splitting between the two hybridized resonances. The SiO$_2$ spacer thickness was found to play an important role in determining the coupling strength. We showed that proper choice of the substrate geometrical parameters enables selective enhancement of different portions of the SERS spectra to be achieved.

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