REVIEW ARTICLE

Nanoantenna effect of surface-enhanced Raman scattering: managing light with plasmons at the nanometer scale

Zhipeng Li\textsuperscript{a} and Hongxing Xu\textsuperscript{b,c}

\textsuperscript{a}The Beijing Key Laboratory for Nano-Photonics and Nano-Structure (NPNS), Capital Normal University, Beijing, China; \textsuperscript{b}School of Physics and Technology, Wuhan University, Wuhan, China; \textsuperscript{c}Division of Solid State Physics/The Nanometer Consortium, Lund University, Lund, Sweden

ABSTRACT

Manipulating light on the nanometer scale is a challenging topic not only from a fundamental point of view, but also for applications aiming toward the design of miniature optical devices. Nanoplasmonics is a rapidly emerging branch of photonics, which offers variable means to manipulate light using surface plasmon excitations on metal nanostructures. As a spectroscopic phenomenon discovered nearly 40 years ago, surface-enhanced Raman scattering (SERS) has been an active topic of fundamental and applied researches. The dominating electromagnetic enhancement in SERS is caused by surface plasmon resonances. This is a typical example of manipulating light intensity with plasmons. Here, we will review the recent SERS studies related to nanoantenna effects on different metal nanostructures based on electromagnetic enhancement. Three aspects will be the focus in this paper: (1) the coupled nanostructures which act as receiving and emitting antenna that can generate enormous SERS enhancement ~E4 even enough for single molecule SERS. (2) The polarization of SERS at the single molecule limit, including the linear and circular polarizations can be manipulated using designed asymmetric antennas. Such an effect can make the traditional 1/2 and 1/4 wave plates miniaturized to the nanometer scale. (3) Combining nanoantenna and waveguiding effects, remote excitation of SERS can be realized, which may open a new area of single molecule SERS on nanophotonic circuits.

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CONTACT
Zhipeng Li zpli@cnu.edu.cn; Hongxing Xu hxxu@whu.edu.cn

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1. Introduction

Antennas, which appeared a century ago, were first used to transmit and collect radio and microwave signals, which now play an essential role in the modern wireless world [1–4]. Optical antennas as the analog at the nanoscale are of great interest due to the unique ability of controlling absorption and emission in the visible and infrared regions [5,6]. Examples are focusing optical fields into sub-diffraction limited volumes [7–10], enhancing the excitation and emission of molecules [11,12], and quantum emitters [13,14], modifying their spectrum and lifetime [15,16]. Propagating light can be converted into a nanoscale enhanced near field [17–20], and vice versa, a localized excitation can be coupled to directed radiation [21]. The efficiency and resonant properties of an optical antenna depend on its shape [22,23], material [24,25], geometry [26–28], and operation frequency [29]. Various optical antennas have been developed experimentally and theoretically, such as individual discs [30], triangles [31,32], flowers [33], as well as coupled antenna such as dimers [4,34,35], bowties [9,15], and trimers [12], etc. [36–38]. Most of these are metallic antennas where surface plasmons (SP) can be excited [39,40]. Single and coupled nanoantennas have been investigated thoroughly by far-field spectroscopy, exploiting two-photon luminescence (TPL) [11,41], and near-field scanning microscopy [6,31,42]. Abundant applications based on nanoantennas and the effects on the near and far fields have been found in optical manipulation [35,43], sensing [44–47], integrated photonic devices [48–50], and notably the surface enhanced Raman scattering (SERS) [7,51]. SERS was first observed by Fleischmann, where molecules adsorbed on roughened silver electrode gave rise to an unexpected huge Raman spectrum [52]. This phenomenon was then recognized physically and chemically by Van Duyne and Creighton [53,54], respectively. It has been generally acknowledged that the physical mechanism of SP gives the main contribution to the SERS enhancement [55]. In closely packed nanostructures, such as a dimer nanoparticle, SERS could reach the single-molecule level due to the strong coupling of SP in nanogaps [7,56–58]. Recently, even single molecules can be spectrally mapped by cutting-edge tip-enhanced
Raman technique based on plasmon enhancement [59]. Generally, the physical mechanism can be understood by the following simple picture. As shown in Figure 1, first, molecules around the surface of metallic structures acting as the receiving antenna will be excited by the hugely enhanced near field and emitting light due to the inelastic scattering, i.e. Raman scattering. The enhancement of the near-field intensity can be expressed as $|E_{\text{local}}(\omega_0)/E_0(\omega_0)|^2$, where $E_{\text{local}}(\omega_0)$ and $E_0(\omega_0)$ are the near and incident field at the excitation frequency ($\omega_0$), respectively. Then, the Raman signals can be enhanced again by the surrounding metal nanoparticles acting as an emitting antenna. The enhancement of an emitting antenna can be estimated by $|E_{\text{local}}(\omega')/E_0(\omega')|$ according to the optical reciprocity, where $\omega'$ is the frequency of the scattered Raman light. For a low-frequency Raman mode when $\omega_0 \approx \omega'$, the SERS enhancement is simply proportional to the fourth power of the localized electromagnetic field enhancement. While, for a high-frequency Raman mode, or particularly in the near-infrared regime, Raman frequencies are far apart from the excitation. Hence, the bandwidth of the plasmon resonance must be considered for the SERS enhancement estimation [60–62]. Generally speaking, the physical enhancement of SERS for roughened surfaces can be $10^2$–$10^6$ [63]. For mesoparticles with rough surfaces, such as 'Flower-like' silver or gold particles, the enhancement factor can be $10^6$–$10^8$ [33,64,65]. Large SERS active surfaces with periodic nanostructures which provide a moderate enhancement of $10^5$–$10^6$ have
been fabricated by nanometer-scale lithography techniques [66]. Enhancements larger than $10^9$ have been accomplished in various coupled structures, such as individual dimers and trimers [7,67] and mildly aggregated colloids of metallic nanoparticles [68]. The antenna effect in SERS makes it a great potential technique for ultra-trace detection [69–75].

In this review, we will focus on the manipulation of the near and far fields at the nanometer scale by nanoantenna effects, that is, the role of nanoantenna on radiative receiving and emitting. We show that the total SERS enhancement has contributions from both the receiving and the emitting antenna effects, which can be quantitatively different, while the normal treatment is as simple as $E^4$ enhancement. Based on these effects, the enhancement factor of SERS is analyzed in detail such as the SERS dependence on incident polarization. The polarization of SERS at the single molecule limit, including the linear and circular polarizations, can be manipulated with designed asymmetric antennas. Such an effect can make the traditional 1/2 and 1/4 wave plates miniaturized to the nanometer scale, and can manipulate the light polarization at the single molecule light scattering and single photon level. Combining nanoantenna and waveguiding effects, remote excitation of single molecule SERS can be realized. This may open a new area of single molecule SERS on nanophotonic circuits.

2. Nanoantenna effects on SERS

2.1. Nanoantenna as a receiver

The antenna can concentrate light around the surface of metallic nanostructures. These nanostructures actually act as the receiving antenna. When the excitation frequency matches the resonance of nanoantenna, an enormous electromagnetic field can be generated in the vicinity of the metal surface. As a simple example, we consider a spherical nanoparticle exited at its resonant frequency. In Figure 2, the near-field intensity distribution around a silver nanoparticle excited at $\lambda = 380$ nm shows that, the near-field intensity is enhanced several tens of times at the two poles of the particles along the incident polarization. As the role of the receiving antenna, the nanoparticle has the ability to concentrate light to the metal surface at the nanometer scale. The near-field enhancement can be larger in a gap between two coupled nanoparticles. As shown in Figure 2, for a 5-nm gap, the near-field intensity enhancement can be as high as 300 times at its resonant wavelength of 508 nm. Actually, the enhancement ability is highly related to the particle size, shape [22,23], geometry [26,27,76], and especially the spacing between nanostructures [6,28]. It is known that the coupling strength of the SP between particles increases enormously as the gap between the particles decreases [77]. The classical electromagnetic theory even predicts an ultrahigh near-field enhancement when the two nanostructures approach each other and form a ultra-small gap [78]. Recent experiments [79–85] and theoretical simulations [86–91] show that the
quantum effects [92–97] such as quantum tunneling and nonlocal effects would prominently reduce the near-field enhancement.

The near-field can be mapped out in experiments such as TPL [11] and scanning near-field optical microscopy (SNOM) [31]. The shape of the antenna influences the near-field properties [31]. Figure 3(a) shows the scattering spectrum of a triangular nanoantenna with a size of 200 nm. Two peaks dominate the spectrum; one is at ~670 nm, the other at ~430 nm, which correspond to the dipole resonance and quadrupole mode. These two modes can be visualized by SNOM. As shown in Figure 3(b), the near-field distribution over a 120 nm nanotriangle obviously shows a dipole resonance under the excitation of 632 nm. For a larger triangle, the quadrupole SP dominates the SP and results in multi bright spots in Figure 3(d). The theoretical simulations with the same configuration of the experiments are shown in Figure 3(c) and (e).

The coupling between these two nanostructures gives rise to strong local enhancement. Experiments and theoretical calculations indicate that the intensity enhancement at the visible frequencies can be as high as $10^3$ when the gap is reduced to a few nanometers. Bow-tie structures [15] are one of the most investigated configurations. The enhancement factor of $|E|^2/|E_0|^2$ at the gap of the bow-tie antenna is evaluated by the surface-enhanced fluorescence which is shown in Figure 4. The size of the gap varies from 15 to 80 nm. The maximum enhancement of fluorescence can reach 1340-fold. Further systematic studies were done by Schnell et al., where they investigated the near-field oscillations of progressively loaded plasmonic antennas at infrared frequencies by scattering-type SNOM [6]. In Figure 5(a), the amplitude signals at both ends of the nanorod and phase change at the rod center clearly reveal the dipolar mode excited on a nanorod. When a wedge is cut in the middle, the dipolar mode of the nanorod still holds, as shown in Figure 5(b). However, if the rod is cut more deeply and even fully cut, the case...
is completely different. In Figure 5(c), the bridge between the two rods is only 2% of the cross section, which cannot support the dipolar mode any more. For the fully cut rod in Figure 5(d), a 80-nm gap is formed in the rod center. Each antenna segment oscillates as a dipole. Hence, there is a phase change between the two segments and the gap.
2.2. Nanoantenna as an emitter

SP excited in nanoparticles effectively increases the cross section interacting with free space radiation. Figure 6(a) shows the absorption and scattering spectra of two different silver nanoparticles, which shows a maximum within the visible range, which is linked to the excitation of dipolar SP. The shape affects the properties of the SP in metallic nanoparticles [5]. The cubic one has a broad peak around 430 nm, whereas in the ring, the peak is shifted to 568 nm, which makes them good candidates for nanoantennas. The anisotropic shape of particles affects the resonant SP modes at different spectral positions, which are shown in Figure 6(b) [29]. The width of the particles is around 55 nm with the length varying from...
Figure 6. (a) Calculated absorption (solid lines) and scattering (dashed lines) efficiencies for a cubic (blue) and a ring (green)-shaped silver nanoparticle. (b) Measured scattering spectra of silver nanobars of lengths 100–200 nm. (c) Electric field intensity enhancement corresponding to the three lowest longitudinal LSPRs supported by 400 nm long silver nanoparticles. Figure adapted from Refs. [5] and [29].
100 to 200 nm. There are two peaks in the scattering spectrum. One is located at 430 nm and does not change with the elongation of the length. This peak is caused by the SP mode of charge oscillating along the short axis of the particle. The other is positioned between 620 and 850 nm depending on the aspect ratio of the particles. This peak corresponds to the charge oscillation along the long axis of the particle, hence red shifts with increasing of particle length. In Figure 6(c), the calculated near field around a gold nanobar shows the excitation of the three lowest SP modes with the incident wavelength 1375, 770 and 630 nm, respectively. The resonance of the nanobar can be understood by Fabry–Pérot oscillation in a cavity. The relation of the wavelength $\lambda_{sp}$ of the SP mode with the rode length $L$ can be written as:

$$L = \frac{n}{2} \lambda_{sp}$$

where $n$ is an integer number. The value of $n$ is shown at the bottom of Figure 6(c).

Controlling the direction of far-field emission from an emitter is another important property of nanoantennas. An example of a strongly coupled bimetallic dimer is shown in Figure 7 [98]. The scattering properties can be tuned by two closely spaced silver and gold disks. Interestingly, the direction of the scattering depends on the wavelength. For blue light at 450 nm and red light at 700 nm, the scattering is in opposite directions, as shown in Figure 7(b), which can be used as an ultra-small ~$\lambda/100$ photon-sorting nanodevice.

If a molecule or quantum dot is positioned close to the nanoantenna, the emission from this molecule or quantum dot such as Raman or fluorescence emission can be enhanced by the antenna. For simplicity, we treat the molecule as a dipole, which emits light at the Raman or fluorescence frequency. As shown in Figure 8, the dipole is put into one of the gaps in a trimer antenna. It is shown that, only when the dipole is oriented along the axis connecting the two nearest particles to the dipole, the emission intensity from the dipole can be enhanced enormously, as high as 10 to the power of 5. The emission direction from a quantum dot emitter can also be tuned by the antenna. To beam the emission, Curto and co-workers...
used a Yagi-Uda plasmonic antenna [13] where a quantum dot is positioned near one of the arms of the antenna. The constructive interference of the emission from each arm excited by the emitter results in a narrow directional radiation pattern.

2.3. SERS enhancement factor

The most notable application of the nanoantenna effects is the surface-enhanced Raman scattering. Although many reports show that the SERS enhancement is proportional to the $E$ field with the power of four, it is still essential to give a detailed model for the SERS enhancement factor. First, without losing the generality, we consider a gap in an aggregate with a molecule position at this junction. This system is excited by incident light. The polarization of excitation is rotated by a 1/2 wave plate. The Raman signal from the system is back scattered, and passes through the plate again. The signal is then split into two orthogonal components denoted as $I_{\parallel}$ and $I_{\perp}$, respectively, and recorded by the spectrometer. The scheme of the experiment setup is shown in Figure 9.

Let the sample plane be the $x$–$y$ plane. Then, the Raman signal generated by the molecule-aggregate complex can be written as follows:

$$
E = \left( \frac{E_{||}}{E_{\perp}} \right) \propto U_{z}^{-1}(\theta)g'(\omega_{0} - \omega_{\text{vib}})\alpha_{\text{vib}}g(\omega_{0})U_{z}(\theta)E_{0} \tag{1}
$$

$E_{0}$ is the incident field. $U_{z}$ is a z-axis rotation operator describing the effect of the 1/2 wave plate. $U_{z}E_{0}$ is the incident electric field on the aggregate. $g$ is the complex-valued tensors describing the enhancement of the laser field at a frequency of $\omega_{0}$, which corresponds to the receiving antenna effect. $\alpha_{\text{vib}}$ is the molecular polarizability tensor of this mode, that feels the enhanced near field and re-emits
Raman light at a frequency $\omega_0 - \omega_{\text{vib}}$, where $\omega_{\text{vib}}$ is the frequency of a particular molecular vibrational mode. Then, the Raman emission from the molecule is enhanced again through the nanoantenna. $g'$ is the complex-valued tensors describing the enhancement of the Raman scattering field at the Raman frequency, which corresponds to the emitting antenna effect. Then we have to determine the value of $g$ and $g'$. Here, we have

$$g = \begin{pmatrix} g_1 & g_2 \\ g_3 & g_4 \end{pmatrix}, \quad g' = \begin{pmatrix} g'_1 & g'_2 \\ g'_3 & g'_4 \end{pmatrix}$$  \hspace{1cm} (2)$$

The relation between $g$ and $g'$ should satisfy the optical reciprocity, [99,100] as shown in Figure 10. A dipole $P$ will induce the near field $E$, and in turn, the near field excited dipole $P'$ will emit light and the electric field of the emission is $E'$ at the position of the excitation dipole. Then we have,

$$E = gP$$

$$E' = g'P'$$  \hspace{1cm} (3)
According to the optical reciprocity, we have

\[ \mathbf{P} = (a, b), \mathbf{P}' = (c, d) \]  \hspace{1cm} (4)

Inserting (2), (3), and (4) into (5), we obtain,

\[ (\mathbf{a}g_1' + \mathbf{b}g_2' + \mathbf{c}g_3' + \mathbf{d}g_4') = (\mathbf{a}g_1 + \mathbf{b}g_2 + \mathbf{a}g_3 + \mathbf{b}g_4). \]

Then it is easy to deduce that \( g_1' = g_1, g_2' = g_2, g_3' = g_3, g_4' = g_4 \). By considering the complex phase and the wave vector for the incidence and emission (\( k = -k' \)), we have

\[ g e^{ikr} = [(g' e^{ik'r})^*]^T \]  \hspace{1cm} (6)

The value of each element in the tensor can be ascertained by the electric relation between the incident light and emission. As shown in Figure 11, the numerical simulations show that the direction of the enhanced local field in the junction is always along the axis of the junction (defined as the \( y \)-axis), irrespective of the incident field polarization. Similarly, the light emitted by the molecular dipole oscillating in the junction is maximally enhanced when the dipole is oriented parallel to the same axis, as shown in Figure 8. Hence, the tensors \( g \) and \( g' \) can be written in the most general way as follows:

\[
g(\omega_0) = \begin{pmatrix} 0 & 0 \\ g_{yx} e^{-i\phi_x} & g_{yy} e^{-i\phi_y} \end{pmatrix}, \quad g'(\omega_0 - \omega_{\text{vib}}) = \begin{pmatrix} 0 & g_{yx}' e^{i\phi_x'} \\ 0 & g_{yy}' e^{i\phi_y'} \end{pmatrix} \]  \hspace{1cm} (7)

where \( g_{yx}, g_{yy}, g_{yx}' \), and \( g_{yy}' \) are the real values of the tensor elements and \( \phi_x, \phi_y, \phi_x' \), and \( \phi_y' \) are their phases. Inserting (7) in (1), we obtain the relation of the SERS signal as a function of the incident polarization angle,
where $\Delta = |\phi_x - \phi_y|$ is the phase differences and $r = \frac{g_{yy}}{g_{yx}}$ is the ratios between tensor components. The intensity depends only on the enhancement tensor $g$.

We first consider a simple dimer case. In the dimer system, we always have $g_{yy} \gg g_{yx}$ due to the highly polarization dependent excitation of bonding modes. Then the relation (8) turns into

$$I = I_{\parallel} + I_{\perp} \propto \frac{1}{2} \left[ 1 + \frac{(r^2 - 1) \cos 2\theta + 2 r \cos \Delta \sin 2\theta}{r^2 + 1} \right]$$

(8)

This relation is confirmed experimentally. Nanocrystal aggregates formed spontaneously in a solution of rhodamine 6G molecules (which serve as the Raman scatterers), and deposited on an indium tin oxide slide meshed with gold grids. The low concentration of molecules used ensures that each aggregate contains no more than a single molecule [102]. Figure 12(a) shows a SEM image of a dimer. It is seen that the angle of the dimer axis is ~130° with respect to the $x$-axis. A R6G molecule sits in the dimer gap. The SERS intensity of the molecule is measured by rotating the 1/2 wave plate, which is shown in Figure 12(b). It is indicated that the maximum Raman intensity (black and red dots) corresponds to the orientation of the dimer. This means that the favorite incident polarization of the laser for the enhancement is along the dimer axis for both Raman shifts (773 and 1650 cm$^{-1}$). This is consistent with the prediction of $g_{yy} \gg g_{yx}$ in the dimer system as there is almost no field enhancement for perpendicularly polarized excitation. The green line is the result of the generalized Mie theory calculation of the normalized local field enhancement factor at $\lambda = 532$ nm, using the geometry from the SEM image as the only input. The agreement of the calculation with the experimental result confirms the relation (9). This relation is also satisfied in the particle-nanowire coupled system as shown in Figure 13 [103]. The calculated SERS enhancements

Figure 12. Polarization response of a nanocrystal dimer. (a) A SEM image showing a dimer of nanoparticles. (b) Normalized SERS intensity at 555 nm (black squares) and 583 nm (red circles) as a function of the angle of rotation by the 1/2 wave plate. Figure adapted from Ref. [12].
between particle and the wire are in good agreement with the experimental measurements. The calculated intensities are found to be proportional to \( \cos^2 \theta \), which is equivalent to \( \sin^2 \theta \) as the orientation is along the \( x \)-axis.

### 3. Manipulation of light polarization

Besides the effect of the field enhancement, SPs excited in nanoparticles can also modulate the polarization of the emission from individual molecules adsorbed on nanoparticles. This modulation can be achieved by a nanocrystal trimer rather than a dimer, as the enhanced Raman of a molecule from a dimer is always polarized along the dimer axis due to the symmetry of the dimer system [104]. With a third nanoparticle close to the dimer, the polarization of the Raman light can be wavelength-dependently rotated with respect to the original dimer axis [12]. This phenomenon is highly correlated to the coupling of the SPs between nanoparticles, which is induced by the molecule dipole in one of the ‘hot sites’ in the aggregates. The degree of the polarization rotation can be sensitively modulated by the separations and sizes of nanoparticles. The degree of the polarization is defined by the depolarization ratio \( \rho = (I_{||} + I_{\perp})/(I_{||} + I_{\perp}) \). Inserting (7), we obtain:

![Figure 13. SERS intensity as a function of polarization angle \( \theta \) defined in the inset for different shape particles adjacent to a wire. The SEM images of the wire-particle system investigated are shown on the left, and the electric field distributions are shown on the right for perpendicular polarization (upper plot) and parallel polarization (lower plot). The scale bar in the SEM images is 1 \( \mu \)m in (a) and 200 nm in (b) and (c). Figure adapted from Ref. [103].](image-url)
The $\rho$ depends only on the emission enhancement tensor $g'$. For the dimer case, $\rho = -\cos 2\theta$. The depolarization ratio reaches its maximum values of ±1 at directions parallel (+1) and perpendicular (−1) to the dimer axis, indicating that the scattered light is linearly polarized, as shown in Figure 14.

In contrast to dimer antennas, the third nanoparticle in the trimer breaks the axial symmetry of the dimer. SPs induced by the incident laser and the molecule dipole oscillation are changed as a consequence. For the SPs at the laser frequency, the electric field distribution for a trimer system with different incident polarization of the laser is shown Figure 15. The electric field in the junction between the second and third particles is oriented along the pair axis irrespective of the polarization of the incident laser (see white arrows in the left figures). For the SPs induced by the molecule dipole, only the component of the dipole parallel to the pair axis can be amplified significantly by the trimer. This is because the parallel oscillation is able to excite the SPs more efficiently. So the tensors $g$ and $g'$ still have the form as in (7), and both $g_{xy}$ and $g_{yy}$ are none zero. The depolarization will be related to the ratio $r'$, which is wavelength dependent.

A trimer antenna is shown in Figure 16. Figure 16(a) is the SEM image of this trimer. The SERS intensity at 555 nm (black squares) and 583 nm (red circles) is shown in Figure 16(b) as a function of the angle of rotation by the 1/2 wave plate. The intensity profile reaches its maximum at an angle of $\sim75^\circ$, which is close to the axis of the first and second nanoparticles. However, the depolarization ratio profiles do not coincide with each other, as shown in Figure 16(c). In addition, they are both rotated with respect to the intensity profile. The depolarization pattern of the 555 nm light is rotated by $\sim45^\circ$, while the 583 nm light is rotated by $\sim75^\circ$.

\[
\rho = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp} = \frac{(r'^2 - 1) \cos 2\theta + 2r' \cos \Delta' \sin 2\theta}{r'^2 + 1^2}
\]
The calculations are performed by assuming that the molecule is placed in each of the three possible junctions in turn. Only when the molecule is set in the junction marked with a red arrow in Figure 16(a), the calculated and experimental results are in good agreement for both the normalized intensity and depolarization. It also confirms the assumption that only one molecule in the junction contributes

**Figure 15.** The local field in one of the junctions of a nanocrystal trimer shown in the upper right inset. The 2D distributions of the light intensity in the red square area are presented on the left. The upper and lower panels show the cases of an external electric field-oriented parallel and perpendicular to the dimer axis, respectively. The polarization of the incident laser is shown by the green arrow. White arrows depict the direction of the enhanced local field. The lower right inset shows the enhancement of the light intensity at the center of the junction between the second and third nanoparticles as a function of the polarization of the incident laser ($\lambda = 532$ nm). The red and black curves are for the cases of trimer and dimer (without the first particle), respectively. Figure adapted from Ref. [12].

**Figure 16.** Polarization response of a nanocrystal trimer. (a) SEM image of the trimer. The red arrow indicates the position of the molecule. (b) Normalized SERS intensity at 555 nm (black squares) and 583 nm (red circles) as a function of the angle of rotation by the 1/2 wave plate. (c) Depolarization ratio ($\rho$) measured at 555 nm (black squares) and 583 nm (red circles). Figure adapted from Ref. [12].

The calculations are performed by assuming that the molecule is placed in each of the three possible junctions in turn. Only when the molecule is set in the junction marked with a red arrow in Figure 16(a), the calculated and experimental results are in good agreement for both the normalized intensity and depolarization. It also confirms the assumption that only one molecule in the junction contributes
to the signal. What should be noted is that this counterintuitive wavelength-dependent polarization rotation is not an accident. The rotation only exists in the cases when the number of particles is larger than two.

The influence of the third nanoparticle is demonstrated in Figure 17. The depolarization of the emission from a dipole is indicated by a red arrow with the wavelength at 555 and 583 nm, respectively. Different distances from the third nanoparticle to the dimer are considered. When the third particle is far away from the dimer (e.g. \( d = 200 \) nm), the property of the depolarization is just like a dimer which is shown by the green curve in Figure 17(b). However, as the third particle moves close to the dimer, the polarization of the emission is rotated effectively with respect to the original dimer axis due to the increasing coupling of the SPs between the third particle (?) and the other two. The degree of the rotation is obviously wavelength-dependent. Simulations above indicate, (i) laser-induced SP in the trimer can create a quasi-isotropic 'hot site' [105,106], (ii) the molecule dipole-induced SP may cause the rotation of the polarization of Raman scattering light, just like we observed in the experiment shown in Figure 17.

The size of the third particle could also have an effect on the SPs excited in the aggregates, which is shown in Figure 18. A third particle with a fixed distance to the dimer radius is varied from 1 to 100 nm, while we still assume the dipole is in the junction of the dimer (between the first and second). When the size of the third nanoparticle is small, the influence of the third particle on the SP of the dimer is very weak, hence the depolarization of the dipole emission is still along the dimer axis. Only when the size of the third particle is relatively large, the behavior of the depolarization deviates from the dimer. Even more interesting, an overall rotation about \( 2\pi \) could be achieved by tuning the distance of third

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**Figure 17.** Polarization rotation as a function of the position of the third particle in a trimer. (a) A calculation showing the polarization rotation as the blue particle in the inset diagram approaches the other two particles. (b) depolarization ratio patterns for \( d = 200, 1.1 \) and 0.5 nm (green, red, and black, respectively). The red arrow indicates the position of the dipole assumed in the calculation. The upper left inset shows the definition of the polarization angle \( \theta \) of the emission. Figure adapted from Ref. [12].
A model for the 1/2 wave plate at the nanoscale is proposed as shown in Figure 19, where the depolarization ratio strongly depends on the position of the third particle. For the linear trimer, in Figure 19(a), the emitted light from the nanoparticle to the original dimer, which actually acts as an equivalent 1/2 wave plate for the Raman emission.

Figure 18. Polarization rotation as a function of the size of the third particle in a trimer. The red arrow indicates the position of the dipole assumed in the calculation. All interparticle distance constants are 1 nm. Figure adapted from Ref. [12].
The polarization angle and the maximum depolarization ratio $\rho_{\text{max}}$ as a function of the wavelength of the dipole emission for the right angle configuration of the silver trimer antenna. The separation between the first and the second particle is 1 and 5 nm, respectively. The separation between the second and the third ones is always 1 nm. Black arrows in the insets: representations of the dipolar polarization excited in each particle. Figure adapted from Ref. [107].

antenna is linearly polarized along the axis, identical to the dimer case. However, the polarization is rotated clockwise when the third particle is positioned to the right of the middle one as shown in Figure 19(b). If the three particles are oriented in an equilateral triangle, the polarization would rotate back due to the symmetric coupling in the trimer, as shown in Figure 19(c). Figure 19(d) shows the polarization angles with respect to the position of the third particle moved around the other two, which indicates a $\sim$40° rotation of the polarization.

Not only the orientation of polarization, but the ellipticity of the far-field emission from trimer antennas can be tuned effectively. The polarization angle and the maximum depolarization ratio $\rho$ as a function of the wavelength of the dipole emission for the right angle configuration of the silver trimer antenna are shown in Figure 20. At the short wavelength, the polarization rotates counterclockwise relative to the dimer axis, while clockwise at long wavelength of the dipole emission. A phase transition occurs around 520 nm, which corresponds to the plasmonic resonance of the trimer. On one hand, the polarization rotation shifts sharply from $-30^\circ$ to $40^\circ$ at the phase transition. On the other hand, the emission from the trimer antenna is almost circularly polarized with the ellipticity $\sim$0.96, which indicates a possibility of 1/4 wave plates plate at the nanometer scale. This phenomenon could also be the origin of the plasmonic circular dichroism (CD), such as Raman optical activity (ROA) of trimers, which is proved experimentally by Chuntonov and Haran [108].

The polarization state of Raman-scattered light measured in the far field can provide information about the interaction of the electromagnetic field generated by a molecule and the plasmon modes of nanoantennas [106]. The origin of this plasmonic ROA in the molecule-aggregates system is also the nanoantenna effect.
of asymmetric particles excited by the Raman emission of the molecule [107]. As mentioned above, in the case of a dimer, this polarization is always aligned along the dimer axis and linear. As for an equilateral triangular trimer, in which only one plasmonic mode is excited, the polarization of the Raman-scattered light of a molecule situated in one of the gaps is similar to the dimer case. Only for an asymmetric antenna, a circular polarized Raman emission is possible [109].

The single-molecule ROA may open a new perspective on the characterization for structural biology and the pharmaceutical industry [110]. Actually, the local field in the nanogap of aggregates could also have CD characteristics, which might result in incident circular polarization ROA [111] and local scattering optical activity [112]. For example, the large scattering optical activity has been observed locally in random fractal aggregates of silver nanoparticles by photon scanning tunneling microscopy. Optical activity of aggregates has been simulated to reproduce the experiment observations [112–114]. However, in the complicated system of coupled nanoparticles [115,116], fundamental insight into the relation between the near field and geometry under the excitation of circularly polarized light is beneficial for the design of plasmonic CD or ROA nanostructures.

The near-field enhancement of the hotspot in a right angle trimer is highly dependent on the polarization rotation, that is, the local CD originating from the near-field interference in the strongly coupled particle system. According to the definition of CD signals for far-field transmission or reflection [109], the local CD can be evaluated by the parameter $\rho$, which is defined as $\rho = (M_{\text{RCP}} - M_{\text{LCP}})/(M_{\text{RCP}} + M_{\text{LCP}})$. The field enhancement at the gap for left-hand circularly polarized light (LCP) and right-hand circularly polarized light (RCP) excitation will be $M_{\text{LCP}}$ and $M_{\text{RCP}}$, respectively. In Figure 21, a near unity $\rho$ is obtained in the right angle trimer excited at $\lambda = 532$ nm, where the near-field excited by RCP is much larger than the LCP case. For the asymmetric trimer

Figure 21. (a) Electric field intensity distributions around the interparticle junction in the right angle trimer excited by LCP and RCP at 532 nm, respectively. (b) Local field intensity and local CD response $\rho$ (black curve, to the right axis) at the hotspot in the interparticle junction as a function of the incident wavelength. Figure adapted from Ref. [101].
In the case, the near-field intensity in the gap could differ up to 1000 times depending on the handedness of light. If a non-chiral molecule is situated in a symmetric dimer, the interaction between the molecule and nanoparticles would result in a far-field plasmonic CD.

This phenomenon exists widely in non-identical trimers, and can be tuned by the rotation of the third particle around the second particle and the interparticle distance. Figure 22(a) shows how the near-field enhancement and CD response \( \rho \) change with the rotation of the third particle around the dimer. When the third particle is rotated around the dimer, a \( C_{2v} \) trimer is formed. Both \( A_1 \) and \( B_2 \) plasmon modes can be excited and result in considerable field enhancement in the dimer gap, irrespective of the incident polarization. Consequently, the local CD response \( \rho \) grows with the

**Figure 22.** Local CD response as a function of the geometry. (a) Local field intensity and CD response at the hotspot as a function of the rotation of the third particle around the second particle. (b) Local field intensity and CD response at the hotspot as a function of the distance \( d \) between the third and second particle. Figure adapted from Ref. [101].

**Figure 23.** Local CD response in different dielectric environments. Black, red and green curves are the trimer in air, water, and oil, with the refractive index \( n_s = 1, 1.33, \) and 1.5, respectively. Figure adapted from Ref. [101].
increase of $\theta$ and reaches its maximum around 90°. After passing 90°, local CD response $\rho$ drops rapidly to zero again when $\theta = 120°$. $\rho$ is also related to the magnitude of the coupling between the second and third particles, which can be tuned by the gap separation $d$ between the second and third particles. As shown in Figure 22(b), when $d$ is only several nanometers, the near-field enhancement for RCP excitation is much larger than the LCP case.

Another important parameter influencing the SP coupling is the environment. Figure 23 shows the spectrum of $\rho$ for the right angle trimer in air, water, and oil. The peak of the wavelength-dependent $\rho$ has an obvious red-shift with increasing $n_s$. Similar to the resonance shift in SP resonance sensors, the CD response in the gap in asymmetric structures is quite sensitive to the environment implying the application of asymmetric nanoantenna to sensitive sensing [22,44,117–119].

**Figure 24.** Coupling between free-space photons and nanowire plasmons. The SPs are launched at a metallic particle adjacent to the nanowires (a), at one end of the nanowire (b), at the kink (c), and at the other end of the nanowire (d). Red arrows show the incident polarization. Figure adapted from Ref. [17].
4. Nanoantenna and waveguiding effects on SERS

Plasmonic waveguides have recently been the subject of intense focus due to their potential applications in miniaturized optical devices for nanoelectronics and nanophotonics [120–126]. Basic optical properties of propagating SPs have been carried out. It was found that the Fabry–Pérot resonances of the forward- and backward-propagating plasmons on the nanowires generate directional emission from the nanowire waveguide [18,127]. The directional emission is also observed by the technique of back confocal Fourier imaging [34]. Depending on the termination shape, a nanowire can serve as either a polarization maintaining waveguide, or a nanoscale polarization-rotating 1/2 plate [128]. Moreover, nanowire-based splitters, routers [121–123] and modulators [19], and even interferometric logic functions have been accomplished [129,130]. The propagating SPs can be coupled in and out through the coupling between a nanoparticle and the nanowire as shown in Figure 24.

This strong coupling could result in the conversion of propagating SPs to highly localized SPs. If a molecule resides in the gap between the particle and wire, strong SERS can be anticipated. As shown in Figure 25, a silver nanowire is attached to

Figure 25. Remote-excitation SERS of MGITC molecules excited through propagating plasmons. (a) SEM image of a nanowire-nanoparticle system. (b) The corresponding optical image. (c) The optical image of the launching and emitting spots. (d) The corresponding Raman image at the Raman peak of 436 cm\(^{-1}\). (e) Raman spectra from the laser spot at the left end of the nanowire and the remote site of the wire/particle junction, respectively. (f) The fluorescence background image of smooth indium tin oxides glass only. (g) The Raman image after background subtraction of panel d from panel f. (h) The remote-excitation SERS spectrum after fluorescence background correction. Figure adapted from Ref. [131].
a nanoparticle. The SPs are excited from the left end of the wire, propagate along the wire and re-emits to the free space at the particle position. A molecule MGITC with a very low concentration is covered on the particle-wire system. It is shown that in Figure 25(e), there is no Raman signal at the excitation end. Surprisingly, the SERS is significant at the particle site, although the incident power is much larger than at the remote site where the particle is. This is direct proof that the SERS is from molecule in the gap between the particle and the wire, rather than the Raman propagating from the excitation at the end. The nanoantenna effect on the SERS is evaluated as shown in Figure 26. For the receiving antenna effect, there is a huge near-field enhancement at the junction of the particle-wire as shown in Figure 26(a). For the emitting antenna effect, Figure 26(b) clearly shows the emission enhancement at the junction. The calculated remote-excitation SERS enhancement at the hotspot can be as high as $10^7 - 10^8$, which may be sufficient for the detection of a few molecules at their resonant frequency. The SERS using propagating plasmons as a remote excitation allows for remote-excitation SERS sensing. As there is no direct excitation at the site where the molecule is, this new method of SERS has a great potential to expand ultrasensitive chemical detection.
and biosensing. It can possibly also be used to probe the greater complexity of intracellular responses at the molecular level in situ, such as an immunological challenge and neural cell signal generation.

5. Summary

Plasmonic antennas have shown the unique ability to manipulate light properties at the nanoscale. With the help of SP coupling, the light intensity, direction and polarization can be well tailored. The enhancement of SERS in particular is highly related to the antenna effects. On one hand, the coupled nanostructures acting as receiving antennas enhance the near field enormously. On the other hand, the emitting antenna effect amplifies the emission from molecule Raman scattering. These two effects can contribute enormous SERS enhancement even for single molecule SERS. We quantify the SERS factor by introducing a simple model including the receiving and emitting antenna effects represented by the corresponding enhancement factors. It is shown that the SERS factor is proportional to the cosine square of the polarization angle, which is the consequence of the receiving antenna effect. The polarization of the SERS emission can be manipulated with designed asymmetric antennas, which is a consequence of the emitting antenna effect. Such effects can make the traditional 1/2 and 1/4 wave plates miniaturized to the nanometer scale, Far-field ROA and near-field CD, and will eventually enable the manipulation of the light polarization at the single molecule light scattering and single photon level. A nanoantenna can also be excited by propagating SP in a nanowaveguide. Remote excitation of single molecule SERS is realized, which may open a new area of single molecule SERS. Although there are still a lot of unsolved problems, there is no doubt that, nanoantennas as a new subject will be further developed, and more applications will be found in, ultra-sensitive sensor, biosensing, integrated photonic devices, etc.

Disclosure statement

No potential conflict of interest was reported by the authors.

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References

[1] J.J. Greffet, Science 308 (2005) p.1561.
[2] P. Mühlenschlegel, H.J. Eisler, O.J.F. Martin, B. Hecht and D.W. Pohl, Science 308 (2005) p.1607.
[3] N.J. Halas, S. Lal, W.S. Chang, S. Link and P. Nordlander, Chem. Rev. 111 (2011) p.3913.
[4] L. Yang, H. Wang, Y. Fang and Z. Li, ACS Nano 10 (2016) p.1580.
[5] V. Giannini, A.I. Fernandez-Domínguez, S.C. Heck and S.A. Maier, Chem. Rev. 111 (2011) p.3888.
[6] M. Schnell, A. García-Etxarri, A.J. Huber, K. Crozier, J. Aizpurua and R. Hillenbrand, Nat. Photonics 3 (2009) p.287.
[7] H.X. Xu, E.J. Bjerneld, M. Käll and L. Börjesson, Phys. Rev. Lett. 83 (1999) p.4357.
[8] Z. Zhang, A. Weber-Bargioni, S.W. Wu, S. Dhuey, S. Cabrini and P.J. Schuck, Nano Lett. 9 (2009) p.4505.
[9] D.P. Fromm, A. Sundaramurthy, P.J. Schuck, G. Kino and W.E. Moerner, Nano Lett. 4 (2004) p.957.
[10] Z.Y. Fang, Q.A. Peng, W.T. Song, F.H. Hao, J. Wang, P. Nordlander and X. Zhu, Nano Lett. 11 (2011) p.893.
[11] P. Ghenuche, S. Cherukulappurath, T.H. Taminiau, N.F. van Hulst and R. Quidant, Phys. Rev. Lett. 101 (2008) p.116805.
[12] T. Shegai, Z.P. Li, T. Dadosh, Z. Zhang, H.X. Xu and G. Haran, Proc. Natl. Acad. Sci. U.S.A. 105 (2008) p.16448.
[13] A.G. Curto, G. Volpe, T.H. Taminiau, M.P. Kreuzer, R. Quidant and N.F. van Hulst, Science 329 (2010) p.930.
[14] M. Ringler, A. Schwemer, M. Wunderlich, A. Nichtl, K. Kurzinger, T.A. Klar and J. Feldmann, Phys. Rev. Lett. 100 (2008) p.203002.
[15] A. Kinkhabwala, Z.F. Yu, S.H. Fan, Y. Avlasevich, K. Mullen and W.E. Moerner, Nat. Photonics 3 (2009) p.654.
[16] J.N. Farahani, D.W. Pohl, H.J. Eisler and B. Hecht, Phys. Rev. Lett. 95 (2005) p.017402.
[17] M.W. Knight, N.K. Grady, R. Bardhan, F. Hao, P. Nordlander and N.J. Halas, Nano Lett. 7 (2007) p.2346.
[18] Z.P. Li, F. Hao, Y.Z. Huang, Y.R. Fang, P. Nordlander and H.X. Xu, Nano Lett. 9 (2009) p.4383.
[19] Z.P. Li, S.P. Zhang, N.J. Halas, P. Nordlander and H.X. Xu, Small 7 (2011) p.593.
[20] Z.P. Li, K. Bao, Y.R. Fang, Z.Q. Guan, N.J. Halas, P. Nordlander and H.X. Xu, Phys. Rev. B 82 (2010) p.241402.
[21] Z.Y. Fang, L.R. Fan, C.F. Lin, D. Zhang, A.J. Meixner and X. Zhu, Nano Lett. 11 (2011) p.1676.
[22] Y. Xia and N.J. Halas, MRS Bull. 30 (2005) p.338.
[23] N. Grillot, D. Manchon, F. Bertorelle, C. Bonnet, M. Broyer, E. Cottancin, J. Lermé, M. Hillenkamp and M. Pellarin, ACS Nano 5 (2011) p.9450.
[24] Q. Zhang, J. Xie, J.Y. Lee, J. Zhang and C. Boothroyd, Small 4 (2008) p.1067.
[25] Y. Ma, W. Li, E.C. Cho, Z. Li, T. Yu, J. Zeng, Z. Xie and Y. Xia, ACS Nano 4 (2010) p.6725.
[26] J.A. Fan, C. Wu, K. Bao, J. Bao, R. Bardhan, N.J. Halas, V.N. Manoharan, P. Nordlander, G. Shvets and F. Capasso, Science 328 (2010) p.1135.
[27] L. Chuntonov and G. Haran, Nano Lett. 11 (2011) p.2440.
[28] K.-H. Su, Q.-H. Wei, X. Zhang, J.J. Mock, D.R. Smith and S. Schultz, Nano Lett. 3 (2003) p.1087.
[29] B.J. Wiley, Y.C. Chen, J.M. McLellan, Y.J. Xiong, Z.Y. Li, D. Ginger and Y.N. Xia, Nano Lett. 7 (2007) p.1032.
[30] C. Langhammer, B. Kasemo and I. Zoric, J. Chem. Phys. 126 (2007) p.194702.
[31] M. Rang, A.C. Jones, F. Zhou, Z.Y. Li, B.J. Wiley, Y.N. Xia and M.B. Raschke, Nano Lett. 8 (2008) p.3357.
[32] J. Nelayah, M. Kociak, O. Stephan, F.J.G. de Abajo, M. Tence, L. Henrard, D. Taverna, I. Pastoriza-Santos, L.M. Liz-Marzán and C. Colliex, Nat. Phys. 3 (2007) p.348.
[33] H.Y. Liang, Z.P. Li, W.Z. Wang, Y.S. Wu and H.X. Xu, Adv. Mater. 21 (2009) p.4614.
[34] T. Shegai, V.D. Miljkovic, K. Bao, H.X. Xu, P. Nordlander, P. Johansson and M. Käll, Nano Lett. 11 (2011) p.706.
[35] F. Svedberg, Z.P. Li, H.X. Xu and M. Käll, Nano Lett. 6 (2006) p.2639.
[36] R.C. Jin, Y.W. Cao, C.A. Mirkin, K.L. Kelly, G.C. Schatz and J.G. Zheng, Science 294 (2001) p.1901.
[37] J. Aizpurua, P. Hanarp, D.S. Sutherland, M. Käll, G.W. Bryant and F.J.G. de Abajo, Phys. Rev. Lett. 90 (2003) p.057401.
[38] F. Hao, C.L. Nehl, J.H. Hafner and P. Nordlander, Nano Lett. 7 (2007) p.729.
[39] H.H. Raether, Surface Plasmons, Springer, Berlin, 1988.
[40] K.G. Lee, H.W. Kihm, J.E. Kihm, W.J. Choi, H. Kim, C. Ropers, D.J. Park, Y.C. Yoon, S.B. Choi, H. Woo, J. Kim, B. Lee, Q.H. Park, C. Lienau and D.S. Kim, Nat. Photonics 1 (2007) p.53.
[41] P.J. Schuck, D.P. Fromm, A. Sundaramurthy, G.S. Kino and W.E. Moerner, Phys. Rev. Lett. 94 (2005) p.017402.
[42] T.H. Tamini, R.J. Moerland, F.B. Segerink, L. Kuipers and N.F. van Hulst, Nano Lett. 7 (2007) p.28.
[43] Z.P. Li, M. Käll and H. Xu, Phys. Rev. B 77 (2008) p.085412.
[44] B. Luk'yanchuk, N. I. Zheludev, S. A. Maier, N. J. Halas, P. Nordlander, H. Giessen, and C. T. Chong, Nat. Mater. 9 (2010), p. 707.
[45] S. Lal, S.E. Clare and N.J. Halas, Acc. Chem. Res. 41 (2008) p.1842.
[46] C. Loo, A. Lowery, N.J. Halas, J. West and R. Dreizk, Nano Lett. 5 (2005) p.709.
[47] Y.J. Bao, Z.J. Hu, Z.W. Li, X. Zhu and Z.Y. Fang, Small 11 (2015) p.2177.
[48] E. Ozbay, Science 311 (2006) p.189.
[49] R. Kirchain and L. Kimerling, Nat. Photonics 1 (2007) p.303.
[50] F.J. García de Abajo, J. Cordon, M. Corso, F. Schiller and J.E. Ortega, Nanoscale 2 (2010) p.717.
[51] W. Wang, Z.P. Li, B.H. Gu, Z.Y. Zhang and H.X. Xu, ACS Nano 3 (2009) p.3493.
[52] M. Fleischmann, P.J. Hendra and A.J. McQuillan, Chem. Phy. Lett. 26 (1974) p.163.
[53] D.L. Jeanmaire and R.P. Van Duyne, J. Electroanal. Chem. Interf. Electrochem. 84 (1977) p.1.
[54] M. Albrecht, M. Grant and J.A. Creighton, J. Am. Chem. Soc. 99 (1977) p.5215.
[55] M. Moskovits, Rev. Mod. Phys. 57 (1985) p.783.
[56] D.K. Lim, K.S. Jeon, H.M. Kim, J.M. Nam and Y.D. Suh, Nat. Mater. 9 (2010) p.60.
[57] D.K. Lim, K.S. Jeon, J.H. Hwang, H. Kim, S. Kwon, Y.D. Suh and J.M. Nam, Nat. Nanotechnol. 6 (2011) p.452.
[58] J.W. Oh, D.K. Lim, G.H. Kim, Y.D. Suh and J.M. Nam, J. Am. Chem. Soc. 136 (2014) p.14052.
[59] R. Zhang, Y. Zhang, Z.C. Dong, S. Jiang, C. Zhang, L.G. Chen, L. Zhang, Y. Liao, J. Aizpurua, Y. Luo, J.L. Yang and J.G. Hou, Nature 498 (2013) p.82.
[60] N.G. Greenelth, M.G. Blaber, G.C. Schatz and R.P. Van Duyne, J. Phys. Chem. C 117 (2013) p.2554.
[61] J. Zhao, J.A. Dieringer, X.Y. Zhang, G.C. Schatz and R.P. Van Duyne, J. Phys. Chem. C 112 (2008) p.19302.
[62] S.Y. Ding, J. Yi, J.F. Li, B. Ren, D.Y. Wu, R. Panneerselvam and Z.Q. Tian, Nat. Rev. Mater. 1 (2016) p.16021.
[63] M.F. Mrozek, D. Zhang and D. Ben-Amotz, Carbohydr. Res. 339 (2004) p.141.
[64] H. Wang and N.J. Halas, Adv. Mater. 20 (2008) p.820.
[65] L.K. Yang, Z.P. Li, P.J. Wang, L.S. Zhang and Y. Fang, Plasmonics 9 (2014) p.121.
[66] C.L. Haynes, A.D. McFarland and R.P. Van Duyne, Ana. Chem. 77 (2005) p.338A.
[67] H. Lee, G.H. Kim, J.H. Lee, N.H. Kim, J.M. Nam and Y.D. Suh, Nano Lett. 15 (2015) p.4628.
[68] P.P. Patra and G.V.P. Kumar, J. Phys. Chem. Lett. 4 (2013) p.1167.
[69] K. Kneipp, Y. Wang, H. Kneipp, L.T. Perelman, I. Itzkan, R. Dasari and M.S. Feld, Phys. Rev. Lett. 78 (1997) p.1667.
[70] Y.W.C. Cao, R.C. Jin and C.A. Mirkin, Science 297 (2002) p.1536.
[71] H.X. Xu, J. Aizpurua, M. Käll and P. Apell, Phys. Rev. E 62 (2000) p.4318.
[72] J.F. Li, Y.F. Huang, Y. Ding, Z.L. Yang, S.B. Li, X.S. Zhou, F.R. Fan, W. Zhang, Z.Y. Zhou, Y. Wu de, Z.L. Wang and Z.Q. Tian, Nature 464 (2010) p.392.
[73] M. Fan, G.F. Andrade and A.G. Brolo, Anal. Chim. Acta. 693 (2011) p.7.
[74] E.C. Le Ru and P.G. Etchegoin, Annu. Rev. Phys. Chem. 63 (2012) p.65.
[75] J.H. Lee, M.H. You, G.H. Kim and J.M. Nam, Nano Lett. 14 (2014) p.6217.
[76] H. Chen, Z. Sun, W. Ni, K.C. Woo, H.Q. Lin, L. Sun, C. Yan and J. Wang, Small 5 (2009) p.2111.
[77] P.K. Jain, W. Huang and M.A. El-Sayed, Nano Lett. 7 (2007) p.2080.
[78] I. Romero, J. Aizpurua, G.W. Bryant and F.J. García De Abajo, Opt. Express 14 (2006) p.9988.
[79] K.J. Savage, M.M. Hawkeye, R. Esteban, A.G. Borisov, J. Aizpurua and J.J. Baumberg, Nature 491 (2012) p.574.
[80] J.A. Scholl, A. García-Etxarri, A.L. Koh and J.A. Dionne, Nano Lett. 13 (2013) p.564.
[81] J. Mertens, A.L. Eiden, D.O. Sigle, F. Huang, A. Lombardo, Z. Sun, R.S. Sundaram, A. Colli, C. Tserkezis, J. Aizpurua, S. Milana, A.C. Ferrari and J.J. Baumberg, Nano Lett. 13 (2013) p.5033.
[82] S. Kadhodazadeh, J.B. Wagner, H. Kneipp and K. Kneipp, Appl. Phys. Lett. 103 (2013) p.083103.
[83] W. Zhu and K.B. Crozier, Nat. Commun. 5 (2014) p.5228.
[84] H. Cha, J.H. Yoon and S. Yoon, ACS Nano 8 (2014) p.8554.
[85] S.F. Tan, L. Wu, J.K.W. Yang, P. Bai, M. Bosman and C.A. Nijhuis, Science 343 (2014) p.1496.
[86] F.J. García de Abajo, J. Phys. Chem. C 112 (2008) p.17983.
[87] J. Zuloaga, E. Prodan and P. Nordlander, Nano Lett. 9 (2009) p.887.
[88] T. Dong, X. Ma and R. Mittra, Appl. Phys. Lett. 101 (2012) p.233111.
[89] G. Toscano, S. Raza, S. Xiao, M. Wubs, A.-P. Jauho, S.I. Bozhevolnyi and N.A. Mortensen, Opt. Lett. 37 (2012) p.2538.
[90] T.V. Teperik, P. Nordlander, J. Aizpurua and A.G. Borisov, Phys. Rev. Lett. 110 (2013) p.263901.
[91] R. Esteban, A.G. Borisov, P. Nordlander and J. Aizpurua, Nat. Commun. 3 (2012) p.825.
[92] D.C. Marinica, A.K. Kazansky, P. Nordlander, J. Aizpurua and A.G. Borisov, Nano Lett. 12 (2012) p.1333.
[93] J.M. McMahon, S.K. Gray and G.C. Schatz, Nano Lett. 10 (2010) p.3473.
[94] C. David and F.J. García de Abajo, J. Phys. Chem. C 115 (2011) p.19470.
[95] T.V. Teperik, P. Nordlander, J. Aizpurua and A.G. Borisov, Opt. Express 21 (2013) p.27306.
[96] M.S. Tame, K.R. McEnery, Ş.K. Özdemir, J. Lee, S.A. Maier and M.S. Kim, Nat. Phys. 9 (2013) p.329.
[97] Y. Luo, A.I. Fernandez-Dominguez, A. Wiener, S.A. Maier and J.B. Pendry, Phys. Rev. Lett. 111 (2013) p.093901.
[98] T. Shegai, S. Chen, V.D. Miljković, G. Zengin, P. Johansson and M. Käll, Nat. Commun. 2 (2011) p.481.
[99] M. Moskovits, L. L. Tay, J. Yang and T. Haslett, Optical Properties of Nanostructured Random Media, Springer, Berlin, Vol. 82, p. 215, 2002.
[100] L. Landau, E. Lifchitz and L. Pitaevskii, Electromagnetics of Continuous Media, Pergamon, Oxford, 1984.
[101] H. Wang, Z. Li, H. Zhang, P. Wang and S. Wen, Sci. Rep. 5 (2015) p.8207.
[102] E.C. Le Ru, M. Meyer and P.G. Etchegoin, J. Phys. Chem. B 110 (2006) p.1944.
[103] H. Wei, F. Hao, Y.Z. Huang, W.Z. Wang, P. Nordlander and H.X. Xu, Nano Lett. 8 (2008) p.2497.
[104] T.O. Shegai and G. Haran, J. Phys. Chem. B 110 (2006) p.2459.
[105] H.X. Xu, J. Opt. Soc. Am. A 21 (2004) p.804.
[106] P.G. Etchegoin, C. Galloway and E.C. Le Ru, Phys. Chem. Chem. Phys. 8 (2006) p.2624.
[107] Z. Li, T. Shegai, G. Haran and H. Xu, ACS Nano 3 (2009) p.637.
[108] L. Chuntonov and G. Haran, Nano Lett. 13 (2013) p.1285.
[109] L. Chuntonov and G. Haran, MRS Bull. 38 (2013) p.642.
[110] L.D. Barron, F. Zhu, L. Hecht, G.E. Tranter and N.W. Isaacs, J. Nanopart. Res. 834–836 (2007) p.7.
[111] Y. Liu, R. Wang and X. Zhang, Opt. Express 22 (2014) p.4357.
[112] V.P. Drachev, W.D. Bragg, V.A. Podolskiy, V.P. Safonov, W.T. Kim, Z.C. Ying, R.L. Armstrong and V.M. Shalaev, J. Opt. Soc. Am. B 18 (2001) p.1896.
[113] H. Zhang and A.O. Govorov, Phys. Rev. B 87 (2013) p.075410.
[114] T. Wu, J. Ren, R. Wang and X. Zhang, J. Phys. Chem. C 118 (2014) p.20529.
[115] A.E. Schlather, N. Large, A.S. Urban, P. Nordlander and N.J. Halas, Nano Lett. 13 (2013) p.3281.
[116] Y. Tanaka, A. Sanada and K. Sasaki, Sci. Rep. 2 (2012) p.764.
[117] J.B. Lassiter, H. Sobhani, J.A. Fan, J. Kundu, F. Capasso, P. Nordlander and N.J. Halas, Nano Lett. 10 (2010) p.3184.
[118] A. Lovera, B. Gallinet, P. Nordlander and O.J.F. Martin, ACS Nano 7 (2013) p.4527.
[119] S.P. Zhang, K. Bao, N.J. Halas, H.X. Xu and P. Nordlander, Nano Lett. 11 (2011) p.1657.
[120] H. Ditlbacher, A. Hohenau, D. Wagner, U. Kreibig, M. Rogers, F. Hofer, F.R. Aussenegg and J.R. Krenn, Phys. Rev. Lett. 95 (2005) p.257403.
[121] P. Tuchscherer, C. Rewitz, D.V. Voronine, F.J. Garcia de Abajo, W. Pfeiffer and T. Brixner, Opt. Express 17 (2009) p.14235.
[122] X. Guo, M. Qiu, J.M. Bao, B.J. Wiley, Q. Yang, X.N. Zhang, Y.G. Ma, H.K. Yu and L.M. Tong, Nano Lett. 9 (2009) p.4515.
[123] Y.R. Fang, Z.P. Li, Y.Z. Huang, S.P. Zhang, P. Nordlander, N.J. Halas and H.X. Xu, Nano Lett. 10 (2010) p.1950.
[124] H. Wei, X.R. Tian, D. Pan, L. Chen, Z.L. Jia and H.X. Xu, Nano Lett. 15 (2015) p.560.
[125] H. Wei and H.X. Xu, Mater. Today 17 (2014) p.372.
[126] H. Wei, S.P. Zhang, X.R. Tian and H.X. Xu, Proc. Natl. Acad. Sci. U. S. A. 110 (2013) p.4494.
[127] Z.X. Wang, H. Wei, D. Pan and H.X. Xu, Laser Photon. Rev. 8 (2014) p.596.
[128] Z.P. Li, K. Bao, Y.R. Fang, Y.Z. Huang, P. Nordlander and H.X. Xu, Nano Lett. 10 (2010) p.1831.
[129] H. Wei, Z.P. Li, R. Tian, Z.X. Wang, F.Z. Cong, N. Liu, S.P. Zhang, P. Nordlander, N.J. Halas, H.X. Xu, Nano Lett. 11 (2011) p.471.
[130] H. Wei, Z.X. Wang, X.R. Tian, M. Käll and H.X. Xu, Nat. Commun. 2 (2011) p.387.
[131] Y.R. Fang, H. Wei, F. Hao, P. Nordlander and H.X. Xu, Nano Lett. 9 (2009) p.2049.