
Molecular Plasmonics: Directional Optical Antennas and Single Molecule SERS

A thesis

*submitted in partial fulfilment of the requirements
for the degree of Doctor of Philosophy*

by

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CERTIFICATE

Certified that the work incorporated in the thesis entitled ("Molecular Plasmonics: Directional Optical Antennas and Single Molecule SERS") submitted by **Sunny Tiwari** was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other university or institution.



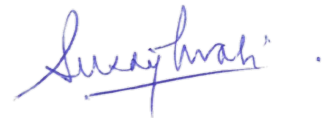
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Declaration

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Abstract

Interaction of light with metal nanoparticles creates large electric field intensity in a small region because of surface plasmons. This interaction also leads to the heating of metal particles because of Joule heating caused by interactions between electrons and phonons. Electric field enhancement provided by metallic structures have been used for understanding the fundamentals of enhanced light-molecular interactions and also for applications such as single molecule detection and strong coupling physics. Metal structures have also been shown to work as a subwavelength heating sources because of enhanced absorption and other thermoplasmonic properties. Concurrently harnessing the field enhancement and heating capabilities will open new avenues in utilization of metallic structures for fundamental studies as well for applications purposes.

In this thesis, first, we will discuss how field confinement is achieved by optical cavities formed in the gaps of two metallic structures. We study emissions such as fluorescence and surface enhanced Raman scattering (SERS) from molecules confined in optical cavities. Specifically, we image the molecular emission wavevectors using Fourier plane and energy-momentum imaging. We show that well designed optical cavities can be used to tune light-matter interaction for designing directional optical antennas for elastic or inelastic light scattering.

Next, we present how light induced heating of subwavelength metal particles can be harnessed for trapping a large number of metallic nanostructures at extremely low input power density. We utilized heat, and temperature gradients produced by a single heated metal nanoparticle to create a large-scale reversible assembly of metallic nanoparticles in a fluidic environment. Furthermore, we study SERS signatures from molecules in such assemblies, down to the level of single molecule limit. We apply bi-analyte technique to statistically confirm the spectroscopic signatures of single molecule SERS from the molecules in the assembly.

List of Publications

Included in thesis:

- **Sunny Tiwari**, Utkarsh Khandelwal, Vandana Sharma, and G V Pavan Kumar, Single Molecule SERS dynamics in a single nanoparticle-driven thermoplasmonic tweezer, *Journal of Physical Chemistry Letters* 12, 11910-11918 (2021)
- **Sunny Tiwari**, Adarsh B. Vasista, Diptabrata Paul, and G V Pavan Kumar, Mirror enhanced directional out-coupling of SERS by remote excitation of a nanowire-nanoparticle cavity, *Journal of Optics* 23(12), 124001 (2021)
- **Sunny Tiwari**, Adarsh B. Vasista, Diptabrata Paul, Shailendra K. Chaubey, and G V Pavan Kumar, Beaming Elastic and SERS Emission from Bent-Plasmonic Nanowire on a Mirror Cavity, *Journal of Physical Chemistry Letters* 12, 6589–6595 (2021)
- **Sunny Tiwari**, Chetna Taneja, and G V Pavan Kumar, Sub-wavelength plasmon polaritons channeling of whispering gallery modes of fluorescent silica microresonator, *Materials Research Bulletin*, 142, 111412 (2021)
- **Sunny Tiwari**, Chetna Taneja, Vandana Sharma, Adarsh B. Vasista, Diptabrata Paul, and G V Pavan Kumar, Dielectric microsphere coupled to a plasmonic nanowire: a self-assembled hybrid optical antenna, *Advanced Optical Materials*, 8(11), 1901672 (2020)

Not included in thesis:

- Vandana Sharma, **Sunny Tiwari**, Diptabrata Paul, Ratimanasee Sahu, Vijayakumar Chikkadi, and G V Pavan Kumar, Superdiffusive pulling, trapping, and assembly of colloids using nanowire plasmons, *Soft Matter*, 17, 10903-10909 (2021)
- Shailendra K. Chaubey, **Sunny Tiwari**, Gokul M. A., Diptabrata Paul, Atikur Rehman, and G V Pavan Kumar, Beaming of WS₂ Photoluminescence from a film coupled microsphere antenna, *arXiv:2110.10387*, (2021)

- Shailendra K. Chaubey, Gokul M. A., Diptabrata Paul, **Sunny Tiwari**, Atikur Rehman, and G V Pavan Kumar, Directional Emission from Tungsten Disulfide Monolayer Coupled to Plasmonic Nanowire-on-Mirror Cavity, *Advanced Photonics Research*, 2100002 (2021)
- **Sunny Tiwari**, Chetna Taneja, and G V Pavan Kumar, Plasmonic nanowire coupled to zero-dimensional nanostructures: A brief review, *Asian Journal of Physics*, (Review Article) 28(10-12), 961-981, (2020)
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- Adarsh B. Vasista, Harshvardhan Jog, Tal Heilpern, M.E. Sykes, **Sunny Tiwari**, Deepak K. Sharma, Shailendra K. Chaubey, G.P. Wiederrecht, S.K. Gray, and G V Pavan Kumar, Differential wavevector distribution of surface-enhanced Raman scattering and fluorescence in a film-coupled plasmonic nanowire cavity, *Nano Letters*, 18, 650-655 (2018)

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Dedicated to Jaun Elia

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Chapter 1

Introduction

Metal particles are known to confine light at subwavelength scales because of their ability to support surface plasmons[1–3]. Plasmonic cavities which are gaps between two closely spaced metallic structures create a region of large local electric field intensity[2, 4, 5]. This enhanced electric field is extensively harnessed to tune light-molecular interactions for fundamental studies as well as for applications such as molecular antenna[6], single molecule detection[7–11], and strong coupling physics[12–15].

Emission properties such as emission rates[16] and wavevectors[6, 17, 18] can be tailored by placing the molecules near well designed cavities. Emission wavevectors are probed to gain insights about molecular behaviour in confined regions. Wavevectors information is also needed in understanding the modes of cavities[6, 17], molecular orientation and dynamics,[19, 20] and in designing subwavelength optical antennas[6, 21].

Furthermore, subwavelength metallic particles can act as thermal sources as they provide very large heating at a low input power density because of enhanced absorption properties[22, 23]. Though earlier considered as a drawback, heating of plasmonic structures has turned out to be an advantageous property in the field of thermoplasmonics[22]. Heat produced by metallic particles have been utilized in harnessing the thermophoretic movement of charged molecules and particles[24, 25], to design optical traps[26–28], and in energy storage[29].

In this thesis, we utilize electric field enhancement by plasmonic particles to enhance and direct molecular emissions. We also show the utilization of heat produced by a single gold nanoparticle to create a thermoplasmonic tweezer. However, to present the content of the thesis in a more clear way, we first discuss molecular processes and various plasmonic effects that will be used frequently in the thesis.

1.1 Light-matter interaction at subwavelength scales

The free space radiation can be focused to subwavelength scales by utilizing metallic antennas[30]. The interaction of light with metallic particles excites plasmons, which are electronic clouds confined in a small region at metal-dielectric interface[1, 2]. Figure 1.1 shows the schematic of a spherical metal particle illuminated by light[31]. The dimension of the particle is considered to be much smaller than the wavelength of the light. The electric field of light drives the electrons in phase of the incoming frequency of light.

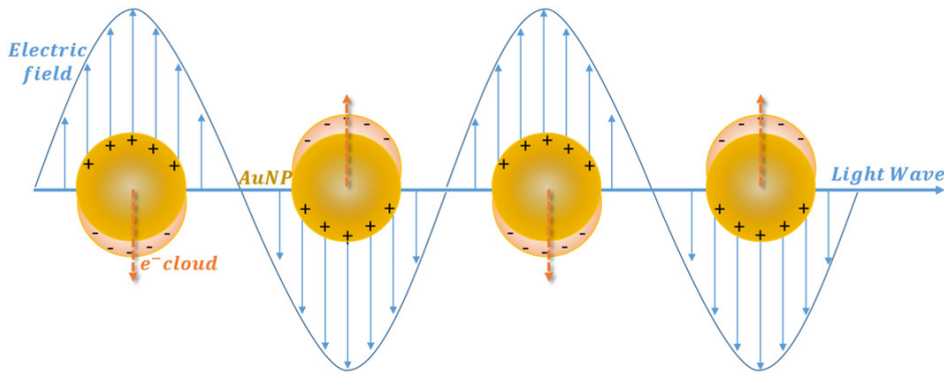


FIGURE 1.1: Schematic showing the oscillation of an electron cloud of a spherical gold particle with respect to the electric field. Figure reproduced from [31].

When the frequency of light matches with the natural frequency of the electronic cloud a resonance condition is achieved. This couples the energy of the incoming light to the electrons which creates a large electric field intensity near the metal-dielectric interface. The collective oscillations of electronic clouds excited by light are known as surface plasmon polaritons (SPPs) and it leads to enhanced absorption and scattering of light.

Placing molecules in a region of enhanced electric field intensity changes the molecular emission properties such as emission rates[2], polarization[32], and wavevectors[21, 33] of emission. Furthermore, optical hotspots or cavities created by placing two plasmonic structures confine light in ultra-small volumes[34] and thus provide a much larger electric field enhancement as compared to field provided by isolated metallic structures. Plasmonic cavities have been used for fundamental physics as well as for application based studies such as strong coupling[12, 15], single molecule surface enhanced Raman scattering[9], optical antenna[6, 35], and large Purcell enhancement[16].

The large electric field intensity in cavities has been used for tailoring molecular emissions such as fluorescence and Raman scattering which will be discussed in next sections. Furthermore, enhanced absorption because of the non-radiative interaction in

the plasmonic structures, such as electron-phonon interaction, is mainly responsible for heating the structure[36].



FIGURE 1.2: Schematic representing plasmon excitation in a gold nanoparticle as well as carrier relaxation and thermal dissipation to the environment upon illumination. Figure reproduced from [31]

The excited plasmon polaritons because of optical excitation, creates a non-equilibrium situation inside the nanoparticle. To restore the equilibrium, the electron-electron interaction takes place. The electrons also interact with phonons to redistribute some portion of energy which is shown in figure 1.2. The phonon-phonon interaction accounts for the dissipation of energy to the environment including the substrate. Finally, because of all these processes, the temperature of the particle increases as compared to the surrounding[36]. This leads to a temperature gradient in the system which can be harnessed for processes such as thermophoresis[22, 24, 25].

1.2 Molecular fluorescence

Molecular fluorescence is the process of relaxation of molecules from higher to lower energy states after optically absorbing electromagnetic radiation[2, 37]. A photon of energy E_L gets absorbed by the molecule present in the ground state S_0 , after which it goes to the state S_1 . The excitation of molecules using light is called optical excitation. As shown in figure 1.3, in each electronic state, there are vibrational sub-levels shown as v_0 , v_1 and so on. The molecule relaxes down to the ground state of S_1 after non-radiating transitions because of various relaxation processes such as solvent interaction and intra-molecular vibrational redistribution[2].

As can be seen in the fluorescence and absorption spectrum of Rhodamine 6G molecules (figure 1.3, right), the absorption is at lower wavelength and the emitted photons (E_S) are at higher wavelengths or at lower energies. The emission is broad in nature and the time scale of transitions are in nanoseconds. The emitted photons in the case of fluorescence are called Stokes shifted photons.

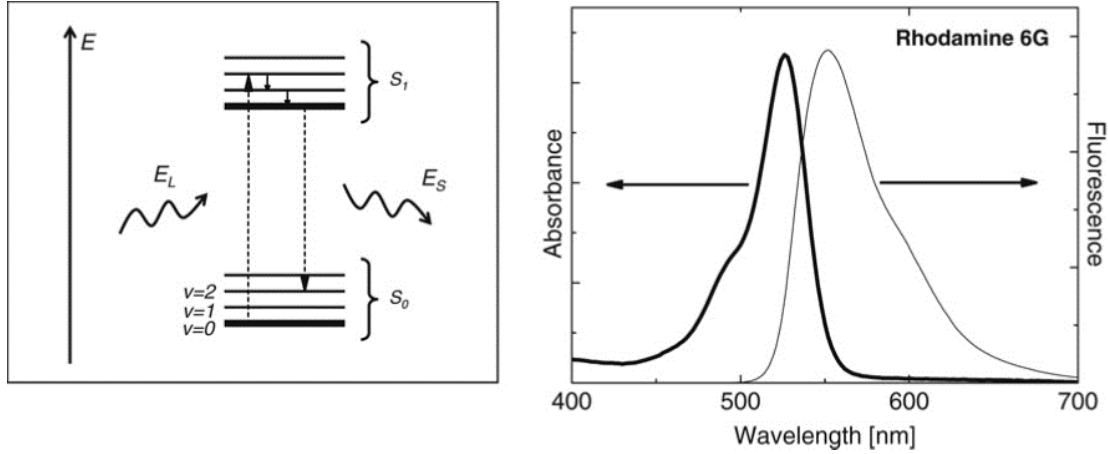


FIGURE 1.3: Schematic showing fluorescence process in a molecule (left). Absorption and fluorescence spectrum of Rhodamine 6G molecules (right). Figure reproduced from [2].

The intensity of the fluorescence radiation depends on the transition probability from the excited state S_1 to S_0 and is known as radiative decay rate. The probability of transition, Γ_{ij} , from state j to i depends on the number of states available, $\rho(f_{ij})$ to the molecule for transition and also to S_{ij} which is the transition matrix element.

It is calculated using Fermi's golden rule[38] as,

$$\Gamma_{ij} \propto S_{ij} \rho(f_{ij}) \quad (1.1)$$

The probability of transition can be increased by changing the environment of the molecules, which in turn changes the density of states available to the molecules. The molecules when subjected to a large local electric field intensity, undergo enhanced absorption. The absorption enhancement which directly effects the fluorescence intensity is related to local electric field intensity as[2],

$$M_{abs}(\omega) = 3 \left| \frac{\mathbf{E}_L}{\mathbf{E}_i} \right| (\mathbf{e}_{mol} \cdot \mathbf{e}_L(\omega))^2 \quad (1.2)$$

Where E_i is the incident electric field and E_L is the field intensity experienced by the molecule. e_{mol} represents the orientation of the molecule with respect to the polarization of the incoming light e_L having a frequency ω .

1.3 Raman scattering

Another type of molecular emission is Raman scattering[39, 40], which is a scattering process and involves an instantaneous emission of photons. In fluorescence, the absorption of a photon is necessary for the inelastic scattering but in Raman scattering,

the inelastic scattering can happen without actual absorption of a photon. Depending on the energy exchange between the incoming photons and molecules, Raman scattering can be divided into two categories:

Elastic scattering: When the energy of incoming photons is equal to the energy of scattered photons ($E_L = E_S$) the process is known as elastic scattering. Though, there is no change in the energy of the elastically scattered photons, there can be changes in the polarization and direction of propagation after scattering. This type of scattering phenomenon is also known as *Rayleigh* scattering.

Inelastic scattering: When the energy of scattered photons is different from the energy of incoming photons, the scattering process is known as inelastic scattering. The molecule can take or give energy to the incoming photons depending on the initial state of the molecule.

Discussing the scattering process quantum mechanically, brings the concept of *virtual* state[2]. The scattering process can be divided into two steps: first the absorption of incoming photons and the second process is the spontaneous emission of the scattered outgoing photons. But in principle, whenever there is an absorption, the molecule should undergo a transition to higher energy levels. This higher energy level may or not exist in the molecule, and thus it can be considered as a *virtual* state.

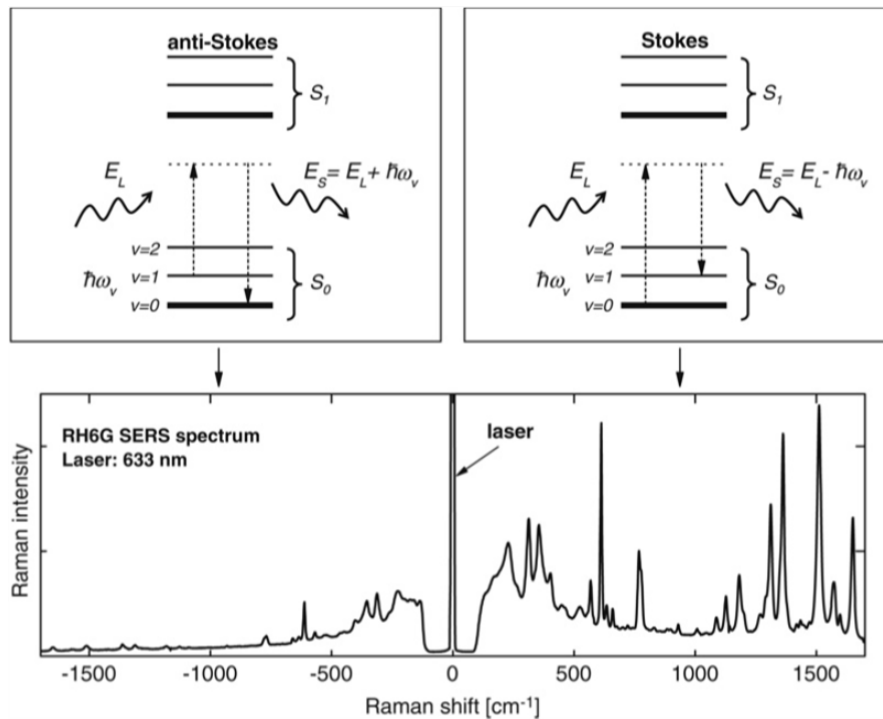


FIGURE 1.4: Schematic showing *anti* – *Stokes* (left top) and *Stokes* (right top) Raman scattering. Raman spectrum of Rhodamine 6G molecules showing anti-Stokes and Stokes shifted photons. Figure reproduced from [2].

If the energy of scattered photon is less than the incoming photon energy ($E_S < E_L$), the process is known as *Stokes* process. This process shows that the molecule was present in the ground state of vibrational sub-levels of state S_0 . After scattering the molecule get excited to the *virtual* state and the *Stokes* shifted photons are emitted at a lower energy after the relaxation of the molecule to the state $v = 1$.

The other inelastic scattering process is when the energy of the scattered photon is more than the energy of the incoming photon ($E_S > E_L$). The process is known as *anti - Stokes* process. For this to happen, the molecule should be initially present in the excited state, say $v = 1$. The molecule gives energy to the incoming photon and thus the scattered photon has energy more than the incoming photon.

Figure 1.4 shows the Raman scattering of Rhodamine 6G molecules. Both *Stokes* and *anti - Stokes* processes are shown. Generally, at room temperature the number of molecules present in the excited states is low and therefore the intensity of *anti - Stokes* peaks is low as compared to *Stokes* shifted peaks. Raman scattering peaks are very sharp in nature as compared to the fluorescence spectrum of the molecules.

The scattering cross-section for Raman scattering is very low and out of 10^7 photons only about one photon undergoes Raman scattering. The power radiated (P_s) by *Stokes* Raman scattering is calculated by,

$$P_s = N\sigma_{RS}I(\nu_L) \quad (1.3)$$

where N is the number of molecules giving Raman photons, σ_{RS} is the Raman scattering cross-section, and $I(\nu_L)$ is the intensity of incident laser with frequency ν_L .

The radiated power and also the radiation pattern can be tuned by changing the environment of the molecules. Placing the molecules near a region of enhanced local electric field drastically modifies the radiated power of Raman shifted photons. The power radiated ($P_{s'}$) by enhanced *Stokes* Raman scattering is calculated by[2]

$$P_{s'} = M \times (N\sigma_{RS}I(\nu_L)) \quad (1.4)$$

Where M is the enhancement factor for enhanced Raman scattering and it incorporates the enhanced local electric field felt by the molecule. It is given by

$$M = \left| \frac{E_{loc(\nu_L)}}{E_{i(\nu_L)}} \right|^2 \times \left| \frac{E_{loc(\nu_{Stokes})}}{E_{i(\nu_L)}} \right|^2 \quad (1.5)$$

Where $E_{i(\nu_L)}$ is the input electric field at the laser frequency ν_L , $E_{loc(\nu_L)}$ is the electric field felt by the molecule at the laser frequency and $E_{loc(\nu_{Stokes})}$ is the electric field at the Stokes shifted frequency.

Since the difference in frequency of *Stokes* shifted photons and laser light is very small, the electric field enhancement at laser light and Stokes shifted frequency can be taken as equal. This makes the enhancement factor M as,

$$M = \left| \frac{E_{loc}(\nu_L)}{E_i(\nu_L)} \right|^4 \quad (1.6)$$

Chemical enhancement: It is the enhancement in the Raman shifted photons because of the change in the chemical properties of the molecules such as polarizability[2], which also incorporates the orientation of the molecule. It provides much lesser enhancement as compared to the electromagnetic enhancement[41].

1.4 Surface enhanced fluorescence and Raman scattering

As discussed in the previous sections, molecular emissions such as fluorescence and Raman scattering can be enhanced by placing the molecules near a region of high electric field intensity. Along with intensity, polarization and wavevectors of emission can also be controlled by placing the molecules near plasmonic geometries. Before going into the details, we first discuss the terminologies that are used in light-molecule interactions related to plasmonics.

Localized and propagating SPPs:

For zero dimensional metallic spherical nanoparticles (diameter $\ll \lambda$), all the surface plasmon polaritons (SPPs) modes decay exponentially[1, 2]. The SPPs modes associated with the nanoparticle are localized only to the surface of the illuminated particle.

Compared to the localized SPPs in the case of small nanoparticles, SPPs can also propagate in some dimensions in elongated systems, where there is a degree of freedom for the SPPs to propagate. Examples of geometries which can support propagating SPPs are one dimensional metallic nanowires[42–44] and two dimensional metallic films[45, 46]. Coupling photons with surface plasmon modes of elongated structures requires special excitation schemes because the momentum of SPPs in the structures is more than the vacuum momentum of photons[2]. A few excitation schemes for coupling light to SPPs are end scattering in nanowires[42, 43], grating based coupling, and high angle excitation on metallic films[1, 3].

Plasmonic cavities:

The field provided by SPPs can be enhanced many folds by creating optical cavities which are small gaps between two plasmonic geometries[1, 2]. The electric field enhancement in such cavities is much more enhanced as compared to the enhancement provided by single plasmonic geometries.

Mirror based plasmonic cavities:

Generally, creating optical cavities requires top down approaches such as electron beam lithography and focused ion beam[11, 47–49], and other processes like binding particles with DNA[50, 51] or chemically binding the particles[52–54]. Of late, mirror based cavities have gained attention because of the ease in preparation and the presence of ultra-small gaps[5, 12, 34]. A plasmonic particle placed on a metallic mirror creates a particle-image particle system with a gap between the two structures that can be controlled with molecular monolayer[55–58].

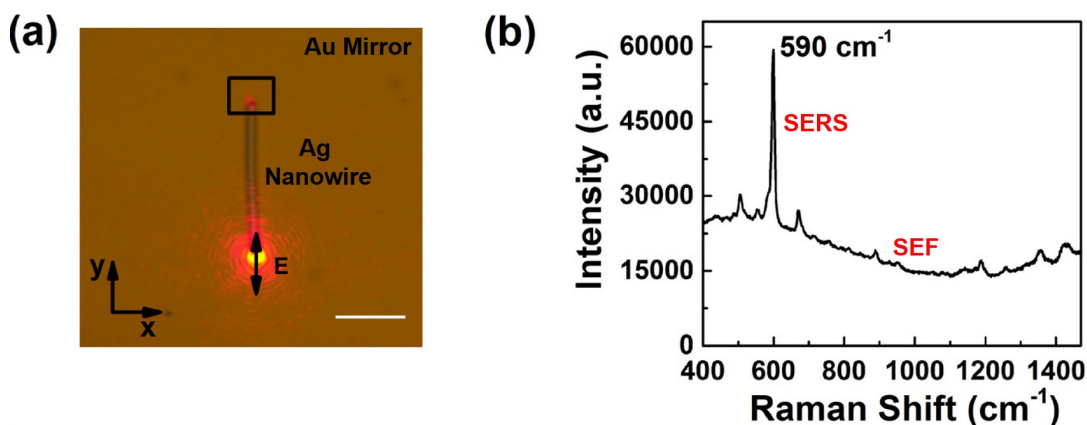


FIGURE 1.5: Exciting SEF and SERS from Nile blue molecules placed in the cavity formed between silver nanowire and gold mirror. One end of nanowire was excited with a focused laser and light from the other end was collected. Figure reproduced from [17].

Figure 1.5 shows surface enhanced fluorescence (SEF) and surface enhanced Raman scattering (SERS) from a mirror based cavity designed by placing an one dimensional silver nanowire on a gold mirror[17]. The molecules are sandwiched between the nanowire and the mirror. The nanowire is excited with a laser at one end, which excites nanowire SPPs propagating along the length of the nanowire. These SPPs out-couple from the nanowire end and excite the SEF and SERS from Nile blue molecules. The broad spectrum is SEF and sharp peaks are SERS of Nile blue molecules.

1.5 Directional emission

The scattering from subwavelength structures such as metallic nanoparticles, quantum dots, or molecules is isotropic in nature[3]. Molecules present on a substrate or in isolation emit light in a large range of angles. This limits the practical utilization of such emission as the collection of the emission depends on the maximum numerical aperture of the objective lens used.

Of late, there is an imperative to tune the direction of light emanating from subwavelength structures in the desired directions for fundamental studies as well for practical utilization[6, 17, 21, 49, 59]. Molecular emission wavevectors are tuned by coupling molecules to plasmonic structures that can scatter light directionally.

Conventional real plane imaging gives information about the spatial coordinates of the structures but does not provide the information about the angles at which light is emanating from the sample. To study the angular distribution of light emanating from subwavelength structures, Fourier plane imaging[59–62] is performed which will be discussed in detail in chapter 2.

Various types of structures that scatter light directionally have been designed such as nanowires[42, 43] and metal film based optical antennas[6, 17]. Out of all, chemically synthesised silver nanowire has gained prominence because of its ability to direct light in a narrow range of angles[43, 63]. The nanowire can also act as a waveguide to direct or route light at subwavelength scales[18, 64]. Light excited at one end out-couples from the other part of the nanowire directionally in the elastic scattering regime[43]. The emission angles of light scattered from silver nanowire can also be tuned by changing the thickness of nanowire or the substrates.

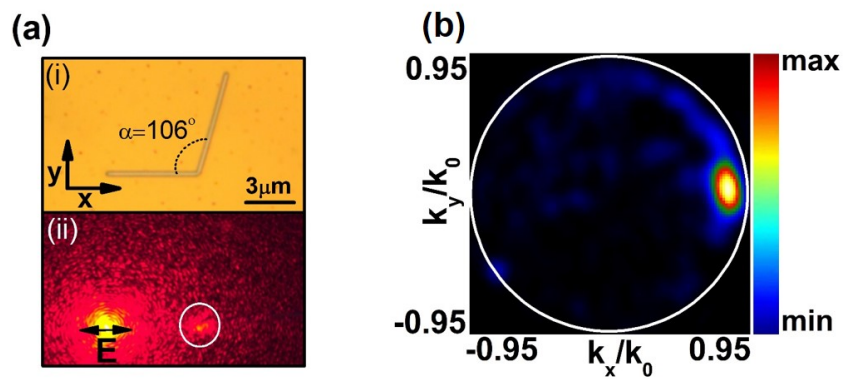


FIGURE 1.6: Directional emission from a bent plasmonic nanowire. (a) (i) Bright field image of a bent nanowire placed on a gold mirror. (ii) Elastic scattering image of the same nanowire upon excitation at one end. (b) Fourier plane image showing directional emission of the light collected from the bent part only. Figure reproduced from [6].

To tailor the directionality of molecular emission, molecules are placed in the vicinity of plasmonic structure such as nanowire. The molecular emission gets coupled to the nanowire SPPs and out-couple directionally[17]. To further achieve better directionality, various designs have been developed such as bending the nanowire[6, 21, 33]. The kink portion of the bent nanowire scatter light in a very narrow range of angles as shown in figure 1.6[6]. Light coupled to nanowire SPPs at one end, out-couples from the kink part of the bent-nanowire. The Fourier plane image shows the confinement of out-coupled light in narrow range of angles.

1.6 Single molecule surface enhanced Raman scattering

The molecular emission can be modified by placing it near a region of enhanced electric field intensity. The scattering cross-sections of molecular processes increases drastically, which facilitates studying the Raman scattering process up-to the level of single molecule and the phenomenon is known as single molecule SERS[7, 8, 10, 65, 66]. Single molecule SERS utilizes the field enhancement provided by hotspots created by plasmonic structures. Generally, SERS is performed by collecting spectra from an ensemble of molecules. This makes it impossible to study the molecular process which gets averaged out in ensemble based study. Studying single molecules provides various insight into the processes at fundamental levels such as molecular orientation in the hotspots[67], electric field enhancement factor for plasmonic hotspots/cavities[2, 68], molecular dynamics such as blinking and movement in the hotspots[69–72].

Various approaches have been used to study the single molecule SERS signatures, out of which bi-analyte SM-SERS technique is widely used because it statistically confirms the detection of SM-SERS[2, 10, 73]. The method uses two types of molecules at higher concentration as compared to the concentration used in the approaches based on low concentration of molecules[7, 8]. Detecting SERS signatures from only one type of molecule, with two types of molecules in the solution at a high concentration, ensures that the emission is only from a single or a few molecules.

Using two types of molecules can lead to four different types of events as shown in figure 1.7[74]. Two types of analytes (Nile blue and Rhodamine 6G) when used can show spectrum from Nile blue molecules, or Rhodamine 6G molecules, no SERS signal or SERS from both the molecules. The bi-analyte method along with modified principal component analysis (MPCA) statistically confirm the single molecule SERS signature. The MPCA method extracts the information about the frequency of SERS collected from only a single type of molecule from a large number of events of SERS from two types of molecules. The MPCA method will be discussed in chapter 2.

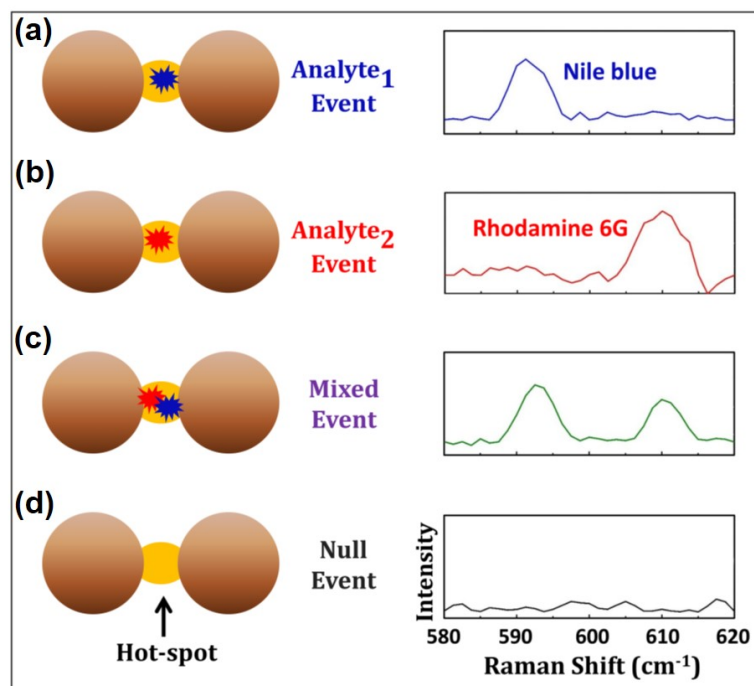


FIGURE 1.7: Schematic showing bi-analyte SERS technique. Four possible events of two molecules competing for a single hot-spot are shown.

Figure adapted from [74].

1.7 Outline of the thesis

The thesis focuses on utilizing the field enhancement and heat produced by plasmonic structures. Field enhancement is used for enhancing and directing molecular emissions. Heat produced by the structures is used to harness the thermophoretic motions of molecules and nanoparticles, to create a single nanoparticle driven thermoplasmonic tweezer. Single molecule SERS is performed on reversible assembly of plasmonic particles.

Chapter 2: Methodology in Fourier plane imaging, numerical modelling, and single molecule SERS spectroscopy

First and foremost, we discuss various methodologies used in the thesis. Fourier plane and energy-momentum imaging are introduced, which are used to image the angular wavevectors of scattered light from subwavelength structures. Further, we present numerical calculations to image near-field, far-field, and temperature increments and gradients based on finite element method using COMSOL Multiphysics. We then conclude the chapter by discussing bi-analyte single molecule SERS technique. A mathematical

description of modified principal component analysis is also presented which is used in chapter 6 to statistically confirm the single molecule SERS signature.

Chapter 3: Beaming elastic scattering light and surface enhanced Raman scattering using bent-plasmonic nanowire on a mirror cavity

In this chapter, we show directional elastic scattering and SERS light from a bent-plasmonic nanowire on a mirror cavity. We used an elongated cavity to enhance and direct SERS from a monolayer of BPT molecules which are self-assembled on a mirror substrate. Gold mirror substrate was not only used for enhancing the emission but also to direct most of the emission in a narrow range of angles with a very high directionality (11.8 dB). Finite element method and finite difference time domain based numerical calculations were used to corroborate and understand the experimental findings. The radiation pattern from the cavity was imaged by individually placing the dipoles in the cavity which gives insights on how to use the cavity for directing inelastic emission in a narrow range of angles.

Chapter 4: Mirror enhanced directional out-coupling of SERS by remote excitation of a nanowire-nanoparticle cavity

We study the effect of confining molecules in nanowire-nanoparticle cavity placed on a gold mirror on the radiation pattern of SERS. The effect of multiple hotspots on the SERS wavevectors was investigated. We study the junction placed on the gold mirror in remote excitation configuration and show that this configuration facilitates directional out-coupling of SERS emission.

Chapter 5: Metallo-dielectric antenna for directional molecular fluorescence

In this chapter, we show how to direct and enhance molecular fluorescence using a self-assembled hybrid metallo-dielectric optical antenna. Morphology dependent resonances of the dielectric microsphere enhances the fluorescence of the molecules coated on the microsphere. Surface plasmon polaritons of silver nanowire remotely excite the modes of the microsphere and also facilitate the directional emission of molecular fluorescence. Finite element method based numerical calculations are performed to understand the individual effects of plasmonic and dielectric structures used in procuring the directional emission.

Chapter 6: Single molecule SERS in a single gold nanoparticle-driven thermoplasmonic tweezer

Herein, we focus on utilizing the heat generated by a single gold nanoparticle when excited with a very low power laser to facilitate a reversible trapping of plasmonic particles. The heat generated by a single nanoparticle initiates a reversible trap. A large scale assembly of plasmonic particles was created and SERS experiments were performed on the molecules in such assemblies. Lee-Meisel silver particles were trapped for performing sensitive single molecule SERS experiments. Bi-analyte SM-SERS method was used to get the SM-SERS signatures which was further confirmed using modified principal component analysis. We utilize the single nanoparticle driven thermoplasmonic trap, as a low power tweezer to trap and move the assemblies to the desired location and to trap single nanoparticle trapping.

Chapter 7: Conclusion and Future directions

The thesis concludes with this chapter. Present challenges and limitations of the work presented in the thesis are discussed. We propose methods and experimental designs to overcome the challenges and to extend the work presented in the thesis, along with the application of the results for future research.

Chapter 2

Methodology in Fourier plane imaging, numerical modelling, and single molecule SERS spectroscopy

Studying light-matter interaction at subwavelength scales needs probing of intensity, phase, polarization, and wavevectors of light. For this, various methods involving experiments, numerical calculations, and statistical analysis are used. Conventional real plane imaging and spectroscopy gives information about the spatial information of the system under study but lacks the information of wavevectors and polarization of scattered light. Of late, there is an imperative to probe wavevectors of scattered light for understanding the molecular interactions in optical cavities. We used Fourier plane and energy-momentum imaging techniques to image the emission wavevectors. Probing wavevectors give information about the angles at which light is emanating from the subwavelength structures, which is further needed for on-chip coupling applications and in understanding the cavity modes and molecular orientation in the cavities.

A detailed discussion on the theory of Fourier plane imaging technique, and experimental setup to image Fourier plane is presented in the first section of this chapter. We then proceed to discuss the finite element method based numerical calculations which are performed to image the near-field and far-field electric field profiles. Details on analyzing temperature increment and distribution around metallic structures using numerical calculations are also discussed.

The chapter concludes with a mathematical foundation of the methods used for spectral studies in the thesis. We study in detail the spectral studies, such as bi-analyte single molecule SERS method and modified principal component analysis which are used to confirm the single molecule SERS signatures.

The chapter is divided into the following three sections:

- Fourier plane imaging
- Numerical calculations

- Single molecule surface enhanced Raman scattering

2.1 Fourier plane imaging

Fourier plane imaging[59–61] is performed to get the information about the angles at which light emanates from the sample plane. It maps the radial and azimuthal angles of the wavevectors. Imaging the wavevectors of molecular emission gives information about the modes of the cavity in which the molecules are confined[75]. The angular distribution of emission from molecules depends primarily on the molecular orientation as well as on the modes of the cavity[18]. In this thesis, Fourier plane imaging was performed on an upright microscope for studying light-molecule interactions to gain insight about how molecules behave when confined to subwavelength plasmonic gaps. Imaging molecular emission also facilitates in designing inelastic optical antennas.

We first study mathematically[60] the Fourier transform property of a lens and then describe how to image Fourier plane experimentally using a single or a combination of lenses.

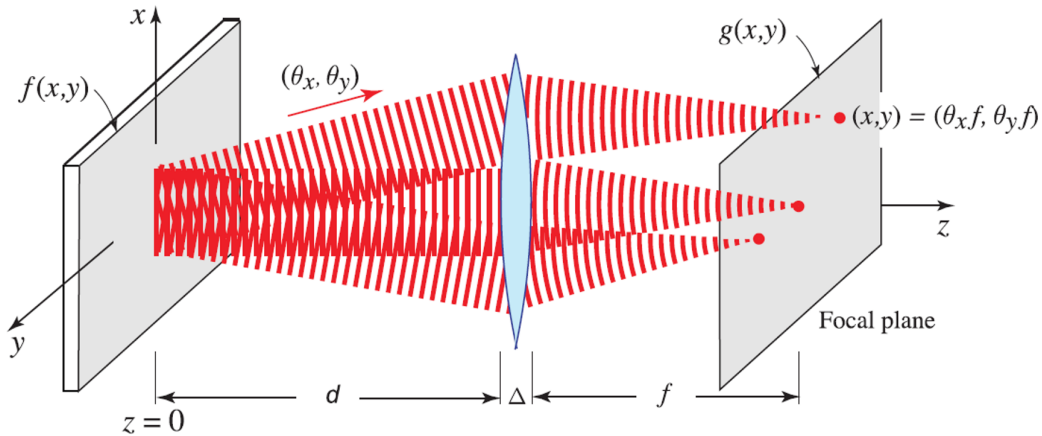


FIGURE 2.1: Schematic showing a lens performing Fourier transform.

Figure reproduced from [60].

A plane wave from the sample plane of a lens coming at small angles (θ_x, θ_y) , meets at a point on the other focal plane of the lens at $(\theta_x f, \theta_y f)$, with f as the focal length of the lens (figure 2.1). This means, that waves coming at same angles from the sample plane meet at one point on the second focal plane of the lens, which is called back focal plane.

The angles can be rewritten as $(\theta_x f, \theta_y f)$ as $\theta_x = \lambda \nu_x$ and $\theta_y = \lambda \nu_y$ where $\nu_x = x/\lambda f$ and $\nu_y = y/\lambda f$.

At $z = 0$, a plane wave $U(x, y, z)$ with a complex amplitude proportional to the Fourier transform $F(\nu_x, \nu_y)$ can be written as,

$$U(x, y, 0) = F(\nu_x, \nu_y) e^{-i2\pi(\nu_x x + \nu_y y)} \quad (2.1)$$

The same plane wave at $z = d$ can also be written as,

$$U(x, y, d) = H(\nu_x, \nu_y) F(\nu_x, \nu_y) e^{-i2\pi(\nu_x x + \nu_y y)} \quad (2.2)$$

where d is the distance of the sample plane from the lens. $H(\nu_x, \nu_y)$ is the transfer function and with $H_0 = e^{-ikd}$ it is defined as

$$H(\nu_x, \nu_y) = H_0 e^{i\pi d(\nu_x^2 + \nu_y^2)} \quad (2.3)$$

Upon crossing the lens of thickness Δ , the complex function will be multiplied with a lens phase factor $e^{i\pi\left(\frac{x^2+y^2}{\lambda f}\right)}$. Note that the phase factor $e^{-ik\Delta}$ because of the thickness of the lens is ignored. Therefore,

$$U(x, y, d + \Delta) = A(\nu_x, \nu_y) e^{i\pi \frac{(x-x_0)^2 + (y-y_0)^2}{\lambda f}} \quad (2.4)$$

with $x_0 = \lambda\nu_x f$, $y_0 = \lambda\nu_y f$, and A as

$$A(\nu_x, \nu_y) = H_0 e^{i\pi\lambda(d-f)(\nu_x^2 + \nu_y^2)} F(\nu_x, \nu_y) \quad (2.5)$$

The expression for $U(x, y, d + \Delta)$ shows complex amplitude of a wave getting focused to a point (x_0, y_0) on the lens focal plane ($z = d + \Delta + f$). After integrating, the complex amplitude can be written as,

$$U(x, y, d + \Delta + f) = h_0(\lambda f)^2 A(\nu_x, \nu_y) \delta(x - x_0) \delta(y - y_0) \quad (2.6)$$

where $h_0 = \frac{i}{\lambda f} e^{-ikf}$. The above equation shows a wave converging to a point (x_0, y_0) on the back focal plane of the lens.

Integrating over all the plane waves gives the total amplitude as,

$$g(x, y) = h_l e^{\frac{i\pi(x^2+y^2)(d-f)}{\lambda f^2}} F\left(\frac{x}{\lambda f}, \frac{y}{\lambda f}\right) \quad (2.7)$$

with $h_l = H_0 h_0 = \left(\frac{i}{\lambda f}\right) e^{-ik(d+f)}$.

Furthermore, since $|h_l| = 1/\lambda f$, we can write the intensity at the output plane as,

$$I(x, y) = \frac{1}{(\lambda f)^2} \left| F \left(\frac{x}{\lambda f}, \frac{y}{\lambda f} \right) \right|^2 \quad (2.8)$$

The above equation shows that the intensity at the back focal plane of the lens is directly proportional to the square of Fourier transform of the amplitude of wave at the first focal plane, which basically shows the Fourier transform property of a lens.

2.1.1 Experimentally imaging the Fourier plane

Figure 2.2 shows a simple description of imaging the Fourier plane[76]. The sample under study is placed at the sample plane and light scattered by the sample plane is collected through the objective lens. The light out-coupling from the sample plane in one direction, shown as light coming from the points, x_1 , x_2 , and x_3 in one direction is focused to a point k_1 at the Fourier plane, which is at the second focal plane of the objective lens.

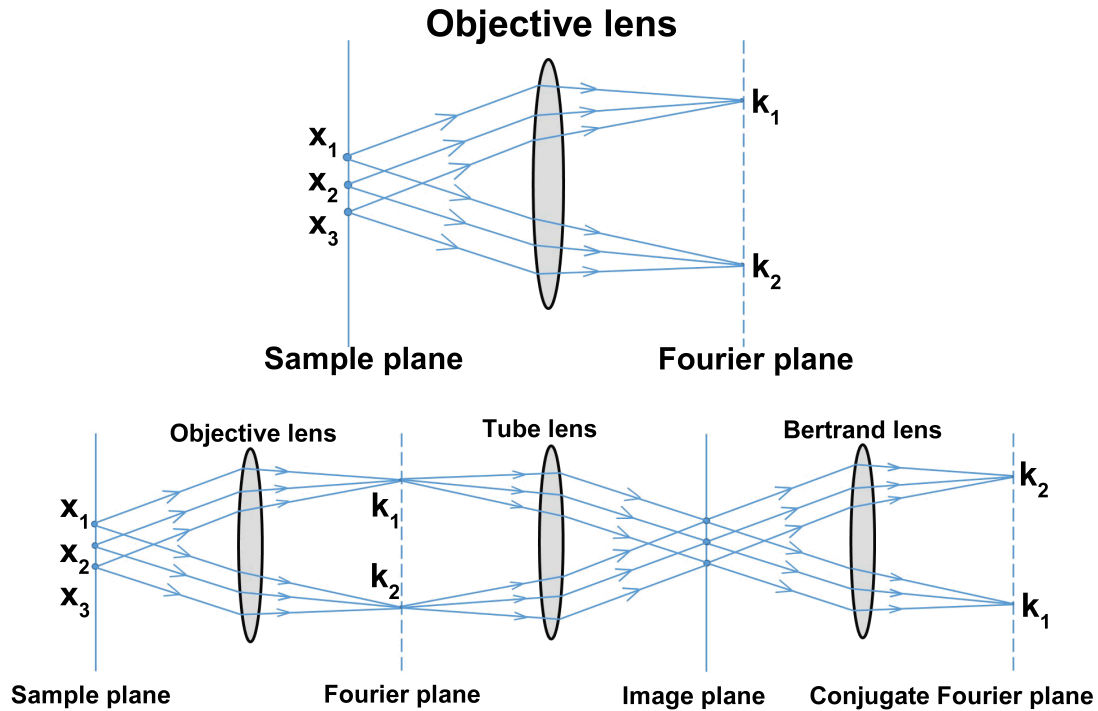


FIGURE 2.2: Schematic showing experimentally imaging the Fourier plane.

Practically, the second focal plane of the objective lens used is very close to the back aperture of the objective lens, and it is not possible to place an imaging device such as a camera there to image the Fourier plane. The Fourier plane is captured by re-imaging it using a combination of lenses. To understand this, we should first discuss the experimental setup used in the thesis to image the Fourier plane and also to perform spectroscopy and energy-momentum imaging.

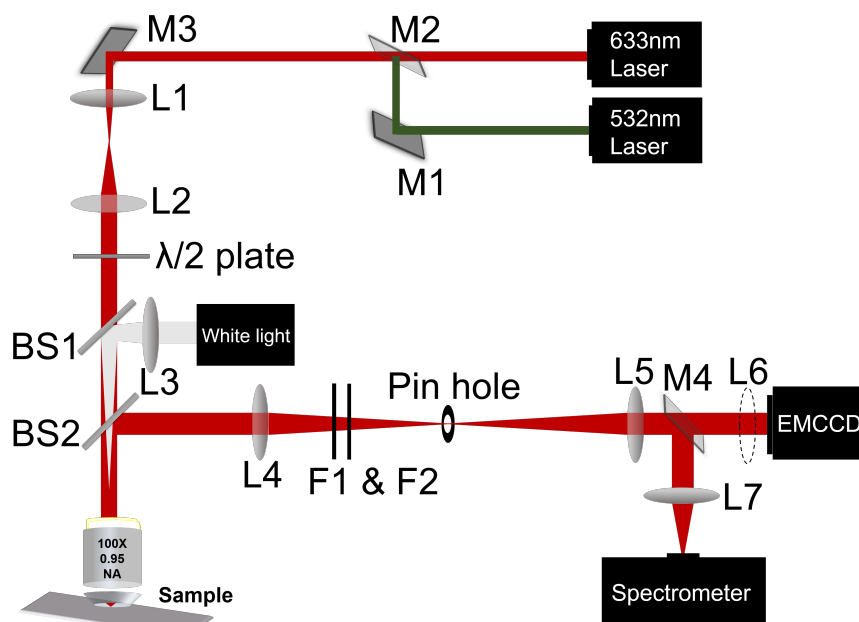


FIGURE 2.3: Schematic of the experimental setup.

Figure 2.3 shows the experimental setup used to study the spectral and wavevector signatures[17, 77]. The sample was excited using either 633 nm or 532 nm laser by a high numerical aperture objective lens and the scattered light was collected using the same lens. M1 and M3 are mirrors and M2 is a flip mirror used to select either of the two lasers. Lenses L1 and L2 were used to expand the beam such that the back aperture of the objective lens was completely filled. The in-plane polarization of the laser was varied using a half wave plate ($\lambda/2$). The sample was observed using a white light source, lightly focused on the sample plane. BS1 and BS2 are beam splitters. L3, L4, L5, and L7 are lenses and L6 is a flip lens. M4 is flip mirror used to switch from collecting spectral signature to wavevector signature. Filters F1 and F2 are used to reject the laser light for collecting only the inelastic imaging. Pinhole in the conjugate image plane is used to perform spatial filtering based measurements.

Since, the back aperture of the lens cannot be imaged directly, we used a combination of lenses to re-image the Fourier plane. A tube lens (L4) was used to again create a image plane, which was also used to place spatial filters and perform remote excitation

studies where the excitation spot need to be discarded before putting the light either into spectrometer or onto camera. To again transform the real image to the Fourier plane image, where a camera can be placed, lens L5 was placed which is called Bertrand lens. And by this a conjugate Fourier plane image is obtained again which is real and inverted in nature. This is shown in the figure 2.2 where the light from the sample plane is imaged to points k_1 and k_2 on the back focal plane of the objective lens. After using tube lens, a Fourier transform was performed to again get the real plane image. Lens L5 was again used to do the Fourier transform and to projected the light onto the camera.

2.1.2 Energy-momentum imaging

Fourier plane imaging gives the information about the angles at which light emanates from the sample plane. For inelastic emissions such as fluorescence and Raman scattering, where there is a large number of wavelengths, the Fourier plane image fails to provide information about the angles corresponding to different wavelengths. It means, we only have momentum information of the collected light and the information related to the wavelength is lost. In certain experiments, different types of molecular emissions are collectively imaged and there comes the necessity to probe the angles related to different molecular emission happening at different wavelengths. To get the energy or wavelength information along with angular information of light from the sample plane, energy-momentum imaging is performed[59, 75]. For this, a portion of Fourier plane image, with a known k value, is projected to the spectrometer and dispersed to get the wavelength information. By projecting the complete Fourier plane by dividing it in slices, the details about the energy information can be achieved.

2.2 Numerical calculations

One more important tool to gain insights about the light-matter interaction at subwavelength scale is to use electrodynamics based numerical calculations. Maxwell's equations are solved with boundary conditions to calculate the electromagnetic fields around the subwavelength structures.

The electric field in the close proximity of the structures is called near-field electric field[3] and generally, this field decays exponentially. Imaging near-field electric fields using conventional microscopes is not possible. Imaging it requires special techniques such as scanning near-field optical microscopy (NSOM)[78]. The other regime is the far-field radiation which will be discussed in detail through-out the thesis. It is the scattering signal that is captured using the objective lens. Illuminating the metallic structures also heats up the particle and the temperature of the particle increases because of

the non-radiative processes such as electron-electron or electron-phonon collisions[22, 23]. We numerically calculate the temperature increment of the structure and also the temperature gradient near the structure which is needed to understand the mechanism behind reversible trapping which will be discussed in detail in chapter 6.

A more involved discussion about the near-field electric field, far-field signatures of scattered light, and temperature increment of plasmonic structure will be done in the subsequent chapters. Here, we discuss the near-field electric field, and the far-field scattering pattern, and the temperature increment of a single 150 nm AuNP. The particle is placed on a glass substrate and is illuminated with a focused Gaussian source of wavelength 633 nm. We discuss the methods used in numerically calculating the field and temperature profiles.

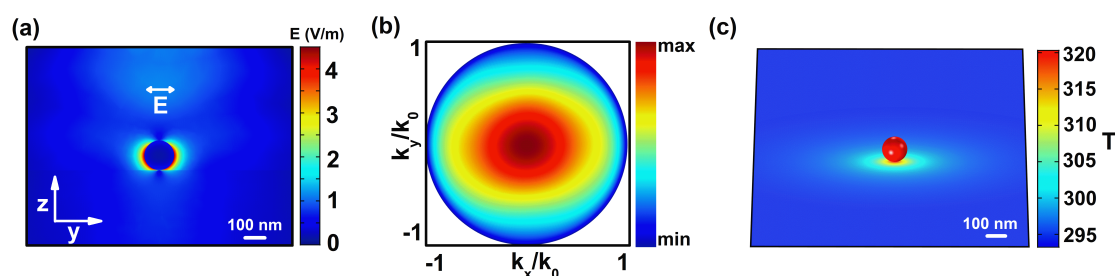


FIGURE 2.4: Calculated near-field (a) and far-field (b) of a 150 nm gold nanoparticle placed on a glass substrate. (c) Calculated temperature increment of a 150 nm gold nanoparticle placed on a glass substrate and suspended in water. The particle is excited with a focused Gaussian laser source of wavelength 633 nm.

Figure 2.4 (a) shows calculated near-field electric field near a gold nanoparticle of size 150 nm which is placed on a glass substrate. The particle is excited with a focused Gaussian source of wavelength 633 with the incoming polarization along the y axis. The wavelength of the incoming laser source is selected to be 633 nm because the plasmon scattering peak of the particle is near 633 nm. As can be seen, a large local electric field is created at the metal dielectric interface and the field intensity decays away from the nanoparticle. For an anisotropic structure such as one dimensional nanowire, the near-field electric field profile looks more complicated and will be discussed in detail in the upcoming chapters. Next, we study the angles at which the particle scatters the light by calculating the far-field images of the scattered light from the nanoparticle using the reciprocity arguments[79]. For this method, first the near-field electric field was calculated by performing finite element method calculations using COMSOL Multiphysics as a solver and then the far-field signature is calculated using a MATLAB based code attached with COMSOL[79] which is based on the reciprocity principle. The Fourier

plane image is shown in figure 2.4 (b) which shows the emission angles in the far-field of the scattered light from the particle. The image is plotted in k_x and k_y axes which are basically the Fourier transform of the spatial coordinates (x and y axes). In further chapters, we will discuss calculation of far-field images of emission from structures which scatter light directionally. Furthermore, by using the calculated electric field, we computed the temperature increment of the nanoparticle. The temperature is computed by first calculating the heat generated and then by applying the boundary conditions.

The heat power density $q(r, t)$ at any time t and at any location r inside an illuminated structure is given by[22],

$$q(\mathbf{r}, t) = \mathbf{J}(\mathbf{r}, t) \cdot \mathbf{E}(\mathbf{r}, t) \quad (2.9)$$

where J is the electronic current density and E is the electric field inside the nanostructure. Taking the time average, and denoting the frequency of the light source illuminating the structure as ω , the heat power density becomes,

$$q(\mathbf{r}) = \left(\frac{\omega}{2}\right) \varepsilon_0 \text{Im}(\varepsilon) |\mathbf{E}(\mathbf{r})|^2 \quad (2.10)$$

Boundary conditions were defined using the equation

$$q_0 = h (T_{ext} - T) \quad (2.11)$$

with $T_{ext} = 293.15$ K and h as the heat transfer coefficient, with external natural convection option for a spherical geometry of diameter 150 nm.

Figure 2.4 (c) shows the temperature increment of a 150 nm gold nanoparticle placed on a glass substrate and is surrounded by water. The particle was excited with a low power density laser ($0.07 \text{ mW}/\mu\text{m}^2$) of wavelength 633 nm. A maximum temperature increment of $\approx 23\text{K}$ was observed near the surface of the nanoparticle.

2.3 Single molecule surface enhanced Raman scattering

SERS is the phenomenon of enhanced Raman signals from molecules in the presence of near-field around plasmonic structures[2, 80, 81]. Generally while performing SERS, spectrum from a large number of molecules is collected. Single molecule SERS (SM-SERS) is to observe the enhanced Raman scattering from only a single molecule. Probing SERS signatures from isolated molecules provides details which are otherwise not possible by a spectrum of ensemble of molecules such as details of the modes of cavities[12], origin of SERS enhancement factors[2, 68], and molecular orientation[67].

We first discuss the early approaches to observe SM-SERS signatures using a low concentration of molecules. We then move to discuss a more accurate and advanced method developed by Eric Le Ru et al., which involves using the bi-analyte single molecule SERS method and modified principal component analysis. The early approaches were based on the fact that to study SERS from a single molecule, a low concentration ($\approx 10^{-15}$ M) of molecules should be added with plasmonic particles for performing SERS. The molecular concentration was gradually reduced to undergo in the regime when there was about one molecule in the scattering volume[7, 8]. If the SERS signal from such a low concentration of molecule is detected then the regime was considered as a single molecule SERS spectroscopic regime. The early approaches to study SM-SERS which were based on analyzing the fluctuations in the intensity of the peaks. The number of molecules on the hotspots were estimated by using the concentration of molecules used and the concentration of the particles in the solution.

The approaches based on using low concentration of molecules are suffered from statistical errors and following are the points which make the methods less accurate:

- SERS fluctuations can also come from a high concentration of molecules.
- Any non-reacted silver particle will lead to wrong molecules/colloid ratio (wrong average number of molecules).
- Number of molecules on hotspots are very low which results in low accuracy of statistical methods used.

Next, we discuss the bi-analyte single molecule SERS method[10] developed by Eric Le Ru and Pablo Etchegoin, which overcomes the above mentioned problems and gives an accurate proof of single molecule SERS signature. The bi-analyte method uses a relatively high concentration of molecules ($\approx 10^{-9}$ M) and thus overcomes the problem of low number of molecules on the hotspots. Two types of different molecules or analytes are added in the solution having plasmonic hotspots, in a relatively high concentration as compared to the concentration used in the single analyte based SM-SERS studies.

Let us say two types of molecules, A and B are added in the solution and SERS spectroscopy is performed. In principle, the signal should come from both types of molecules A and B . But if the collected spectrum is from only one type of molecule (say molecule A), then the signal is essentially from a single or few molecules of only one type (molecule A).

For example:

- If the signal is from 5 molecules; then the probability that the signal is only from one type of molecule is 1/32.
- If the signal is from 10 molecules; then the probability that the signal is only from one type of molecule is 1/1064 and so on.

So, using a higher concentration of two types of molecules and detecting SERS spectrum from only one type of molecule, makes sure that the collected SERS emission is from a few or single molecules.

To statistically confirm the single molecule signature, first a large number of spectra with two types of molecules are collected. After this, the frequency of SERS spectra from only one type of molecule is extracted. This is achieved by performing modified principal component analysis (MPCA) developed by Etchegoin et al.[73]. We discuss the mathematical analysis of the MPCA which is used in chapter 6 for confirming single molecule SERS signature. A detailed method can be found in ref[73].

The collected spectra is decomposed in a rectangular matrix M having T number of spectrum and N number of wavenumber where $M = T \times N$. In terms of intensity, M can be written as,

$$M = \begin{pmatrix} I_{t_1}^{v_1} & I_{t_1}^{v_2} & \dots & \dots & I_{t_1}^{v_N} \\ I_{t_2}^{v_1} & I_{t_2}^{v_2} & \dots & \dots & I_{t_2}^{v_N} \\ \dots & \dots & \dots & \dots & \dots \\ I_{t_T}^{v_1} & I_{t_T}^{v_2} & \dots & \dots & I_{t_T}^{v_N} \end{pmatrix} \quad (2.12)$$

Next, the mean of the row is subtracted from each element to produce at each time t_i , a spectrum with zero mean intensity.

With this, the matrix M becomes,

$$\hat{M} = \left(\hat{I}_{t_i}^{v_j} \right) \quad (2.13)$$

where $\hat{I}_{t_i}^{v_j} = I_{t_i}^{v_j} - \overline{I_{t_i}}$ and $\overline{I_{t_i}} = \frac{1}{N} \sum_{j=1}^N I_{t_i}^{v_j}$.

After this, a covariance matrix V is calculated as,

$$V = \left(\text{cov} \left(\hat{I}_t^{v_j}, \hat{I}_t^{v_k} \right) \right) \quad (2.14)$$

where $\text{cov} \left(\hat{I}_t^{v_j}, \hat{I}_t^{v_k} \right) = \text{cov} \left(\hat{I}_t^{v_k}, \hat{I}_t^{v_j} \right)$ and is calculated as

$$\text{cov} \left(\hat{I}_t^{v_j}, \hat{I}_t^{v_k} \right) = \sum_{i=1}^T \frac{\left(\hat{I}_{t_i}^{v_j} - \langle \hat{I}^{v_j} \rangle \right) \left(\hat{I}_{t_i}^{v_k} - \langle \hat{I}^{v_k} \rangle \right)}{(T-1)} \quad (2.15)$$

where the symbol $\langle \dots \rangle$ denotes the time average.

As we can see, the matrix V is a square matrix having a dimension of the number of wavelengths and is independent of the number of spectra (T) collected. But, the accuracy of the analysis increases when a large number of spectrum are recorded.

Eigenvectors corresponding to the largest eigenvalues are called principal components and in the bi-analyte SERS, generally the first two components are used. This means that, any spectrum in the bi-analyte SERS spectra, can be expressed as a linear combination of the first two principal components ($f_1^{v_j}$ & $f_2^{v_j}$).

For concluding the standard PCA, we need to have a table of coefficients. Two coefficients per spectrum is needed, which can tell us which specific linear combinations of eigenvectors we need to represent any spectrum. The matrix operation required to obtain the table of coefficient is

$$C = \begin{pmatrix} \alpha_1 & \beta_1 \\ \alpha_2 & \beta_2 \\ \dots & \dots \\ \alpha_T & \beta_T \end{pmatrix} = \hat{M} \begin{pmatrix} f_1^{v_1} & f_2^{v_1} \\ f_1^{v_2} & f_2^{v_2} \\ \dots & \dots \\ f_1^{v_N} & f_2^{v_N} \end{pmatrix} \quad (2.16)$$

With this, the reconstructed spectral data can be expressed as,

$$I_{t_i}^{v_j} = \alpha_i f_1^{v_j} + \beta_i f_2^{v_j} + \overline{I_{t_i}} \quad (2.17)$$

Furthermore, C matrix is plotted in the coefficient space for getting the distribution of SERS from the molecules. While performing bi-analyte SM-SERS, a pattern in the coefficient space shows two axes. But to get the spectroscopic information of the data, two eigenvectors are needed, to represent SM-SERS spectra. For this, the axes in the coefficient space is rotated to get the pure SM-SERS spectra from one type of molecule along one axis. To perform this, two eigenvectors are defined as $\vec{e}_1$ and $\vec{e}_2$ as unit vectors along the two directions.

Next, a linear transformation factor matrix R is defined which rotates the two obtained axes as $\vec{e}_1$ to $\vec{e}_x$ and $\vec{e}_2$ to $\vec{e}_y$. Matrix R can be written as,

$$R = \begin{pmatrix} k_1 n_1^x & k_2 n_2^x \\ k_1 n_1^y & k_2 n_2^y \end{pmatrix}^{-1} \quad (2.18)$$

with,

$$\begin{pmatrix} k_1 \\ k_2 \end{pmatrix} = \begin{pmatrix} c_1 n_1^x & c_2 n_2^x \\ c_1 n_1^y & c_2 n_2^y \end{pmatrix}^{-1} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (2.19)$$

If the concentration of two types of molecules used is same then $c_1=c_2$.

Therefore, the new coefficient matrix now becomes,

$$C = C \left({}^t R \right) \quad (2.20)$$

Furthermore, the first two eigenvectors $f_1^{v_j}$ and $f_2^{v_j}$ get transformed as,

$$\begin{pmatrix} g_1^{v_j} \\ g_2^{v_j} \end{pmatrix} = \left({}^t R \right)^{-1} \begin{pmatrix} f_1^{v_j} \\ f_2^{v_j} \end{pmatrix} \quad (2.21)$$

Finally, a histogram is plotted to show the distribution of SERS events. The probability of SERS from one type of molecule is then defined as,

$$p_1 = x/(x + y) = 1/(1 + \text{abs}(y/x)). \quad (2.22)$$

This completes the modified principal component analysis. An information on how many times a single molecule event is recorded is deduced by collecting a large number of spectra from two types of molecules.

Chapter 3

Beaming elastic scattering light and surface enhanced Raman scattering from a bent-plasmonic nanowire on a mirror cavity

In this chapter, I will discuss directional elastic scattering light, and surface enhanced Raman scattering from molecular monolayer, using an extended bent-plasmonic nanowire on a mirror cavity. The chapter is an adaptation of the research article "Journal of Physical Chemistry Letters, 2021, 12, 6589–6595 (2021)".

3.1 Introduction

Designing structures which can direct elastic scattering light as well as inelastic scattering emission from subwavelength structures is at the heart of nanophotonics[30, 82, 83]. There is a continuous need to design structures which can scatter light directionally but with a narrow angular spread. Such geometries with directional scattering properties can be harnessed to provide control on the properties of light for efficient detection and on-chip coupling. To this end, various metallic structures supporting surface plasmons have been utilized to confine and scatter light efficiently at subwavelength scales[3, 43, 84, 85]. One such structure is chemically synthesized silver nanowires which act as a waveguide for efficient propagation of light and have been utilized in remote detection of molecules, strong coupling physics, and as a subwavelength channel of molecular emission.

Furthermore, plasmonic cavities that are formed by coupling two plasmonic structures enhance light-matter interaction by confining the optical field to volumes less than 1 nm^3 [4, 16, 34, 86, 87]. Thus, plasmonic nano-cavities are utilized to probe single molecule surface enhanced Raman scattering (SERS)[2, 81], strong coupling

physics[12], and in designing optical sensors[88]. Of late, mirror based plasmonic cavities have gained special attention because of the ease in preparation and the ultra-small mode volume supported by them[89, 90]. The mirror based cavities can be prepared by just placing a plasmonic particle on the mirror which creates a cavity between the particle and the image particle.

Directional antennas have also been used to enhance, detect and direct molecular emission such as fluorescence and SERS signals in a direct or a remote excitation configuration[21, 33, 64]. But, there was a minimal control over placement and orientation of the molecules on these structure which reduced the directionality of the antenna by increasing the angular spread of emission. Moreover, since most of these geometries are individual structures, the field enhancement supported by them are minimal because of the absence of hotspots. Thus, there is a demand to design geometries which can scatter elastic and inelastic light with high directionality and narrow angular distribution, without compromising the field enhancement.

Motivated by this, here we utilize a bent-plasmonic nanowire placed on a gold mirror for directing elastically scattered light and SERS emission. We show beaming of the elastically scattered light and the SERS to a very narrow range of wavevectors with the excitation and the collection points separated by few microns. We used a monolayer of biphenyl-4-thiol molecules with an out-of-plane orientation and self-assembled on the mirror to utilize maximum field enhancement in the cavity for SERS enhancement and in achieving beaming SERS.

3.2 Architecture of the system

A schematic of the experimental configuration is shown in figure 3.1. A single crystalline, chemically synthesized bent silver nanowire (AgNW) was placed on a gold mirror making an extended bent-nanowire on a mirror cavity (B-NWoM cavity). One end of the nanowire was excited with a tightly focused 633 nm laser using a high numerical aperture objective lens which excites nanowire surface plasmon polaritons (SPPs) along with the gap plasmon modes between the nanowire and the mirror. The plasmon polaritons propagating along the nanowire out-couple as free-space photons at the kink and were spatially filtered and projected onto the EMCCD for Fourier plane imaging. For SERS studies, a monolayer of biphenyl-4-thiol (BPT) molecules was assembled on the gold mirror, using self-assembled monolayer technique, following that bent-nanowires were dropcasted. The system was then excited on one end with a focused 633 nm laser beam. Out-coupled light from the kink was spatially filtered and was projected onto the

EMCCD or spectrometer for Fourier plane and energy-momentum imaging and spectroscopy[59, 61, 75].

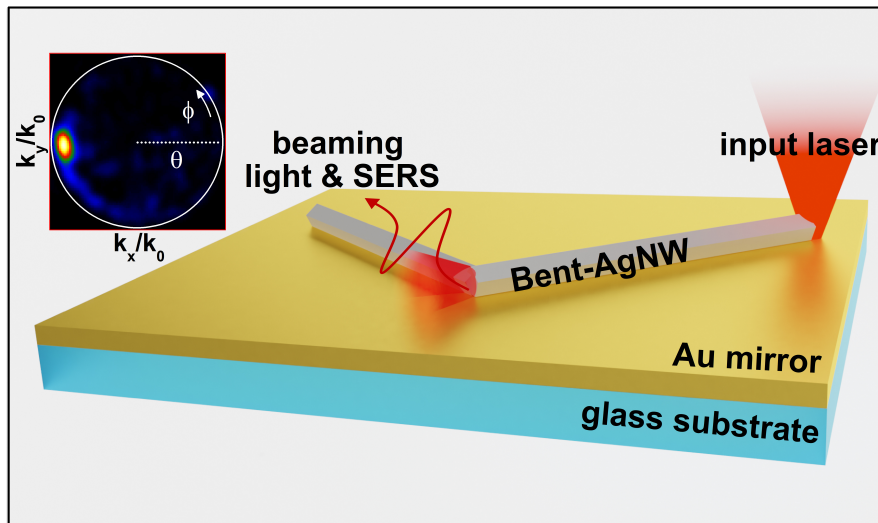


FIGURE 3.1: Schematic of the experimental configuration. A bent silver nanowire was placed on a gold mirror and one end of the nanowire was excited with a focused laser. The out-coupled light from the kink of the nanowire was spatially filtered and was projected onto the EMCCD for Fourier plane imaging. For SERS experiments, a monolayer of biphenyl-4-thiol molecules was sandwiched between the wire and the mirror. The light out-coupled from the kink was projected onto the EMCCD and spectrometer for Fourier plane and energy-momentum imaging after rejecting the laser line. Figure reproduced from [6].

3.2.1 Preparing the geometry

Silver nanowires were synthesized using polyol process[91]. For making bent-nanowires, nanowires dispersed in ethanol solution were ultra-sonicated for 30 seconds. The complete process of bending the nanowires using ultra-sonication can be found in ref[92]. Figure 3.2 shows multiple bent-nanowires with different inter-arm angles. These bent-nanowires were dropcasted on a 160 nm thick gold mirror for making B-NWoM geometry. For directing SERS emission from BPT molecules, a single layer of vertically oriented molecules was assembled on a 160 nm thick mirror using self-assembled monolayer technique. For preparing the self-assembled monolayer of BPT molecules on mirror, a gold coated glass cover slip was left in a solution of 1 millimolar solution of BPT molecules in ethanol for 24 hours. The cover slip was cleaned with ethanol before use for removing the molecules which were not assembled. Over the monolayer, bent-nanowires were dropcasted for making B-NWoM cavity.

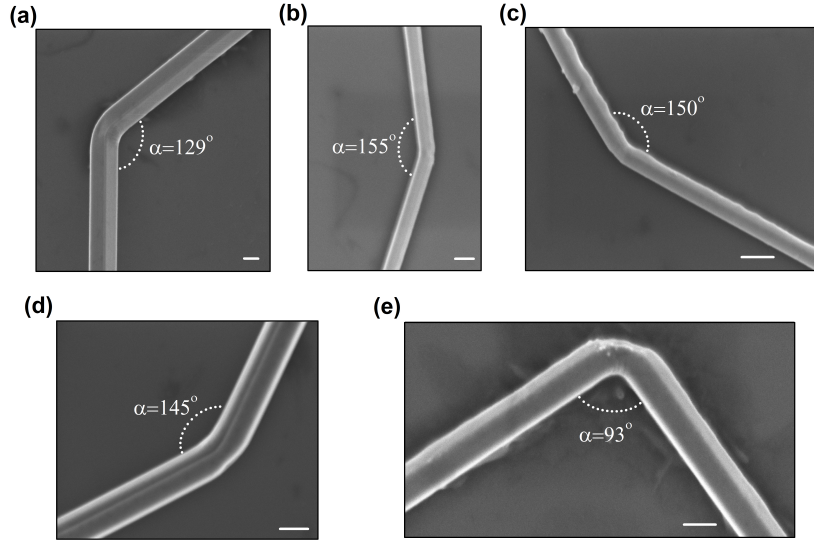


FIGURE 3.2: Scanning electron microscopy (SEM) image of bent silver nanowires with different inter-arm angles. (a-e) SEM image of bent-nanowires with bending angles, $\alpha=129^\circ$, 155° , 150° , 145° and 93° respectively. Scale bar (a-e) is 200 nm. Figure reproduced from [6].

3.3 B-NWoM cavity as a directional elastic antenna

Figure 3.3 (a) shows bright field image of a bent-nanowire with an inter-arm angle $\alpha=106^\circ$, placed on a 160 nm thick gold mirror. One end of the nanowire was excited with a 633 nm laser with polarization along the axis of the nanowire using a high numerical aperture objective lens (see figure 3.3 (a)(ii)). Nanowire SPPs scatter out as free space photons at the kink. We collected the emission only from the kink using a spatial filter and projected the light to the EMCCD to perform Fourier plane imaging which maps the angular distribution in terms of radial and azimuthal angles. The Fourier plane image shown in figure 3.3 (b) indicates that the wavevector spread of out-coupled elastic scattered photons are narrow in terms of radial and azimuthal angles. This implies that scattered light is beaming in the form of a small lobe and it is directed towards higher k-values.

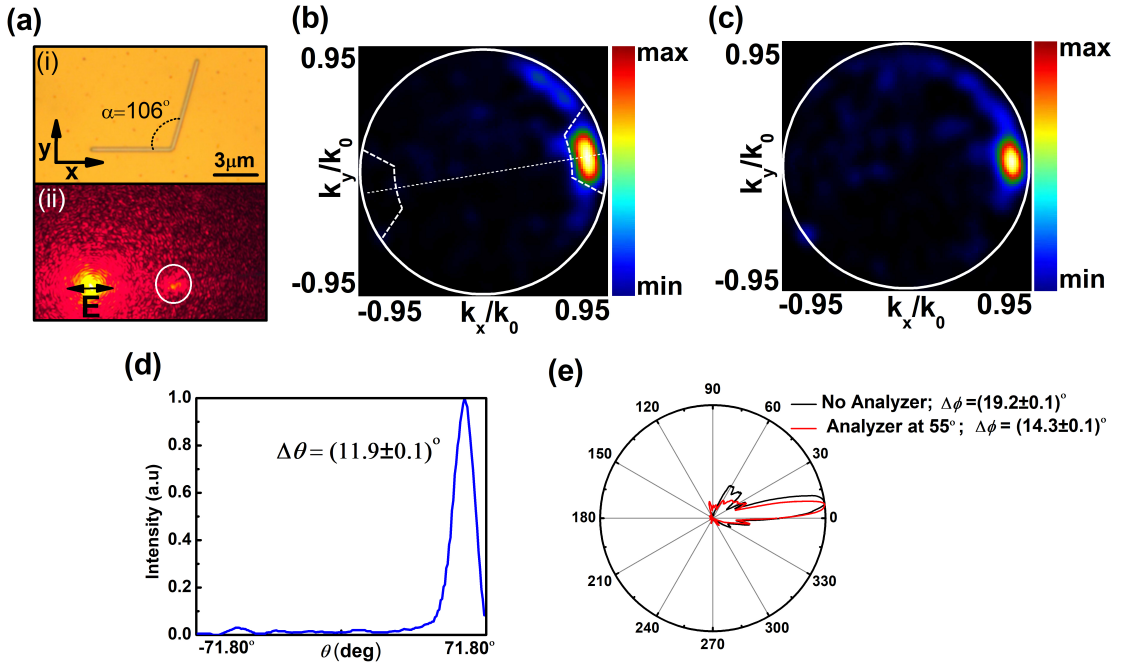


FIGURE 3.3: Directional elastic emission from B-NWoM geometry. (a) (i) Bright field optical image of a bent-nanowire with an inter-arm angle $\alpha=106^\circ$ placed on a 160 nm thick gold mirror. (ii) Corresponding image of the same nanowire excited at one end with a 633 nm laser. (b) Fourier plane image of elastic scattering light from the kink of the nanowire (shown as white circle in (a)(ii)). (c) Polarization resolved Fourier plane image when the emission is analyzed at an angle of 55° with respect to nanowire axis. (d) Intensity cross-cut along the white dotted line in Fourier plane image showing the confinement of light with a FWHM, $\Delta\theta$, of 11.9° . (e) The intensity profile of azimuthal angles (ϕ) for θ corresponding to maximum intensity in the Fourier plane images (c) and (d). The FWHM are only 19.2° and 14.3° for unanalyzed and analyzed emission respectively. Figure reproduced from [6].

3.3.1 Quantifying the elastic emission

To quantify the emission, we define directionality (Dir), using the ratio of forward and backward intensity of emission in the Fourier plane[84], as

$$\text{Dir} = 10\log_{10} \frac{\int \int_{(\theta_m-\delta_1, \phi_m-\delta_2)}^{(\theta_m+\delta_1, \phi_m+\delta_2)} I(\theta, \phi) \sin(\theta) d\theta d\phi}{\int \int_{(\theta_m-\delta_1, \phi_m-\pi-\delta_2)}^{(\theta_m+\delta_1, \phi_m-\pi+\delta_2)} I(\theta, \phi) \sin(\theta) d\theta d\phi} \quad (3.1)$$

where θ_m and ϕ_m are the radial and azimuthal angles with maximum emission. $I(\theta, \phi)$ is the intensity in the Fourier plane image. For the white dotted region in the Fourier plane image (see figure 3.3 (b)), with $\delta_1=7.5^\circ$ and $\delta_2=10^\circ$ the calculated directionality of the emission is (16.2 ± 0.1) dB, which is an excellent number for a structure prepared using bottom-up approach.

In addition to high directionality, an antenna should provide narrow angular distribution along the azimuthal angles. Various structures acting as directional optical antennas have shown high directionality but the spreading in the azimuthal angles of out-coupled emission is very large[21, 33, 43]. The unwanted signatures of leaky modes are also present in the far-field radiation patterns, which reduces the directionality and angular confinement of emission, for example, bent-nanowires placed on glass substrate shows considerably large angular spread along the azimuthal angles. Furthermore, collecting the emission through the air side reduces the collection efficiency, as majority of the emission leaks into the substrate having higher refractive index. The gold substrate used in our experiments acts as a mirror thus minimizes the photon loss due to leakage while decreasing the angular spread of emission.

Intensity cross-cut (figure 3.3 (d)) along the white dotted line in figure 3.3 (b) shows that the emission is confined to a narrow range of radial angles with a full width at half maxima (FWHM) ($\Delta\theta$) of only $(11.9 \pm 0.1)^\circ$. In addition, the intensity profile of azimuthal angles (ϕ) for θ corresponding to maximum intensity in the Fourier plane image shows that the majority of emission is going towards higher wavevectors with a very narrow range of azimuthal angles with a FWHM ($\Delta\phi$) of only $(19.2 \pm 0.1)^\circ$ (see figure 3.3 (e)). Although the propagation of nanowire plasmon polaritons is along the nanowire axis which is along $k_y/k_0=0$ the presence of the kink shifts the out-coupled emission towards higher $+k_y/k_0$.

3.3.2 Polarization resolved Fourier plane imaging

For straight silver nanowires, the emission wavevectors of the out-coupled SPPs from the distal end show interesting polarization signatures[93]. When the out-coupled light from the distal end is analyzed, for a particular polarization the emission is relatively narrow. We show how at a certain angle of analyzer, the angular spread of the emission from B-NWoM geometry can be further reduced. For this, we performed polarization resolved Fourier plane imaging on elastic scattering light from the bent-nanowire. The FWHM of azimuthal spreading in the emission wavevectors reduces from 19.2° to 14.3° at an analyzer angle of 55° with respect to the nanowire axis. The variation of emission wavevectors in Fourier plane images and change in $\Delta\phi$ with respect to analyzer angle is shown in figure 3.4. Also, see table 3.1 for the value of analyzer angle for obtaining minimum $\Delta\phi$ spreading with a change in the inter-arm angles α . In addition, for bent-nanowire, with obtuse inter-arm angles, the value of analyzer for obtaining minimum $\Delta\phi$ spreading is approximately half of the inter-arm angle of the nanowire (Table 3.2). Whereas for acute inter-arm angles, the value of analyzer angle for minimum $\Delta\phi$ spreading changes peculiarly which shows that the far-field radiation pattern and

polarization dependence of emission depends on the exact geometry of the kink of the bent-nanowire.

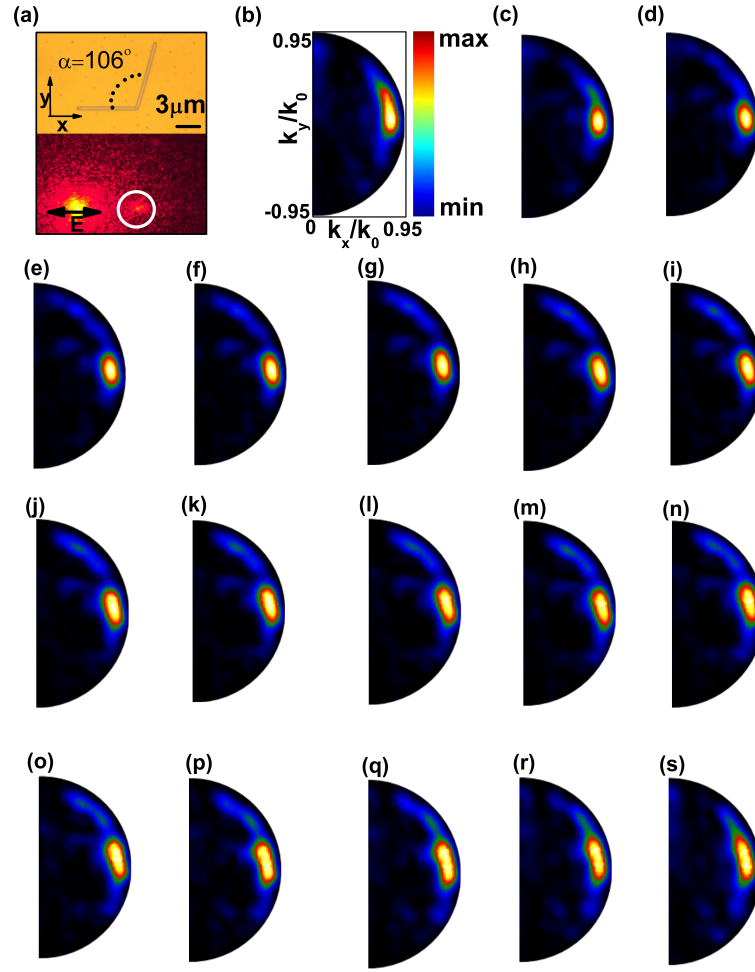


FIGURE 3.4: Variation of emission wavevectors in Fourier plane images with respect to analyzer angle. (a) (i) Bright field optical image of a bent-nanowire with an angle $\alpha=106^\circ$ placed on a 160 nm thick gold mirror. (ii) Elastic scattering image of the same bent-nanowire when one end was excited with 633 nm laser. (b-s) Polarization resolved Fourier plane image of emission from kink part of the bent-nanowire when the emission was analyzed. The analyzer angle was changed from 35° to 205° with a step size of 10° with respect to the nanowire axis. The minimum ϕ spreading was obtained at an analyzer angle of 55° which is nearly half of α . Figure reproduced from [6].

Analyzer angle (°)	$\Delta\phi$ (°)	Analyzer angle (°)	$\Delta\phi$ (°)
No analyzer	19.2	125	19.7
35	26.2	135	19.1
45	15.3	145	19.5
55	14.3	155	19.9
65	14.7	165	21.7
75	15.5	175	24.0
85	16.4	185	25.7
95	16.8	195	25.8
105	18.2	205	23.8
115	20.0	—	—

TABLE 3.1: Variation of $\Delta\phi$ with a change in the analyzer angle.

α (°)	Analyzer angle for minimum $\Delta\phi$ spreading (°)
59	40
106	51
113	80
124	50
125	65

TABLE 3.2: Variation of analyzer angle for minimum $\Delta\phi$ spreading for bent-nanowires with different inter-arm angles α .

3.4 Understanding the mechanism behind directional emission using a chain of dipoles model

To understand the effect of substrate on the far-field wavevector distribution of emission from B-NWoM, we studied far-field radiation pattern from a chain of dipoles[43], to model the waveguiding of light, placed on a glass and a gold substrate, at a distance of $\lambda/200$ from the substrate and oscillating at 633 nm in x, y, or z directions. Although, the exact emission pattern depends on the geometry of the waveguide, yet the effect of substrate on the waveguiding of light using these simulations can be understood. The length of the chain was 1 μm and the distance between consecutive dipoles was 100 nm. The phase retardation between the dipoles was set according to the plasmon propagation wavelength calculated using COMSOL Multiphysics for the thickness of the nanowire used in the experiments (see figure 3.5). AgNW was modelled with a pentagonal cross-section with an edge to edge thickness of 350 nm and length of 10 μm . The gap between the nanowire and substrate was set to be 5 nm. This 5 nm

gap is to model the PVP coating on the AgNW. The refractive indices of the material were taken from ref[94]. The nanowire was excited with a focused Gaussian laser beam of wavelength 633 nm with polarization along the length of the nanowire. The plasmon propagation wavelength (λ_{spp}) for nanowire placed on glass substrate λ_{spp} was calculated to be 557 nm, whereas for nanowire placed on the gold substrate λ_{spp} was 613 nm.

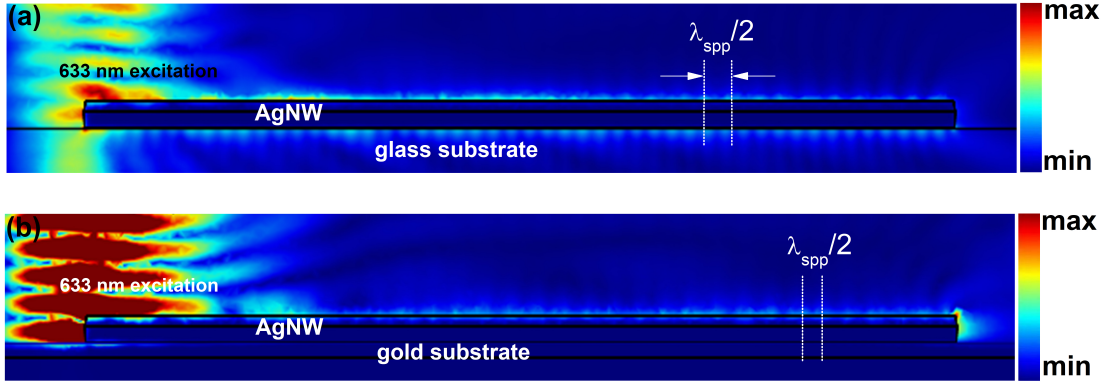


FIGURE 3.5: Calculated near-field electric field and plasmon propagation wavelength for nanowire placed on glass and gold substrate. Near-field electric field of nanowire placed on a glass (a) and gold (b) substrate. The nanowire was excited with a wavelength of 633 nm using a Gaussian excitation with polarization along the length of the nanowire. The plasmon propagation wavelength was 557 nm on a glass substrate and 613 nm on a gold substrate. The length of nanowire in (a) and (b) was 10 μm .

Figure reproduced from [6].

For calculating the far-field radiation pattern, the near-field electric field for a series of dipoles, calculated using FEM based simulations, was transformed to the far-field using reciprocity arguments. Figure 3.6 (a) and (e) show the geometry of the system used in the simulations. The calculated Fourier plane image for a chain of dipoles, oriented along z axis, placed on a glass substrate and oscillating at 633 nm is shown in figure 3.6 (b). The emission is confined to higher $+k_x/k_0$ values which is along the direction of wave propagation. Intensity cross-cuts along the $k_y/k_0 = 0$ value in Fourier plane images for a chain of x , y , and z oriented dipoles show that the emission is more confined in terms of radial angles when the orientation of dipoles is along z (see figure 3.6 (c)). The in-plane oriented dipoles give relatively broader emission. Comparison between the intensity profile of azimuthal angles (ϕ) for θ corresponding to maximum intensity in the Fourier plane images for x , y , and z oriented dipoles shows that the spreading is approximately same for all the orientations (see figure 3.6 (d)).

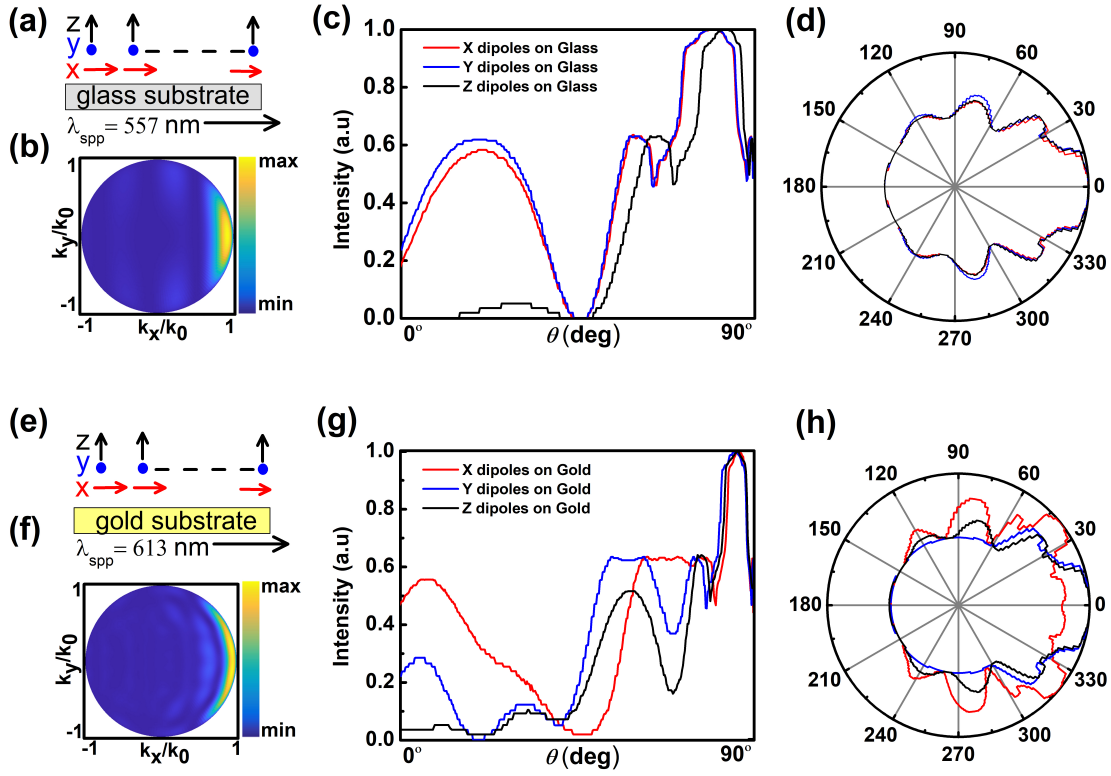


FIGURE 3.6: Effect of substrate on the far-field radiation pattern of the emission from a chain of dipoles. (a) A chain of 10 dipoles (x, y, or z oriented) placed at a distance of $\lambda/200$ from glass substrate. The phase retardation between the dipoles are set according to the plasmon propagation wavelength of 557 nm. (b) Calculated Fourier plane image for a series of z oriented dipoles on glass substrate. (c) Intensity cross-cuts along the $k_y/k_0 = 0$ in the calculated Fourier plane images for a series of x, y, and z oriented dipoles. (d) Intensity profiles of azimuthal angles (ϕ) for θ corresponding to maximum intensity in the Fourier plane images. (e) Chain of 10 dipoles (x, y, or z oriented) placed at a distance of $\lambda/200$ from gold substrate. The phase retardation between the dipoles are set according to the plasmon propagation wavelength of 613 nm. (f) Calculated Fourier plane image for a series of z oriented dipoles on gold substrate. (g) Intensity cross-cuts along the $k_y/k_0 = 0$ in the calculated Fourier plane images for a series of x, y, and z dipoles. (h) Intensity profiles of azimuthal angles (ϕ) for θ corresponding to maximum intensity in the Fourier plane images. The complete length of the chain is $1 \mu\text{m}$ and the dipoles are oscillating at 633 nm. Figure reproduced from [6].

The above mentioned results suggest that for a waveguide placed on a substrate, the emission will be more confined in the Fourier plane, for an intense z field, which can be achieved by using a gold substrate. For this, we simulated the far-field radiation pattern from a chain of x, y, and z oriented dipoles placed on a gold substrate at a distance of $\lambda/200$ from the substrate. Even for a gold substrate, the emission is more confined

in radial and azimuthal angles for z oriented dipoles as compared to in-plane x or y oriented dipoles (see figure 3.6 (g) and (h)). The results suggest the importance of gold substrate and intense z field in providing better directionality for waveguides.

3.5 Utilizing the cavity for beaming SERS emission

Using three-dimensional electrodynamics simulations, we studied how B-NWoM cavity can be used to enhance and direct secondary emission from molecules. For calculating near-field electric field, we performed three-dimensional finite difference time domain (FDTD) calculations in Lumerical software. The details of the geometry and other parameters used in the simulations are given in figure 3.7. Near-field electric field and far-field radiation pattern were simulated in Lumerical FDTD software. The nanowire was modelled as a cylindrical rod of length $6\ \mu\text{m}$ and radius of cylinder was set to be $125\ \text{nm}$. The end radius of the cylindrical rod was set to be $110\ \text{nm}$ to match the geometry of the kink part of the bent-nanowire. The nanowire was placed on a $100\ \text{nm}$ thick gold substrate and the gap between the nanowire and gold substrate was set to be $5\ \text{nm}$. This $5\ \text{nm}$ gap is to model the PVP coating on the AgNW. The radiation pattern was calculated by projecting the near-field to the far field from a small region of the nanowire which contains the kink part of the bent-nanowire.

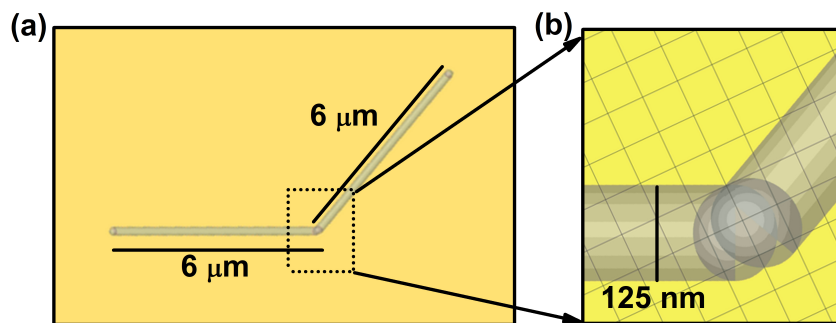


FIGURE 3.7: Geometry of the system used in FDTD simulations. Figure reproduced from [6].

Figure 3.8 (a-c) show the component wise magnitude of near-field electric field (E_z , E_y , and E_x respectively) in the B-NWoM cavity when one end of the nanowire was excited with a focused Gaussian beam of wavelength $633\ \text{nm}$ with polarization along the length of nanowire. Though the cavity is excited with a laser having in-plane polarization along the nanowire, the magnitude of out-of-plane, E_z field in the cavity is much stronger than in-plane E_x and E_y fields. The results show that for utilizing the maximum field present in the cavity for enhanced scattering, the orientation of the molecule should be out-of-plane or in the z direction.

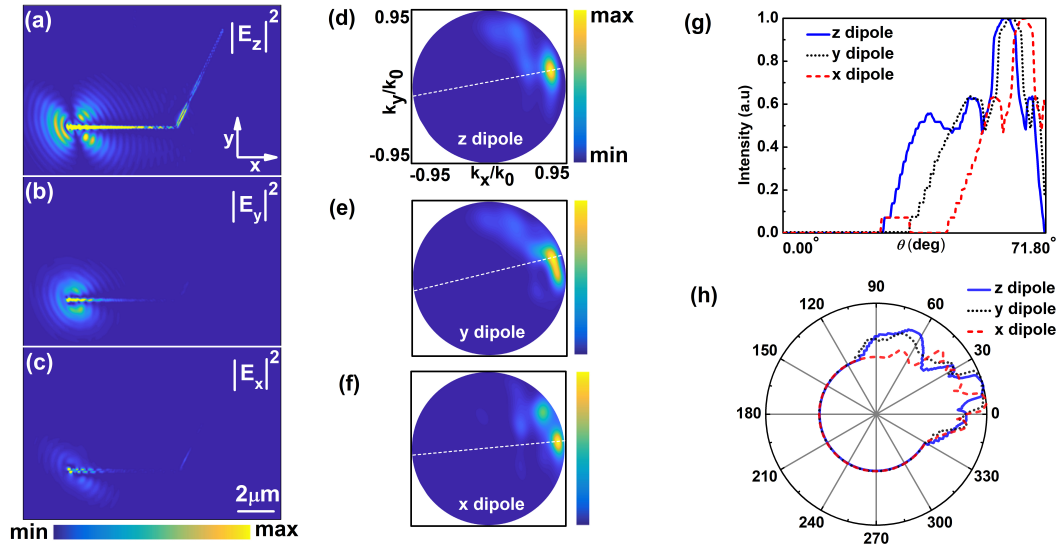


FIGURE 3.8: Calculated component wise near-field electric field magnitude in the B-NWoM cavity and Fourier plane images of emission from the kink upon excitation of one end of nanowire with different orientation of molecules. (a-c) Calculated component wise near-field electric field inside the cavity for magnitude of E_z , E_y , and E_x respectively, upon excitation of nanowire end with 633 nm Gaussian excitation with polarization along the nanowire length. (d-f) Calculated Fourier plane images of the emission from kink when nanowire end is excited with z, y, and x dipoles respectively by individually placing a dipole at a wavelength of 703 nm in the B-NWoM cavity. (g) Intensity cross-cuts along the white dotted line in Fourier plane images (d-f). Only positive angular values are shown. (h) The intensity profile of azimuthal angles (ϕ) for θ corresponding to maximum intensity in the Fourier plane images (d-f). Figure reproduced from [6].

Next, we studied for which orientation of the dipole, the out-coupled emission from the kink is more directional and confined. For this, we calculated Fourier plane images of emission from the kink. We placed dipoles with x, y, and z orientations in the B-NWoM cavity, near the end of the nanowire and projected the near-field electric field of the kink region to the far-field. Figure 3.8 (d-f) show the calculated Fourier plane images from the kink region of the B-NWoM cavity, when an individual z, y, or x dipole oscillating at a wavelength of 703 nm is placed in the cavity respectively. The wavelength of dipole oscillation is chosen to be 703 nm as the BPT molecules used in the SERS experiments has a prominent Raman mode at 703 nm. Quantitatively, the intensity cross-cuts along the white dotted lines in the Fourier plane images (figure 3.8 (d-f) shows that the emission is more confined in the radial direction for x and z dipoles as compared to the y dipole (see figure 3.8 (g)). The intensity profile of azimuthal angles (figure 3.8 (h)) (ϕ) for θ corresponding to maximum intensity in the Fourier plane images (d-f) show that the azimuthal spreading for the z and x dipoles is relatively less

as compared to y dipole. This makes the z oriented dipoles to be extremely beneficial for utilizing the B-NWoM cavity for enhancement and high directionality as the E_z field is more intense in the cavity and the emission is narrower when the dipole orientation in the cavity is along z direction.

3.5.1 B-NWoM cavity for beaming SERS from molecular monolayer

To utilize the B-NWoM cavity for enhancing and directing SERS emission from molecules, we used a monolayer of vertically oriented self-assembled monolayer of BPT molecules on gold mirror. Figure 3.9 shows a bent-nanowire with an inter-arm angle of 133° drop-casted on a gold mirror over which there is a self-assembled monolayer of vertically oriented BPT molecules. One end of the nanowire was excited using a high numerical aperture objective lens with a 633 nm laser with polarization along the nanowire (figure 3.9 (a)(ii)). Due to the presence of cavity between the nanowire and mirror the molecules undergo SERS emission which gets couples to the nanowire plasmons. These plasmons get out-coupled as free-space photons from the kink. In addition, the SPPs propagating along the nanowire also get out-coupled from the kink of the nanowire, exciting the molecules present at the kink. The out-coupled emission from the kink was spatially filtered and projected to the spectrometer after rejecting the elastic scattered light for spectroscopy and energy-momentum imaging and to EMCCD for Fourier plane imaging.

The spectrum (figure 3.9 (b)) collected from the kink of the nanowire shows the SERS signatures of BPT molecules riding over a broad background. To study the directionality of the wavevector of remotely collected SERS spectrum from the BPT molecules, we performed Fourier plane imaging on SERS emission by spatially filtering the kink region and projecting it to EMCCD. The Fourier plane image (figure 3.9 (c)) shows that the SERS emission is beaming towards higher k-values in a small lobe having very narrow angular spreading. The emission is slightly shifted towards higher $+k_y/k_0$ values and is not along the axis of nanowire because of the presence of kink.

Along with sharp SERS lines in the spectrum there is also an inelastic background emission from the PVP molecules of the nanowire[95], which also gets captured undesirably in the Fourier plane image. To confirm that the emission at higher values was indeed SERS and not inelastic background emission, we performed energy-momentum imaging[17, 75], where selected portion of Fourier plane image is dispersed in the spectrometer to get the wavelength or energy information. We projected a part of Fourier plane image around the white dotted line to the spectrometer and dispersed it in terms of wavelength. The energy-momentum image (figure 3.9 (d)) has greater intensity counts

at higher k -values which confirms the out-coupling of both SERS and background from the kink at higher k -vectors.

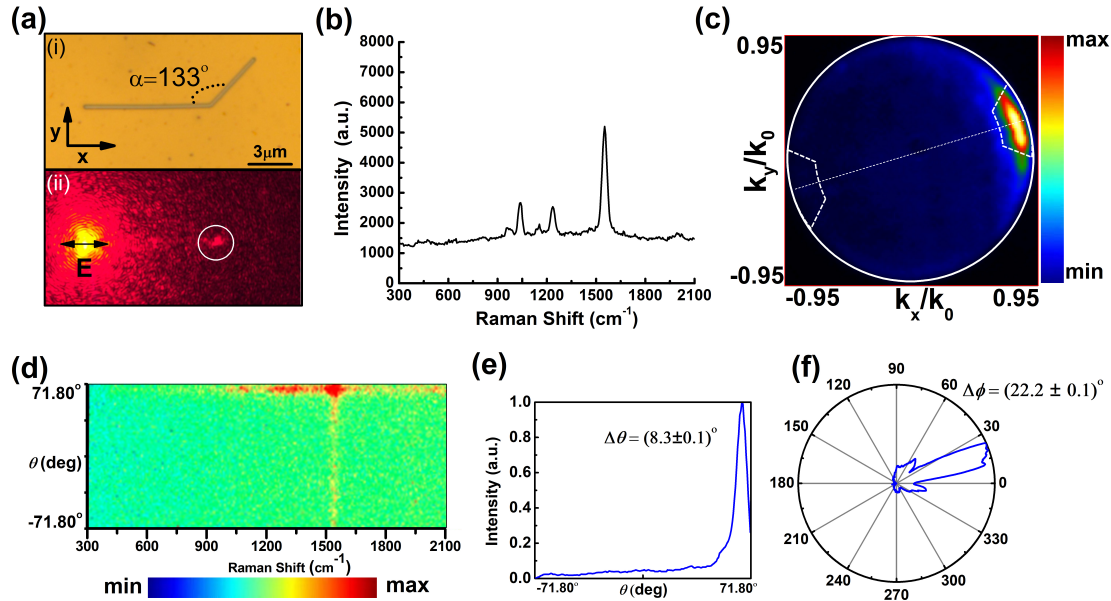


FIGURE 3.9: Directional SERS emission from B-NWoM cavity. (a) Bright field optical image of a bent-nanowire with an inter-arm angle $\alpha = 133^\circ$ placed on a gold mirror over which there is a self-assembled monolayer of BPT molecules. Elastic scattering image of the same bent-nanowire when one end was excited with 633 nm laser. (b) SERS spectrum from a monolayer of BPT molecules collected remotely from the white circle shown in (a)(ii). (c) Fourier plane image of SERS emission collected from the white region in (a)(ii) after rejecting elastic scattering light. (d) Energy-momentum imaging showing the directional out-coupling of the Raman lines and inelastic background to higher angles. (e) Intensity cross-cut along the white dotted line in Fourier plane image showing the confinement of light with a FWHM of only 8.3° . (f) The intensity profile of azimuthal angles (ϕ) for θ corresponding to maximum intensity in the Fourier plane image. The emission is very sharp with FWHM of only 22.2° . Figure reproduced from [6].

3.5.2 Quantifying the SERS emission

To quantify the emission, we used equation (3.1) to calculate the directionality of the emission. For the white dotted region in Figure 3.9 (c), with $\delta_1 = 7.5^\circ$ and $\delta_2 = 12.5^\circ$, the calculated directionality is (12.5 ± 0.1) dB which is greater than the maximum values reported for directionality calculation for inelastic antennas[21, 96, 97] because of the presence of single orientation of molecules in the B-NWoM cavity.

The intensity cross-cut (figure 3.9 (e)) along the white dotted line in the Fourier plane image shows that the emission is very narrow in radial angles with a FWHM of only $(8.3 \pm 0.1)^\circ$. Furthermore, the intensity profile of azimuthal angles (figure 3.9 (f))

(ϕ) for θ corresponding to maximum intensity in the Fourier plane image shows that the emission has a FWHM of only $(22.2 \pm 0.1)^\circ$ which is relatively less as compared to other reported values[21, 96] because of the presence of only one orientation of molecules in the B-NWoM cavity.

3.5.3 Straight and bent-silver nanowire on a mirror with dropcasted BPT molecules in the cavity

As compared to the emission wavevectors from B-NWoM using BPT molecular monolayer, the emission wavevectors from the dropcasted molecules are relatively broader when used either with nanowire on mirror or kink-nanowire on mirror cavities because of the preferred in-plane orientation of the dropcasted molecules.

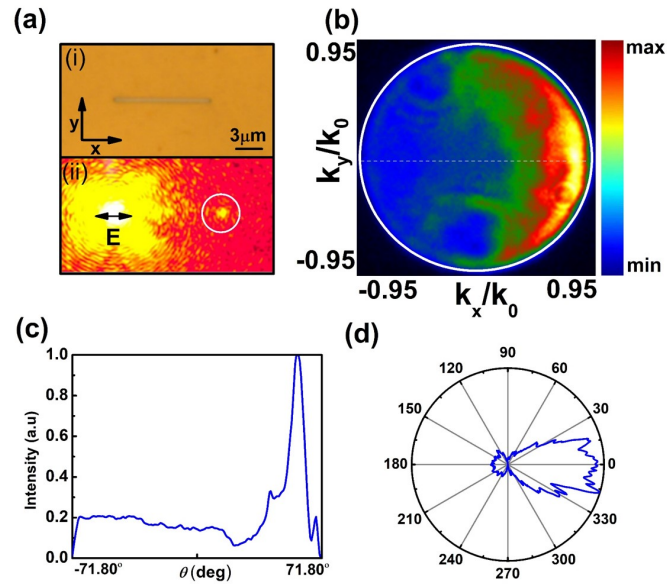


FIGURE 3.10: Fourier plane imaging of SERS emission collected remotely from the nanowire end with BPT molecules dropcasted on mirror. (a) Optical image of a silver nanowire dropcasted on a 160 nm thick gold mirror. (i) Bright field image. (ii) Elastic scattering image of the same nanowire when one end of nanowire was excited using a 633 nm laser. (b) Fourier plane image of SERS emission collected remotely from the nanowire end. (c) Intensity cross-cut along the $k_y/k_0=0$ line. (d) The intensity profile of azimuthal angles (ϕ) for θ corresponding to maximum intensity in the Fourier plane image (b). Figure reproduced from [6].

Figure 3.10 shows the Fourier plane imaging of SERS emission collected from the nanowire end. The BPT molecules are dropcasted on a 160 nm thick gold mirror and were left to dry. Silver nanowire was dropcasted on the BPT molecule coated gold mirror. One end of the nanowire was excited using a high numerical aperture objective lens and the out-coupled light from the distal end was collected using the same

objective lens. The emission was projected was projected to the EMCCD for Fourier plane imaging. The Fourier plane image shows that the emission is directed towards higher wavevectors. Since the molecules are dropcasted on the mirror, majority of the molecules are distributed in plane and the chances of molecules standing vertically on the mirror is negligible. Therefore, the emission is distributed broadly in terms of angles in the Fourier plane image. The intensity cross-cut (figure 3.10 (c)) along the white dotted line shows that the emission is confined in terms of radial angles with a FWHM of 8.8° . But the backward emission is also prominent [43] which reduces the directionality of the emission. The intensity profile of azimuthal angles (figure 3.10 (d)) (ϕ) for θ corresponding to maximum intensity in the Fourier plane image shows that the emission is very broad in azimuthal angles with a FWHM of 62.4° .

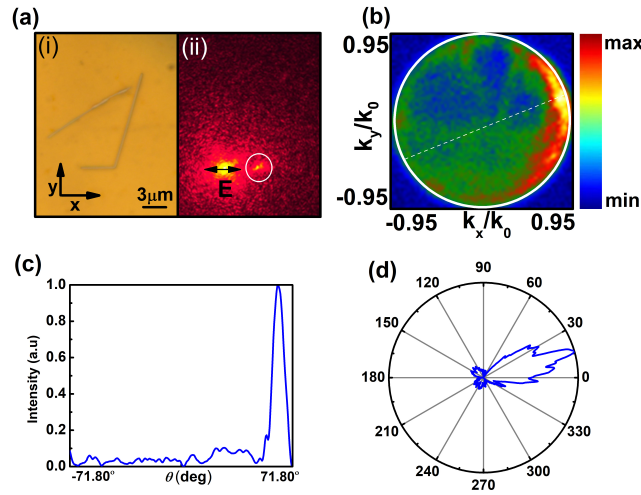


FIGURE 3.11: Fourier plane imaging of SERS emission from kink nanowire on mirror cavity with dropcasted BPT molecules. (a) Optical image of a bent-nanowire dropcasted on a 160 nm thick gold mirror. The inter-arm angle is 106° . The BPT molecules are dropcasted on the gold mirror. (i) Bright field optical image. (ii) Elastic scattering image of the same bent-nanowire when one end of nanowire was excited using a 633 nm laser. (b) Fourier plane image of SERS emission collected remotely from the kink part of the bent-nanowire end using spatial filtering. (c) Intensity cross-cut along the $k_y/k_0=0$ line in the Fourier plane image shows the biasing of light in one direction in a narrow range of radial angles (ϕ). (d) The intensity profile of azimuthal angles (ϕ) for θ corresponding to maximum intensity in the Fourier plane image (b). Figure reproduced from [6].

Figure 3.11 shows the Fourier plane imaging of SERS emission from dropcasted molecules on a 160 nm thick gold mirror in B-NWoM cavity. The preferred orientation of dropcasted molecules are in-plane and thus the directionality in the emission is because of x and y oriented dipoles which is relatively broad as compared to the z oriented

dipoles. The cross-cut along the white dotted line in the Fourier plane image shows that the emission is confined in terms of radial angles (FWHM of 8.8°) but the emission in other regions is prominent. Similarly, the intensity profile of azimuthal angles (ϕ) for θ corresponding to maximum intensity in the Fourier plane image (b) also shows relatively broad emission (FWHM of 42.2°) as compared to spreading with z oriented molecules as shown in figure 3.9 (FWHM of 22.2°).

3.5.4 Silver nanowire on a mirror with monolayer of BPT molecules in the cavity

The confinement of wavevector increases when silver nanowire is used with BPT molecular monolayer but because of finite reflection[43] from the end of nanowire the back scattered light also increases which reduces the directionality of emission. Whereas, with B-NWoM geometry, the kink part of the bent-nanowire does not efficiently reflect the light in the backward direction and majority of the emission is only projected to the forward direction which results in high unidirectionality of the emission.

Figure 3.12 shows the Fourier plane imaging of SERS emission collected from the nanowire end. Silver nanowire was dropcasted on a self-assembled monolayer of BPT molecule coated gold mirror. One end of the nanowire was excited using a high numerical aperture objective lens and the out-coupled light from the distal end was collected using the same objective lens. The emission was projected to the EM-CCD for Fourier plane imaging. The Fourier plane image shows that the emission is directed towards higher wavevectors.

Since the molecules are vertically oriented the emission is relatively narrow in terms of radial and azimuthal angles. The emission in the backward direction is still prominent in the backward direction. The intensity cross-cut along the white dotted line in the Fourier plane image shows that the emission is relatively narrow in radial angles (FWHM of 8.6°) as compared to the spreading when the molecules are dropcasted on the mirror. Even for azimuthal angles, the spreading reduces (FWHM of 49.4°) as compared to the case when the molecules are dropcasted.

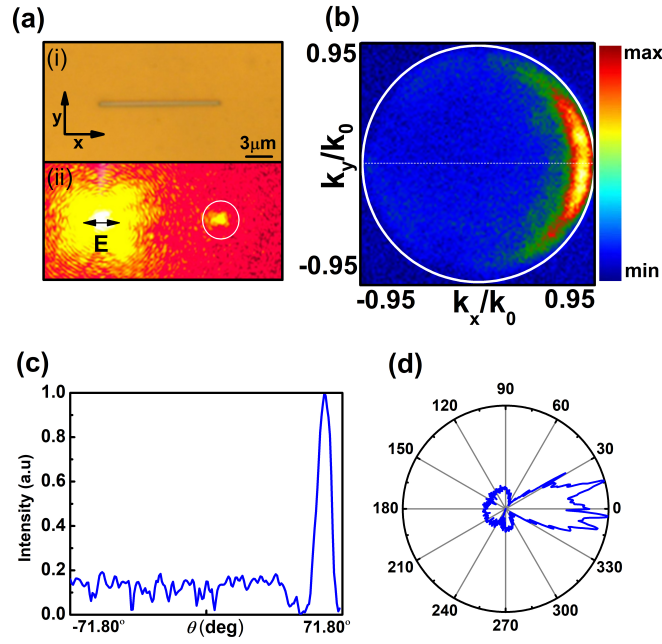


FIGURE 3.12: Fourier plane imaging of SERS emission collected remotely from the nanowire end. (a) Optical image of a silver nanowire dropcasted on a 160 nm thick gold mirror with a self-assembled monolayer of BPT molecules. (i) Bright field optical image of nanowire placed on a gold mirror. (ii) Elastic scattering image of the same nanowire when one end of nanowire was excited using a 633 nm laser. (b) Fourier plane image of SERS emission collected remotely from the nanowire end using spatial filtering. (c) Intensity cross-cut along the $k_y/k_0=0$ line in the Fourier plane image shows the biasing of light in one direction in a narrow range of radial angles (θ). (d) The intensity profile of azimuthal angles (ϕ) for θ corresponding to maximum intensity in the Fourier plane image (b). Figure reproduced from [6].

3.6 Variation of far-field radiation angles with a change in the bending angle

Finally, we show that the far-field angular distribution can be tuned by changing the bending angles of nanowire. We performed experiments and FDTD based simulations to study the variation of radiation pattern for elastic and SERS emission with a change in the inter-arm angle of the nanowire. Figure 3.13 shows the geometry used in the simulation and a representative calculated Fourier plane image of elastic emission from the bent-nanowire on mirror geometry. Table 3.3 shows the variation of ϕ_m (the azimuthal angle, where the emission is maximum in Fourier plane image) for elastic scattering and SERS emission (both experimental and FDTD calculations) with a change in the inter-arm angle of bent-nanowire.

In the case of elastic scattering, for bent-nanowire with acute or right angle inter-arm angles, ϕ_m is along the length of nanowire. For obtuse angles, the emission changes from 152° (for $\alpha=125^\circ$) to 171° (for $\alpha=106^\circ$). The exact angular pattern depends on the geometry of the kink of the bent-nanowire. The calculations suggest that the emission is mainly directed towards angles slightly towards upper side of the nanowire and is always greater than 170° . For SERS, the emission is along the nanowire axis for acute angles, and for obtuse angles it varies from 157° (for $\alpha=108^\circ$) to 166° (for $\alpha=156^\circ$). The calculations for radiation pattern for SERS emission shows a good agreement with the experimentally obtained data and the slight difference can be attributed because a slight change in the geometry can result in the radiation pattern at different angles. On one hand the straight nanowires are unable to provide good directionality to the emission, on the other hand, when the kink region becomes distorted the emission again becomes broader in nature. For bending angle near 90° , the area of the kink region becomes larger as compared to the area of the kink for bending angles 135° . For bending angles approaching 180° , the bent-nanowire starts to act as a straight nanowire, and the spreading of the emission start to increase[21].

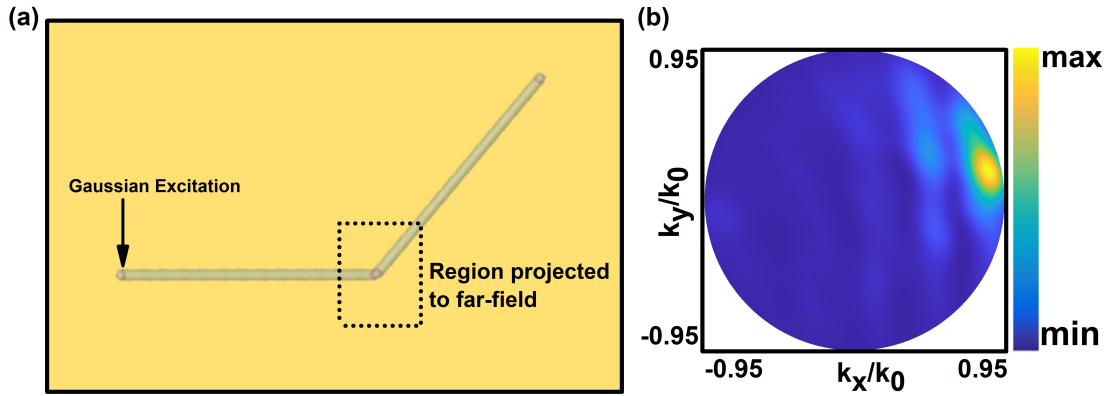


FIGURE 3.13: Calculated Fourier plane image of elastic emission from the bent-nanowire on mirror geometry. (a) Geometry used in the calculations. The end of the nanowire is excited using a Gaussian excitation and the near-field from the kink part of bent-nanowire (shown in a rectangular dotted box) was projected to the far-field. (b) Calculated Fourier plane image of elastic emission from a bent-nanowire on mirror geometry with inter-arm angle 130° showing the out-coupled emission in a narrow range of wavevectors. Figure reproduced from [6].

Elastic (Exp) $\alpha(^{\circ})$, $(\phi_m)(^{\circ})$	Elastic (Sim)	SERS (Exp)	SERS (Sim)
84, 180	84, 174	50, 178	50, 187
93, 179	93, 174	69, 179	69, 172
106, 171	106, 176	108, 157	108, 175
114, 169	114, 172	133, 156	133, 165
119, 174	119, 173	135, 154	135, 167
125, 152	125, 174	152, 158	152, 170
143, 168	143, 173	15, 166	156, 168

TABLE 3.3: Variation of ϕ_m with a change in the inter-arm angle of bent-nanowire.

3.7 Conclusion

To conclude, we have shown beaming elastic and SERS emission with extremely narrow wavevector distribution using B-NWoM cavity. Instead of using conventional substrate with high refractive index, we utilized gold mirror for procuring beaming elastic scattering light from the kink portion of bent-nanowire. In addition, we utilized an extended B-NWoM cavity formed between nanowire and mirror to direct SERS emission from a monolayer of vertically standing molecules sandwiched between nanowire and mirror. We used three-dimensional numerical simulations to corroborate the experimental results and to get insights on how to use the cavity for directing inelastic emission from molecules with a good control on the orientation of molecules. The B-NWoM geometry provides excellent angular confinement to the emission in the far-field with radial and azimuthal spreading with a FWHM of only 11.9° and 14.3° for elastic and 8.3° and 22.2° for SERS emission. The results presented here will readily be extrapolated to study and direct emission from two-dimensional materials placed in the elongated B-NWoM cavity. The strong electric field generated at the kink of the B-NWoM structures can also be used to remotely detect single molecule SERS signatures in fluid-phase and to study strong coupling physics.

Chapter 4

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

This chapter is an adapted version of the research article "Journal of Optics, 23(12), 124001 (2021)". This article discusses how a nanowire-nanoparticle on a mirror cavity can direct SERS emission in remote excitation configuration.

4.1 Introduction

Controlling photo-physics of molecules has far reaching implications in understanding many aspects of quantum physics[3] and in applications such as biomedical imaging[98], designing molecular antennas[30, 82, 83], and catalysis[99]. A simple way to achieve this control is to couple molecules to confined optical fields like plasmonic cavities[4, 16], whispering gallery microcavities[100] and Fabry-Pérot cavities[101].

In the previous chapter, the wavevectors of SERS emission from molecular monolayers were directed by utilizing an extended mirror based plasmonic cavity. The molecular monolayer was sandwiched between the bent-nanowire and the mirror. The molecules were present both in the excitation and collection regions.

Here, we show SERS emission from a different kind of geometry where the cavity is designed in such a way that the molecular monolayer is present away from the excitation region. This ensures, no collection of emission from the direct excitation which can otherwise deteriorate the directionality of the antenna.

We placed a molecule coated nanoparticle near a plasmonic nanowire to utilize the localized electric field provided by the cavity formed between the particle and nanowire.

Coupling nanoparticle with a plasmonic nanowire[102–106] offers the possibility of remotely exciting[64, 107] the cavity using nanowire as a waveguide which eliminates the damage caused to the molecules in the direct excitation of cavity. Placing the nanowire-nanoparticle on a metallic mirror generates particle-mirror particle cavity having ultra-small mode volumes[34, 108]. In addition to the enhancement, metal substrates direct majority of the emission to the collection objectives[11, 49], because of the absence of leakage radiation which occurs in using high refractive index substrates[3].

Motivated by this, we study nanowire-nanoparticle junction, by placing it on a gold substrate. The geometry provides a superior control on the placement of molecules in the cavity. We study the junction placed on a gold mirror in remote excitation configuration. The fields generated in the NW-NP and NP on mirror (NP-Mirror) cavities enhance the Raman scattering from the molecules coated on the nanoparticle and also reduce the angular spread of emission.

4.2 Architecture of the system

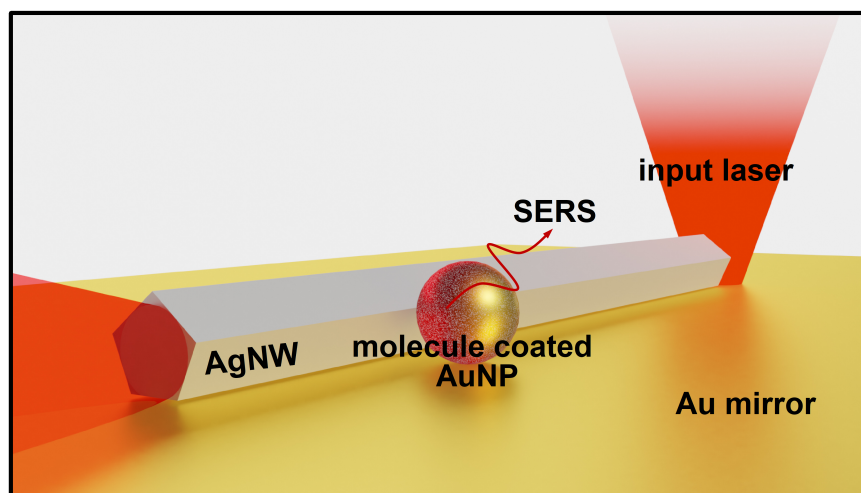


FIGURE 4.1: Schematic of the experimental configuration. A BPT coated AuNP was assembled near an AgNW placed on a gold mirror using self-assembly. One end of the AgNW was excited with a focused 633 nm laser. The SERS emission from the NW-NP junction was collected and its spectral and wavevector distribution were studied using spectroscopy and Fourier plane and energy-momentum imaging. Figure reproduced from [109].

A schematic of the experimental configuration is shown in figure 4.1. One end of the AgNW was excited with a 633 nm laser using a 100x, 0.95 numerical aperture objective lens. AgNW surface plasmon polaritons (SPPs) get scattered by NW-NP junction and

out-couple as free space photons and also excites 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. 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 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.

4.2.1 Preparing the junction

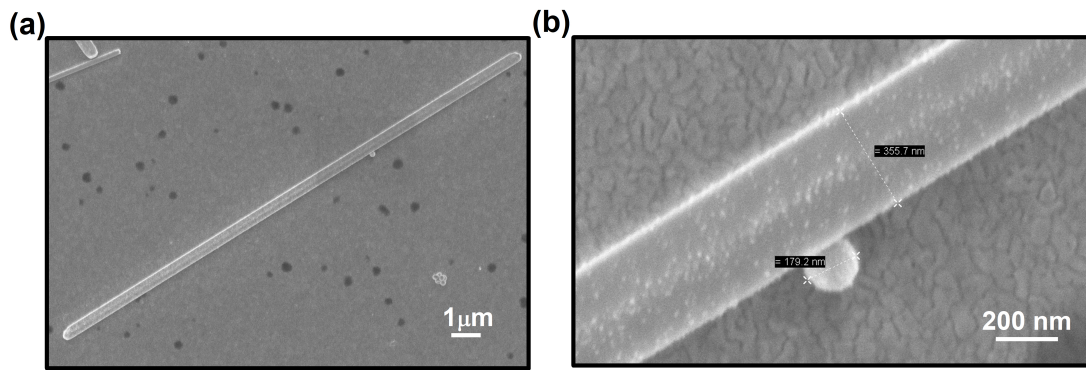


FIGURE 4.2: Scanning electron microscope image of a self-assembled NW-NP junction formed using a 356 nm thick silver nanowire and ≈ 180 nm gold particle placed on a 160 nm thick gold mirror. Figure reproduced from [110].

Single crystalline silver nanowires were prepared using polyol process[91]. The nanowires have a pentagonal cross-section with an average thickness (edge to edge) of ≈ 350 nm. Gold film of thickness 160 nm was deposited on a 2 nm chromium coated glass coverslip using thermal vapor 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 hours. Because of the presence of thiol bonds, the molecules get attached to the gold surface strongly. 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 in ethanol solution. NW-NP junction was prepared using self-assembly technique[111]. Silver nanowires dispersed in ethanol solution were dropcasted on a

gold mirror and left to dry. After this, molecules coated gold nanoparticles were drop-casted on the gold substrate. Gold nanoparticles tend to sit near the nanowire forming a self-assembled junction (figure 4.2). To confirm the presence of molecules only in the cavity and not elsewhere, we performed SERS experiments by exciting the junction and only the nanowire. The spectra from the wire and the junction show that the emission originates only from the junction as the molecules are present only on the nanoparticle (figure 4.3).

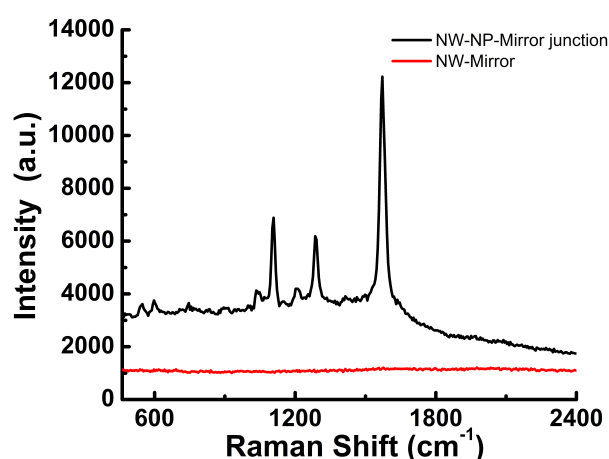


FIGURE 4.3: Spectra collected from the NW-NP on mirror cavity (black curve) and only from the nanowire on mirror cavity (red curve) with the same input intensity and exposure time. The spectra show that the emission originates only from the junction as the molecules are present only on the nanoparticle. Figure reproduced from [110].

4.3 Directional SERS emission from the cavity

Figure 4.4 (a) (i) shows bright field image of a ≈ 180 nm NP coated with BPT molecules, assembled near an AgNW of thickness ≈ 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 4.4 (a)(ii). Figure 4.4 (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 AgNW and the metal film remotely excite the gap plasmons in the NW-NP and NP-Mirror cavities respectively. Intense electric field in the cavities due to these generated gap plasmons, results in the enhanced Raman scattering from the BPT molecules coated on the particle. We used a thick nanowire, diameter ≈ 350 nm, to get better waveguiding properties[43, 63], as we probed the NW-NP using 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 4.4 (a)(iii)) was collected. The remotely excited SERS spectrum of the BPT molecules from NW-NP junction on mirror is shown in Figure 4.4 (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.

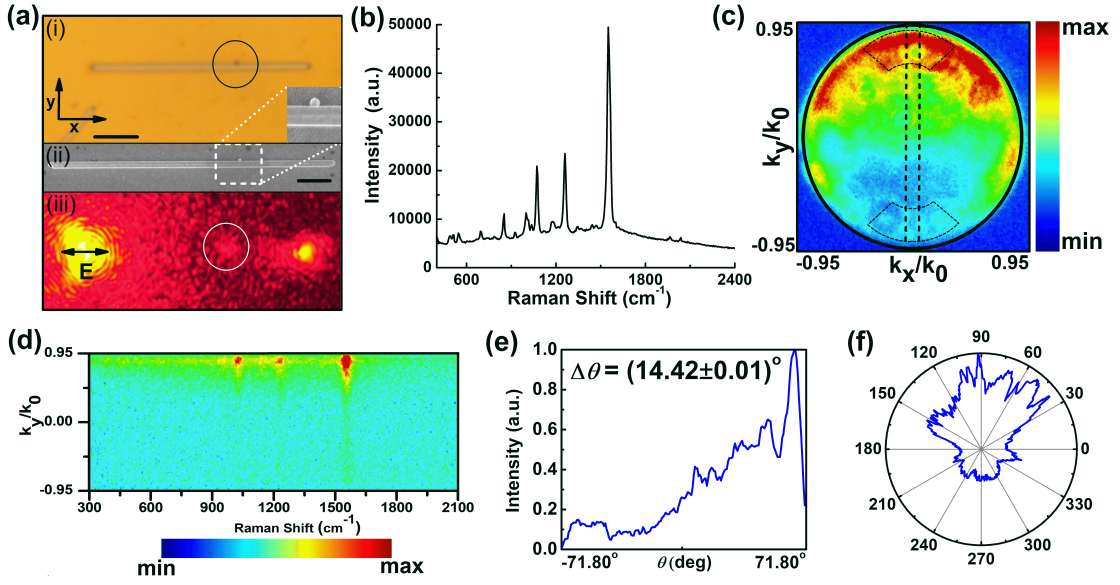


FIGURE 4.4: Remote excitation and Fourier plane imaging of SERS emission. (a) Optical imaging: (i) Bright field image of a ≈ 180 nm AuNP coated with BPT molecules coupled to an AgNW placed on a gold mirror. Scale bar is $3 \mu\text{m}$. (ii) Scanning electron microscopy image of the same NW-NP junction. Scale bar is $3 \mu\text{m}$. (iii). Elastic scattering image upon excitation of one end of AgNW with incident light polarized along the AgNW. (b) SERS spectrum of remotely excited BPT molecules collected from the NW-NP on mirror junction. (c) Fourier plane image of SERS emission collected from the NW-NP junction. (d) Energy-momentum image captured after dispersing a small portion of Fourier plane image (shown in dotted black rectangle around $k_x/k_0=0$) shows the directional out-coupling of the Raman lines and inelastic background. (e) Intensity cross-cut along the $k_x/k_0=0$ line in the Fourier plane image. (f) The intensity profile of azimuthal angles (ϕ) for θ corresponding to maximum intensity in the Fourier plane image (c). Figure reproduced from [110].

To study the wavevector distribution of remotely excited SERS emission, we performed Fourier plane imaging, which quantifies the directionality of emission in terms

of radial (θ) and azimuthal angles (ϕ). The Fourier plane image (figure 4.4 (c)) shows that the maximum SERS emission is biased towards higher k_y/k_0 . Along with the SERS emission from the BPT molecules, there can also be an inelastic background emission from the PVP coating on the nanowire[95] which can also out-couple at higher angles.

To further confirm that the majority of emission at higher $+k_y/k_0$ angles is the SERS emission from the molecules, we performed energy-momentum imaging[59, 75] on the emission from the junction. A small portion of the Fourier plane image along $k_x/k_0=0$ was projected onto the slit of the spectrometer and dispersed to get the image shown in figure 4.4 (d). The energy- momentum image reveals that both SERS signal and the inelastic background from the junction out-couples at higher wavevectors.

4.3.1 Quantifying the SERS emission

To quantify the emission, we defined directionality (Dir), using the ratio of forward and backward intensity of emission in Fourier plane[84], as

$$\text{Dir} = 10\log_{10} \frac{\int \int_{(\theta_m-\delta_1, \phi_m-\delta_2)}^{(\theta_m+\delta_1, \phi_m+\delta_2)} I(\theta, \phi) \sin(\theta) d\theta d\phi}{\int \int_{(\theta_m-\delta_1, \phi_m-\pi-\delta_2)}^{(\theta_m+\delta_1, \phi_m-\pi+\delta_2)} I(\theta, \phi) \sin(\theta) d\theta d\phi} \quad (4.1)$$

Where θ_m and ϕ_m are the radial and azimuthal angles with maximum emission. $I(\theta, \phi)$ 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 directionality changes from 7.7 to 8.2 dB for different values of δ_1 and δ_2 . Intensity cross-cut along $k_x/k_0=0$ in the Fourier plane image (figure 4.4 (c)) shows that the emission is sharp with a full width at half maxima (FWHM) of $(14.42 \pm 0.01)^\circ$ (figure 4.4 (e)). The intensity profile of azimuthal angles (ϕ) for θ corresponding to maximum intensity in the Fourier plane image shows that majority of emission is going along the NW-NP junction.

4.4 Remote excitation: A necessity for directional SERS

To show the importance of remotely exciting the junction in procuring the directional emission, we performed Fourier plane imaging of emission from the junction in direct excitation configuration. The Fourier plane image (figure 4.5 (a)) shows that the emission is biased towards the higher k_y/k_0 values which is along the junction, but covers a very large range of wavevectors. The direct excitation configuration excites molecules in a large spatial region, which leads to the out-coupling of emission at relatively large range of wavevectors. The intensity cross-cut (figure 4.5 (c), black curve) along $k_x/k_0=0$

in the Fourier plane image (figure 4.5 (a)) shows that the emission is biased towards higher k_y/k_0 values but spread in a large area in the Fourier plane image as compared to the spreading obtained in the remote excitation configuration (figure 4.4 (c)).

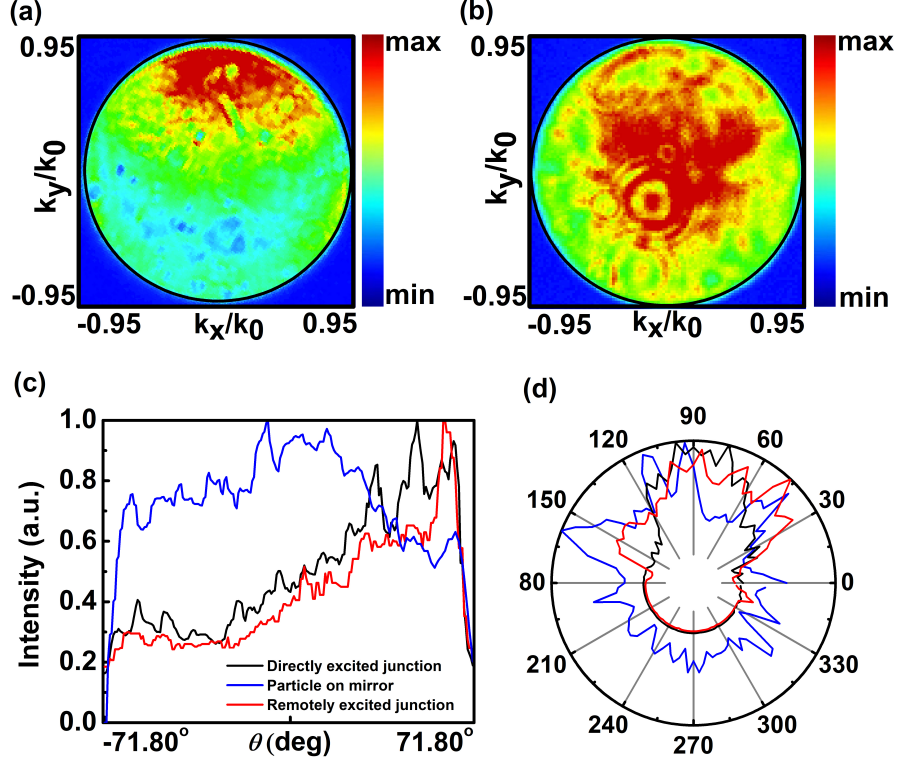


FIGURE 4.5: Fourier plane imaging of SERS emission from direct excitation of nanowire-nanoparticle junction on mirror and nanoparticle on mirror cavities. (a) Fourier plane image of SERS emission from molecules in direct excitation of the junction on the mirror. (b) Fourier plane image of SERS emission from molecules in direct excitation of an isolated nanoparticle on mirror cavity. (c) Intensity cross-cuts along $k_x/k_0=0$ in the Fourier plane image for direct excitation of junction (black curve), isolated nanoparticle on mirror (blue curve) and remote excitation of junction (red curve). (d) The intensity profile of azimuthal angles (ϕ) for θ corresponding to maximum intensity in the Fourier plane images for excitation of junction (black curve), isolated nanoparticle on mirror (blue curve) and remote excitation of junction (red curve). Figure reproduced from [110].

In addition to this, we performed Fourier plane imaging on the emission wavevectors from molecules placed in the cavity formed between isolated nanoparticle on a mirror. The Fourier plane image (figure 4.5 (b)) and intensity cross-cut (figure 4.5 (c), blue curve) along the $k_x/k_0=0$ line in the Fourier plane image show that the emission is isotropic in nature and covers a very large range of wavevectors as compared to the

emission wavevectors obtained in the case of remote excitation configuration. The intensity profiles of azimuthal angles (figure 4.5 (d)) (ϕ) for θ corresponding to maximum intensity in the Fourier plane images show that the emission from nanoparticle on a mirror cavity (blue curve) covers 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_y/k_0 values with comparable spreading in both the direct and remote excitation configuration.

4.5 Metallic substrate for confining SERS wavevectors

To understand the effect of the ground plane on SERS emission from NW-NP junction, we imaged the wavevectors of emission from NW-NP junction placed on a glass substrate. Figure 4.6 (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 633 nm laser with polarization along the AgNW, the AgNW plasmons out-couple from the AgNW end and NW-NP junction. The SERS emission from the junction (figure 4.6 (b)) was spatially filtered and was projected onto the Fourier plane. The Fourier plane image (figure 4.6 (c)) shows that the emission is biased towards the higher k_y/k_0 values, but the angular spread in emission is broader as compared to the spreading in the presence of gold substrate (see figure 4.4 (c)).

We calculated the near-field electric field using 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 reciprocity argument[79]. We place oscillating x, y and z oriented dipoles to mimic the molecular emission at the hotspots of the geometry. AgNW was modelled with a pentagonal cross-section with an edge to edge thickness of 350 nm and length of 5 μm . AuNP of diameter 180 nm is placed at a distance of 5 nm from the AgNW. This 5 nm gap is to model the PVP coating on the AgNW and molecular coating on the AuNP. The refractive indices of the material were taken from reference[94].

Figure 4.6 (d) shows the calculated near-field at the NW-NP junction placed on a glass substrate in remote excitation configuration. One end of the AgNW was excited using focused Gaussian source of 633 nm. The field at the junction is only concentrated in the NW-NP cavity (shown as α), 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 Fourier

plane image after incoherently adding the far-field radiation patterns from individual dipoles.

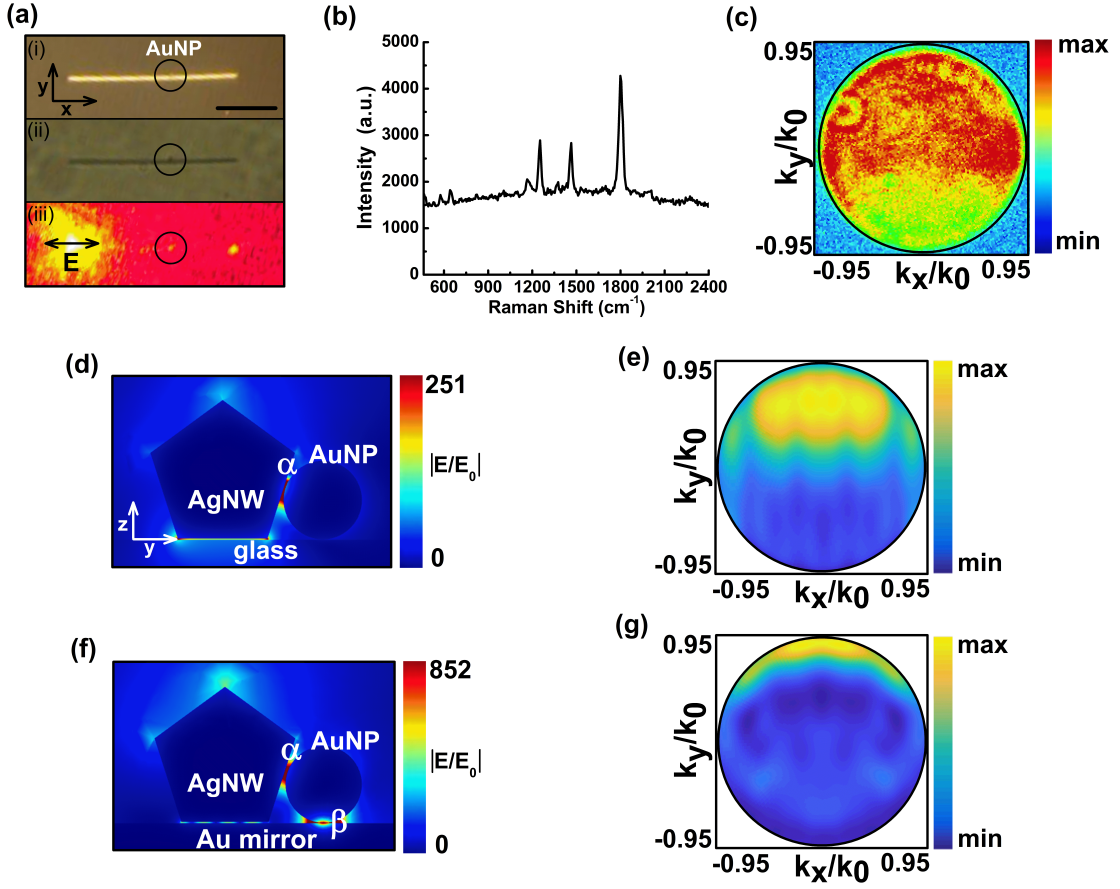


FIGURE 4.6: Role of Au mirror in influencing SERS wavevectors. (a) Optical imaging. (i) Bright field image of a BPT coated ≈ 180 nm AuNP assembled near a ≈ 350 nm thick AgNW placed on a glass substrate. Scale bar is $3 \mu\text{m}$. Transmission image of the same system. Elastic scattering image of the same system upon excitation of AgNW end using a 633 nm laser with polarization along the AgNW. (b) SERS spectrum of remotely excited BPT molecules collected from the NW-NP junction on glass. (c) Fourier plane image of SERS emission collected from the NW-NP junction on glass substrate after rejecting the elastically scattered light. (d) Calculated normalized near-field electric field at the NW-NP junction placed on a glass substrate in remote excitation configuration. (e) Calculated Fourier plane image after incoherently adding the far-field radiation patterns of x, y and z oriented dipoles placed in the gap between NW-NP (α). (f) Calculated normalized near-field electric field at the NW-NP junction on mirror in remote excitation configuration. (g) Calculated Fourier plane image after incoherently adding the far-field radiation patterns of x, y and z oriented dipoles placed in the gap between NW-NP (α) and in the gap between NP-mirror (β). The wavelength of emission of dipolar source is 703 nm. Figure reproduced from [110].

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 4.6 (e)) corroborates the experimentally observed wavevector distribution of SERS. The emission is broad in terms of wavevectors and covers large range of angles. In the case of gold substrate, along with a high field at the NW-NP cavity, there is also a hotspot in the NP-Mirror cavity (shown as β) (figure 4.6 (f)). The presence of two cavities in the case of NW-NP junction on mirror geometry, makes the SERS emission more enhanced (figure 4.4 (b)) as compared to the SERS intensity obtained with a glass substrate (figure 4.6 (b)). In this case, we placed oscillating x, y and z oriented dipoles at a wavelength of 703 nm in both NW-NP and NP-Mirror cavities and incoherently add the far-field radiation patterns from individual dipoles. The simulated Fourier plane image (figure 4.6 (g)) shows that the emission is biased towards NW-NP junction and is confined to narrow range of wavevectors. The results show the importance of metallic substrates for enhancement and in directing the SERS emission.

4.6 Effect of nanowire reflectance on SERS wavevectors

To study how AgNW influence the SERS emission wavevectors we study the change in the directionality of the emission when the distance between the AgNW and NP is varied. Figure 4.7 (a) shows the geometry of the system used in the calculations. Oscillating x, y, and z oriented dipoles at a wavelength of 703 nm (λ) are placed at the base of 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 mirror cavity is isotropic in nature. When the distance between the nanoparticle is changed to $\lambda/3$ the emission is no longer directional in nature but is still biased towards the higher k vectors. At a distance of λ , the influence of AgNW on the emission wavevectors is minimal and the emission is 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 narrow range of angles.

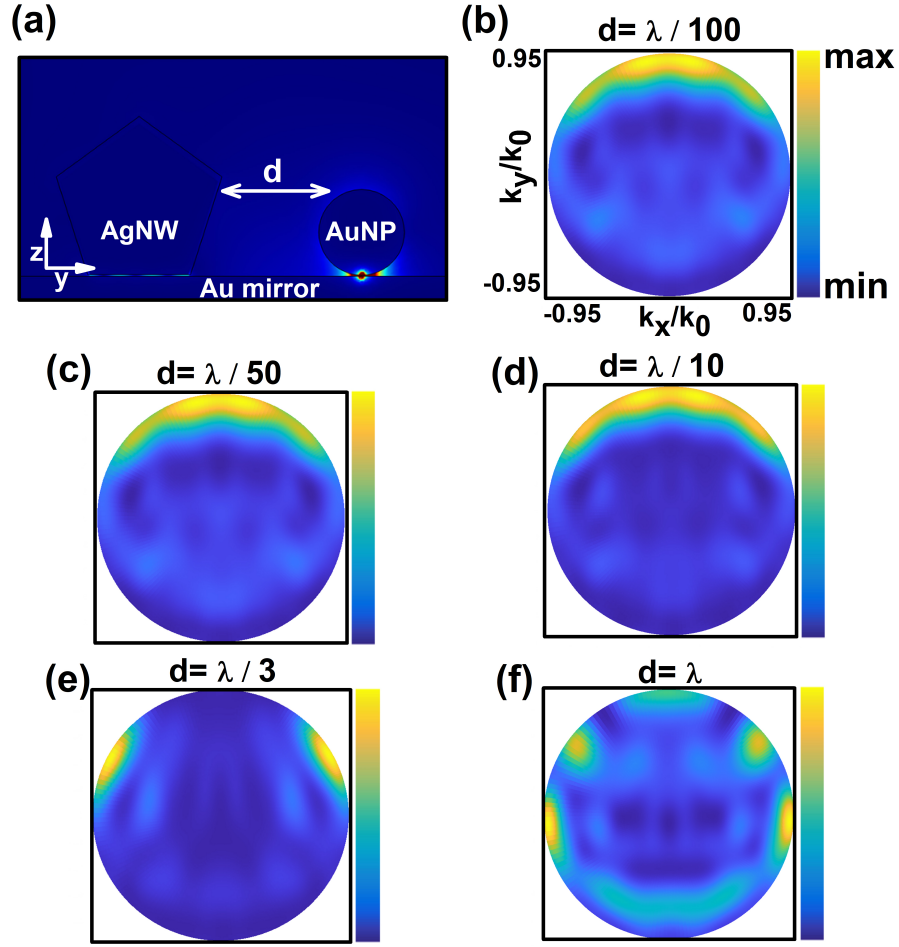


FIGURE 4.7: Variation in the directionality of emission with varying distance between nanoparticle and nanowire. (a) Geometry of NW-NP on mirror cavity with a distance 'd' between nanowire and nanoparticle. The nanowire (350 nm thickness) and nanoparticle (180 nm diameter) are placed on a gold mirror. (b-h) Calculated Fourier plane image when the distance between nanoparticle and nanowire is $\lambda/100$, $\lambda/50$, $\lambda/10$, $\lambda/3$ and λ respectively. In each case, oscillating x, y and z oriented dipoles at wavelength of 703 nm (λ) are placed at the base of the nanoparticle and the Fourier plane image is calculated by incoherently adding the emission from individual dipoles. Figure reproduced from [110].

4.7 Conclusion

To conclude, we have shown how unidirectional SERS emission can be achieved by NW-NP junction on mirror cavity in remote excitation configuration. The nanowire and gold mirror helps in providing enhancement and directing the SERS emission to a narrow range of wavevectors. Calculated forward-to-backward emission ratio for 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 letter will be extrapolated for studying strong interaction of molecules with extremely small cavities in remote excitation configurations. The NW-NP junction on mirror excited by nanowire plasmons will be a good test bed for remote detection of single molecules and studying quantum electrodynamics effects.

Chapter 5

Metallo-dielectric antenna for directional molecular fluorescence

In this chapter, we discuss how a hybrid structure (metal nanowire-dielectric microsphere) can be utilized for directing molecular fluorescence emission. The chapter is an adaptation of the research article "Advanced Optical Materials, 8 (11), 1901672 (2020)".

5.1 Introduction

In the past two chapters, we have seen how to efficiently direct SERS from molecular monolayer placed in the cavities. The molecules used in the experiments were non-resonant and contain a thiol group which can tightly attach to the gold surfaces. To enhance and direct emission from molecules which are resonant in nature and does not bind to the surface of metals strongly, require different techniques.

Plasmonic structures supports localized electric field to a small mode volumes but they suffer Ohmic losses. In the chapter 6, we will discuss how to harness the heat produced by plasmonic structures. Dielectric structures, on the other hand, supports morphology dependent modes having high quality factors, without producing much heat. Dielectric structures such as microspheres[112], disks[113], and toroids[114] have been fabricated/synthesized, and their optical properties have been extensively studied. Specifically, the high-quality factors provided by these microresonators have been harnessed for various applications including lasing[115], non-linear photonics[116] and (bio) chemical sensors[117].

Plasmonic and dielectric structures can be combined[118, 119] to simultaneously utilize the high quality factor of dielectric resonators for enhancing molecular emission, and metallic properties of plasmonic structures such as reflectance and waveguiding.

With the motivation of coupling whispering gallery modes (WGMs) of a dielectric microsphere with a plasmonic structure with waveguiding property, we experimentally

study a dye coated SiO_2 microsphere coupled to a silver nanowire. Specifically, we demonstrate remote excitation of WGMs of the microsphere via nanowire surface plasmon polaritons (SPPs), and study their spectral signature, and wavevector distribution using Fourier plane imaging[59, 61, 62].

5.2 Architecture of the system

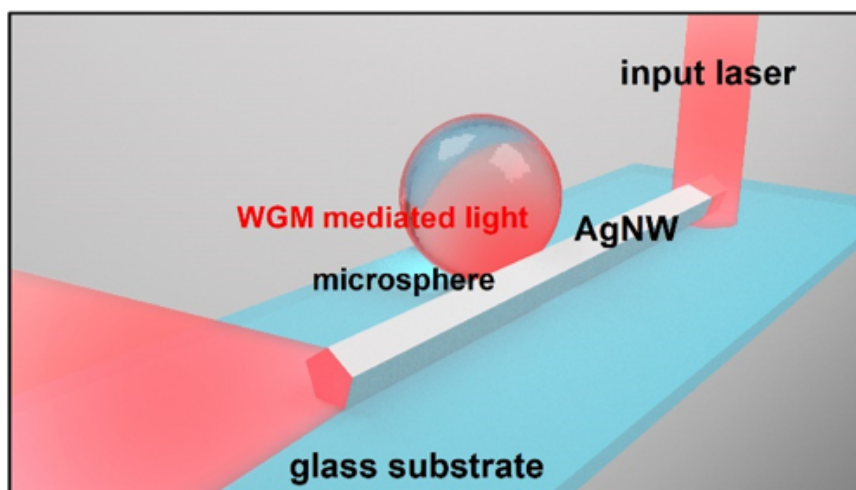


FIGURE 5.1: Schematic of the experimental configuration. a) A Nile blue molecules coated μS is coupled to AgNW using self-assembly methodology. One end of AgNW is excited using a high numerical aperture lens and outcoupled light was collected from the silver nanowire–dielectric microsphere (AgNW– μS) junction. Figure reproduced from [110].

Figure 5.1 shows the schematic of the experimental configuration. A Nile blue molecules coated dielectric microsphere (μS) is coupled to a silver nanowire (AgNW) using self-assembly methodology[111]. A high numerical aperture objective lens (0.95 NA, 100x) was used to focus laser at one end of NW for the generation of SPPs. SPPs outcouple as free photons from the distal end of NW and the AgNW– μS junction. The outcoupled light from the junction was spatially filtered and was projected onto the spectrometer and EMCCD for Fourier plane imaging. The near-field of SPPs and the outcoupled photons at the junction excite the fluorescence emission of molecules coated on the μS . This resulting broad fluorescence emission acts as a local source to generate the WGMs of the μS .

5.2.1 Preparing the geometry

Chemically synthesized AgNWs[91] in ethanol solution were dropcasted on a glass substrate and were left to dry. Over this sample, dye molecules coated μ S were dropcasted. After evaporation of solvent, the sample contained capillary force assisted self-assembled μ S coupled AgNW (figure 5.2 (a)). Figure 5.2 (b) shows scanning electron microscope image, dark field image and bright field images of some AgNW- μ S junction. We have probed one such junction which was prepared using AgNW of thickness ≈ 350 nm and a dielectric μ S of diameter ≈ 3 μ m coated with Nile blue (NB) molecules as shown in figure 5.2 (c)(i). Figure 5.2 (c)(ii) shows the propagation of SPPs along AgNW at 633 nm excitation wavelength which is near to the absorption maxima of NB molecules. We have maintained polarization along the long axis of AgNW for efficient generation of SPPs throughout our experiments. As can be seen in figure 5.2 (c)(iii), near field of SPPs and the out-coupled photons at the junction excite the fluorescence emission of molecules coated on the μ S.

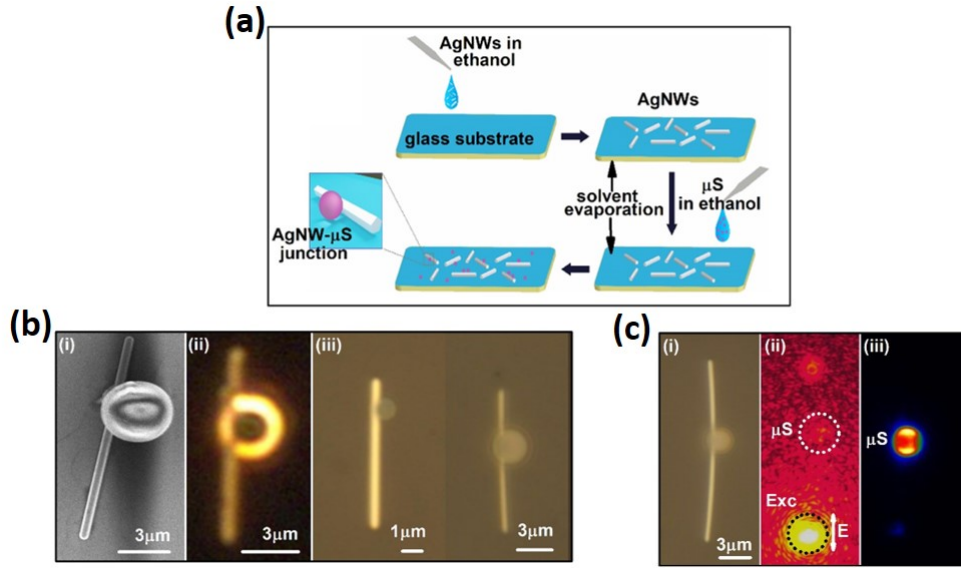


FIGURE 5.2: (a) Methodology for preparing self-assembled AgNW- μ S junction. (b) (i and ii) Scanning electron microscope and dark field image of a ≈ 3 μ m diameter microsphere coupled to ≈ 350 nm thick silver nanowire respectively. (iii) Bright field images of AgNW- μ S junctions with ≈ 350 nm diameter thick AgNW coupled to a ≈ 1 μ m diameter μ S and ≈ 250 nm diameter thick AgNW coupled to a ≈ 3 μ m diameter microsphere. (c) (i) Bright field image and (ii) elastic scattering image of the junction with ≈ 350 nm wire and ≈ 3 μ m sphere. (iii) Fluorescent image after rejecting the excitation wavelength, when plasmons along the nanowire are excited using a 633 nm laser. Figure reproduced from [110].

5.2.2 A short note on whispering gallery modes

Whispering gallery modes (WGMs)[100, 120] are electromagnetic modes of a structure which depends on the morphology of the structures. The waves suffer total internal reflection at the surface of the sphere and thus get confined in a region of small volume. This creates a region of large local electric field.

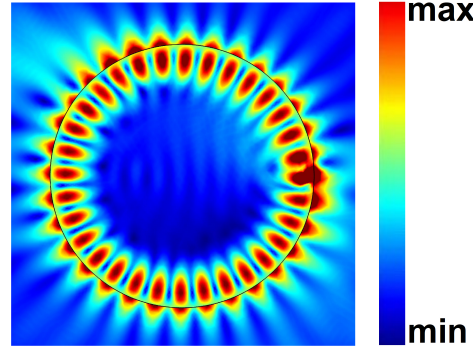


FIGURE 5.3: Calculated near field electric field distribution for a $TM_{16,1}$ mode of a $3\ \mu\text{m}$ dielectric microsphere placed on a glass substrate, using finite element method in COMSOL Multiphysics software. For excitation of the modes, we placed a dipole at the microsphere glass interface. The electric field is calculated at a wavelength of 656 nm which coincides with the position of a transverse magnetic (TM) mode with radial quantum number ' n ' and orbital quantum number ' l ' equals 16 and 1 respectively. Figure reproduced from [110].

The modes of a microsphere are labeled by two types of polarization, transverse electric (TE) and transverse magnetic (TM), and three quantum numbers n , l , and m . n is the radial quantum number which represents the number of intensity maxima along the radius of the sphere. l represents called the orbital quantum number which is equal to half of the intensity maxima along the perimeter of the microsphere. m which represents the azimuthal quantum number, is the projection of orbital quantum number on the quantization axis. The extinction cross-section for an interaction between a microsphere and electromagnetic field is given by,

$$Q_{ext} = \frac{2}{(ka)^2} \sum_{n=1}^{\infty} (2n+1) \text{Re}(a_n + b_n) \quad (5.1)$$

where, k is the wavenumber and a is the radius of the microsphere. Coefficients a_n and b_n are known as Mie coefficients. Putting $a_n=0$ gives modes which are called transverse electric, whereas setting $b_n=0$ gives transverse magnetic modes. Figure 5.3 shows the calculated near-field electric field distribution for a $TM_{16,1}$ mode of a $3\ \mu\text{m}$ dielectric microsphere placed on a glass substrate, using finite element method simulations[121].

5.3 Remote excitation of whispering gallery modes using nanowire SPPs

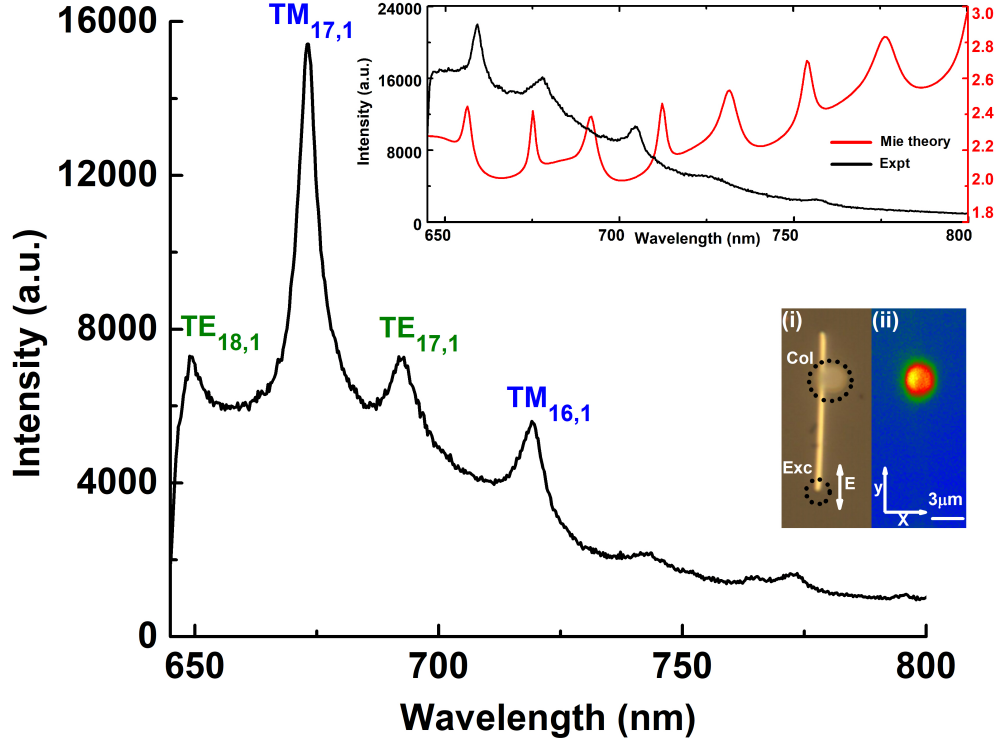


FIGURE 5.4: Spectral signatures of the hybrid photonic structure. We remotely excited whispering gallery modes (WGMs) of Nile blue-coated microsphere using surface plasmon polaritons of the nanowire. The spectrum shows sharp WGMs of a $\approx 3 \mu\text{m}$ microsphere. Inset: (i) Bright field image. (ii) Fluorescent image of the junction. Plots in inset show calculated Mie resonances of an isolated microsphere of diameter $3 \mu\text{m}$ in air and experimentally measured spectrum of a microsphere of diameter $\approx 3 \mu\text{m}$ placed on a glass substrate. Figure reproduced from [110].

To probe the spectral signature of a remotely excited dye coated μS coupled to an AgNW, we spatially filtered the junction using pinhole, placed at the image plane and projected the emission to the spectrometer. The spectrum shows the fluorescence of the molecules coupled to the WGMs of the μS (figure 5.4). The WGMs of the μS ride over the fluorescence spectrum and thus we see relatively intense modes near the fluorescence maxima of molecular emission. Since WGMs of μS are very sensitive to the environment, we numerically calculated WGMs of a μS of diameter $3 \mu\text{m}$ in air and compared it with the experimentally observed modes of NB molecules coated μS

on glass substrate or near an AgNW (inset in figure 5.4). Placing the microsphere on the glass substrate or near a silver nanowire shifts the peak position associated with the modes[122]. Along with the change in the peak position, the full width at half maxima of the peaks also broadens because of the interaction of near field of the μ S with the environment.

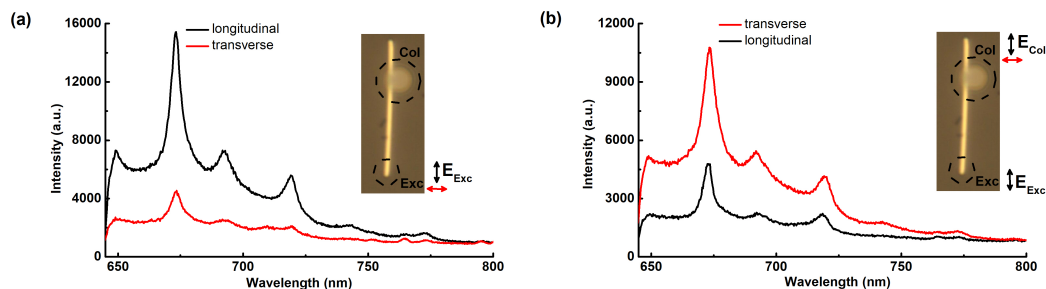


FIGURE 5.5: Input and output polarization resolved spectrum of molecular emission from silver nanowire-dielectric microsphere junction. Figure reproduced from [110].

To understand the polarization dependence of the coupled structures, we performed input and polarization dependence spectroscopy (figure 5.5). The input polarization dependence of the spectrum from Nile blue coated microsphere shows that the molecular emission is more enhanced with input polarization along the nanowire. Silver nanowire when excited using a laser with polarization along the longitudinal axis results in efficient excitation of propagating SPPs as compared to when the polarization is kept perpendicular to the long axis[43]. Thus, with longitudinal input polarization, near field coupling of the SPPs with molecules increases and leads to more emission from the junction. For output polarization dependence, input polarization is kept longitudinal to the nanowire. Majority of emission from the junction is polarized transverse to the nanowire although the input polarization is longitudinal to the nanowire.

5.4 Directional emission of remotely excited whispering gallery modes

After probing the spectral signatures, we perform Fourier plane imaging to study the emission wavevectors from the AgNW- μ S junction. Emission from the spatially filtered junction was projected to the EMCCD placed at the Fourier plane of the objective lens using relay optics. Fourier plane image of emission from the junction shows that the majority of the emission is directed perpendicular to the length of AgNW and covers a short range of angles (figure 5.6 (a-c)). The full width at half maxima (defined as α)

which relates to the distribution in the radial angles of emission in the $+k_x/k_0$ direction is 0.34.

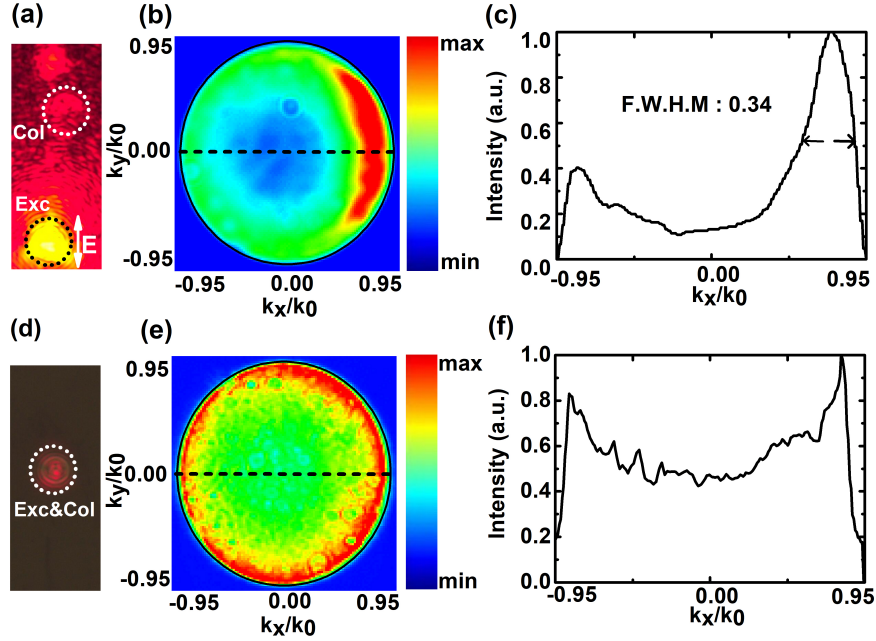


FIGURE 5.6: Comparison of the Fourier plane images of whispering gallery modes of remotely and directly excited dielectric microsphere. (a) Elastic scattering image of remotely excited silver nanowire–dielectric microsphere (AgNW– μ S) junction using a 633 nm laser. (b) Fourier plane image of the spatially filtered, remotely excited fluorescence emission from AgNW– μ S junction. Fourier plane image shows that the majority of the emission is confined to higher $+k_x/k_0$ values. (c) Intensity profile (black dash line) along the $k_y/k_0=0$. The emission is confined to a short range of k vectors with a full width at half maxima (α) of 0.34 in the forward direction ($+k_x/k_0$). (d) Elastic scattering image of a NB molecules coated microsphere on glass substrate. (e) Fourier plane image of the fluorescence emission from the microsphere shown in (d). (f) Intensity profile (black dash line) along the $k_y/k_0=0$.

Figure reproduced from [110].

For quantitatively measuring the directionality of emission from the junction, we used forward to backward ratio in dB given by,

$$\beta = 10 \left(\log \frac{l_+}{l_-} \right) \quad (5.2)$$

where l_+ and l_- is the intensity along $+k_x/k_0$ and $-k_x/k_0$ respectively. The emission from the junction is directional with a gain of 3.87 dB. In contrast to this result, when a NB molecules coated isolated μ S placed on glass is directly excited, the Fourier plane image of the emission shows isotropic emission. The emission wavevectors cover a relatively large range of angles (figure 5.6 (d-f)). Comparing both the Fourier plane images in

figure 5.6 (b) and (e), we infer that remotely excited WGMs of the microsphere through SPPs in silver nanowire are directional in nature. Emission from the μ S is confined to a narrow range of radial angles (θ), thus aiding optical antenna effect. To study the effect of direction of SPPs along AgNW, on the directionality of emission, SPPs were launched individually from both the ends of AgNW and Fourier plane imaging was performed on the emission from the junction. Since, the point of μ S in contact with AgNW is constant for both the excitation, the far field emission wavevectors are independent of the direction of propagating SPPs along the AgNW.

5.4.1 Controlling the angular spreading using nanowire thickness

Since the emission from the AgNW- μ S junction is directional, we ask whether the thickness of AgNW or μ S diameter can be used as a parameter to tune the angular distribution of emission from the junction. For this study, we varied AgNW thickness for a constant μ S size and performed Fourier plane imaging of emission from the junction.

Figure 5.7 (a) shows the bright field image of the junction prepared by NB molecules coated μ S of diameter $\approx 3 \mu\text{m}$ and an AgNW with thickness $\approx 120 \text{ nm}$. Fourier plane image of the emission from the junction shown in figure 5.7 (a) spans a large range of angles both in terms of θ and ϕ (figure 5.7 (b)). At a defined radial angle $\theta=51^\circ$, the intensity profile along the red dotted line in figure 5.7 (c) shows a large distribution of emission along the azimuthal angles.

Upon increasing the thickness of AgNW to $\approx 250 \text{ nm}$, Fourier plane image (figure 5.7 (e)) shows that the emission is biased in the forward direction ($+k_x/k_0$) with a reduced azimuthal distribution (figure 5.7 (f)). As AgNW thickness was further increased to $\approx 350 \text{ nm}$, majority of the emission can be seen to be confined in the $+k_x/k_0$ direction with a minimal azimuthal angle distribution as shown in figures 5.7 (g-i).

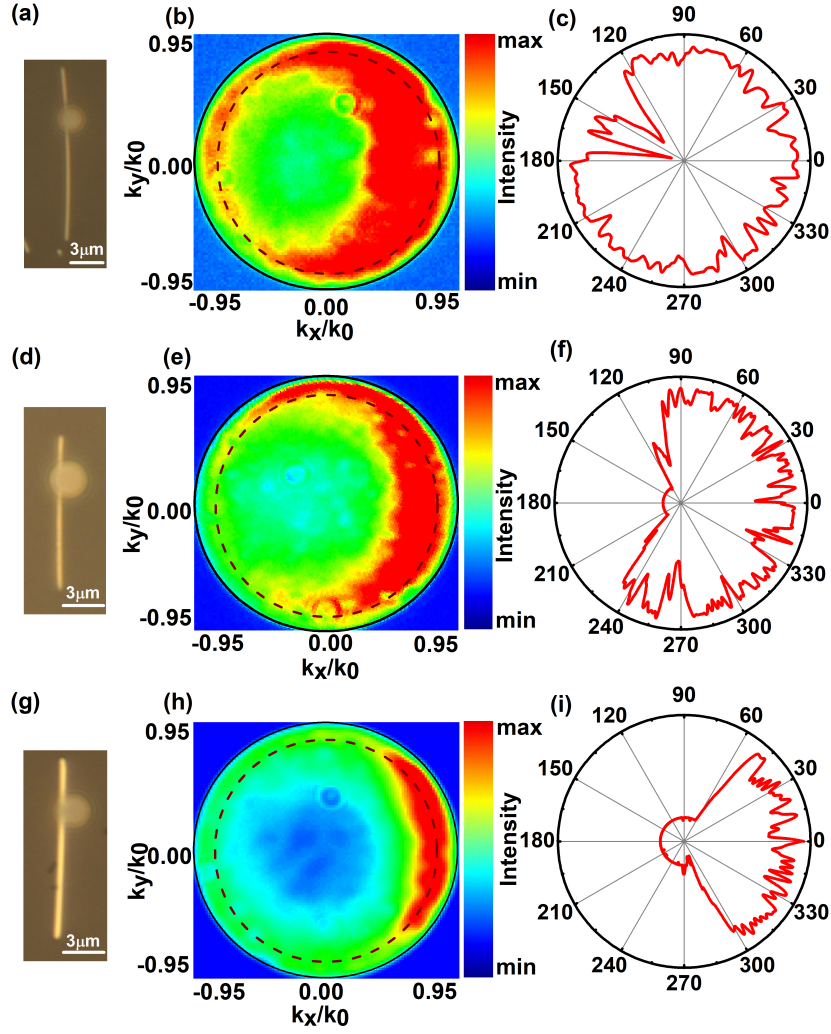


FIGURE 5.7: Controlling the azimuthal (ϕ) distribution of the emission by tuning the nanowire thickness. (a) Bright field image of an $\approx 3 \mu\text{m}$ microsphere coupled to an $\approx 120 \text{ nm}$ thick nanowire. (b) Fourier plane image of emission from the junction spanning a large range of angular emission. (c) The intensity profile of azimuthal angle along a defined radial angle, $\theta=51^\circ$ (black dotted curve in Figure 5.7 (b)). (d–f) Bright field image, respective Fourier plane image and intensity profile for an $\approx 3 \mu\text{m}$ microsphere coupled to a nanowire of thickness $\approx 250 \text{ nm}$. (g–i) Bright field image, respective Fourier plane image and intensity profile for an $\approx 3 \mu\text{m}$ microsphere coupled to a thick nanowire of diameter $\approx 350 \text{ nm}$. Figure reproduced from [110].

For a constant AgNW thickness, by changing the μS dimension the wavevector distribution of emission from the junction can also be tuned. This in turn, changes the angular distribution of emission and gain in the directionality because of the change in the defect point or the contact point with nanowire.

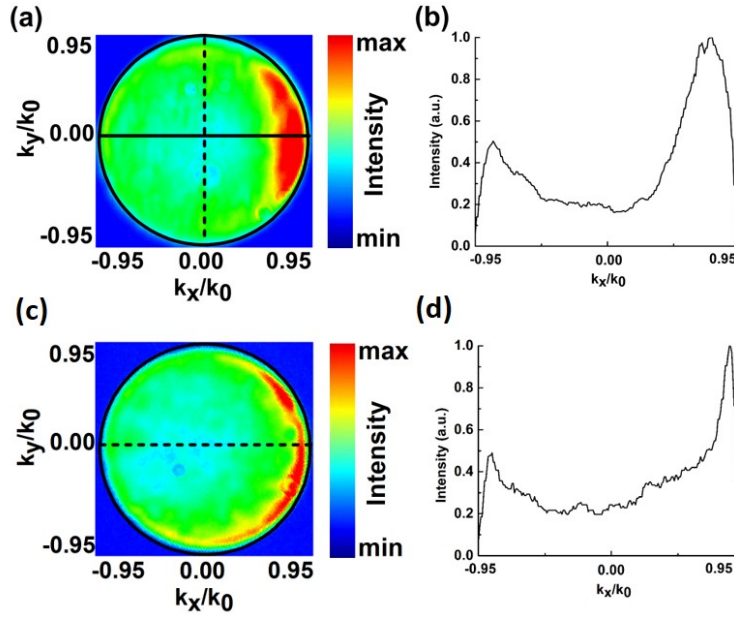


FIGURE 5.8: Fourier plane imaging of emission from a dye coated 2 and 1 μm diameter microsphere placed near a silver nanowire of thickness ≈ 350 nm. Propagating surface plasmon polaritons along the nanowire are excited using a 532 nm laser. (a) and (c) Emission wavevectors of molecular emission from silver nanowire-dielectric microsphere junction with a 350 nm nanowire and microsphere of size 2 and 1 μm . (b) and (d) are intensity profile along the black horizontal line in (a) and (c) respectively. The emission from the junction is directed in a specific narrow range of wavevectors. Figure reproduced from [110].

AgNW thickness (nm)	3 μm μS	2 μm μS	1 μm μS
350	$\alpha=0.34, \beta=3.87$	$\alpha=0.41, \beta=3.01$	$\alpha=0.18, \beta=3.10$
250	$\alpha=0.34, \beta=3.87$	—	—
120	$\alpha=0.34, \beta=3.87$	—	—

TABLE 5.1: Variation of full width at half maxima (α) of emission and forward to backward gain (β) in dB as a function of silver nanowire thickness and microsphere size.

For a fixed nanowire thickness, we performed the experiments using microspheres of two different sizes (1 and 2 μm). The Fourier plane images of the emission from the junction is shown in figure 5.8. The emission wavevectors become narrow when the size of the microsphere is reduced for a constant nanowire thickness. Variation of α and β with different AgNW thickness and μS size is given in the table 5.1.

5.5 FEM simulations to understand the roles of AgNW and microsphere in directional emission

To understand the origin of directionality in emission, we perform finite element method simulations in COMSOL Multiphysics software. An AgNW of diameter 350 nm and length 5 μm , with pentagonal cross section was modeled on a glass substrate. A dielectric μS of diameter 1 μm is placed equidistant from AgNW ends. The separation between dielectric μS and AgNW was 4 nm from one of the vertex of AgNW. The 4 nm separation represents the coating of polyvinylpyrrolidone (PVP) on the AgNW[91]. We have used refractive index for silver from the reference[94]. For launching propagating SPPs, one end of AgNW was excited using a plane wave of wavelength 633 nm with polarization along the long axis of AgNW (figure 5.9 (a)).

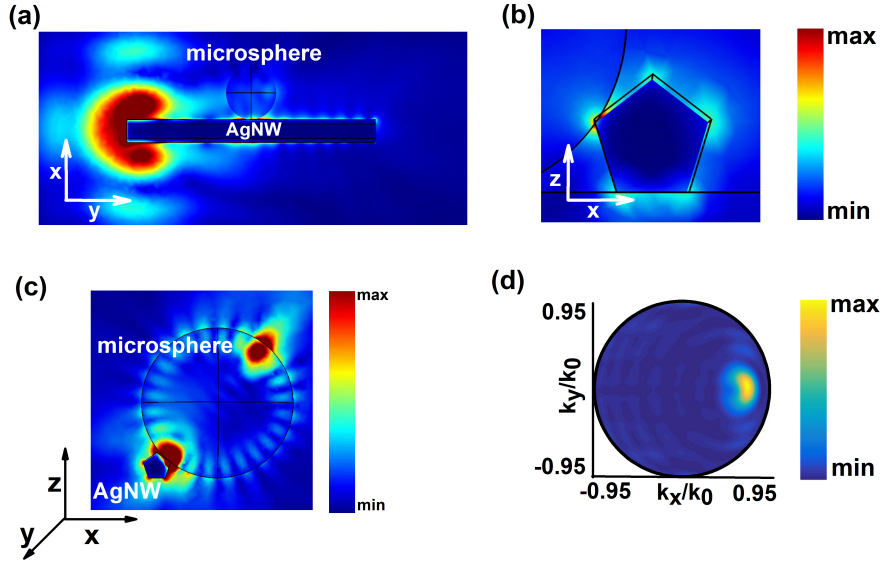


FIGURE 5.9: Finite element method simulations on silver nanowire coupled to a dielectric microsphere. (a) Near-field electric field at the junction of a 1 μm diameter microsphere placed near a nanowire of thickness 350 nm on a glass substrate. Propagating surface plasmon polaritons along the nanowire were launched by a 633 nm laser using a plane wave excitation with polarization along the longitudinal axis of nanowire. (b) Electric near field at the junction shows that field at one of the vertex of nanowire is interacting with the microsphere creating a relatively large local electric field as compared to the other vertices. (c) Near-field electric field at the junction of 350 nm thick nanowire and a microsphere of 2 μm diameter. The emission is mimicked by placing three mutually orthogonal excitation dipoles near the junction. (d) Far field radiation pattern calculated using transformation of near field to far field of the system shown in (c). Figure reproduced from [110].

At an excitation wavelength of 633 nm, a 350 nm thick AgNW placed on a glass substrate supports two leaky modes and one bound mode[63] as discussed in figure 5.10. Bound mode has an electric field confined between AgNW and the glass substrate, whereas the leaky modes have majority of the electric field confined on the vertices which are not in contact with the substrate. Thus, we deduce that the interaction between nanowire and μS is mainly because of leaky modes of nanowire.

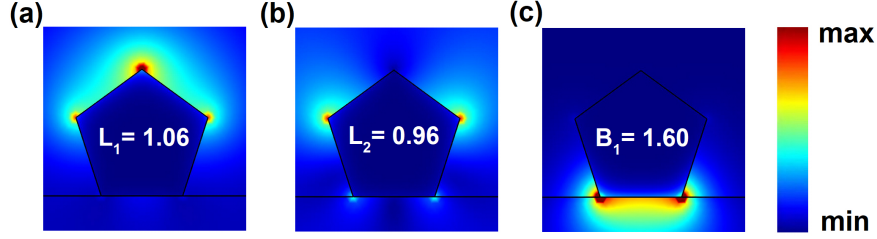


FIGURE 5.10: Modes of a silver nanowire of thickness 350 nm diameter placed on a glass substrate, at an excitation wavelength of 633 nm. (a) and (b) Near-field electric field profile of two leaky modes L_1 and L_2 with an effective refractive index of 1.06 and 0.96 respectively. (c) Bound mode, B_1 , with an effective refractive index of 1.60. Figure reproduced from [110].

As shown in Figure 5.9 (b), the field at the vertex where the μS is coupled to the nanowire is relatively more intense as compared to the other vertex. Thick nanowires will support more intense field at the junction compared to thin nanowires as the number of leaky modes reduces with a decrease in AgNW thickness as shown in simulated field profile of modes with variation of AgNW thickness and excitation wavelength in figure 5.11. Figure 5.11 shows the modes of silver nanowire of thickness 150 nm and 250 nm diameter at an excitation wavelength of 633 nm and 532 nm. Figure 5.11 (a) – (h) show numerically simulated near field electric field using finite element method. For an excitation wavelength of 633 nm, (a) and (b) show a leaky mode of effective refractive index 1.06 and a bound mode of effective refractive index 1.62 respectively, for a silver nanowire of thickness 150 nm diameter. (c) and (d) show a leaky mode of effective refractive index 1.05 and a bound mode of effective refractive index 1.63 respectively, for a silver nanowire of thickness 250 nm diameter. With a nanowire of thickness 250 nm and 150 nm, the number of modes, both leaky and bound, are less as compared to a thicker nanowire of thickness 350 nm. For a silver nanowire of thickness 350 nm and excitation wavelength of 532 nm, (e)-(h) show two leaky modes, L_1 and L_2 , of effective refractive index 1.10 and 1.01 and two bound modes of refractive index 1.51 and 1.72 respectively.

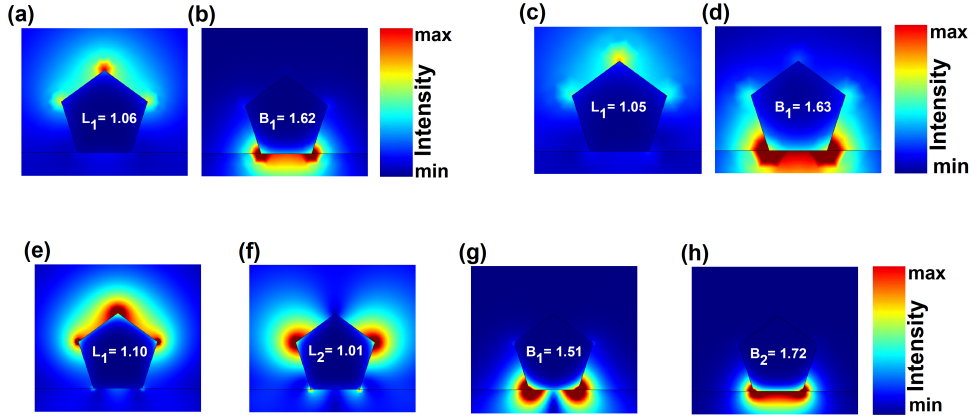


FIGURE 5.11: Modes of silver nanowire of thickness 150 nm and 250 nm diameter at excitation wavelength of 633 nm and 532 nm. Figure reproduced from [110].

The WGMs emission from a microsphere is isotropic in nature but can be made directional by introducing a scatterer near to the surface[123, 124]. The microlensing property of the microsphere focuses incoming plane wave to a region of small space, a process known as photonic nanojet effect[125]. Reversely, because of the scatterer, the WGMs get collimated in a direction opposite to the scatterer which leads to a directional emission. In this case, the nanowire acts as a scatterer and helps in collimating the emission. To further understand the directionality of emission, we modelled a $2\ \mu\text{m}$ diameter μS placed at a distance of 4 nm from a 350 nm thick silver nanowire without substrate (because of computational limit). We placed three mutually orthogonal dipoles near the surface of μS (figure 5.9 (c)), to mimic the molecular emission at the junction which is coupling to the WGMs of the microsphere. We performed near to far field transformation of electric field at the junction using reciprocity theorem[79]. The far-field pattern shows that the majority of the emission from the junction is directed to higher k_x/k_0 .

The analysis performed in figure 5.9 (c) and (d) was repeated for a nanowire of glass and without nanowire, to understand the individual role of nanowire and μS in directional emission. Results suggest that even without silver nanowire, the emission is biased to higher k vectors but silver nanowire acts as a scatterer and helps in narrowing down the spreading of emission, thus making the emission relatively more directional. For a constant nanowire diameter, the size of the μS is changed to study the effect of excitation point on μS . This suggests that the spread in the wavevectors depends on the location of the excited dipoles at the surface of μS . Hence, by changing either the size of μS or the nanowire coupled to the μS , directionality of WGMs emission can be tuned.

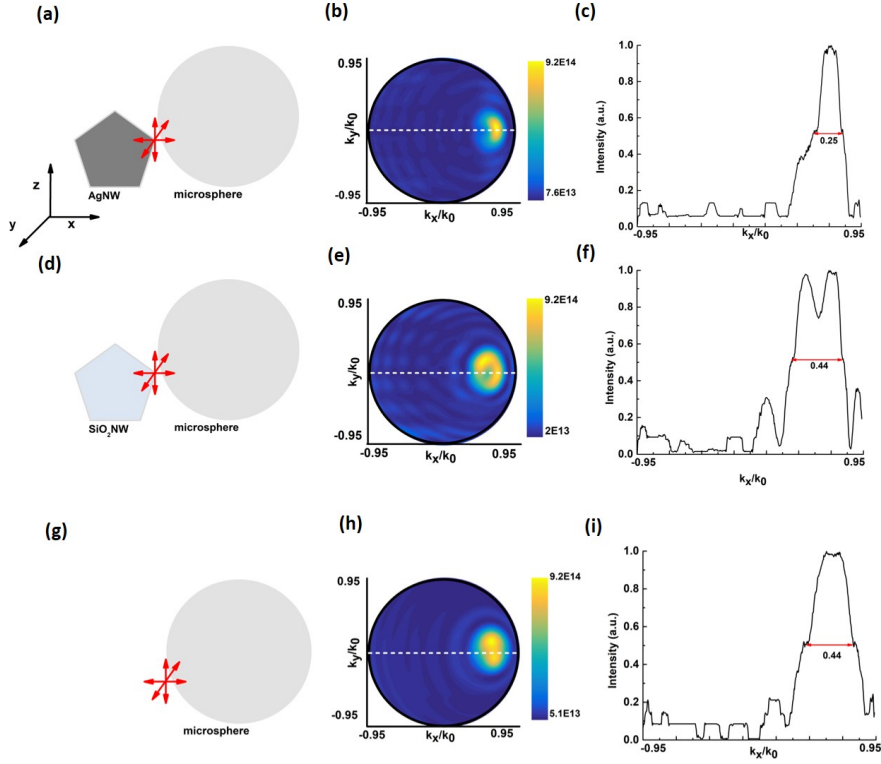


FIGURE 5.12: Numerically simulated far field pattern. (a) Schematic showing three mutually orthogonal dipoles placed at the junction of silver nanowire and dielectric microsphere. (b) Far field pattern captured in the x-y plane showing the biasing of emission to higher k_x/k_0 values. (c) Intensity profile along the white dotted line in (b). (d) Schematic showing three mutually orthogonal dipoles placed at the junction of SiO₂ nanowire and dielectric microsphere. (e) Far field pattern showing biased emission with a relatively large spreading in angles as compared to (b). (f) Intensity profile along the white dotted line in (e). Figure reproduced from [110].

Figure 5.12 shows the effect of silver nanowire on the emission wavevectors as compared to a SiO₂ nanowire. To study the effect of reflectance on wavevectors, we performed numerical calculations with a nanowire made up of SiO₂. With both silver nanowire and SiO₂ nanowire, the emission is biased towards higher k vectors, but with silver nanowire the emission is confined to relatively narrower range of wavevectors. In the case of silver nanowire, full width at half maxima (FWHM) of emission in the $+k_x/k_0$ is 0.25 while with SiO₂ nanowire FWHM is 0.44. Thus, silver nanowire provides additional directionality and gain to the emission. Figure 5.12 also shows the effect of individual microsphere on the emission wavevectors. The numerical modelling was same as performed in figure 5.9. Without silver nanowire the emission is biased towards higher k vectors but silver nanowire helps in narrowing down the emission to shorter range of wavevectors. Without nanowire, full width at half maxima (FWHM)

of emission in the $+k_x/k_0$ is 0.44 which is more than FWHM (0.25) of emission with silver nanowire. Thus, the emission is directional because of the focusing of emission through microsphere. Silver nanowire reduces the spread in the directional emission.

5.6 Subwavelength propagation of whispering gallery modes using nanowire

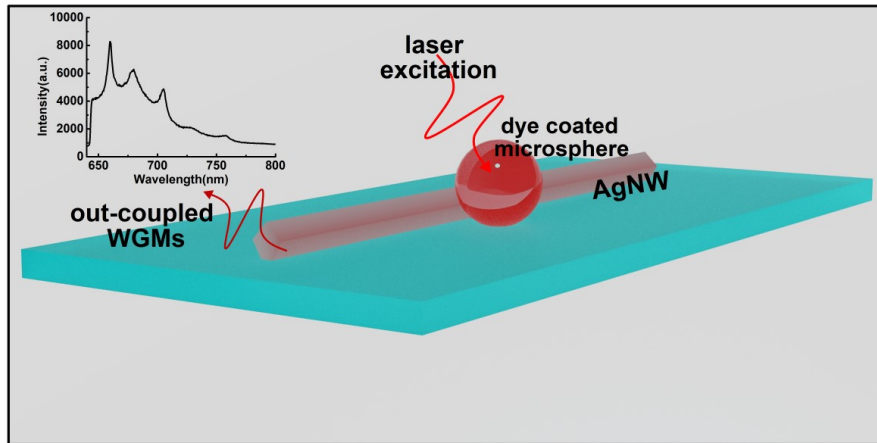


FIGURE 5.13: Schematic of the experiment configuration. A dye coated microsphere is assembled near a silver nanowire using self-assembly. The nanowire-microsphere junction is excited with a 633 nm laser. The emission from the molecules excites the whispering gallery modes (WGMs) of the sphere which gets coupled to nanowire SPPs. At the distal end of nanowire, plasmons get out-couple as WGMs of the microsphere in a directional manner. Figure reproduced from [126].

In addition to showing the directional emission of remotely excited WGMs, we have also explored the possibilities of subwavelength channeling WGMs using nanowire SPPs[126]. For this, we performed experiments in which the junction was excited directly and because of the near-field coupling, the WGMs of the microsphere couple to the nanowire SPPs. Figure 5.13 shows the schematic of the experimental configuration. We achieved subwavelength propagation of WGMs by converting WGMs to nanowire SPPs. In addition, the WGMs also out-couple in a directional manner from the ends of the nanowire when the SPPs out-couple from the nanowire ends as free space photons.

5.7 Conclusion

In conclusion, we have experimentally shown how a capillary-force assisted self-assembled process can be utilized to couple a dye-coated μ S to a plasmonic AgNW. The realized

hybrid photonic structure was shown to act like a remotely excitable optical antenna. The nanowire coupled with the dielectric microstructure facilitates SPPs for the remote excitation of WGMs and selective location of molecular excitation on microsphere provides the directionality to the emission by collimating the WGMs to a short range of wavevectors. We quantified the directional emission from the hybrid structure and found that the thickness of the AgNW and size of the μ S can be harnessed as parameters to control the emission angles of the out-coupled WGMs. Given that our geometry facilitates both propagating optical component via SPPs and a localized component in the form WGMs resonance, we envisage its utility as a directional photonic out-couplers on a micro-chip. Such directional emitters may find applications in nonlinear hybrid nanophotonics, random lasing and nano-optical sensing.

Chapter 6

Single molecule SERS in a single gold nanoparticle-driven thermoplasmonic tweezer

In this chapter, we will discuss how to simultaneously utilize the heat generated in plasmonic particles and the electric field enhancement for creating a reversible assembly of nanoparticles and to detect single molecules SERS from the molecules in the assembly. This chapter is an adaptation of the research article " Journal of Physical Chemistry Letters, 12, 11910-11918 (2021)".

6.1 Introduction

In the past three chapters, we have seen how to efficiently harness the electric field enhancement provided by plasmonic structures for enhancing molecular emission and also to direct the emission in a narrow range of angles. In this chapter, we will utilize the non-radiative part of light-matter interaction.

Plasmonic structures have been extensively designed and utilized for near-field interaction with the molecules[127, 128], and thereby influencing their optical emission not only in terms of their intensity[12, 16, 129] but also in terms of their directivity[6, 17]. Optical trapping[130–132] and assembly of nanoparticles in a fluid[133–136] is one of the effective ways to create large-scale electromagnetic enhancement with re-configurable nano-constructs that can be deterministically transported within the fluidic environment[26, 137].

In this context, performing SERS in an optical or an optothermal trap has emerged as an interesting prospect[26, 138–140]. Many of the SERS studies in optical traps require multiple lasers operating at relatively high powers[141, 142]. For single molecule studies, this may not be a conducive condition. Plasmonic tweezers have emerged as an alternative to trap nanoscale entities with a low power budget[143, 144]. In recent

times, the thermoplasmonic fields around a metal film[26, 27] or other designed nanostructures[28, 145, 146] have been utilized to optically trap nano and micro objects at extremely low powers.

Although, a large number of studies have shown the capabilities of thermoplasmonic tweezer[147–151] to manipulate nanoscale objects, there is still a requirement of tweezer strategies that can be mobile in a fluid and can adapted for biological conditions such as on a cell. One of the simplest possible thermoplasmonic nanostructure that can be introduced in a variety of environment is a chemically prepared gold nanoparticle that can be directly dropcasted from solution phase[22, 152, 153].

Motivated by these requirements, we show how SM-SERS can be performed in a thermoplasmonic trap driven by a single, dropcasted gold nanoparticle. This dropcasted nanostructure acts as an anchor trap to create an assembly of plasmonic particles which can be further utilized for SM-SERS studies. By utilizing bi-analyte[10] SERS technique, we provide experimental proof of SM-SERS signature in such a thermoplasmonic traps. Furthermore, we show how such nanoparticle based thermoplasmonic trap can be utilized for single nanoparticle trapping and optical transport of nanoparticle assemblies, all at a very low laser power density.

6.2 Architecture of the geometry

A schematic of the experimental configuration is shown in figure 6.1. A single 150 nm diameter gold nanoparticle (AuNP) was dropcasted on a glass substrate to work as an anchor particle to create an assembly of plasmonic structures. The AuNP was surrounded with an aqueous solution of plasmonic particles, molecules, surfactant cetyltrimethylammonium chloride (CTAC) and potassium chloride (KCl). The plasmonic particle assembly provides the electromagnetic enhancement for the SM-SERS [2]. The CTAC and the KCl were used as assisting agents for thermoplasmonic trapping and SM-SERS, respectively. We will discuss their role later in the chapter.

A single, low power-density laser was used to simultaneously heat the anchor metal nanoparticle[22] for thermoplasmonic trapping of plasmonic particles, and as an excitation source for SERS. For SM-SERS validation, we used bi-analyte technique. Two types of molecules were added in the solution after which modified principal component analysis (MPCA) was performed to statistically confirm the SM-SERS signature[73].

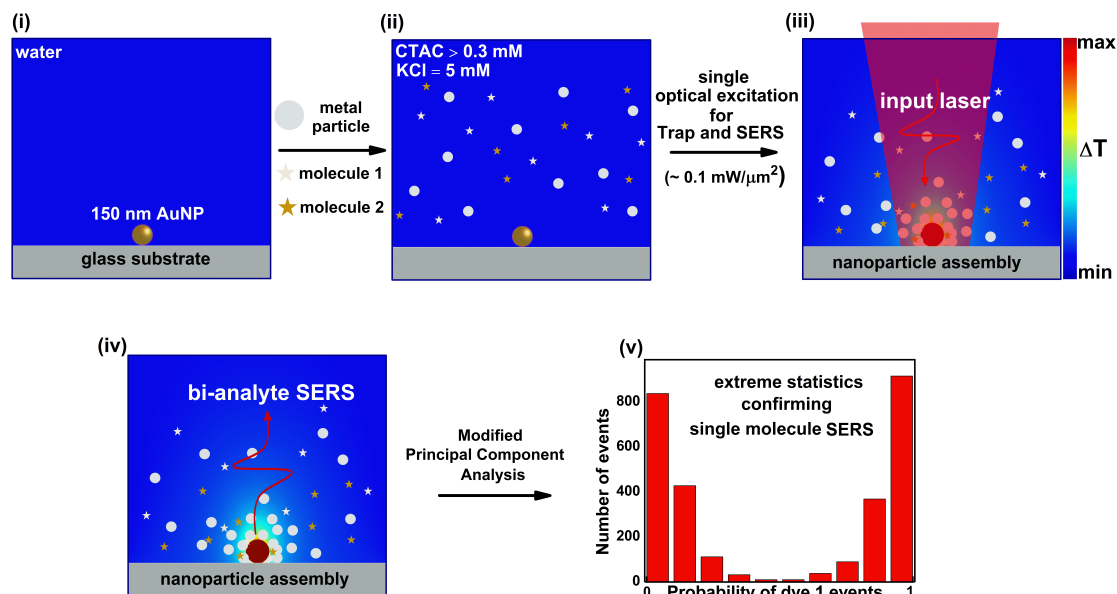


FIGURE 6.1: Schematic of the experimental configuration to perform SM-SERS in a low power, single nanoparticle driven thermoplasmonic tweezer. (i) A single 150 nm AuNP dropcasted on a glass substrate to be operated as an anchor particle for trapping. (ii) The AuNP was surrounded by a solution containing CTAC and KCl mixed with molecules and plasmonic particles (AuNPs or Lee-Meisel AgNPs). (iii) A low power density laser source ($\approx 0.1 \text{ mW}/\mu\text{m}^2$) was used to heat the AuNP for achieving reversible assembly of plasmonic particles. (iv) SERS was performed on the molecules in the assembled plasmonic particles using the same laser source. (v) Modified principal component analysis was performed to statistically confirm SM-SERS signature. Figure reproduced from [77].

6.2.1 Thermoplasmonic tweezer coupled with SERS setup

Figure 6.2 shows schematic of the experimental setup. The sample was illuminated using a 50x, 0.50 NA air objective lens for trapping and 60x, 1.2 NA water immersion objective lens for simultaneous trapping and SERS. The backscattered light was collected using the same lenses. The laser light was expanded using a set of two lenses L1 and L2. M1 and M3 are mirrors and M2 is a flip mirror to choose either of the lasers. BS1 and BS2 are beam splitters to simultaneously excite the sample with laser and its visualization using white light for bright field imaging. Lens L3 is used to loosely focus white light on the sample plane. Notch filter is used to reject the elastically scattered light for SERS spectroscopy and dark field and bright field imaging. Lenses L4 and L5 are used to focus the emission onto the spectrometer or CCD. M4 is a flip mirror to route light for the imaging or the SERS. For dark field imaging the sample was excited with a dark field condenser from the bottom and the scattered light was collected from

the top objective lens. A spacer of height $120\ \mu\text{m}$ was used while performing trapping experiments and no spacer was used while performing simultaneous trapping and SERS.

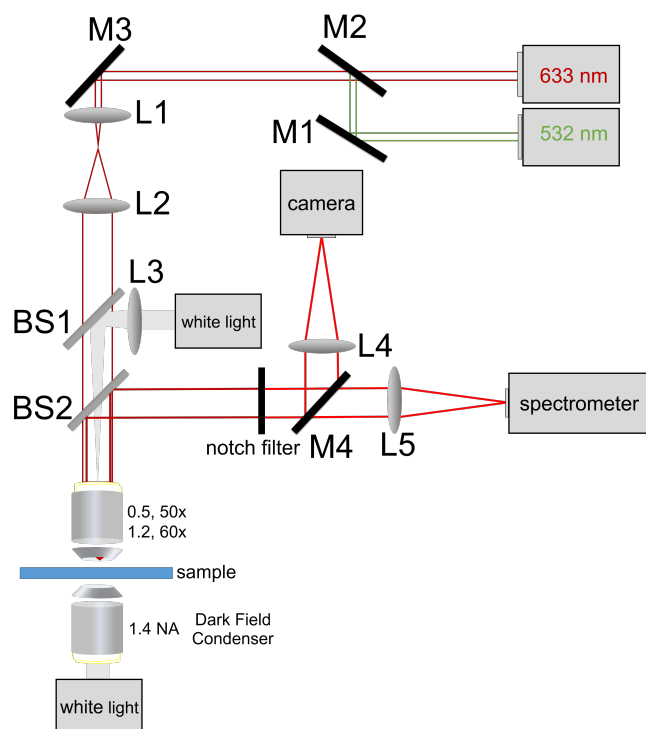


FIGURE 6.2: Schematic representation of the optical setup. Figure reproduced from [77].

6.3 Reversible assembly of plasmonic particles

First, we discuss the experiments on reversible trapping of 250 nm AuNPs in a CTAC solution. Figure 6.3 (a) and (b) show the trapping and release sequence of 250 nm AuNPs. A 150 nm AuNP was excited by focusing a 0.74 mW laser of wavelength 633 nm at a $3.34\ \mu\text{m}$ spot size by using a 50x, 0.50 NA objective lens. The AuNP was surrounded with an aqueous solution having 12 mM CTAC. As the laser was turned on, the plasmonic particles were seen to be trapped near the anchor AuNP and within 10 s, an assembly of size greater than $5\ \mu\text{m}$ was achieved. The assembly disappears within a few seconds after turning off the laser. This process can be reproduced over multiple cycles.

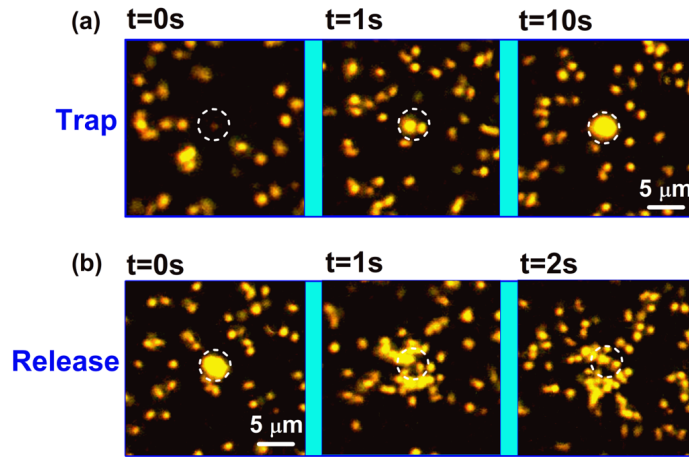


FIGURE 6.3: Reversible trapping of plasmonic particles in the low power thermoplasmonic tweezer. Time series dark field images of (a) assembly of 250 nm AuNPs and (b) disassembly of the same AuNPs when the laser was turned off. The dotted, white circle represents the location of the anchor 150 nm AuNP. Excitation at 633 nm laser with a power density of $0.08 \text{ mW}/\mu\text{m}^2$. Figure reproduced from [77].

In the absence of the CTAC, trapping of plasmonic particles was not observed at the same input power density[26]. The particles get scattered away because of the large scattering force when they enter the excitation volume. Furthermore, in the absence of anchor AuNP and CTAC, trapping of plasmonic particles was not observed upon the excitation of only glass substrate. This shows that conventional optical trapping at such a low power density cannot trap the plasmonic particles because of the absence of sufficient temperature gradient in the system. Assembly of nanoparticles of size as large as 400 nm were also created efficiently at low power density, using the single nanoparticle driven thermoplasmonic trapping. A slightly more efficient trapping at 532 nm was achieved with a laser source of 532 nm which is nearer to the absorption maxima of the anchor particle.

6.4 Mechanism of the trapping

To understand the mechanism behind the reversible trapping of the particles using single nanoparticle driven thermoplasmonic trapping, we first characterise the absorption and scattering cross-sections of the nanoparticle. Figure 6.4 shows the scattering and absorption cross-sections of a 150 nm diameter nanoparticle. The scattering spectrum was experimentally measured using slant angle excitation and the scattered light was collected using a low numerical aperture objective lens. To experimentally calculate the absorption cross-section, the peak of the calculated scattering spectrum was recorded

by tuning the refractive of the surrounding medium in which the gold particle was suspended. Refractive index of the medium was chosen by taking the effective refractive index of the medium as the particle was placed on a glass substrate and was surrounded by water. The peak position of experimentally measured and numerically calculated scattering spectrum matches at an effective refractive index of 1.365. Finally, at a refractive index of 1.365 of the medium the absorption cross-section was calculated and is shown in figure 6.4 (c).

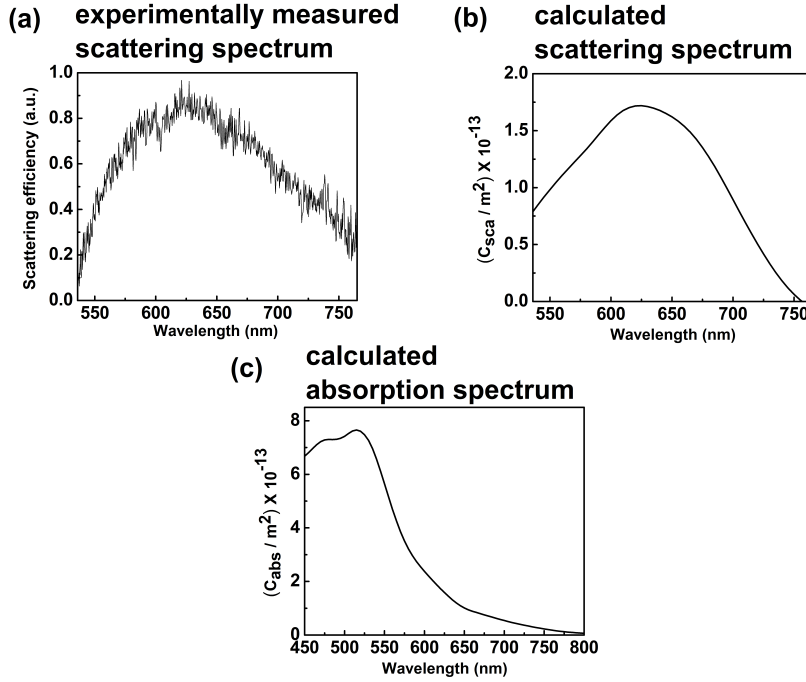


FIGURE 6.4: Scattering and absorption cross-sections of a 150 nm AuNP placed on a glass substrate and surrounded by water. (a) Experimentally measured scattering spectrum of the AuNP in water and placed on a glass substrate. (b) Calculated scattering spectrum of a 150 nm AuNP in a material of refractive index 1.365. (c) Calculated absorption of a 150 nm AuNP in a material of refractive index 1.365. Figure reproduced from [77].

Next we studied the effect of laser illumination on the heating of the nanoparticle. The heat power density at power density $q(r, t)$ at any time t and at any location r inside an illuminated structure is given by,

$$q(\mathbf{r}, t) = \mathbf{J}(\mathbf{r}, t) \cdot \mathbf{E}(\mathbf{r}, t) \quad (6.1)$$

where J is the electronic current density and E is the electric field inside the nanostructure.

Taking the time average, and denoting the frequency of the light source illuminating the structure as ω , the heat power density becomes,

$$q(\mathbf{r}) = \left(\frac{\omega}{2}\right) \varepsilon_0 \text{Im}(\varepsilon) |\mathbf{E}(\mathbf{r})|^2 \quad (6.2)$$

Calculation for electric field intensity inside the metal structures and thus temperature increment and temperature gradient upon illumination were performed using finite element method based study using COMSOL Multiphysics as solver. Electromagnetic power loss density option was selected to account for the heating source. Boundary conditions were defined using the equation

$$q_0 = h(T_{ext} - T) \quad (6.3)$$

with ($T_{ext} = 293.15$ K and h is the heat transfer coefficient, with external natural convection option for a spherical geometry of diameter 150 nm. The particle was excited with a focused Gaussian beam with values of power and beam waist size were put in, by measuring the experimental power at the sample plane and beam spot size. The refractive index of the metal particle was taken from ref[94].

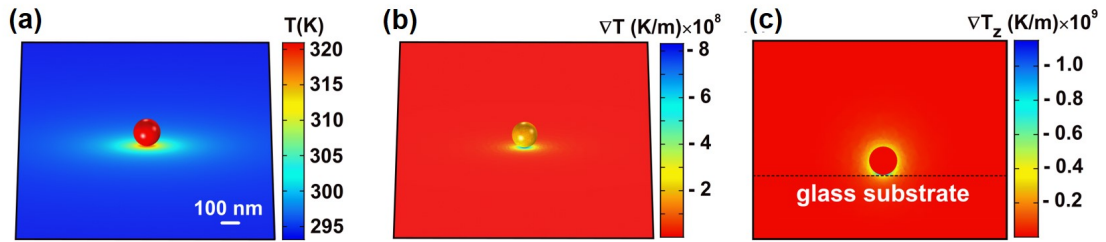


FIGURE 6.5: (c) Calculated temperature distribution around a 150 nm AuNP placed on a glass substrate and surrounded by water. Excitation at 633 nm laser with a power density of $0.08 \text{ mW}/\mu\text{m}^2$ (d) Calculated temperature gradient ∇T for the same geometry. (e) Calculated temperature gradient ∇T in the z-plane. Figure reproduced from [77].

Figure 6.5 (a) shows the calculated temperature distribution of a 150 nm AuNP placed on a glass substrate and surrounded with water. A temperature increment of ≈ 27 K was obtained by exciting the AuNP with a laser of power density $0.08 \text{ mW}/\mu\text{m}^2$. In addition, there was a temperature gradient, both in-plane and out-of-plane of our geometry, because of the heating of AuNP as shown in figure 6.5 (b) and (c) respectively. This gradient has an important connection to CTAC in the solution. The plasmonic particles in the fluid and the anchor particles were coated with a positive CTAC double layer because of the addition of CTAC in the solution[154]. Since, the concentration of

CTAC is greater than critical micelle concentration(0.3 mM), the solution also contains CTAC micelles and negatively charged chlorine ions.

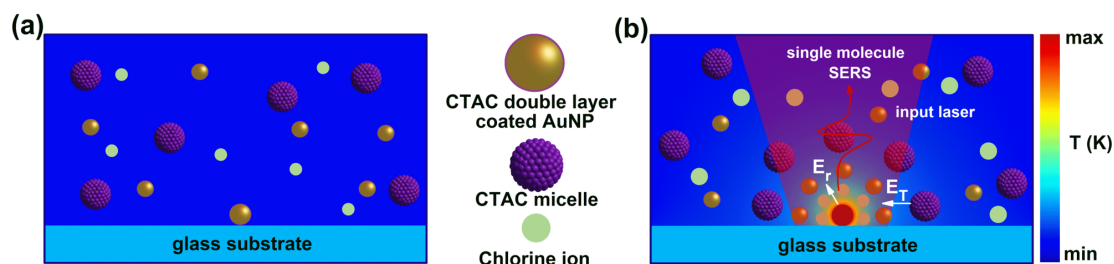


FIGURE 6.6: Detailed mechanism of the reversible trapping using single nanoparticle driven thermoplasmonic trap. Figure reproduced from [77].

Figure 6.6 shows the mechanism of the reversible trapping. 150 nm gold nanoparticles in ethanol solution were dropcasted on the glass substrate and were left to dry. The AuNPs were surrounded with an aqueous solution containing plasmonic particles, and CTAC molecules at a concentration greater than critical micelle concentration. The plasmonic particles suspended in the solution and the anchor metal particle get coated with a CTAC double layer which is positive in charge[154]. The solution also contains negatively charged chlorine ions. A distribution of the ions is shown in figure 6.6 (a). As the anchor particle is illuminated with the laser source, the temperature of the particle increases. This also creates a temperature gradient near the anchor metal particle. This temperature gradient leads to the thermophoretic motion of the charged ions in the solution. This causes a redistribution of Cl^- ions and CTAC micelles, and CTAC double layer coated plasmonic particles. The thermoelectric force E_T between the Cl^- ions present near the anchor particle and the positively charged CTAC micelles forces the plasmonic particles to move towards the anchor particle. An interaction between the CTAC coated anchor particle and CTAC micelle creates a repulsive force E_r which balances the E_T and the plasmonic particles get trapped near the anchor particle. After the laser is turned off the repulsive force in addition with the Brownian motion of the plasmonic particles causes the particles to move away from the anchor particle.

6.5 Versatility of the nanoparticle-driven trap

Can our tweezer platform assemble and transport plasmonic structures? Can such a platform trap single nanoparticles at the low laser power densities? In order to address these questions, further experiments were performed to make the trap a more versatile in terms of trapping and tweezing and are discussed in next sections.

6.5.1 Tweezer driven by the nanoparticle

We trapped and transported an assembly of 250 nm AuNPs along two different axes, as shown in figure 6.7. We performed this transport by holding the trap at its position and moving the motorized-stage of the optical microscope. An interesting aspect of this transport is that once assembled, the plasmonic particles do not need the assistance of the anchor nanoparticles for further trapping. This may be due to temperature increment and gradient facilitated by the assembly and hence acting as a ‘self-sufficient’ trap.

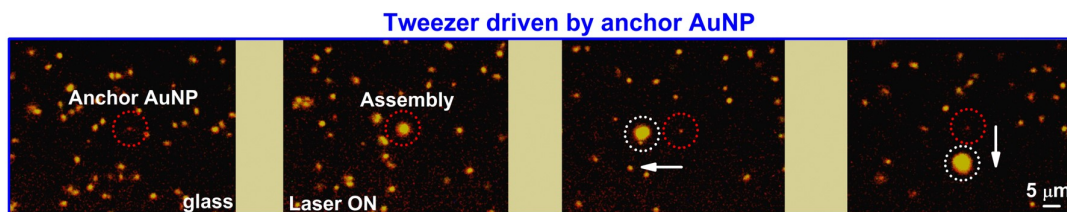


FIGURE 6.7: Tweezer driven by anchor AuNP. Time series dark field images of assembly and its translation along two axes. Figure reproduced from [77].

6.5.2 Tweezer driven without the nanoparticle

We show that the assembly can also be created without the assistance of anchor NP (figure 6.8). Although we could trap and transport the assembly of plasmonic particles, we found the trapping process to be stochastic and can take much longer times when compared to anchor AuNP based tweezers (figure 6.7). The figure 6.8 shows the formation of the assembly when the laser was illuminated on a glass substrate. Initially, a single particle comes under the excitation volume and gets pushed towards the glass substrate because of scattering force, and it stays there for finite duration. Within that time, the temperature of the particle increases, which leads to the formation of a thermal gradient, and hence a trap.

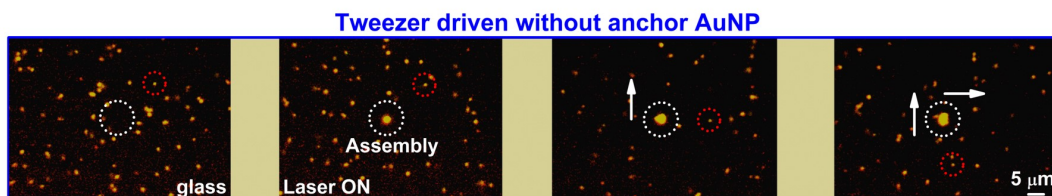


FIGURE 6.8: Tweezer driven without anchor AuNP. Time series dark field images of assembly and its translation along two axes. Note that this assembly process is stochastic and takes longer duration compared to the previous case. Figure reproduced from [77].

6.5.3 Single gold nanoparticle trapping

We show how a single 250 nm plasmonic particle can also be trapped using a single, anchor AuNP, thus forming a dynamic, plasmonic dimer. Figure 6.9 shows the reversible trapping and release of a single 250 nm AuNP. Turning off the laser results in the release of the trapped particle from the anchor location. Turning on the laser again, further traps the nanoparticle thus confirming the reversibility.

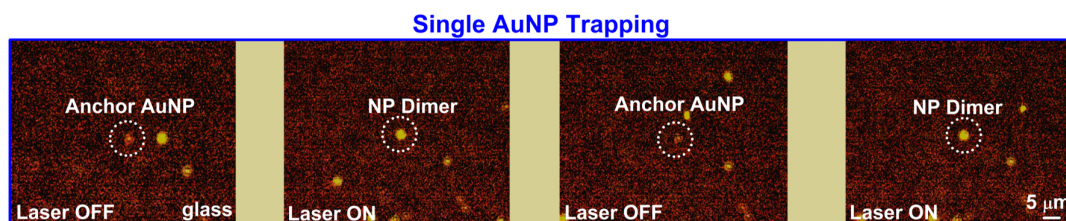


FIGURE 6.9: Single particle trapping and release. A reversible dimer formation was observed. Excitation wavelength: 633 nm at a power density of $0.08 \text{ mW}/\mu\text{m}^2$, anchor AuNP: 150 nm, trapped plasmonic particles: 250 nm AuNPs, for all the observations. Figure reproduced from [77].

6.6 SERS from the assembly

Having shown the formation of large scale assembly, next we show how the assembly can be utilized for performing SERS of rhodamine 6G (Rh6G) molecules and compare its performance for various plasmonic particles. A schematic of the experimental design is shown in figure 6.10 (a). A reversible assembly of plasmonic particles (250 or 100 nm AuNPs or Lee-Meisel AgNPs) was achieved by heating a 150 nm AuNP. The anchor AuNP was illuminated with a water immersion 1.2 NA, 60x objective lens by focusing a 0.80 mW, 633 nm laser to a spot size of $2.70 \mu\text{m}$. For this optical excitation, the temperature distribution, and gradients are shown in figure 6.11.

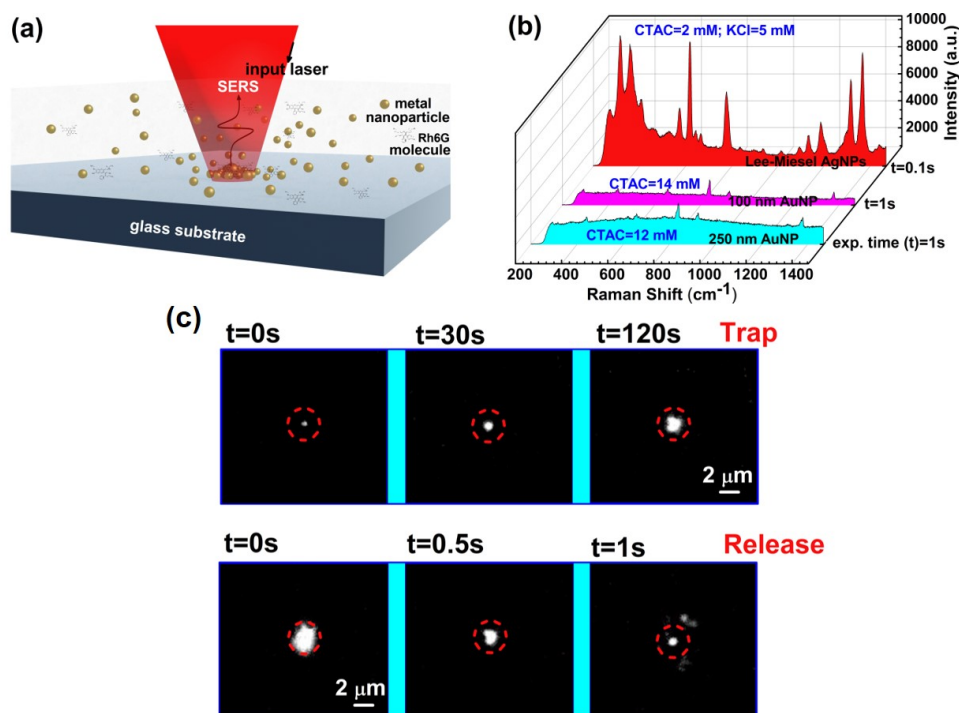


FIGURE 6.10: Optimization of experimental configuration for SM-SERS. (a) Schematic of the SERS performed for different plasmonic particles (250 nm and 100 nm AuNPs, and Lee-Miesel AgNPs) with Rh6G molecules. (b) Comparison of the SERS spectra at same input power using 250 nm AuNPs, 100 nm AuNPs and Lee-Miesel AgNPs (with varied concentrations of CTAC and KCl). Time series images of (c) assembly and disassembly of the Lee-Miesel AgNPs. Figure reproduced from [77].

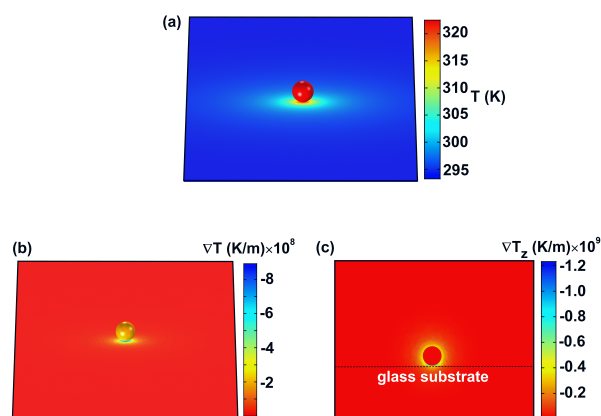


FIGURE 6.11: Calculated temperature and temperature gradient upon illumination of a single nanoparticle with a 633 nm wavelength laser at a power density of $0.14 \text{ mW}/\mu\text{m}^2$. (a) Temperature increment of the nanoparticle. (b) Calculated temperature gradient ∇T in the x-y plane and near the surface of the nanoparticle. (c) Calculated temperature gradient ∇T_z in the z plane. Figure reproduced from [77].

After an assembly formation of about the spot size, SERS spectroscopy of Rh6G molecules was performed in the backscattering configuration using the same excitation laser used for the trapping purpose. Figure 6.10 (b) compares the SERS spectrum collected from 10^{-6} M Rh6G molecules in the assembly of 250 nm AuNPs, 100 nm AuNPs and Lee-Meisel AgNPs. As can be seen from the SERS spectra figure 6.10 (b), the SERS sensitivity was superior for Lee-Meisel AgNPs in the presence of CTAC and KCl. From the past work, it is well known that Lee-Meisel AgNPs are excellent substrates for achieving large SERS enhancement[2, 155], when a small amount of KCl is added to the solution [156–158].

Therefore, Lee-Meisel AgNPs were first mixed with KCl (3 mM) and then with Rh6G molecules by following half-half dilution method[159]. Again using half-half dilution method, a low concentration of CTAC (2 mM) was then added to the solution containing molecules and AgNPs.

Figure 6.10 (c) shows the trap and release of large scale assembly of Lee-Meisel AgNPs using nanoparticle driven thermoplasmonic trap. An assembly of few microns was formed within tens of seconds after the anchor particle was illuminated with the laser source. The assembly disappears very fast after the laser is turned off.

6.7 Single molecule SERS from the assembly

To push the limit of single nanoparticle driven thermoplasmonic trap, we performed SM-SERS spectroscopy on the assembly of trapped Lee-Meisel AgNPs using bi-analyte technique, whose details can be found elsewhere [9, 10, 160]. Figure 6.12 (a) shows the schematic of the experimental configuration to perform bi-analyte SERS experiments using two types of molecules, which compete for the same hotspot[10]. A 3 mM KCl solution was added with Lee-Meisel AgNPs and was left for 10 minutes. The molecules were then added in the solution using half-half dilution method[159]. Finally, CTAC was added to the solution again using half-half dilution method. The solution contains two types of molecules, Nile Blue (NB) and Rh6G, with a final concentration of 5 nM. As discussed earlier, the illuminated anchor AgNPs drives the assembly and SERS was performed from the assembly in the presence of CTAC and KCl.

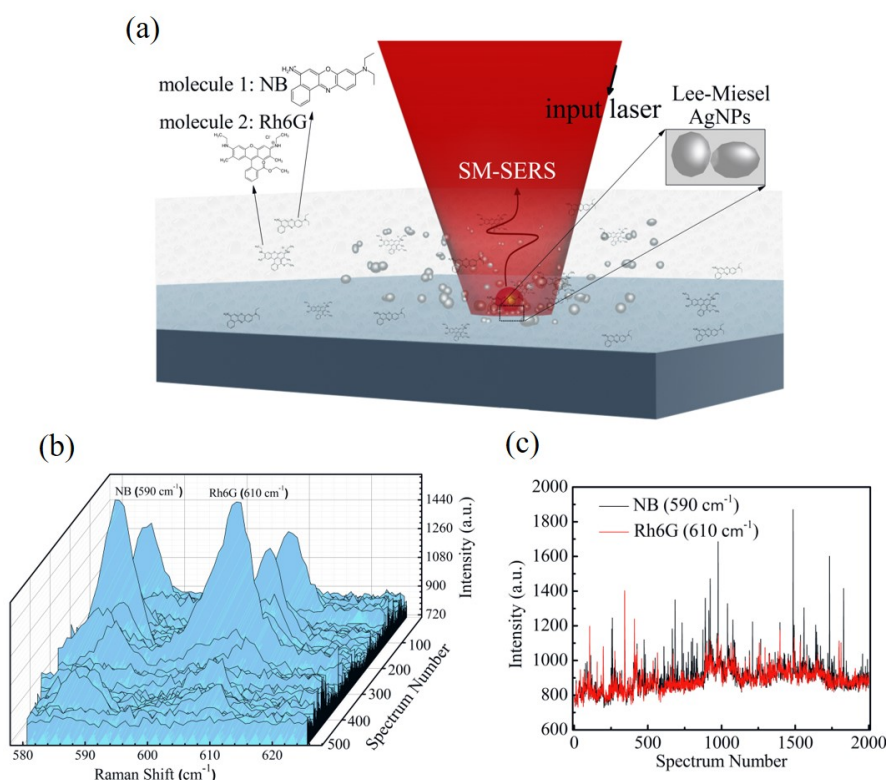


FIGURE 6.12: (a) Schematic of SM-SERS using bi-analyte method at 633 nm laser. The trapping configuration included the following: 150 nm anchor AuNP, Lee-Miesel AgNPs in solution, NB and Rh6G molecules in the presence of CTAC (2 mM) and KCl (3 mM). (b) 500 bi-analyte SERS spectra recorded from a solution containing 5 nM of both NB and Rh6G molecules. The integration time for single spectrum was 0.3 s and the dwell time between two consecutive spectra was 1 s. (c) SERS intensity variation of 590 cm^{-1} and 610 cm^{-1} peaks of NB and Rh6G molecules, respectively, as a function of spectrum number. Figure reproduced from [77].

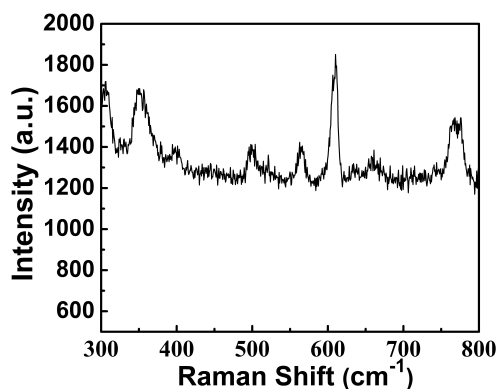


FIGURE 6.13: Bi-analyte SERS from assembly of trapped Lee-Miesel AgNPs without adding KCl in the solution. Figure reproduced from [77].

In addition, without adding KCl in the solution results in a low SERS enhancement of molecular emission. Figure 6.13 (a) shows bi-analyte SERS experiments performed without adding KCl in the solution. The final concentration of NB and Rh6G molecules in the solution was 5 nM. The exposure time for each spectrum was 5 s. The SERS enhancement was very low as compared to the enhancement obtained from trapped Lee-Meisel AgNPs with added KCl. Also, intensity and occurrence of SERS peaks from molecules reduces when the spectra are collected away from a location of the assembly because the number of hotspot away from the assembly was lower as compared to the hotspots present in the assembly.

Next, we discuss the obtained SERS spectra. A waterfall plot of 500 spectra containing closely spaced NB SERS peak 590 cm^{-1} and Rh6G SERS peak (610 cm^{-1}) is shown in figure 6.12 (b). The exposure time for each spectrum was 0.3 s and dwell time between two consecutive spectra was 1 s. The variation in the peak intensity can be seen clearly. Figure 6.12 (c) shows the occurrence and variation in the intensity of both 590 cm^{-1} peak of NB and 610 cm^{-1} peak of Rh6G molecules as a function of spectrum number. These fluctuating individual events suggest that the single nanoparticle driven thermoplasmonic trap can be used to perform SM-SERS.

To statistically confirm the single molecule SERS signature, we performed modified principal component analysis (MPCA)[9, 73, 160] on 2000 spectra collected from the solution containing both NB and Rh6G molecules. Figure 6.14 (a) shows the plot of calculated eigenvalues and eigenvectors, where the first two elements are the principal eigenvalues. Figure 6.14 (b) shows the scatterplot of two covariant matrix coefficients α and β , with two axes shown as NB and Rh6G. Each data point in the scatterer plot represents an event. The re-oriented scatterer plot (α' and β') in figure 6.14 (c) shows two orthogonal axes Rh6G and NB axes, where events on both axes represent pure events of SERS from only one type of molecule. Events in between the two axes represent mixed events which are signals from both the types of molecules. To calculate the frequency of single molecule events, a histogram was plotted in figure 6.14 (d) where the frequency of only NB molecule was plotted after removing noisy mixed events as shown by a black box in figure 6.14 (c). The extreme left part of the histogram represents the events where SERS from only Rh6G molecules was recorded. The spectrum in figure 6.14 (e)(iii) shows such a type of an intense pure event from only Rh6G molecules. The center part of the histogram shows the mixed events from both types of molecules and one such event is shown in figure 6.14 (e)(i). The extreme right part of the histogram displays the probability of only NB molecule events and one such event is shown in figure 6.14 (e)(ii). Along with these three events, a relatively less probable null event was also observed, which is shown in figure 6.14 (e)(iv).

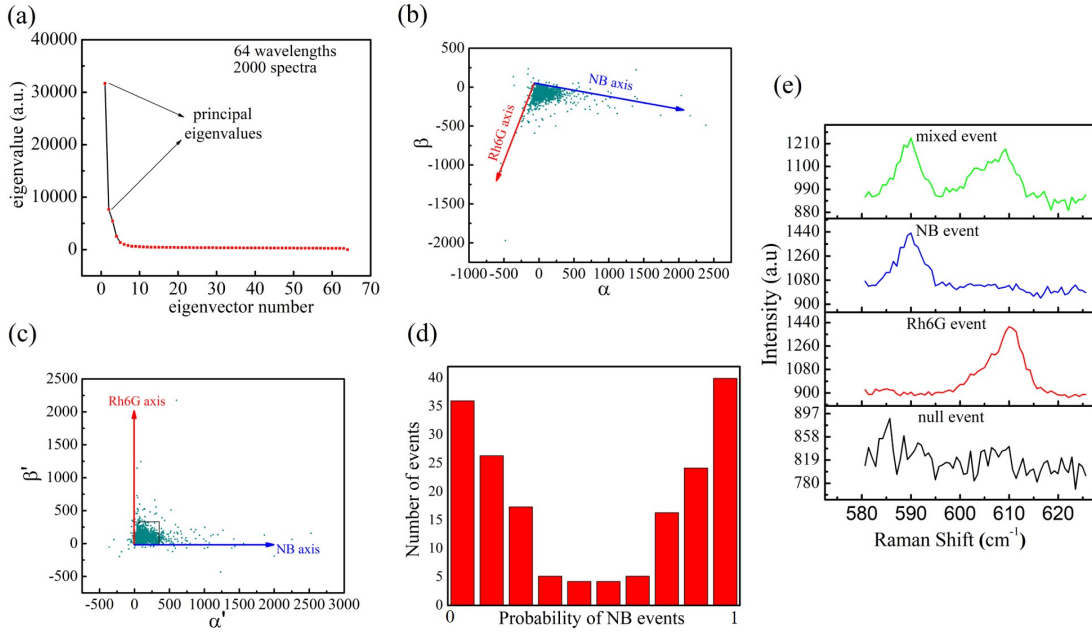


FIGURE 6.14: Modified principal component analysis of bi-analyte SM-SERS. (a) Eigenvalues obtained from PCA of 4000 spectra consisting of 64 wavelengths containing the 590 cm^{-1} and 610 cm^{-1} peaks of NB and Rh6G, respectively. (b) Distribution of the covariant matrix coefficients (α and β) obtained after PCA showing two Rh6G and NB axes. (c) Distribution of the transformed matrix coefficients α' and β' showing two orthogonal Rh6G and NB axes. (d) Probability of NB events plotted using (c) after removing the mixed dye events shown in a black region in (c). (e) Four possible events: (i) Mixed event obtained near the center of the histogram (d). (ii) NB event obtained near the region of probability of NB event=1 (iii) Rh6G event obtained near the region of probability of NB event=0. (iv) No event obtained when probabilities of both NB event and Rh6G event are 0. Figure reproduced from [77].

6.8 Conclusion

To conclude, we have shown how a single dropcasted gold nanoparticle on a glass substrate can be utilized as a thermoplasmonic tweezer to reversibly assemble plasmonic nanoparticles for SM-SERS experiments. By employing bi-analyte SERS technique we have revealed the single-molecule spectral dynamics and its extreme statistical signatures in the assembly of nanoparticles. We have emphasized the relevance of surfactant and salt solution in creating a conducive environment for trapping and SM-SERS at low laser powers ($\approx 0.1\text{ mW}/\mu\text{m}^2$). Furthermore, we have revealed the capability of the tweezer to not only trap single plasmonic nanoparticles, but also to transport plasmonic nanoparticle assembly to a desired location. Such an assembled plasmonic entity can be potentially harnessed as components of plasmonic meta-fluid. We envisage its utility

as a flexible trapping and transport platform *in-vivo*, and anticipate further exploration on colloidal plasmonic tweezers sensitive to single-molecule reactions in physiological conditions.

Chapter 7

Conclusion and Future Directions

In conclusion, the work presented in this thesis was focused on harnessing the field enhancement and heat generated by subwavelength plasmonic structures. Field enhancement was utilized to enhance the molecular emission, and to design directional elastic and inelastic optical antennas with high gain and narrow angular spreading. Mirror based plasmonic cavities were designed to enhance the SERS emission from molecular monolayers. Furthermore, the geometries were designed in such a way that they out-couple light in a very narrow range of angles, without compromising the field enhancement. Fourier plane and energy-momentum imaging were performed to image the wavevectors of scattered light from the cavities. FDTD and FEM based simulations were performed to understand the cavity modes to efficiently make use of the cavities for enhancement and directionality purposes.

On the other hand, heat generated because of the non-radiative interactions in the plasmonic structures was studied to harness the thermophoretic movement of molecules and plasmonic particles. The directed motion of molecules because of temperature gradient was utilized to create a large-scale assembly of plasmonic structures which further was used for detecting single molecule SERS signatures. The assembly was initiated by the heat generated in a single gold nanoparticle. The presented results based on a single nanoparticle driven optothermal trap can be easily extrapolated for applications and fundamental based studies such as in single molecule waveguiding, *in-vivo* applications and in strong coupling physics.

We summarize the different topics covered in the thesis and present some outlines to extrapolate the results for future studies. Importantly, we will also discuss a few challenges that exist in the results presented in the thesis. We envisage that overcoming these challenges will deepen the understanding of light-matter interaction at subwavelength scales.

Directing SERS from molecular monolayer:

In chapter 3 and 4, we presented how to efficiently enhance and direct SERS emission from a self-assembled molecular monolayer. In chapter 3, we utilized bent-plasmonic nanowire on a mirror cavity to direct SERS emission from molecules assembled as a monolayer on a metallic substrate. The geometry also scatters elastic scattering light in a narrow range of angles. The results presented will help in designing more efficient Raman antennas and for efficient on-chip coupling. The wavevectors of scattered radiation also give insights into how light is confined in the hotspots. After this, in chapter 4, we used a metallic particle coated with a molecular monolayer and assembled near a plasmonic nanowire using self-assembly. In this geometry, the molecules were only present in the cavities away from the excitation region and were excited remotely using nanowire plasmon polaritons. We utilized the mirror substrates not only for conventional field-enhancement purposes but also for providing directionality to the enhanced molecular emissions.

Present challenges and future directions:

The cavity used in chapter 3 uses bent nanowires which were prepared using ultrasonication. As mentioned in the chapter, there was no control on the bending angles of the nanowires. Furthermore, though the light scattered from the kink part of the bent-nanowire was collected for imaging and spectroscopy, the molecules were also present at the region of the excitation. This light can also couple to the collection schemes, if performed without spatial filtering techniques. Recently, there are some trapping based studies[27, 161] where two nanowires are trapped and are assembled in such a way that they form an end-to-end couple nanowire junction. This geometry can potentially work in the same manner as bent nanowires but with a better control on the bending angles.

We resolved the problem of molecular presence at the excitation region by designing a geometry where the molecules were present only in the cavities away from the excitation region. We used nanowire-nanoparticle on mirror based cavity used in chapter 4, where the molecules were excited by nanowire plasmon polaritons. Although the molecules were assembled as a monolayer on a gold particle, yet there was no control on the molecular orientation which were excited in the cavity. Furthermore, the particle was coupled to the nanowire using self-assembly technique. The placement of the particle along the nanowire was not controllable. We propose that the nanowire itself can work as an opto-thermal source[162] and the particle can be trapped at any location along the length of the nanowire using the same trapping techniques we discussed in chapter 6 and in the reference[77]. One of the remaining questions that need

to be addressed is what are the wavevectors signatures of elastic scattering light from the junction. The question can also be proposed in such a way that how a nanoparticle on a mirror geometry scatters the nanowire plasmon polaritons. Answering these questions will help in understanding the plasmon hybridisation in momentum space and in studying plasmon scattering by metallic particles.

Directing molecular fluorescence using hybrid metallo-dielectric optical antenna

In chapter 5, we presented how to direct fluorescence from a molecules coated dielectric microsphere. We used the waveguiding property of nanowire to excite the fluorescence and to direct the emission. Since the molecules were coated on the microsphere, no secondary emission was emanated from the excitation region. In addition, the microsphere enhances the fluorescence by coupling the emission to whispering gallery modes of the microsphere. In this work, we have essentially explored the spontaneous emission process in the form of whispering gallery modes mediated fluorescence, but we anticipate that the realized dielectric-metallic hybrid structure can be harnessed for stimulated emission studies, where a hybrid optical antenna can boost the directivity of symmetric resonators.

Present challenges and future directions:

Self-assembly was used to couple the microsphere to the nanowire. There was not much control on the placement of the microsphere near the nanowire. To overcome this problem, an optical trapping technique can be used to trap the microsphere and place the microsphere at any desired location near the nanowire. In addition to this, for preparing a self-assembled microsphere-nanowire junction, the non-radiative interactions of the nanowire plasmon polaritons can also be utilized. Recently, we have utilized a silver nanowire based opto-thermal trap to assemble microspheres near the nanowire[162]. This technique can also work to trap a single microsphere on any desired location near the nanowire. Performing these experiments may also open new avenues for studying the forces acting on the microsphere because of the nanowire plasmon polaritons.

Single molecule SERS in a single nanoparticle-driven thermoplasmonic tweezer:

In chapter 6, we utilized both heating in plasmonic structures and field enhancement produced by metallic structures to create a reversible large-scale assembly. We also detected sensitive single molecule SERS signatures from molecules in the assembly. We used a very low power input laser for both trapping and spectroscopy. Using the heat produced by a single nanoparticle, we trapped a single nanoparticle to make a dynamic plasmonic dimer. The field in the cavity of the dimer created can be used to study the plasmon hybridization phenomenon. Given that our tweezer platform is based on a colloidal gold nanoparticle, it can be chemically functionalized for targeted trapping of nano-objects including bio-molecules.

Present challenges and future directions:

The anchor particle which was working as an optothermal trapping source was a single spherical nanoparticle. For the same input power density, using an anisotropic structure can result as a better heating source[163]. In plasmonic structures, the heating is due to the field penetration inside the structures. Cavities like structures can be designed to generate more efficient heating, which can reduce the power density needed.

In the experiments the anchor particle was first made static on the glass substrate and then was used as a heating source. Once made static, the anchor particle working as a heat source becomes immobile. Of late, there is an imperative to design heating sources which can be made mobile by using optical tweezers. Some experiments are also initiated by us, where the anchor trap is made up of dielectric materials and thus can be trapped using gradient forces of focused laser beam. The trapped anchor particle can be utilized as a low power optical tweezer. Furthermore, the temperature increment and gradient in the system was quantified using numerical calculations. Presently, it is very difficult to accurately estimate or calculate the temperature increment of a plasmonic structure using numerical based calculations. Optical thermometry[164–166] is an experimental technique which can measure the temperature of the particle under illumination with very high accuracy. It is a non-perturbative method which provides temperature of plasmonic structures by collecting the *anti* – *Stokes* shifted emission.

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