Mirror-enhanced directional out-coupling of SERS by remote excitation of a nanowire-nanoparticle cavity

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Abstract

We report on the experimental observation of mirror-enhanced directional surface-enhanced Raman scattering (SERS) from a self-assembled monolayer of molecules coupled to a nanowire-nanoparticle (NW-NP) junction on a mirror in a remote excitation configuration. Placing the NW-NP junction on a metallic mirror generates multiple gap plasmon modes that have unique momentum space-scattering signatures. We perform Fourier plane imaging of the SERS from the NW-NP on a mirror to understand the effect of multiple hotspots on molecular emission. We systematically study the effect of the ground plane on the directionality of emission from the NW-NP junction and show that the presence of a mirror drastically reduces the angular spread of emission. The effect of multiple hotspots in the geometry on the directionality of the molecular emission is studied using 3D numerical simulations. The results presented here will have implications in understanding plasmon hybridization in the momentum space and its effects on molecular emission.

Keywords: plasmonic cavities, remote excitation, directional emission, surface enhanced Raman scattering

(Some figures may appear in colour only in the online journal)

1. Introduction

Controlling the photophysics of molecules has far-reaching implications in understanding many aspects of quantum physics [1] and in applications such as biomedical imaging [2], designing molecular antennas [3–5], and catalysis [6, 7]. A simple way to achieve this control is to couple molecules to confined optical fields like plasmonic cavities [8–10], whispering gallery microcavities [11], and Fabry–Pérot cavities [12].

When a molecular dipole is placed inside an optical cavity, its emission characteristics, such as rate of spontaneous emission [9, 13], polarization signatures [14, 15], and direction of emission [4, 14], can be influenced. The ability to engineer plasmon-matter interactions has been extensively utilized to design and develop optical antennas to direct optical emission from molecules [1, 5, 16]. An important aspect of optical antenna design is to achieve low angular spread without compromising the enhancement of light–molecule interactions. To this end, a variety of antennas have been studied to influence secondary emission from molecules and quantum dots [17–19].

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Of interest to this study is the emission of secondary photons through Raman scattering [20, 21]. Thanks to developments in nanoscale fabrication and synthesis, routing Raman scattered light from molecules by designing plasmonic geometries has gained prominence [22, 23]. Most of the studies in the context of Raman optical antennas use lithographically fabricated structures and arbitrarily couple molecules to ‘top–down’ nanostructures [24, 25]. A relatively less explored approach is to create Raman optical antennas by self-assembling chemically prepared colloidal nanostructures that are pre-coated with molecules. A molecule-coated particle can be placed near a plasmonic structure to utilize the localized electric field provided by the cavity formed between the particle and nanostructures for enhanced spectroscopies. A unique nanostructure in this regard is a one-dimensional plasmonic nanowire. Coupling a nanoparticle with a plasmonic nanowire [26–30] offers the possibility of remotely exciting the cavity using the nanowire as a waveguide, which eliminates the damage caused to the molecules in the direct excitation of the cavity [31–33]. Such geometries have been used in our past works to show enhanced directional spectroscopic signals [25, 34]. Placing the nanowire-nanoparticle (NW-NP) on a metallic mirror can generate a particle-mirror particle cavity with ultra-small mode volumes [35, 36]. These types of cavities formed using a mirror have been used for various purposes, such as strong coupling at room temperature [37], for large Purcell enhancement [38], and in tailoring the spectral signatures of two-dimensional materials [39]. In addition to the enhancement, metal substrates direct the majority of the emission to the collection objectives [16, 40, 41] because of the absence of leakage radiation, which occurs in using high refractive index substrates [1].

Motivated by this, we modify the geometry of a NW-NP junction used in our past studies [25, 34] by placing the junction on a gold mirror. As compared to our recent study [41] on an extended bent-plasmonic nanowire on a mirror (B-NWoM) cavity, the localized cavity in the NW-NP geometry provides superior control on the placement of molecules in the cavity. The absence of molecules at the excitation region allows us to remotely excite the molecules present only in the NW-NP cavity, as compared to the excitation of molecules throughout the extended cavity in the B-NWoM geometry. The fields generated in the NW-NP and NP on the mirror (NP-mirror) cavities enhance the Raman scattering from the molecules coated on the nanoparticle and also reduce the angular spread of emission, which is probed using Fourier plane imaging.

2. Materials and architecture of the system

Single crystalline silver nanowires were prepared using the polyl process [42]. The nanowires have a pentagonal cross-section with an average thickness (edge to edge) of ∼350 nm. Gold film with a thickness of 160 nm was deposited on a 2 nm chromium coated glass coverslip using thermal vapour deposition. Gold nanoparticles were purchased from Sigma Aldrich.

To coat the molecules on the nanoparticles, the particles were first cleaned with acetone several times to remove the surfactant coating from the particles. The particles were then soaked in 1 millimolar solution of biphenyl-4-thiol (BPT) in ethanol for 24 h. Because of the presence of a thiol bond, the molecules get strongly attached to the gold surface. The solution was then centrifuged and washed several times to remove the excess BPT molecules and then particles coated with the BPT molecules were transferred to an ethanol solution.

The NW-NP junction was prepared using a self-assembly technique [43]. Silver nanowires dispersed in ethanol solution were dropcasted on a gold mirror and left to dry. After this, molecules coated with gold nanoparticles were dropcasted on the gold substrate. Gold nanoparticles tend to sit near the nanowire, forming a self-assembled junction.

A schematic of the experimental configuration is shown in figure 1. One end of the silver nonwire (AgNW) was excited with a 633 nm laser using a 100×, 0.95 numerical aperture objective lens. AgNW surface plasmon polaritons (SPPs) get scattered by the NW-NP junction and out-couple as free space photons; they also excite the gap plasmons in the NW-NP cavity. By focusing light onto one end of the nanowire, we also excite SPPs on the metal film. These propagating plasmons on the metal film excite the gap mode between the nanoparticle and the mirror [44]. The gap plasmons generated at both the cavities enhance the Raman scattering signatures of the molecules coated on the NP and influence its far-field scattering signatures. Out-coupled free space emission only from the junction was collected by the same objective lens by spatially filtering the region and was projected onto the Fourier plane to study the spectral and wavevector signatures. For the complete experiment setup, refer to our previous works [41, 45].

![Schematic of the experimental configuration.](image-url)
3. Results and discussion

Figure 2(a)(i) shows the bright field image of a ~180 nm AuNP coated with BPT molecules, assembled near an AgNW with a thickness of ~350 nm placed on a 160 nm thick gold mirror. The black circle indicates the NW-NP junction. The corresponding scanning electron microscopy image of the junction is shown in figure 2(a)(ii). Figure 2(a)(iii) shows the same AgNW when one end was excited with a focused 633 nm laser polarized along the axis of the nanowire. SPPs on the AgNW and the metal film remotely excite the gap plasmons in the NW-NP and the NP-mirror cavities, respectively. Intense electric field in the cavities due to these generated gap plasmons results in enhanced Raman scattering from the BPT molecules coated on the particle. We used a thick nanowire, diameter ~350 nm, to get better waveguiding properties [46, 47], as we probed the NW-NP using a remote excitation mechanism. The size of nanoparticle was chosen such that the localized plasmon resonance of the NP overlapped with the wavelength of the excitation to generate maximum response from the system. The out-coupled SERS emission from the junction (shown in a white circle in figure 2(a)(iii)) was collected. The remotely excited SERS spectrum of the BPT molecules from the NW-NP junction on the mirror is shown in figure 2(b). The sharp Raman lines are clearly visible with a broad inelastic background emission. Since the molecules are present only on the nanoparticle, the SERS emission originates only from the junction and not from the nanowire on the mirror cavity.

To study the wavevector distribution of remotely excited SERS emission, we performed Fourier plane imaging [48–51], which quantifies the directionality of emission in terms of radial (θ) and azimuthal angles (ϕ). The Fourier plane image (figure 2(c)) shows that the maximum SERS emission is biased towards higher kx/k0. Along with the SERS emission from the BPT molecules, there can also be an inelastic background emission from the polyvinylpyrrolidone (PVP) coating [52] on the nanowire, which can also out-couple at higher angles. To further confirm that the majority of emission at higher +kx/k0 angles is the SERS emission from the molecules, we performed energy-momentum imaging [14, 53] on the emission from the junction. A small portion of the Fourier plane image along kx/k0 = 0 was projected onto the slit of the spectrometer and dispersed to get the image shown in figure 2(d). The energy-momentum image reveals that both the SERS signal and the inelastic background from the junction out-couples at higher wavevectors.

To quantify the emission, we defined directionality (Dir), using the ratio of forward and backward intensity of emission in the Fourier plane [54], as:

$$\text{Dir} = 10 \log_{10} \frac{\int \int (\theta_u + \delta_1, \phi_u + \delta_2) I(\theta, \phi) \sin(\theta) d\theta d\phi}{\int \int (\theta_u - \delta_1, \phi_u - \pi + \delta_2) I(\theta, \phi) \sin(\theta) d\theta d\phi},$$

where θm and φm are the radial and azimuthal angles with maximum emission. I(θ, ϕ) is the intensity in the Fourier plane image. For the black dotted region in the Fourier plane image, the calculated directionality is 8.0 ± 0.2 dB. The value of the
The intensity profiles of azimuthal angles ($\phi$) for $\theta$ corresponding to maximum intensity in the Fourier plane images show that the emission from a nanoparticle on a mirror cavity (blue curve) covers a large range of angles, whereas for the case of direct (black curve) and remote excitation (red curve) configurations, the emission is directed towards the higher $k_x/k_0$ values with comparable spreading in both the direct and remote excitation configuration.

To understand the effect of the ground plane on the SERS emission from the NW-NP junction, we studied the wavevector of emission from the NW-NP junction placed on a glass substrate. Figure 4(a) shows the bright field and transmission image of a BPT molecule coated ~180 nm AuNP assembled near an ~350 nm thick AgNW placed on a glass substrate. Upon excitation of one end using a 633 nm laser with polarization along the AgNW axis, the AgNW plasmons out-couple from the AgNW end and the NW-NP junction. The SERS emission from the junction (figure 4(b)) was spatially filtered and was projected onto the Fourier plane. The Fourier plane image (figure 4(c)) shows that the emission is biased towards the higher $k_x/k_0$ values, but the angular spread in emission is very broad as compared to the spreading in the presence of the gold substrate (see figure 2(c)).

We calculated the near-field electric field using the finite element method with COMSOL Multiphysics as a solver to study the effect of different hotspots on emission wavevectors. Fourier plane images were then calculated by projecting the near-field to the far-field using the reciprocity argument [55]. We placed oscillating $x$, $y$, and $z$ oriented dipoles to mimic the molecular emission at the hotspots of the geometry. The AgNW was modelled with a pentagonal cross-section with an edge-to-edge thickness of 350 nm and length of 5 $\mu$m. The AuNP of diameter 180 nm was placed at a distance of 5 nm from the AgNW. This 5 nm gap was to model the PVP coating on the AgNW and the molecular coating on the AuNP. The refractive indices of the material were taken from [56]. Figure 4(d) shows the calculated near-field electric field at the NW-NP junction placed on a glass substrate in a remote excitation configuration. One end of the AgNW was excited using a focused Gaussian laser of 633 nm. The field at the junction is only concentrated in the NW-NP cavity (shown as $\alpha$), from where the SERS signal will originate. To study the effect of this cavity on the emission wavevector, we placed oscillating $x$, $y$, and $z$ oriented dipoles at a wavelength of 703 nm in the NW-NP cavity and calculated the Fourier plane image after incoherently adding the far-field radiation patterns from individual dipoles. The wavelength of the dipolar source was set at 703 nm because the BPT molecules have a prominent Raman mode at this wavelength. The calculated Fourier plane image (figure 4(e)) corroborates the experimentally observed
wavevector distribution of the SERS. The emission is broad in terms of wavevectors and covers a large range of angles. In the case of the gold substrate, along with a large electric field at the NW-NP cavity, there is also a hotspot in the NP-mirror cavity (shown as $\beta$) (figure 4(f)). The presence of two cavities in the case of the NW-NP junction on the mirror geometry makes the SERS emission more enhanced (figure 2(b)) compared to the SERS intensity obtained with a glass substrate (figure 4(b)). In this case, we placed oscillating $x$, $y$, and $z$ oriented dipoles at a wavelength of 703 nm in both the NW-NP and NP-mirror cavities and incoherently added the far-field radiation patterns from individual dipoles. The calculated Fourier plane image (figure 4(g)) shows that the emission is biased towards the NW-NP junction and is confined to a narrow range of wavevectors. The results show the importance of metallic substrates for enhancement and directing of the SERS emission.

To study how the AgNW influences the SERS emission wavevectors, we studied the change in the directionality of the emission when the distance between the AgNW and the NP is varied. Figure 5 shows the geometry of the system used in the calculations. Oscillating $x$, $y$, and $z$ oriented dipoles at a wavelength of 703 nm ($\lambda$) were placed at the base of the NP and the calculated near-field electric field was projected to the far-field. The calculated Fourier plane images show that the emission wavevectors are directional in nature when the distance between the nanowire and nanoparticle is between $\lambda/100$ to $\lambda/10$ as the nanowire reflects the emission along higher $k_y$ values. Without the presence of the nanowire, the emission pattern from an isolated nanoparticle on the mirror cavity is isotropic in nature. When the distance between the nanoparticle is changed to $\lambda/3$, the emission was no longer directional in nature but was still biased towards the higher $k_y$ vectors. At a distance of $\lambda$, the influence of the AgNW on the emission wavevectors was minimal and the emission was no longer biased or directional in any specific direction because, at larger distances, the reflection from the AgNW reduces. This shows that the nanowire not only facilitates the SERS enhancement but also directs emission in a narrow range of angles.
Figure 5. Variation in the directionality of emission with varying distance between the nanoparticle and nanowire. (a) Geometry of the NW-NP on the mirror cavity with a distance ‘d’ between the nanowire and nanoparticle. The nanowire (350 nm thickness) and nanoparticle (180 nm diameter) were placed on a gold mirror. (b)–(f) Calculated Fourier plane image when the distance between the nanoparticle and nanowire was λ/100, λ/50, λ/10, λ/3, and λ, respectively. In each case, oscillating x, y, and z oriented dipoles at a wavelength of 703 nm (λ) were placed at the base of the nanoparticle and the Fourier plane image was calculated by incoherently adding the emission from individual dipoles.

4. Conclusion

To conclude, we have shown how unidirectional SERS emission can be achieved by a NW-NP junction on a mirror cavity in a remote excitation configuration. The nanowire and gold mirror help in providing enhancement and directing the SERS emission to a narrow range of wavevectors. Calculated forward-to-backward emission ratio for the SERS emission is ~8 dB. Three-dimensional numerical calculations reveal the influence of electromagnetic hotspots generated in the geometry on the wavevectors of out-coupled SERS emission. We believe that the results shown in this paper will be extrapolated for studying the strong interaction of molecules with extremely small cavities in remote excitation configurations. The NW-NP junction on a mirror excited by nanowire plasmons will be a good testbed for remote detection of single molecules and for studying quantum electrodynamics effects.

Data availability statement

The data underlying the results of this study are available from the corresponding author upon request.

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Conflict of interest

The authors declare no conflicts of interest.

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