
Plasmonic Nanowire Photonics: Light Propagation and Field Enhancement

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 ("Plasmonic Nanowire Photonics: Light Propagation and Field Enhancement") submitted by **Chetna Taneja** 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.



Date: October 13, 2022

(G V Pavan Kumar)
Supervisor

Declaration

I declare that this written submission represents my research work in my own words and where others' ideas or works have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will be caused for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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A handwritten signature in blue ink, appearing to read 'Chetna', with a long horizontal stroke extending to the right.

(Chetna Taneja)

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Abstract

For future generation optical components such as couplers, antennas and waveguides, we need nanoscale control and confinement of the electromagnetic fields. Over the years, metallic nanostructures have been studied intensely to confine light beyond the diffraction limit of light. Resonant oscillations of surface charge density in metallic nanostructures with incident laser field offer hugely enhanced and confined field at the surface of metal-dielectric interface. These oscillations are called ‘surface plasmon polaritons’ (SPPs). Of all nanostructures supporting SPPs, silver nanowire (AgNW) gains particular importance owing to the low loss SPP waveguiding leading to potential application as an optical antenna which forms the bedrock for on-chip photonic circuitry. In addition, uniform geometry, ease of synthesis, and wide range of resonance tunability ensure ease of implementation for various nanophotonic applications on any substrate. This thesis focuses on studying the light confinement and propagation in subwavelength plasmonic AgNW. We intensely explore the existence of transverse spin in SPPs propagating in AgNW and show the spin-momentum locking phenomenon due to evanescent nature of SPPs which can add to a more complete description of many effects due to SPPs such as directional coupling, and spin-Hall effect. Further, to overcome losses associated with light propagating in metals, we show that combining plasmonic and dielectric photonic structures can offer interesting opportunities in hybrid nanophotonics. We study subwavelength SPP propagation mediated via whispering gallery modes (WGMs) of dielectric microsphere (μ S) for hybrid nanowire-microsphere (AgNW- μ S) system.

From the surface of metallic nanostructures, field confinement has been pushed to few nanometers (nm) inside the nanogap between two metallic nanostructures by utilising metallic nanocavities. We study the tightly confined plasmon inside the nanogap supported by Nanowire over mirror (NWoM) geometry. Utilising the cavity plasmons, we probe spatial inhomogeneities of the nanogap which are often inaccessible in experimental characterisation. Furthermore, we observe local morphological changes on the surface of AgNW placed on a mirror forming NWoM geometry. We show that these changes are non-reversible and can be controlled on atomic scales using the optical excitation at room temperature. Presented findings could pave the way towards an atomic scale lithography for plasmonic nanostructures using metallic nanocavities.

List of Publications

Included in thesis:

- **Chetna Taneja**, Diptabrata Paul, G. V. Pavan Kumar , Experimental observation of transverse spin of plasmon polaritons in a single crystalline silver nanowire, *Applied Physics Letters* 119, 161108 (2021)
- Sunny Tiwari*, **Chetna Taneja***, G. V. Pavan Kumar, Sub-wavelength plasmon polaritons channeling of whispering gallery modes of fluorescent silica microresonator, *Materials Research Bulletin*, 6(1), 148-153 (2021). (**Contributed equally to this work*)
- **Chetna Taneja**, Eoin Elliott, G V Pavan Kumar, Jeremy J Baumberg, Rohit Chikkaraddy, Mapping 1-D extended nanocavities using light scattering from molecular monolayers, *manuscript under preparation* (2022).
- **Chetna Taneja**, G V Pavan Kumar, Jeremy J Baumber, Rohit Chikkaraddy, Non-reversible local structural change inside 1-D extended nanogap, *manuscript under preparation* (2022).

Not included in thesis:

- Sunny Tiwari*, **Chetna Taneja***, Vandana Sharma, Adarsh Bhaskar Vasista, Diptabrata Paul, G. V. Pavan Kumar, Dielectric Microsphere Coupled to a Plasmonic Nanowire: A Self-Assembled Hybrid Optical Antenna, *Advanced Optical Materials*, 8, 1901672 (2020). (**Contributed equally to this work*)
- Sunny Tiwari, **Chetna Taneja**, G V Pavan Kumar, Plasmonic nanowire coupled to zero-dimensional nanostructures: A brief review, *Asian Journal of Physics*, 28(10-12), 961-981, (2020). (**Review Article**)
- Tamaghna Chowdhury, **Chetna Taneja**, Aastha Vasdev, Prasenjit Ghosh, Goutam Sheet, G V Pavan Kumar, Atikur Rahman, Stacking Engineered Room Temperature Ferroelectricity in Twisted Germanium Sulfide Nanowires, *Advanced Electronic Materials* 8 (5), 2101158 (2022).

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Dedicated to my parents

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Chapter 1

Introduction : Silver nanowire and field confinement beyond diffraction limit of light

The realisation of miniaturized nanophotonics devices would require components such as antennas, couplers and waveguides for light at subwavelength scales. For all these components there is a necessity of confining the electromagnetic fields at scale much beyond the diffraction limit of light. The advanced nanofabrication techniques have pushed this confinement limit up to few nanometer (< 2 nm) using metallic nanostructures. In this chapter, we introduce confinement of light at subwavelength scales in metallic nanostructures with intensely focussed discussion on silver nanowires (AgNWs).

1.1 Metallic nanostructures : Guiding light through SPPs

Metallic nanostructures support surface charge density oscillations at the metal-dielectric interface called 'surface plasmon polaritons (SPPs)' [1–3]. The Resonant oscillations of charge density with incident field results in enhanced and confined field at the interface which has been utilised to strongly increase light-matter interaction at nanoscale [4–8]. These SPPs are evanescent waves with field propagating along the interface and decaying exponentially in both the metal and dielectric medium (Fig. 1.1).

Upon solving the Maxwell equations for the metal-dielectric interface (metals having larger and negative real part of relative permittivity (ϵ_m)), SPPs wave-vector's real component (k_{spp}) can be described as

$$k_{SPP} = k_0 \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} \quad (1.1)$$

where ϵ_d and k_0 are the relative permittivity of dielectric material and wave-vector of free space photon respectively [9]. It is clear from the Eq. 1.1 that SPPs momentum is greater than the free space photon. This momentum mismatch would require extra momentum for a photon to couple into SPPs. There are many methods that have been used to satisfy this mismatch condition such as coupling the light through prism [10, 11], using scattered light with grating fabricated on metallic nanostructures [12, 13] and near-field coupling [14, 15].

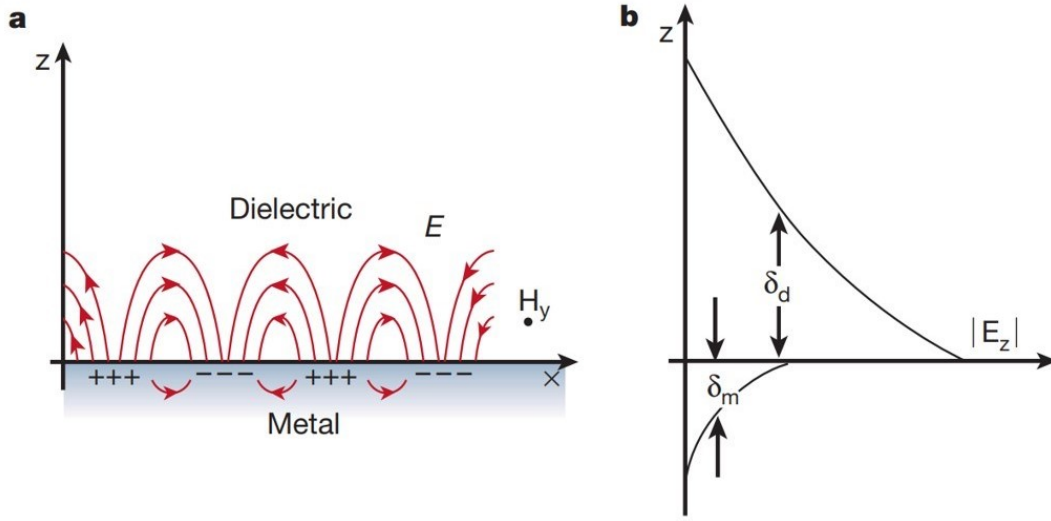


FIGURE 1.1: (a) Schematic of SPPs propagating at metal-dielectric interface (b) Schematic showing evanescent decay of SPPs electric field into both metal and dielectric medium during propagation. Figure has been reproduced with permission from [2].

1.2 Plasmonic silver nanowire as SPP waveguide

Of all the structures that support SPPs such as thermally evaporated metallic film (~ 50 nm thick) [16, 17], plasmonic nanoslits [18, 19], gold (Au) nanowires (NWs)/plate [20–23], chemically prepared quasi-one-dimensional single-crystalline AgNW gains particular importance because of their low loss SPP waveguiding property [24, 25]. One of the most important aspect of SPP propagation in AgNW is the directional out-coupling of SPPs at NW end leading to potential applications as an optical antenna which forms the bedrock for on-chip photonic circuitry [26, 27]. Further, uniform geometry and ease of synthesis ensures implementation for various nanophotonic applications on any substrate [28]. Scanning electron micrograph (SEM), zoomed-in SEM image of one end and optical bright-field image of one such chemically prepared AgNW are shown in Fig. 1.2 (a)-(c). SPPs launched at one end (scattering at the NW end provide extra momentum) using high numerical aperture objective lens out-couple directionally at the other end (Fig. 1.2(d)).

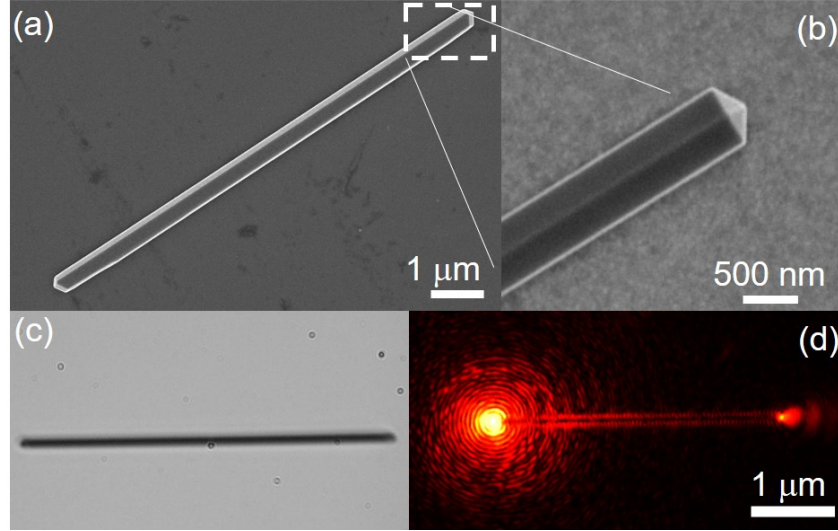


FIGURE 1.2: (a) SEM image of AgNW placed on a glass substrate (b) Zoomed-in image of the ends of AgNW (c) Optical bright-field image of AgNW in transmission mode (d) Elastic scattering image of AgNW showing the SPP propagation upon excitation at one end. Figure is prepared using our data collected during experiments.

In addition, electromagnetic hot-spots (region of enhanced field) along the length of the AgNW during the SPP propagation have been utilized in various fields, such as strong coupling [29], nonlinear optics [30], remote molecular emission [31], single photon sources [32], and cavity electrodynamics [33] (Fig. 1.3).

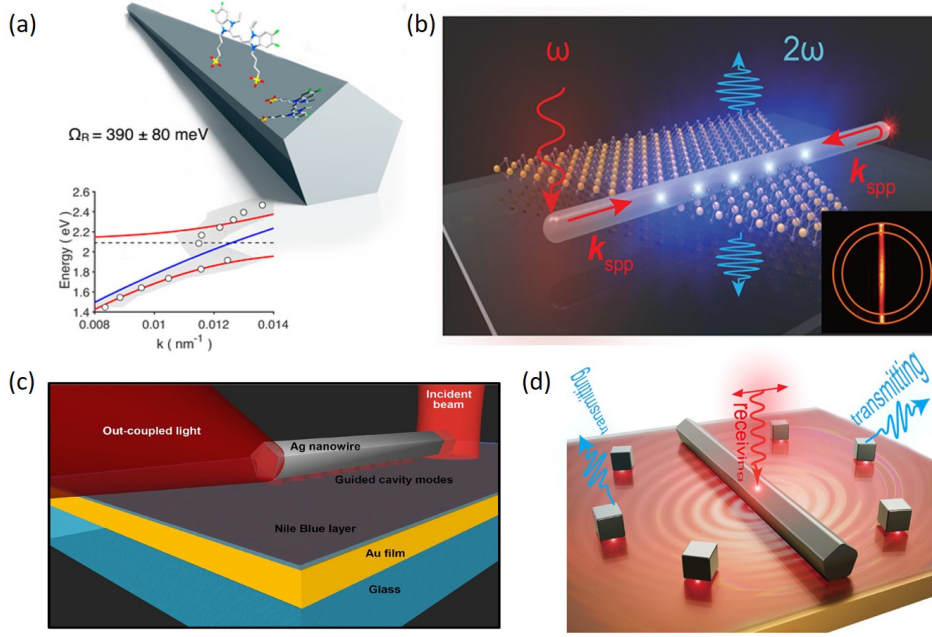


FIGURE 1.3: Schematic of AgNW used for (a) strong coupling (b) second harmonic generation (SHG) from AgNW-transition dichalcogenides hybrid structure (c) AgNW over mirror structure for directing Raman and fluorescence wave-vectors (d) AgNW over mirror geometry for remotely exciting molecular emission. Figures (a), (b), (c) and (d) are reproduced with permission from [29–31, 33].

1.2.1 Bound and leaky surface plasmon modes

Chemically prepared AgNWs placed on a dielectric substrate (with refractive index n_{sub}) can support SPPs which can be classified as Bound or Leaky surface plasmon modes depending on their effective refractive index (n_{eff}) [25]. Bound mode with $n_{eff} > n_{sub}$ does not radiate during propagation whereas leaky mode with $n_{eff} < n_{sub}$ leaks into the substrate while propagating along the length of AgNW [34, 35].

The simulated effective refractive index of fundamental bound and leaky mode of AgNW placed on a glass substrate as a function of NW radius is shown in Fig. 1.4(b) [36]. Excitation of number of plasmon modes and their n_{eff} in a given NW strongly depends on the radius of NW used for experiment [25]. It can also be seen from COMSOL mode analysis for NW with diameter of 350 nm (thick NW) placed on a glass substrate, the near-electric field of bound mode is confined at glass-air interface (thick dashed white line) whereas for two supported leaky mode field is maximum for upper three vertices of the NW (thin dashed white line) (Fig. 1.4).

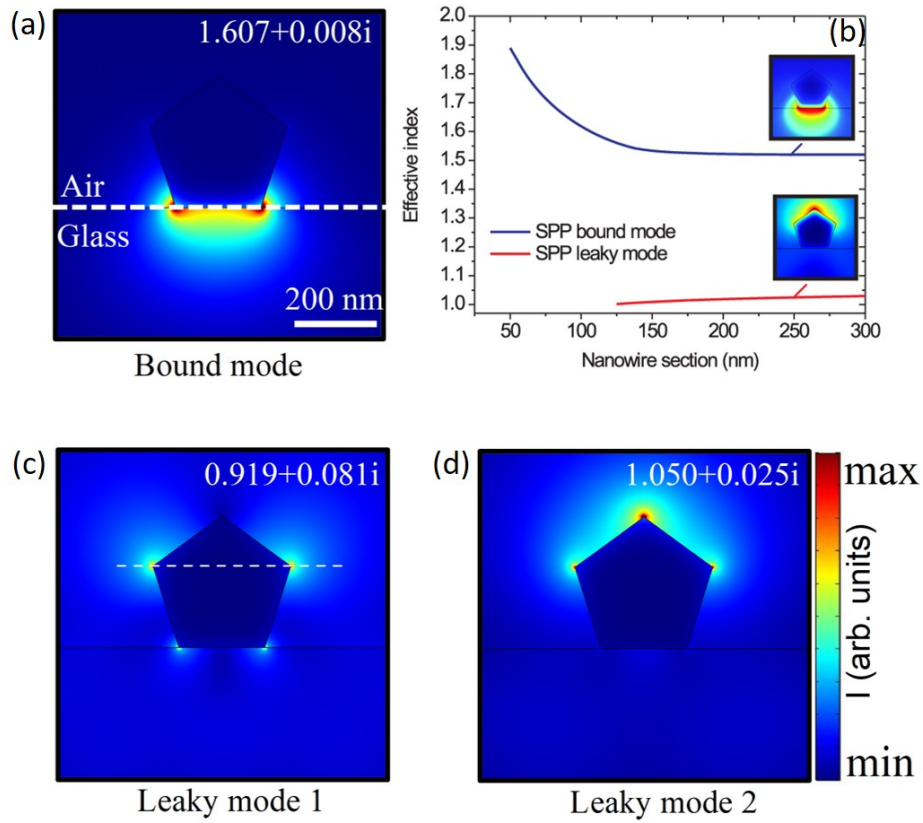


FIGURE 1.4: Numerically calculated near-field of the (a) bound, (c) and (d) leaky SPP modes excited in an AgNW of 350 nm diameter placed on a glass substrate (refractive index 1.518). A bound mode with field components localized at the interface [shown in (a)], whereas for the leaky modes with refractive index lower than the substrate, the field accumulation is more around the upper vertices (white dotted line in (c)) of the AgNW. (b) The simulated effective refractive index of fundamental bound and leaky mode of AgNW placed on a glass substrate as a function of NW radius. Figures (a), (c)-(d) are prepared using our data.

1.3 Hybrid nanostructures with silver nanowire

An interesting prospect that is of relevance to nanophotonics is the coupling between quasi-zero dimensional (0-D) nanostructures (such as metal nanoparticle) with quasi-one dimensional (1-D) nanostructures (AgNWs). Such coupling can lead to some optical properties that are otherwise not present in the individual nanostructures taken in isolation.

1.3.1 Silver nanowire coupled to a nanoparticle: Nanowire-nanoparticle junction

Coupling between 1-D plasmonic AgNW and 0-D nanoparticles forms nanowire-nanoparticle (NW-NP) junction [37–40]. As discussed in earlier, AgNWs support delocalized propagating plasmons, however nanostructures like metallic nanoparticles exhibit localised plasmons at the

metal-dielectric interface called 'localised surface plasmon' [41–44]. Coupling these two structures together provides the platform to utilise both localised and delocalised plasmons in the same geometry.

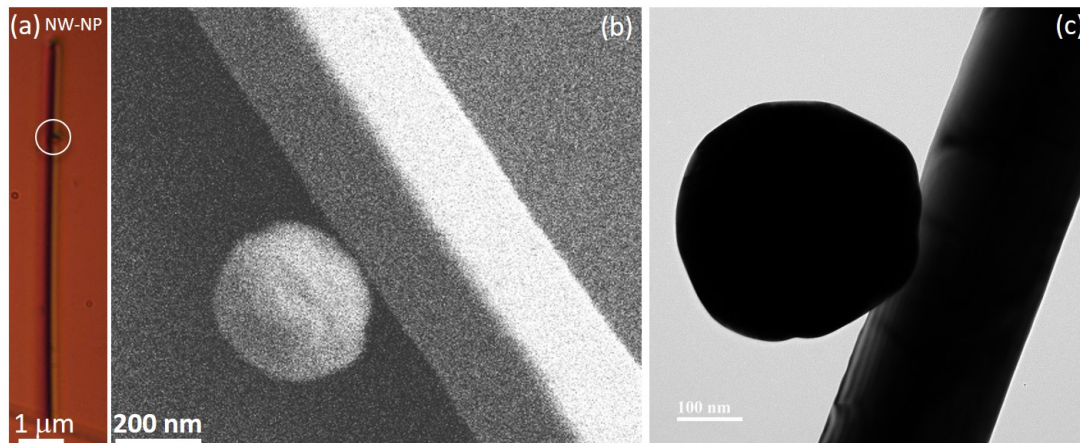


FIGURE 1.5: (a) Optical bright field image of a NW-NP junction where a 400 nm diameter gold nanoparticle is coupled to an AgNW with average diameter 300 nm. (b) SEM and (c) TEM image of the NW-NP junction. Figure is prepared using our data collected during experiments.

Fig. 1.5(a) shows the optical bright-field image of the NW-NP junction where we couple a single 400 nm diameter Au nanoparticle to an AgNW (300 nm diameter). To better visualise the coupling or NW-NP junction, we take SEM (Fig. 1.5(b)) and Transmission electron microscope (TEM) image (Fig. 1.5(c)) of the junction. It is clear from the images that nanoparticle rests on the side facets of the AgNW.

Different NW-NP junctions shown in Fig. 1.5 are prepared using **capillary force based self-assembly processes**. Capillary forces are used intensely for self-assembly process [45, 46] and coupling two metallic nanostructures [47, 48]. A preparation protocol, we first disperse 7 μl of AgNW solutions in ethanol on a glass substrate, followed by drop-casting 7 μl of Au nanoparticles in ethanol on the same sample. Upon visualising the sample, some AgNW would be seen coupled to a single nanoparticle forming NW-NP junction. During the drying process of Au colloids near AgNWs, the capillary force provides a long range interaction between NW-NP. There has been reports with detailed calculation on the capillary forces between the NW and nanoparticle [49]. The force calculated between AgNW and nanoparticle is shown to be of the order of 10^{-8} N which can easily overcome the effect of gravity on nanoparticle which assembles near AgNW forming NW-NP junction. The schematic of forming NW-NP junction using capillary force based self-assembly process can be seen in Fig. 1.6 which is adapted with permission from [49].

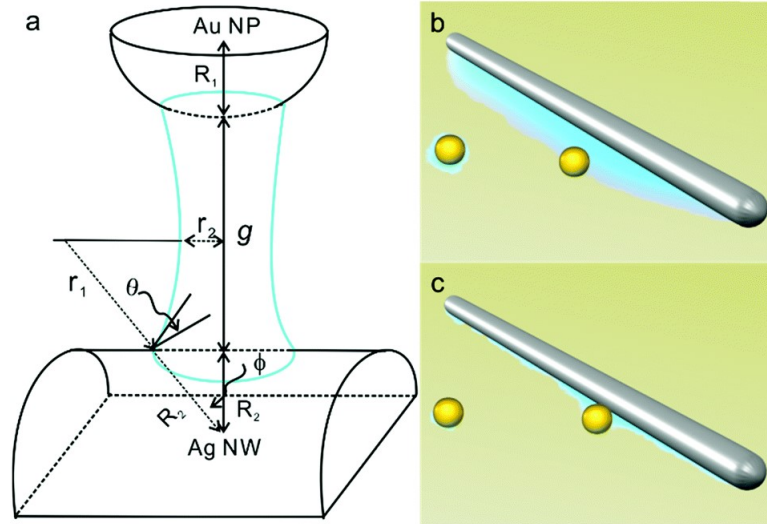


FIGURE 1.6: Liquid-bridge between AgNW and gold nanoparticle dispersed in ethanol and representative images of a capillary force induced self-assembled single NW-NP junction. Figure is reproduced with permission from [49].

It is important to mention that we can not control exactly the number of nanoparticles attached to a single AgNW or the point of coupling nanoparticle along the length of NW. There are other methods such as optical trapping where nanoparticle is trapped using optical tweezers and placed in contact with AgNW to form NW-NP junction [50]. Junction can also be formed by moving a nanoparticle using optical fibre and thus micromanipulating a nanoparticle closer to AgNW [51]. Although both methods provide much more control over the distance and position of nanoparticle forming NW-NP junction, large scale production would not be possible. More information on the NW-NP junction assembly and its application can be found in the review article from our group [52].

1.3.2 Hybrid metallo-dielectric antenna: Silver nanowire coupled with dielectric microsphere

The ability of AgNWs to propagate and direct optical fields at subwavelength scale can be utilised to provide directionality to otherwise symmetric emission from dielectric optical resonators which would be essential for hybrid metal-dielectric nanophotonics [53]. In this regard, we study a self-assembled AgNW- silica microsphere (AgNW- μ S) structure for sub-wavelength propagation of microsphere's optical modes while simultaneously tuning the directionality using AgNW. The protocol for preparing these AgNW- μ S system remains the same as discussed earlier for NW-NP junction. SEM images of various AgNW- μ S junction prepared using self-assembly processes are shown in Fig. 1.7.

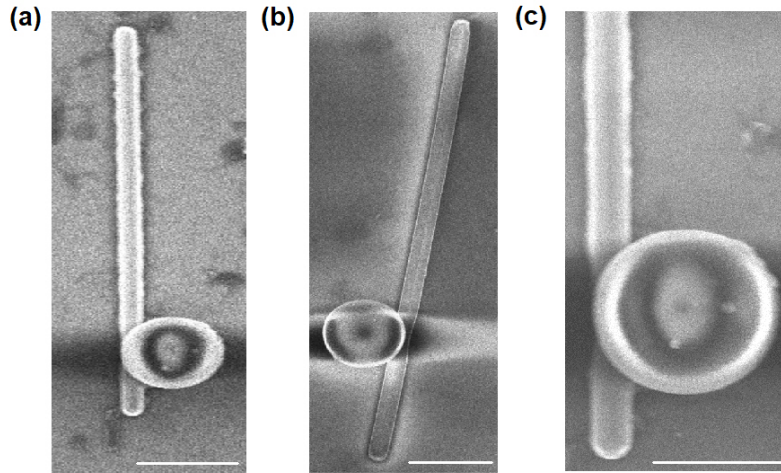


FIGURE 1.7: (a)-(b) SEM images of AgNW- μ S prepared using self-assembly processes where AgNW with average diameter 300 nm is coupled to a microsphere of diameter 3 μ m. Scale bar is 3 μ m. Figure is prepared using our data collected during experiments.

1.3.3 Whispering gallery modes (WGMs)

Coupling light into a dielectric microstructure at an angle greater than the critical angle ($\theta > \theta_c$) (for microstructure and surrounding medium interface) results in light undergoing total internal reflection (TIR) at the inner boundary of microstructure (Fig. 1.8) [54]. The light trapped inside interfere constructively with itself only for specific frequencies and results in high quality factor modes. These modes are called whispering gallery modes (WGMs) [55–57]. Modes are named after the whispering gallery effect at St. Paul’s Cathedral where Lord Rayleigh discovered the WGMs for accoustic waves [58].

The simulated near-field of a WGM supported by a glass microsphere suspended in air with diameter of 3 μ m is given in Fig. 1.8(c). Light is coupled into the structure using near evanescent field of dipole placed at the boundary of the microsphere. The enhanced and confined field is visible at the boundary. WGMs are extremely sensitive to shape, size and local environment of the microstructure which have been used for many applications such as biological sensing [59], non-linear optics [60, 61], lasing [62] and many more.

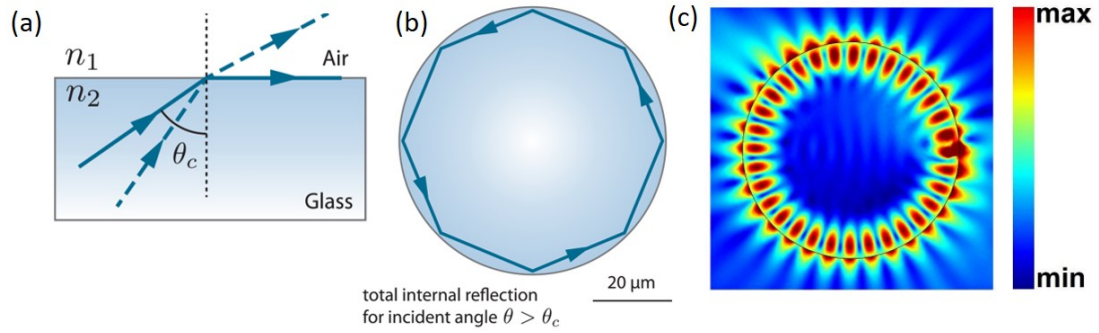


FIGURE 1.8: (a) Schematic of TIR at air-glass interface with air having refractive index n_1 and glass with refractive index n_2 . At incident angle greater than θ_c light gets totally internally reflected from the interface inside the glass medium. (b) Schematic of light propagating inside the dielectric microsphere undergoing TIR (c) Near-electric field of WGM supported by a dielectric microsphere of average diameter = 3 μm simulated using COMSOL. Fig. (a) and (b) have been reproduced with permission from [57].

1.4 Metallic nanocavities for extreme field confinement

As discussed, metallic nanostructures offer optical field confinement at subwavelength scale. Confinement limit can be pushed to the minimum possible dimension of plasmonic nanostructures. Metallic nanoparticles such as Au and Ag support localised plasmon resonances with resonance position dependent on the shape, material composition and size [63–65]. However confinement on the scales of few nanometers (around 1 nm) (for strong coupling of light-matter) is really difficult given the fabrication limitations of particles in both colloidal and lithographical approaches [66–68].

Metallic nanocavities between two metallic nanostructures offer extreme field enhancement and confinement inside the dielectric gap (few nm gap) due to plasmon hybridization [69, 70]. Strongly confined electromagnetic field inside the nanogap has been harnessed to enhance molecular emission from the nanocavity for many applications such as single molecule detection [71], strong coupling [72], mid infra-red detection [73].

Metallic nanocavities can be of different kinds such as metal nanoparticles placed on a mirror (Fig. 1.9(a)) where the nanocavity is formed between a single nanoparticle and mirror. The field is confined inside the nanogap (1 nm) between nanoparticle and mirror [74]. Instead of a single nanoparticle, there can also be nanoparticle dimer placed on a mirror (Fig. 1.9(b)) where nanocavities will be formed between the nanoparticles, a single nanoparticle between the mirror. Instead of placing a metal nanostructure over mirror, top-down approaches can also be utilised using complex fabrication techniques to form metal nanocavities such as Bow-tie antenna (Fig. 1.9(c)) [75]. Top-down approach provides extreme control over fabrication but are harder to prepare and surface scattering leads to a lot of losses. Fig. 1.9(d) shows the nanocavities formed by placing a chemically prepared AgNW placed on a mirror, where the nanogap is extended along the length of NW [76]. This nanocavity does not require complex fabrication and single crystalline nature of chemically prepared AgNW ensures minimal losses.

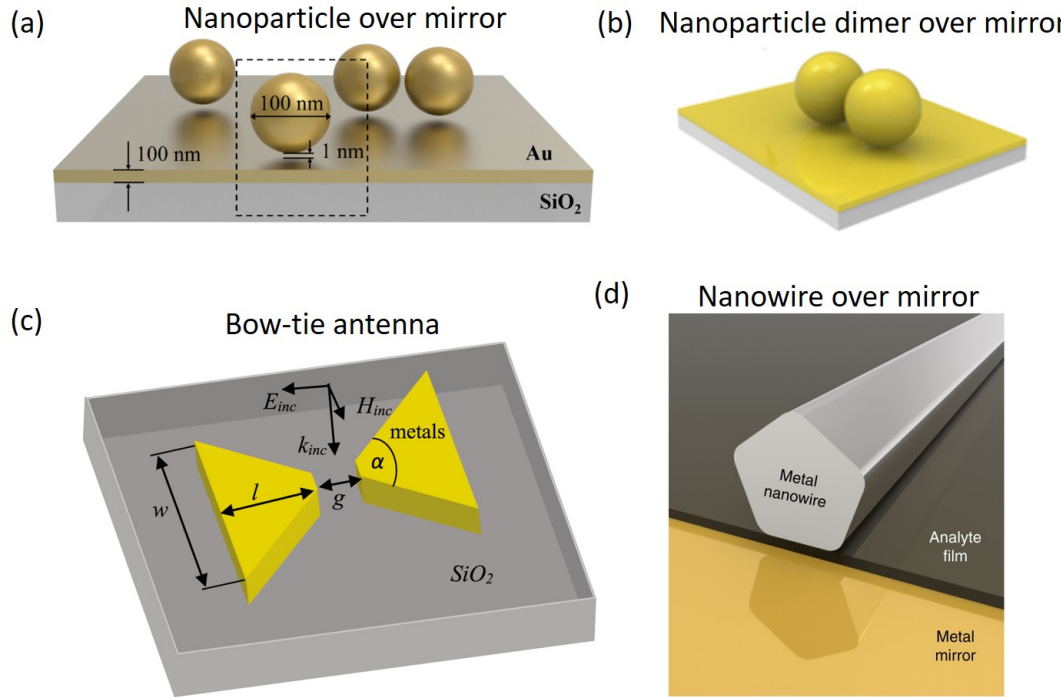


FIGURE 1.9: (a) Schematic of nanoparticles dispersed on a mirror thermally evaporated on a glass substrate forming nanoparticle over mirror nanocavity (NPoM) (b) Nanoparticle dimer placed on a mirror geometry. Geometry supports two nanocavities one between the nanoparticles and a nanocavity formed between the nanoparticle and mirror (c) Schematic for Bow-tie antenna prepared on a glass substrate (d) Schematic of nanowire over mirror (NWoM) geometry.

Figures have been reproduced with permission from [74–76].

1.4.1 Metallic nanostructures over mirror nanocavity

Metallic nanostructure over mirror has gained particular importance due to their ease of fabrication and extremely small gap plasmon mode volume [77]. Ease of fabrication also ensures the reproducible nanogap of the order of 1 nm which is very difficult to achieve with nanocavities prepared using other approaches [70, 78]. As can be seen from the near-field profiles, nanocavities (nanoparticle over mirror (NPoM)) provide much better confinement and enhancement of optical fields than a bare Au nanostructure or a Au film (Fig. 1.10) [79].

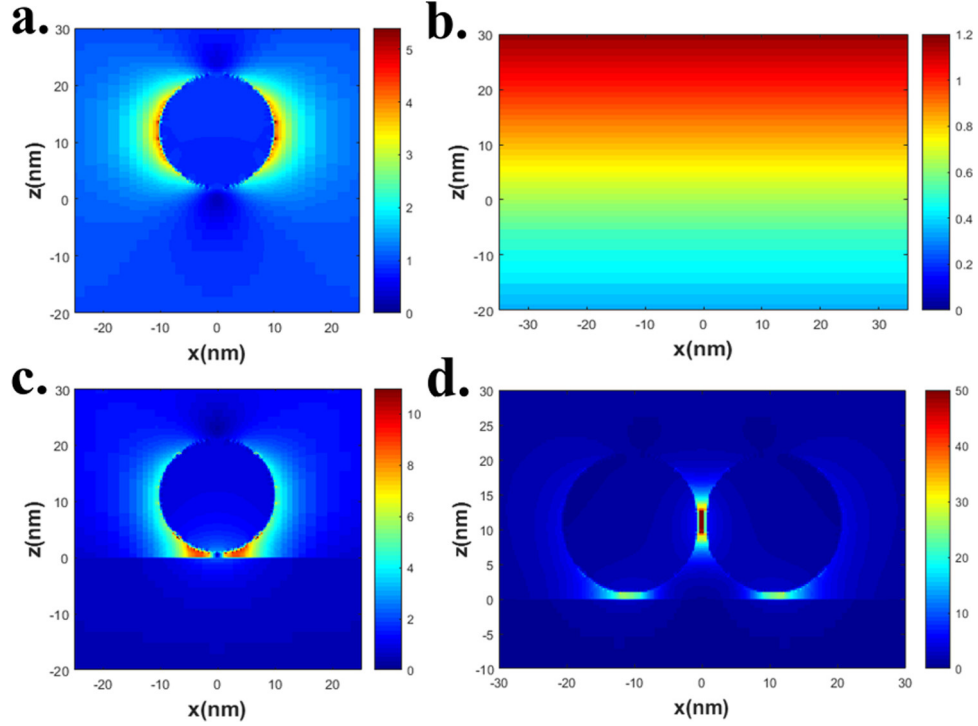


FIGURE 1.10: Simulated near-electric field for (a) a Au nanoparticle (b) a Au film (c) Au NPoM nanocavity (d) two Au NPoM nanocavities at 532 nm incident laser wavelength using finite difference time domain (FDTD). Figure has been reproduced with permission from [79].

1.4.2 Picocavities: sub-nanometer scale optical cavities

In recent times, the atomic presurisons within the nanocavity has introduced 'picocavities' where field enhancement and confinement has reached sub nanometer scale [80]. Picocavities are formed with a single-atom surface defects (adatoms) at metallic facets within a nanocavity. These are consistently reported and studied for NPoM nanocavity where the optical field inside the cavity is large enough to move a single atom from the facet of nanoparticle forming the nanocavity (Fig. 1.11(a)) [81].

As formed picocavities offer unprecedented values of confinement and enhancement of optical fields which is visible in the simulated near-field enhancement near the region of adatom of NPoM geometry with faceted Au nanoparticle (Fig. 1.11(b)). Inset provides the zoomed-in view of picocavity. Fig. 1.11(c) compares the near-field enhancement with or without atomic protrusion inside the nanocavity. The optical fields can be seen hugely increased in the case of picocavities [82].

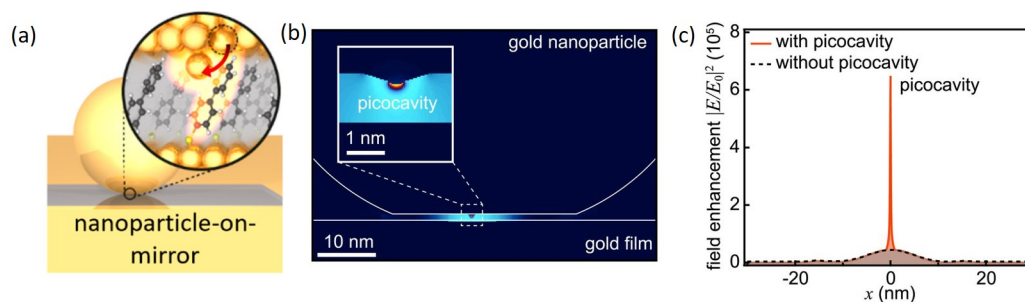


FIGURE 1.11: (a) Schematic of picocavity formation with atomic protrusion from the faceted Au NPoM system (b) Simulated near-field for picocavity with inset showing the zoomed-in image (c) near-electric field enhancement inside NPoM nanocavity with or without the formation of picocavity. Fig. (a), (b) and (c) have been reproduced with permission from [80] and [82].

Thus far, picocavities has been observed using the enhanced molecular emission from molecules sandwiched inside the nanocavity. Since, molecular emission strongly depends on the local near-electric field strength experienced by the molecules, it is a robust and good indicator of field strength inside the nanogap. Next, we discuss some molecular emissions relevant to our discussion.

1.4.3 Molecular Fluorescence

Upon optical absorption (by an incident laser) electrons in the molecules can be moved to an excited state. When this optical absorption results in a emission during the relaxation of molecule, process is called luminescence. One of the most common type of luminescence is 'fluorescence' [83, 84]. The process can be understood by following steps (Fig. 1.12):

- Since, energy of a molecule is divided into electronic, vibrational and rotational energies, any absorption of electromagnetic radiation does not only cause transitions between electronic states but also transitions within vibrational states of molecules. When an incident field with energy E_L greater than the energy difference between molecule's electronic ground S_0 and excited state S_1 is absorbed, electron is excited from S_0 to S_1 .
- The excited electron undergoes some relaxation within few picoseconds (0.1-10 ps) through non-radiating transitions within S_1 (within vibrational sublevels $v=0,1,2$ etc) and reaches the lowest energy level of S_1 .
- Excited electron relaxes back to one of the vibrational level of the ground state S_0 and emits an electromagnetic radiation with energy lower than E_L .

Emitted photons through this process is called fluorescence of the molecules and wavelength dependence of their intensities is called fluorescence spectrum'.

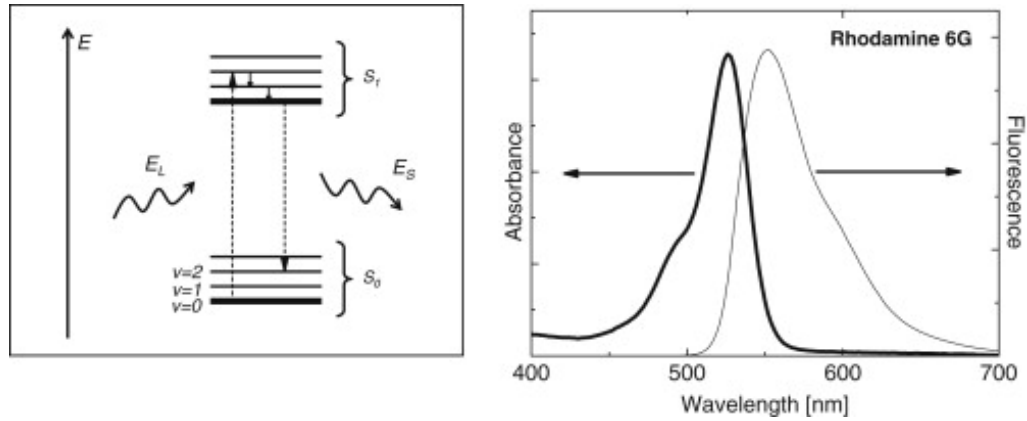


FIGURE 1.12: Jablonski diagram of fluorescence in a molecule (left), absorption and fluorescence spectrum for Rhodamine 6G molecule (right). For fluorescence molecule is excited at 514 nm (maximum absorption). Figure has been reproduced with permission from [83].

1.4.4 Raman Scattering

There are optical scattering processes where emission of photon happens spontaneously upon optical excitation (scattered photon). This spontaneous process does not need to involve an electronic transition (as in the case of fluorescence) and can be understood as the excitation to a virtual state and relaxing back to ground state by the emission of scattered photons. The process can also be understood as the coupling of incident photons to a vibrational state of the molecule.

The scattered photon can have same or different energy than the incident photon. The scattered photon with energy either greater or lower than incident energy is called 'Raman scattered' photon [83, 85]. Raman scattered photon can further classified into two categories:

- **Stokes Raman** If the scattered photon has energy lower than the incident photon energy ($E_S < E_L$), the process is called stokes scattering and photon is called stokes shifted photon. The energy difference ($E_L - E_S$) is called Raman shift which corresponds to vibrational state energy $\hbar\omega_{vib}$ of the molecule coupled to the incident photon.
- **Anti-stokes Raman** If the scattered photon has energy greater than the incident photon energy ($E_S > E_L$), the process is called anti-stokes scattering and photon is called anti-stokes shifted photon. For this process to occur, the molecules should be in an excited states before the optical excitation to provide extra energy to scattered photon. This can be due to thermal excitation and hence, anti-stokes photons intensity depends strongly on temperature of the system. However, at room temperature, most molecules are in ground state and hence in a typical Raman spectrum anti-stokes photons would have much less intensity than stokes photons.

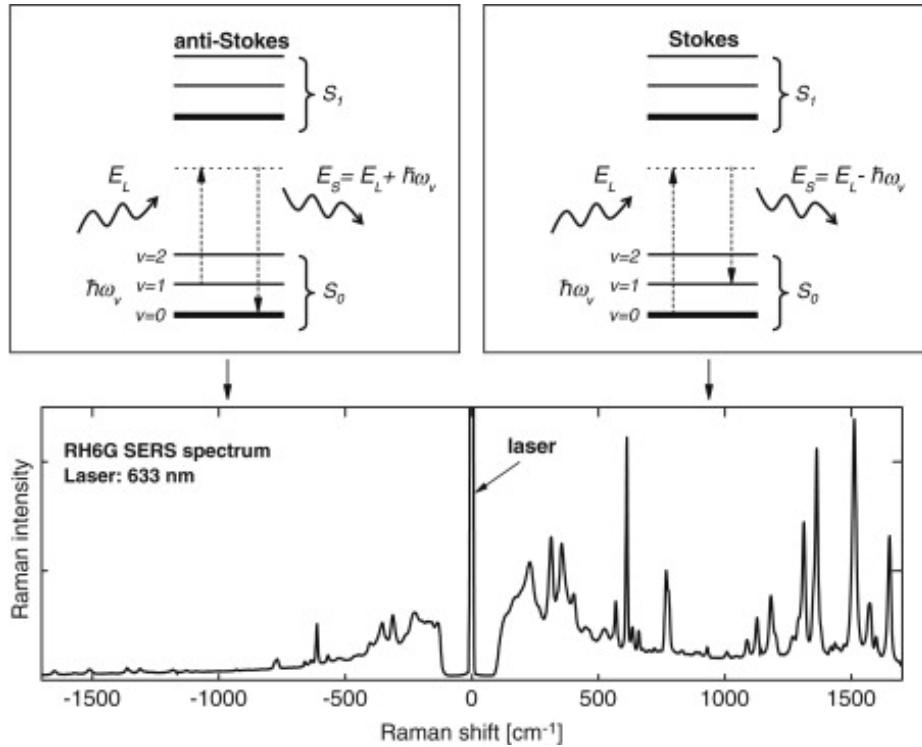


FIGURE 1.13: Jablonski diagram of anti-stokes and Stokes Raman process for a molecule. (b) Typical Raman spectrum of rhodamine 6G molecules showing both Stokes and anti-Stokes Raman peaks. Figure has been reproduced with permission from [83].

The schematic of Stokes and anti-Stokes Raman processes are shown in Fig. 1.13 along with a typical Raman spectrum of rhodamine 6G molecule. The excitation light is blocked for a clear view of Raman scattered photons. Raman peaks in the spectrum are generally displayed as a function of Raman shifts (cm^{-1}) from the excitation laser. It can be seen from the Fig. 1.13 that positive Raman shifts ($E_S < E_L$) show more intense Stokes peaks whereas anti-Stokes peaks ($E_S > E_L$) are weaker in the negative Raman shift region.

1.4.5 Surface enhanced Raman Scattering (SERS)

As discussed in the previous section, each peak corresponds to a specific vibrational mode of the molecule and thus Raman spectrum provides molecular fingerprint which is very useful for chemical and biosensing [85, 86]. However, not every vibrational mode provides strong Raman signal as inelastic scattering process itself is a very weak phenomenon. If 10^7 photons are incident on a molecule, only about 1 photon would result in inelastic scattering. Hence, Raman cross-section σ_{RS} which describes incident beam's area over which photons are scattered as Raman photons [87] is very low.

Surface enhanced Raman scattering (SERS) combines weak Raman scattering process with enhanced optical fields at the surface of metallic nanostructures to increase σ_{RS} which results in increased Raman signal from the molecule. Overall SERS enhancement factor (EF) provided by metallic nanostructures can be **electromagnetic enhancement** (EM) due to increased local

optical fields and **chemical enhancement** (CE) due to chemical interaction between molecules and metal nanostructures.

It has been shown that EM EF is proportional ($|\vec{E}(\omega)|^4/|\vec{E}_0|^4$) at the molecules when plasmons at the metallic surface are excited with frequency ω . As discussed previously, metallic nanocavities provide much more field enhancement than bare metallic nanostructures such as nanoparticle or film, SERS obtained by placing the molecules between the nanogap of metallic nanocavities provides EM enhancement upto 10^5 – 10^6 . The schematic of SERS where Au nanoparticles are dispersed onto the substrate to provide localized electromagnetic hot-spots at the surface of nanoparticles or inside the gap between two nanoparticles is shown in Fig. 1.14 (a). Fig 1.14(b) shows the NPoM geometry formed with faceted Au nanoparticle (optical image in the inset). A self-assembled monolayer of Biphenyl-4-thiol (BPT) molecules are sandwiched inside the nanocavity and time trace of SERS from BPT molecules with 633 nm excitation wavelength shows three characteristic BPT SERS peak (Fig. 1.14(c)) [88].

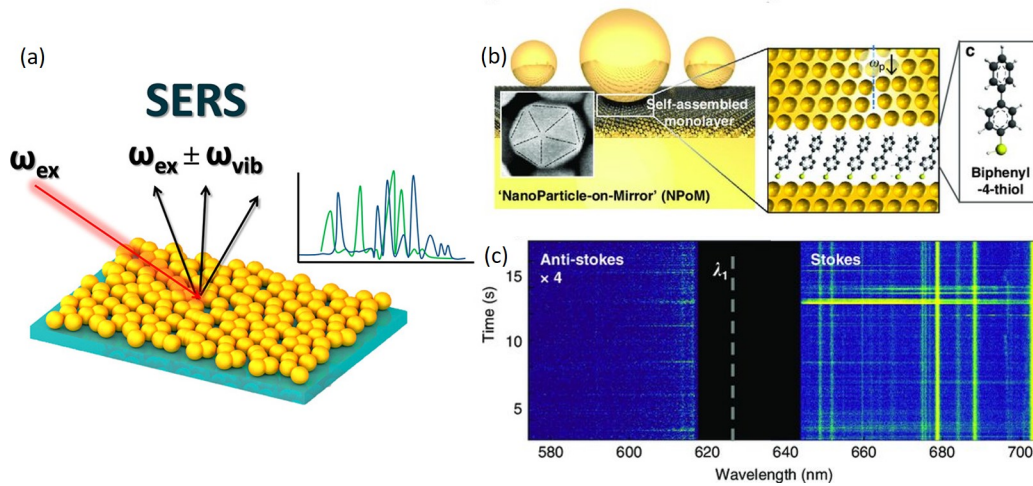


FIGURE 1.14: (a) Schematic of SERS where field enhancement is provided from the plasmons excited in metallic nanoparticles. (b) Schematically showing NPoM nanocavity with a molecular layer of BPT sandwiched inside the nanogap. Inset shows the zoomed-in view of BPT molecules inside the nanogap and the chemical structure of BPT molecule. (c) Time trace of SERS from BPT molecules inside NPoM nanocavity showing three characteristic SERS peaks

Figure (a), (b) and (c) have been reproduced with permission from [87, 88].

1.5 Outline of the thesis

The emphasis of this thesis is to study the light propagation and confinement at subwavelength scale for plasmonic AgNW and nanowire over mirror (NWoM) nanocavity. Thesis is divided into seven chapters. Chapter wise description of the work included in the thesis is given below:

Chapter 2 (Methodology: Dual channel microscopy, Fourier plane imaging and Spectroscopic measurements)

The work in this thesis has been performed with different experimental optical set-up which include upright, inverted microscope and also a home-built dual channel microscope. In addition many experimental techniques such as Fourier plane imaging, Dark-field scattering, Spectroscopic SERS measurements are crucial. This chapter provides overview of the optical set-up, experimental techniques and numerical modelling as described below:

- The architecture of dual-channel microscope.
- Fourier plane imaging and implementation of spin measurement in Fourier plane imaging.
- Simultaneous measurement for polarisation resolved Dark-field scattering spectra and SERS from nanocavities.

Chapter 3 (Transverse spin and associated spin-momentum locking of plasmon polaritons in a single crystalline silver nanowire)

In this chapter, we investigate the transverse spin of SPPs propagating in a quasi-one-dimensional AgNW by analyzing the circular polarisation state of the collected evanescent mode signal through a high numerical aperture objective lens. We show that both experimentally measured and numerically calculated real plane and Fourier plane field distribution corresponding to left and right circularly polarised components of the total field exhibit biasing. Furthermore, our results indicate existence of spin-momentum locking of the evanescent wave.

Chapter 4 (Sub-wavelength channeling of whispering gallery modes into silver nanowire as plasmon polaritons)

In this chapter, we study subwavelength propagation and directionality of WGMs of fluorescent silica microresonator coupled to AgNW. Fourier plane imaging is performed to study the directionality of wavevectors out-coupling from NW ends. Leakage radiation microscopy reveals the mechanism behind the directional emission of WGMs from NW ends. It is found that WGMs of microsphere couple to the NW as propagating modes and out-couples from the NW end. The emission is directional in nature and spans a very narrow range of radial and azimuthal angles making the system a directional hybrid antenna.

Chapter 5 (Mapping 1-D nanocavities using light scattering from molecular monolayers)

In this chapter, We show that mapping of polarisation resolved Dark-field and SERS intensity can be used as a tool to reveal the spatial changes of the nanometre scale inside the nanogap for NWoM nanocavity. We correlate these spatial changes to resultant SERS signal variation inside the elongated nanogap between the AgNW and Au mirror. We are able to track the SERS signal variation at the scale of <3 nm change inside the nanogap for NWoM system. We further show that SERS signal from different positions of nanocavity increases significantly when the gap plasmon mode of NWoM redshifts upto >50 nm inside the nanogap.

Chapter 6 (Non-reversible local structural change for 1-D extended nanogap)

In this chapter, we report fluctuations in SERS intensity from BPT molecules sandwiched inside the NWoM nanocavity. Time traces indicate increasing SERS as a function of time from molecules excited with diffraction limited spot along the nanocavity. Correlating SERS intensity

from Dark-field scattering spectra suggests non-reversible local change in the gap size between AgNW and Au mirror. We show that structural change can be attributed to diffusion of Ag atoms inside the nanocavity, reducing the gap which in turn results in increased near-field strength giving rise to increased SERS intensities. Other possibilities such as melting or reorganisation of polymer coated on AgNW are also discussed.

Chapter 7 (Conclusion and future directions)

Chapter concludes the thesis and provides futures directions related to the light propagation in AgNW and their nanophotonics applications.

Chapter 2

Methodology: Dual channel microscopy, Fourier plane imaging and Spectroscopic measurements

Controlling and studying various parameters of light such as polarisation, phase, amplitude and directionality at the nanoscale is crucial not only for nanophotonic devices [2, 89] but also for fundamental understanding of light-matter interaction [6]. This requires sophisticated optical techniques and modifications to conventional optical microscope which is limited to optical imaging [90, 91]. For studying light-matter interaction, we have to focus onto the excitation (incident laser beam) and collection of the light after the interaction with matter (comparable to wavelength of light). Both excitation and collection would require careful considerations at these length scales. This chapter contains the techniques utilised for efficient excitation and collection of the scattered light for various studies reported in this thesis work.

- We introduce a home-built dual channel optical microscope and understand the capabilities of the microscope simultaneously working as both commercialised inverted and upright microscope. We show that microscope is equipped with two orthogonally aligned objective lens which can both be utilised for excitation of nanostructures and collection of scattered light. Depending on the objective lens used for experimental measurements, microscope can be operated in forward and backward scattering configurations. Optical set-ups for all possible configurations of dual-channel microscope are discussed in this chapter.
- In regards to the collection of light, specifically for studying the directionality of the wave-vectors of the collected light, we employ Fourier plane (FP) imaging techniques [92, 93]. FP provides the in-plane angular distribution of emitted light and thus is also called momentum space imaging. We will discuss the concept of FP imaging and how we experimentally implement the technique to our dual-channel microscope system.
- In addition to FP imaging, we make use of dark-field (DF) scattering spectra to characterise the gap plasmon modes and surface enhanced Raman scattering (SERS) to study the molecular emission from molecules inside the nanocavity. We will discuss the optical set-up used for simultaneous measurement of SERS and DF.

2.1 Dual channel microscope

Commercial microscopes have one objective lens to focus the light onto the sample and collect the scattered light back from the same objective lens. The objective lens can be in upright or inverted position depending on the microscope however, these configurations limits the excitation and collection efficiency. For example, as discussed in the previous chapter leaky modes supported by silver nanowire (AgNW) placed on a glass substrate leaks into the glass while propagating. Upon excitation and collection of plasmon using high numerical aperture lens through air medium (upright configuration), it would only collect light scattered in air (bound mode's optical field). For leaky mode, we have to collect the light leaking into the substrate using oil immersion objective lens. These limitations motivated us to work on a home-built dual channel microscope.

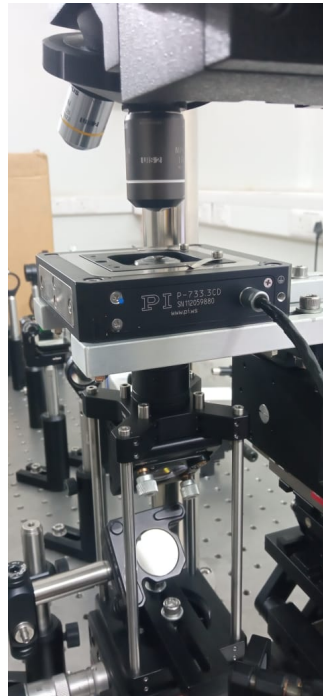


FIGURE 2.1: Picture of the dual-channel microscope with excitation and collection capabilities through both objective lens.

The image of the microscope is shown in Fig. 2.1. Our dual-channel microscope consists of two vertically aligned objective lens and the substrate is placed on a piezo-electric stage. Lower objective lens is placed on linear stages providing fine x , y and z -axis movement to align and adjust the focus, whereas upper objective lens has been mounted on a periscope for only z movement.

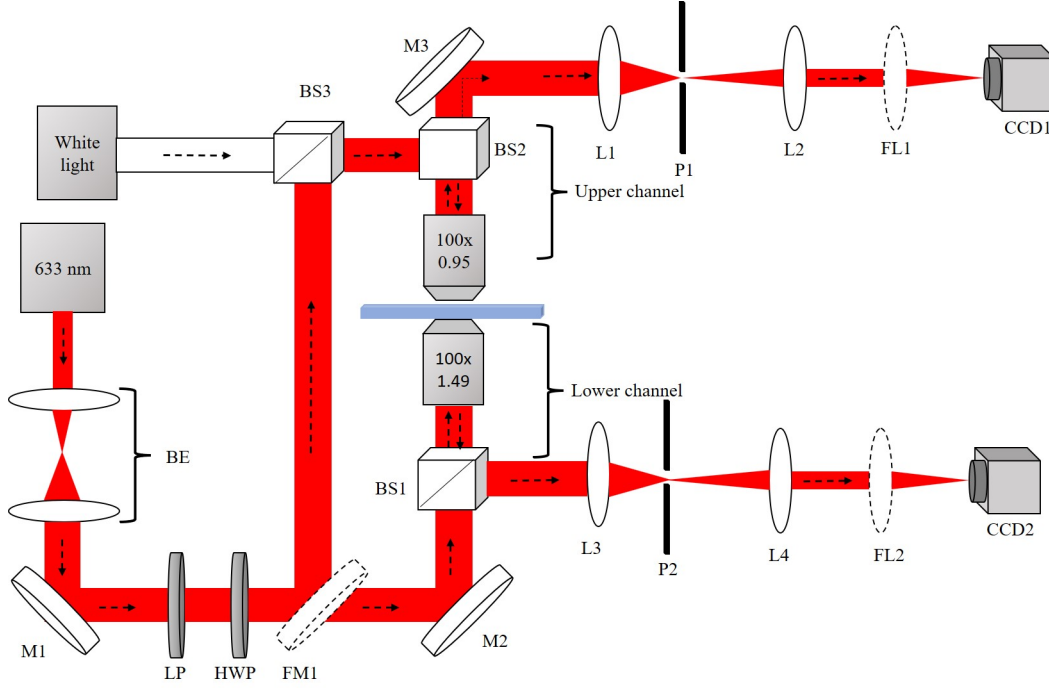


FIGURE 2.2: Optical schematic of dual-channel set-up. Here BE is beam expander, M1-M3 are mirrors, BS1-BS3 are beam splitters, FL1-FL2 are flip mirrors. P1-P2 are pinholes, L1-L4 are lens.

The optical schematic of the dual-channel set-up is shown in Fig. 2.2. As shown in the image above, set-up consists of two objective lenses associated with two channels termed as upper and lower channel. The upper channel consists of objective lens 100x 0.95 mounted (vertically above, air side) and relay optics used for excitation and collection of the back scattered light. Whereas, lower channel uses an oil immersion 100x 1.49 objective lens to excite and collect the scattered light into the substrate (Fig. 2.2).

A laser with wavelength $\lambda = 633$ nm is expanded using a beam-expander (BE) to overfill the back aperture of the excitation objective lens. It is important to note the flip mirror (FM1) in the path of the laser beam after reflection through mirror M1. FM1 projects the beam to upper or lower channel depending on whether it is placed in the optical path or removed. If FM1 is in the path of the beam, laser beam enters upper channel through beam splitter BS2 after getting reflected by BS3. White light has been set to come through upper channel for visualization of the sample using BS3 and BS2. Without FM1, laser beam reflects through M2 and goes to lower channel through BS1. Linear polariser (LP) and half wave plate (HWP) are kept before FM1 for polarisation control of the excitation beam. We can collect the scattered light using any of the lower and upper channel. The collected scattered light from the sample through objective lens in both channels is focussed using tube lens (L3, L1) and bertrand lens (L4, L2) onto the cameras (CCD). We have implemented FP imaging in both channels to quantify scattered light which we will discuss later in this chapter along with the concept of tube and bertrand lens.

Depending on the channels used for excitation and collection, this optical set-up can be used in forward and backward scattering configurations. Next, we discuss both these scattering configurations in details.

2.1.1 Forward scattering configuration

In this configuration, we excite the sample by focusing the light using dry 100x 0.95 objective lens through air side (upper channel). Forward scattered light leaking into the glass substrate is collected by using the oil immersion 100x 1.49 objective lens (lower channel). For this configuration, we do not need to the upper channel for the collection of scattered light, hence collection optics for the upper channel has been removed. The simplified optical schematic of forward scattering configuration with above mentioned considerations is given in Fig. 2.3.

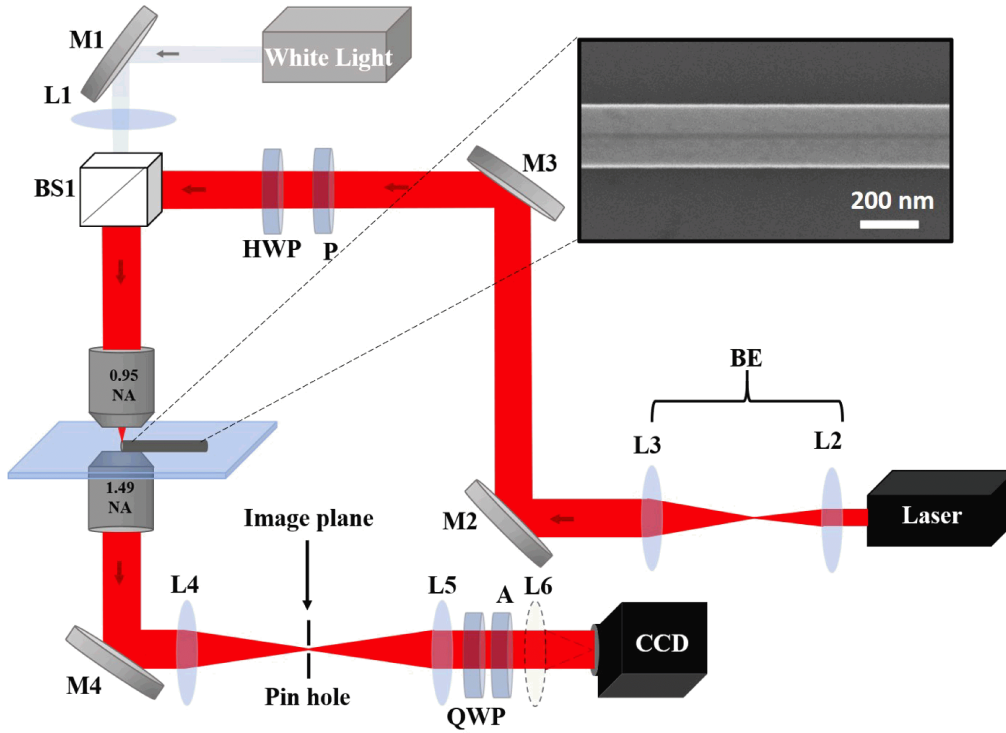


FIGURE 2.3: Simplified optical schematic of dual-channel set-up operated in forward scattering configuration. Half wave plate (HWP) and Polariser (P) are placed in the excitation path to control the polarisation of the excitation beam. Collection optics for the upper channel is removed and is only used for excitation the sample. The scattering light is collected through lower channel using oil-immersion objective lens. Here BE is beam expander, M1-M4 are mirrors, BS1 is beam splitters, L1-L6 are lens. Half wave plate (HWP) and Polariser (P) are placed in the excitation path to control the polarisation of the excitation beam.

2.1.2 Backward scattering configuration

Upon exciting the sample using dry 100x 0.95 objective lens through air side (upper channel) and collecting the backward scattered light using the same objective lens, configuration is called backward scattering configuration. For this configuration, lower channel can be completely removed. Optical schematic of backward scattering configuration is given in Fig. 2.4.

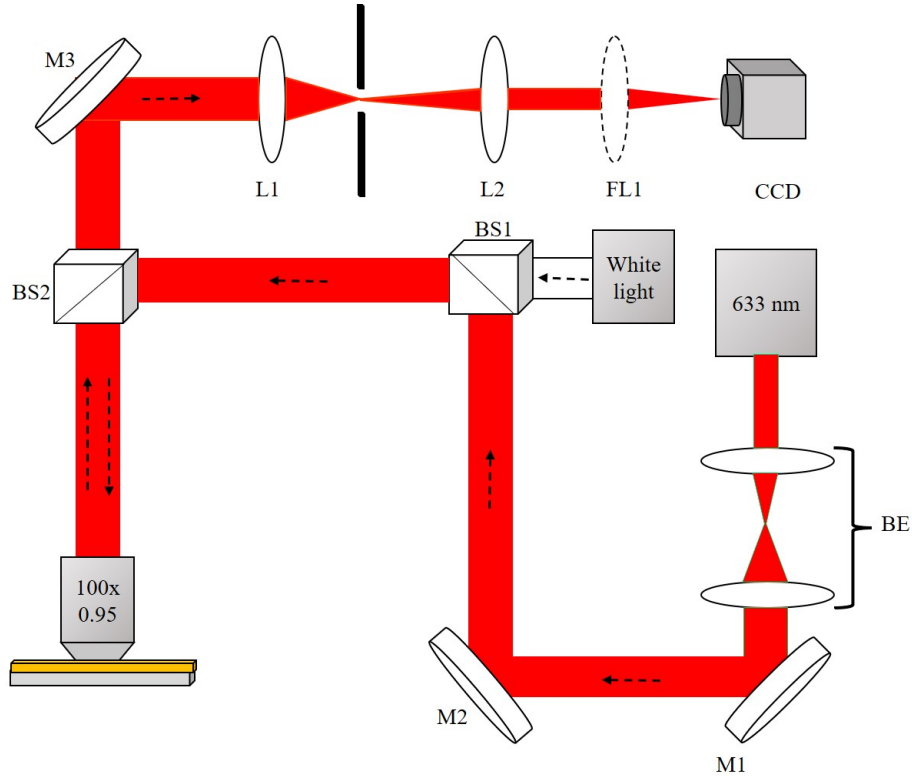


FIGURE 2.4: Simplified optical schematic of dual-channel set-up operated in backward scattering configuration. Here BE is beam expander, M1-M3 are mirrors, BS1- BS2 are beam splitters. L1-L2 are lens, FL1 is a flip lens.

There can also be a different configuration for backward scattering where we excite the sample through lower channel and collect the scattered light using the same objective lens. Given the structure of the microscope in this case upper channel can not be totally removed as the white light illumination for visualisation would still be focused through upper channel. However, in this case, there is no need for the excitation and collection optics for laser beam through the upper channel. The optical set-up corresponding to this configuration is given in Fig. 2.5. As can be seen from the Fig. 2.5, the sample is excited by focussing the laser beam using lower channel through 100x 1.45 objective lens and we collect the scattered light leaking into the substrate using the same lower channel. The collection optics remains the same in the lower channel as discussed in previous configuration.

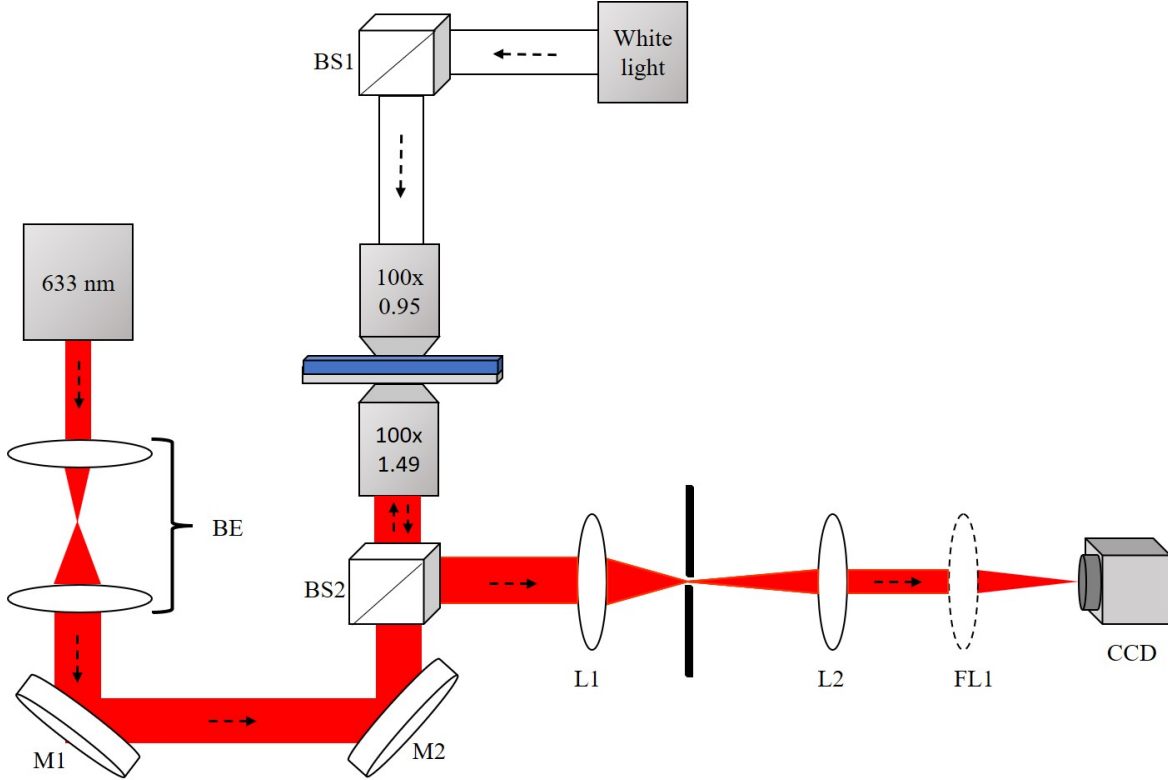


FIGURE 2.5: Simplified optical schematic of dual-channel set-up operated in backward scattering configuration. Here BE is beam expander, M1-M2 are mirrors, BS1- BS2 are beam splitters, L1-L2 are lens and FL1 is a flip lens.

2.2 Fourier plane imaging: Concept and experimental implementation

It is known that when we incident a plane wave onto a thin spherical lens at an angle θ_x , it will get focused to a point $(x = \theta_x f)$ on the focal plane of the lens, where f is the focal length of the lens. Similarly if we have a complex amplitude at a distance $z = d$ from the lens, this would be divided into plane waves. If a Wave is arriving with (θ_x, θ_y) , lens would project them to a focused spot $(x, y) = (\theta_x f, \theta_y f)$ at the focal plane ($z = f$) (Fig. 2.6). The amplitude of the wave at the point (x, y) is proportional to the Fourier transform of the amplitude at $(z = 0)$, which is called Fourier transform property of a lens [94].

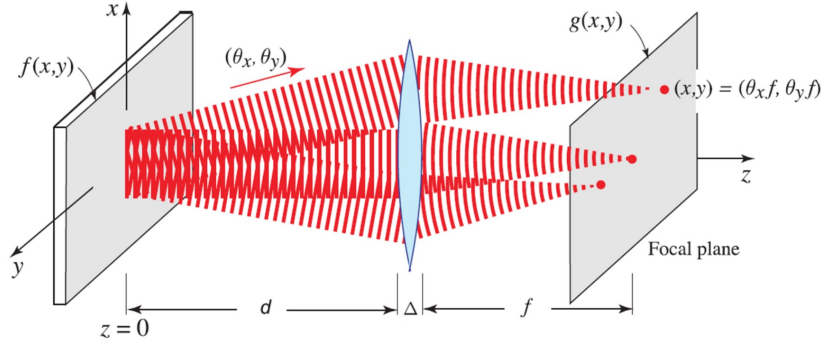


FIGURE 2.6: Plane waves arriving with different angles onto thin spherical lens and getting focused at different point on the FP defined by focal length and incident angle. Figure has been reproduced with permission from [94].

2.2.1 Fourier plane imaging for microscope systems

The ability of guide SPPs in metallic nanostructures makes them ideal candidate for optical antenna in nanophotonics devices, however would require studies on whether or not guided light at subwavelength scale outcouples directionally.

Utilising the Fourier transform property of lens, imaging back focal plane of a lens would provide us information of directionality (angles) of the wavevectors of light emitted from metallic nanostructures [95, 96]. However, for metallic nanostructures the scattered light is collected through objective lens using a microscope system which makes the back focal plane inaccessible for imaging. So we use relay optics to project the focal plane of the objective lens to our CCD. A Tube lens (TL) (spherical lens) is used to Fourier transform the information at back focal plane (angles to spatial co-ordinates) and Bertrand lens (BL) to again Fourier transform (spatial co-ordinates to angles) and project the back focal plane onto CCD. Different experimental configurations using TL and BL used for FP imaging is given in Fig. 2.7 [97].

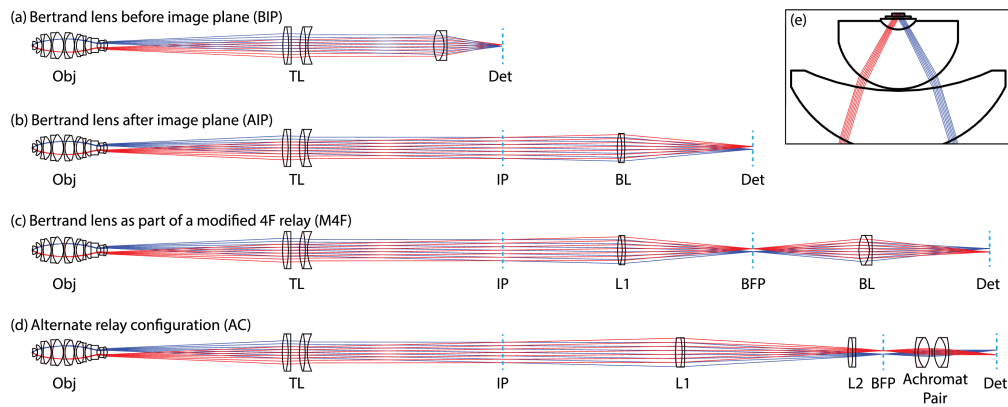


FIGURE 2.7: Different experimental configurations to image back focal plane of the objective lens onto the imaging camera. Figure has been reproduced with permission from [97].

For our forward scattering geometry, optical schematic of the collection path with FP imaging is given in Fig. 2.8. We introduce addition flip lens (FL1) along with TL and BL to image

both back focal plane and real plane image onto the camera. When FL1 is inserted in the optical path, it provides real plane image and removing it from the path gives FP image. The optical path is similar for upper channel in backward scattering configuration.

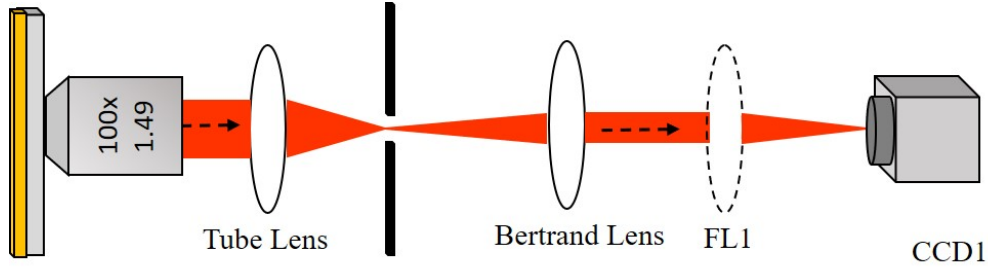


FIGURE 2.8: optical schematic of the collection path with FP imaging.

2.2.2 Fourier plane images for forward and backward scattering

Using the above scheme, we have implemented FP imaging in both lower and upper channel of dual channel microscope. The FP images collected in forward and backward scattering configuration are given in Fig. 2.9(a) and (b) respectively. Boundary of FP image is defined by the numerical aperture of the objective lens used for imaging. Since, the FP provides angular projection of wavevectors, x and y axis of FP image represent k_x/k_0 and k_y/k_0 respectively.

For **forward scattering geometry** inner dotted black circle represents critical angle of glass-air interface ($NA=1.0$) and outer dotted circle defines the boundary at $NA=1.49$ (objective lens's NA used for FP imaging). In this FP image, the unscattered light will be collected upto a circle with boundary at $NA=0.95$ (excitation objective lens) which can be blocked by placing a black disk in the collection path.

For **backward scattering geometry** solid black circle defines the boundary with $NA=0.95$ (objective lens's NA used for FP imaging).

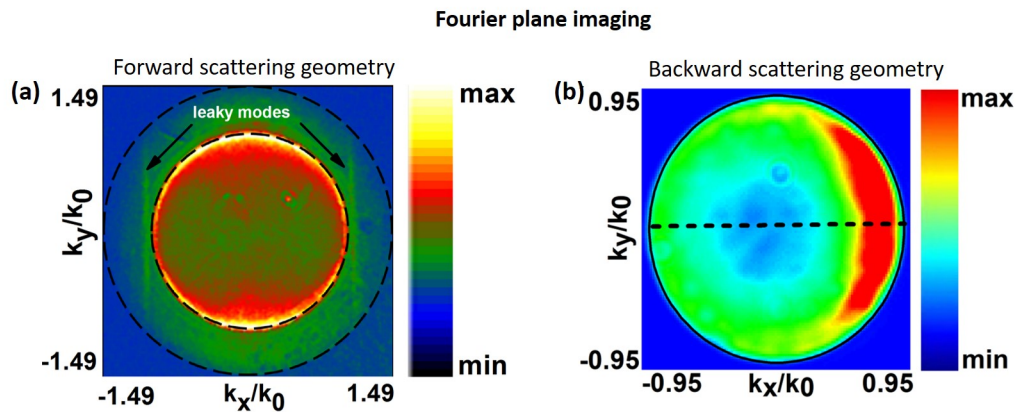


FIGURE 2.9: FP images collected in (a) forward and (b) backward scattering configuration. Fig. (b) has been reproduced with permission from [53].

2.3 Optical set-up for dark-field scattering and SERS

DF imaging has been widely used for imaging metallic nanostructures difficult to image using convention optical objective lens (50-200 nm) [98, 99]. In this imaging method, sample is excited with halogen lamp at very high angles with a broadband light and only scattered light emitted at small angles is collected (Fig. 2.10(a)). Only collecting scattered light provides DF scattering image of the sample. DF scattering image of NW over mirror (NWoM) systems are given in Fig. 2.10(b). Since, background does not scatter any light it appears black whereas scattering NWs are bright.

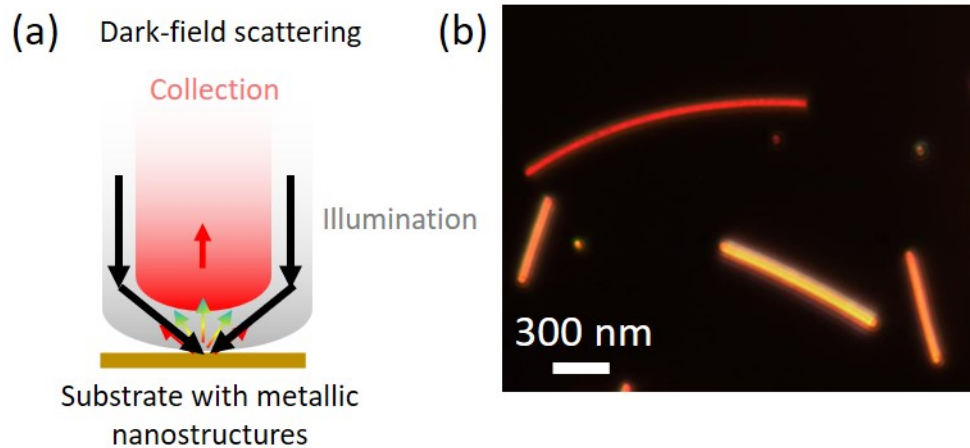


FIGURE 2.10: Schematic of the DF imaging technique with black arrows showing incident light at high angles and red arrows represent collection at small angles. (b) DF scattering image for silver nanowire over mirror system.

2.3.1 Dark-field scattering spectra

DF scattering spectra is obtained by collecting the scattered light and dispersing in wavelengths using a spectrometer [100]. In the case of metallic nanostructures, wavelength resonant with the plasmon modes are scattered more strongly and we observe peaks in DF scattering spectra [101]. Thus, DF scattering is very important for studying the plasmon modes of metallic nanostructures.

Optical schematic for DF imaging and scattering is shown in Fig. 2.11(a). The sample is kept on a computer controlled motorised stage in Olympus BX51 microscope. DF objective lens is used to excite a particular geometry using a halogen lamp and scattered light is collected using the same objective lens. Scattered light is split into a fibre coupled (Ocean Optics QEPRO) spectrometer and camera for DF spectroscopy and imaging. A typical scattering spectra is shown in Fig. 2.11(b) for NWoM geometry where y and x axis show scattering intensity (in %) and wavelength (in nm) respectively. DF spectra are background subtracted and referenced by collecting the reference for a broadband white light scatterer to account for instrument's wavelength response. Two plasmon modes in DF scattering spectra supported by the NWoM geometry are clearly visible.

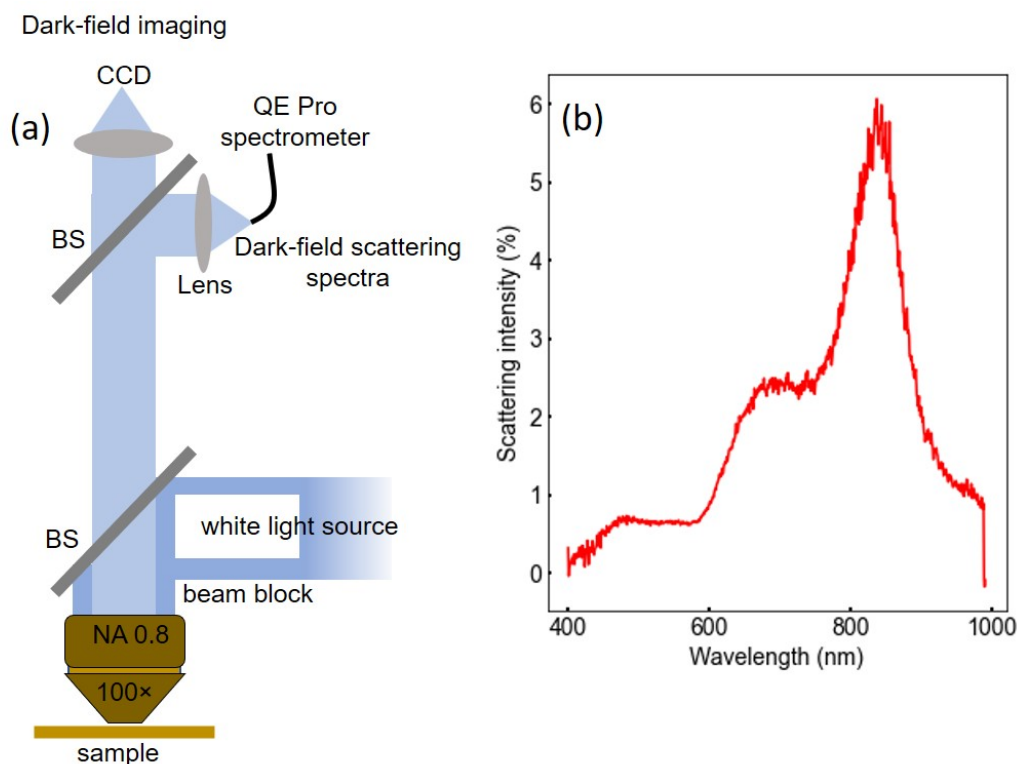


FIGURE 2.11: (a) Optical set-up for measuring DF scattering images and spectra (b) DF scattering spectra for silver NWoM system.

2.3.2 Optical set-up for SERS and DF

We study SERS from the molecules sandwiched inside the nanocavity between AgNW and mirror for NWoM geometry. For a better understanding, We correlate DF scattering and SERS intensities along the extended gap. The complete optical-set used for the experiments is shown in Fig. 2.12. Set-up for DF scattering spectra measurement is unchanged and similar to discussed above. We introduce a 632.8 nm laser for SERS measurements. We excite a particular location on the NW with a diffraction limited spot using 632.8 nm wavelength (diode matchbox laser) after passing through a laser line filter. We use a half -wave plate in the excitation path to control the polarisation state of the incident light. The collected back-scattered light is focussed on the 300 lines/mm grating of Andor Shamrock i303 spectrograph using a tube lens. Elastically scattered light is rejected using two notch filters. For the polarisation resolved measurements an analyser was kept in both DF and SERS path just before the spectrometers.

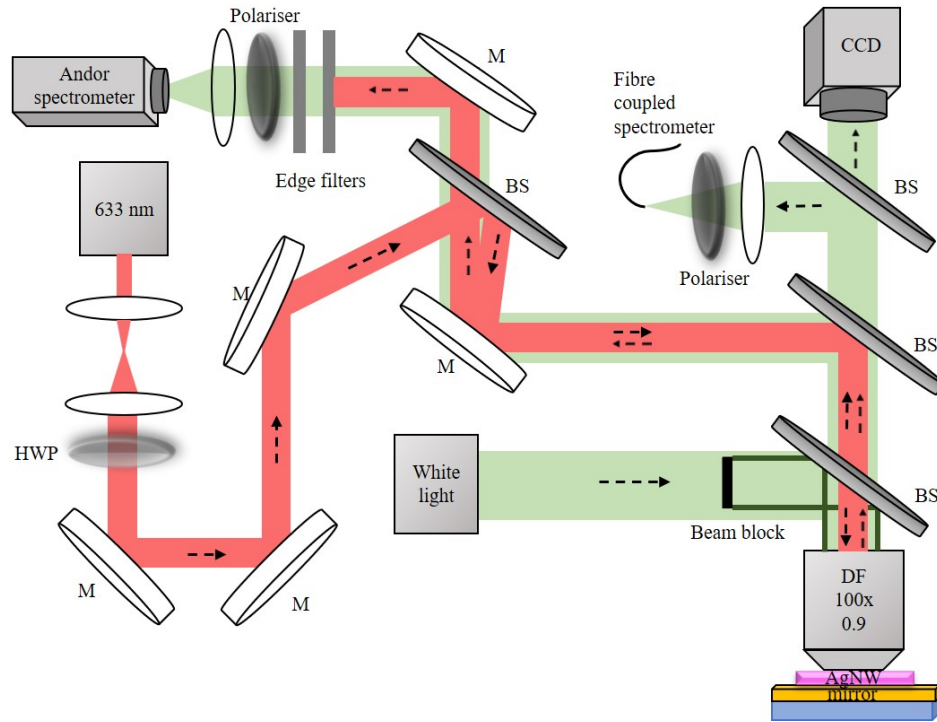


FIGURE 2.12: (a) Optical set-up for measuring DF scattering spectra and SERS. Here, M is mirror, BS is beam splitter, HWP is half wave plate.

2.4 Conclusion

In conclusion, this chapter provides an overview of the dual-channel microscope system and various scattering configurations used for probing metallic nanostructures. We show that microscope can be utilized in mainly forward and backward scattering configurations. Optical set-up for both configurations are discussed in details. We employ FP imaging for investigating the directionality of the scattered light from nanostructures. Starting from the Fourier transform property of a lens, various configuration to implement the FP imaging in microscopic systems are discussed. Specific to our measurements, FP images for forward and backward scattering configurations are presented. In addition to FP imaging, spectroscopic measurements such as DF imaging/spectra and SERS are used in this thesis work. We discuss optical set-up used for DF imaging and show scattering spectra revealing the plasmon modes for the metallic nanostructures. Lastly, optical set-up used for simultaneous measurements of DF spectra and SERS is presented.

Chapter 3

Transverse spin and associated spin-momentum locking of plasmon polaritons in a single crystalline silver nanowire

In this chapter, I discuss experimental observation of a spin density component (transverse spin) which is perpendicular to the direction of propagation and independent of the polarisation for surface plasmon polaritons (SPPs) propagating in silver nanowire (AgNW). The chapter is an adaptation of the research article "Appl. Phys. Lett. 119, 161108 (2021)".

3.1 Introduction

Angular momentum (AM) is one of the important parameters to characterize any optical electromagnetic field [102–104]. The AM can be further decomposed into two parts, spin angular momentum (SAM) [104], related to the circular polarisation of the field and orbital angular momentum (OAM), determined by the helical wave front of the field [103, 105, 106]. In paraxial beams SAM is aligned parallel to the wave-vector, [107] whereas for non-paraxial optical fields such as strongly focused beams or evanescent waves, SAM can have both longitudinal and transverse components with respect to the wave-vector [108–110]. The field components spinning in the longitudinal plane lead to generation of transverse SAM, whereas the longitudinal SAM stems from field components spinning in the transverse plane [111]. In recent years, transverse SAM has been investigated in context of spin-orbit interactions (SOIs) in strongly focused beams and in evanescent waves [112–118]. Specifically, for evanescent waves the helicity of the SAM component gets dictated by the decay as well as the propagation direction leading to "spin momentum locking", similar to the electronic counterpart quantum spin-Hall effect [119–122]. Different configurations have been studied in this regard such as, surface electromagnetic waves generated due to total internal reflection at an interface [123–125], optical fibers [126], dielectric wave guides [121, 127, 128], and structured guided modes [129]. The studies reveal potential utilization of SAM in various photonic applications such as spin-directional coupling

[113, 130–132], optical nano-probing [133–135], optical tweezers [136], and longitudinal field detection [137].

As discussed previously, evanescent SPPs propagating in AgNW are of special interest due to their various emergent properties and applications in nanophotonics [28, 138]. For all the applications, transverse spin can play an important role in modifying the phenomena and add to a more complete description of the resultant effects such as directional coupling [139, 140], spin-Hall effect [118, 141].

Motivated by this, herein we study transverse spin of SPP field excited in a quasi-one-dimensional AgNW placed on a glass substrate (Fig. 3.1). The experimental measurement of the transverse spin component along z axis (s_z) relies on polarisation analysis of the directly measured NW SPP mode signal excited through a tightly focused linearly polarized Gaussian beam, in both real plane and Fourier plane (FP). Although the directly measured SPP signal do not exhibit any biased intensity distribution with respect to the NW long axis (x axis), the analyzed signal exhibits opposite bias for left circularly polarized (LCP) component with respect to the right circularly polarized (RCP) component, revealing the spin-momentum locking of SPPs. Finally, the difference between the LCP and RCP analyzed intensity distribution in both real and FP quantifies the transverse spin density distribution. The experimental observation of transverse spin of SPPs and the resultant spin-momentum locking are also corroborated with numerical calculations.

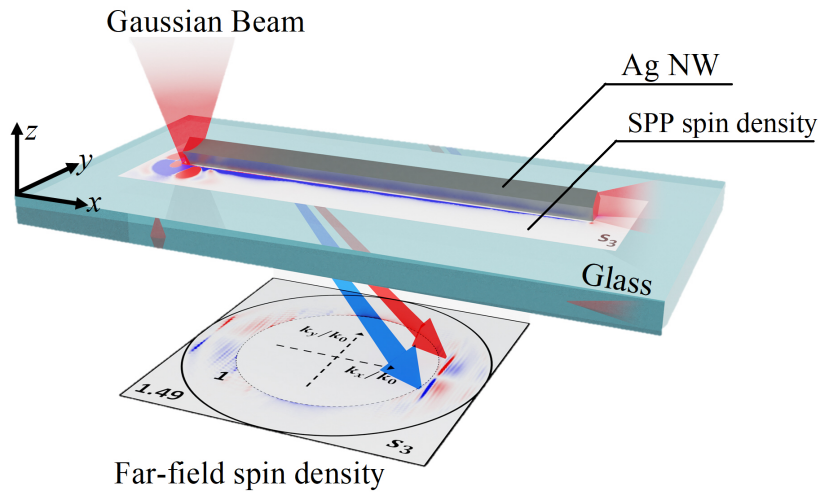


FIGURE 3.1: Schematic of the measurement of the transverse spin of SPPs, excited through focused Gaussian beam in an AgNW placed on a glass substrate.

3.2 Silver nanowire: Ideal for transverse spin measurements of surface electromagnetic waves

Unlike SPPs excited on a planar metal-dielectric interface (x - z), SPPs excited in an AgNW propagating along x axis can simultaneously decay along two longitudinal planes (x - y and x - z

planes), leading to corresponding transverse spin density components (s_z and s_y) (see Fig. 3.2) [123].

The wave-vector corresponding to a propagating wave along any direction can only have real components, whereas for evanescent wave(s) it must also possess imaginary component(s) orthogonal to the propagation direction. For example, evanescent SPP wave propagating at metal film placed on a dielectric interface (x - z plane) can have imaginary wave-vector component in the $z > 0$ direction leading to decay along z axis. On the other hand, evanescent SPP waves propagating along x axis on a quasi-one-dimensional metallic nano-structure can decay along both z (x - z plane) and y (x - y plane) axis. It is well known that transverse spin density (s_y) exists for an evanescent wave which is decaying along z axis [108], however it is not possible to study (s_y) using far-field imaging and require very complex near-field imaging techniques. AgNW provides the test-bed for experimentally studying transverse spin of evanescent wave because of the existence of s_z which can be studied experimentally in far-field for SPPs propagating along x axis and decaying along the $y > 0$ direction.

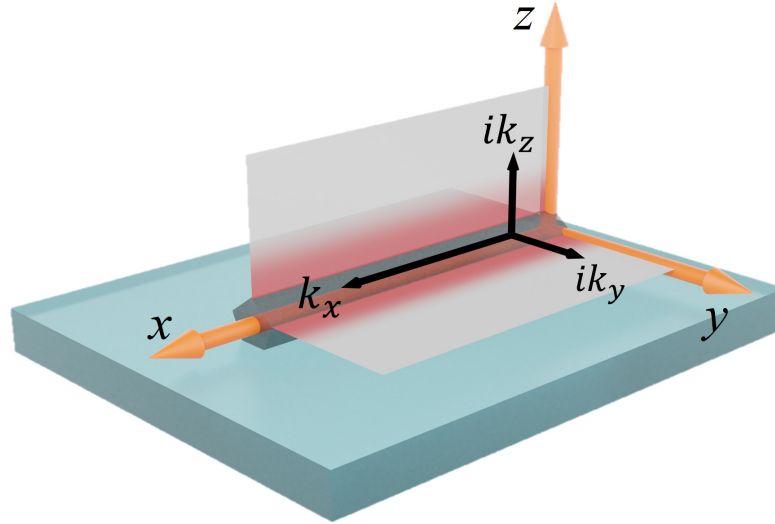


FIGURE 3.2: Schematic of evanescent field of the SPPs propagating in an AgNW along x axis with complex wave-vector $\mathbf{k} = k_x\hat{\mathbf{x}} + ik_y\hat{\mathbf{y}} + ik_z\hat{\mathbf{z}}$ decaying along both x - y ($y > 0$ half space) and x - z planes ($z > 0$ half space).

3.3 Field calculation for the SPPs propagating along silver nanowire

Consider an electromagnetic wave propagating along x axis with wave-vector $(k,0,0)$. The complex electric and magnetic field components can be written as

$$\mathbf{E}(\mathbf{r}) = \frac{E_0\sqrt{\mu}}{\sqrt{1+|\alpha|^2}} \begin{pmatrix} 0 \\ 1 \\ \alpha \end{pmatrix} e^{ikx} \quad (3.1)$$

$$\mathbf{H}(\mathbf{r}) = \frac{E_0\sqrt{\epsilon}}{\sqrt{1+|\alpha|^2}} \begin{pmatrix} 0 \\ -\alpha \\ 1 \end{pmatrix} e^{ikx} \quad (3.2)$$

Here, E_0 denotes the amplitude of the wave in the medium with permittivity ϵ and permeability μ . α determines the polarisation state of the wave. The polarisation state can be classified into three parameters, defined as: $\tau = \frac{1-|\alpha|^2}{1+|\alpha|^2}$, $\eta = \frac{2\text{Re}\alpha}{\sqrt{1+|\alpha|^2}}$ and $\sigma = \frac{2\text{Im}\alpha}{1+|\alpha|^2}$. We have omitted the factor $e^{i\omega t}$ for our analysis.

An evanescent wave propagating along x axis and decaying along $y > 0$ direction (along x - y plane) can be obtained by rotational transformation of optical fields (Eq. 3.1, 3.2) by an angle $i\phi$ about z axis. The transformation matrix for such rotation is given as:

$$\hat{\mathbf{R}}(i\phi) = \begin{pmatrix} \cosh \phi & -i \sinh \phi & 0 \\ i \sinh \phi & \cosh \phi & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (3.3)$$

The transformation matrix is applied to both vector and scalar components of the fields: $\mathbf{E}(\mathbf{r}) \rightarrow \hat{\mathbf{R}}(i\phi)\mathbf{E}[\hat{\mathbf{R}}(-i\phi)\mathbf{r}]$ and $\mathbf{H}(\mathbf{r}) \rightarrow \hat{\mathbf{R}}(i\phi)\mathbf{H}[\hat{\mathbf{R}}(-i\phi)\mathbf{r}]$. The electric and magnetic field components for evanescent waves result as following:

$$\mathbf{E}(\mathbf{r}) = \frac{E_0\sqrt{\mu}}{\sqrt{1+|\alpha|^2}} (-ik_y/k \hat{\mathbf{x}} + k_x/k \hat{\mathbf{y}} + \alpha \hat{\mathbf{z}}) e^{ik_x x - k_y y} \quad (3.4)$$

$$\mathbf{H}(\mathbf{r}) = \frac{E_0\sqrt{\epsilon}}{\sqrt{1+|\alpha|^2}} (-i\alpha k_y/k \hat{\mathbf{x}} - \alpha k_x/k \hat{\mathbf{y}} + \hat{\mathbf{z}}) e^{ik_x x - k_y y} \quad (3.5)$$

Here, $k_x = k \cosh \phi$ and $k_y = k \sinh \phi$ are the wave-vectors along x and y axis respectively. The spin density components corresponding to electric and magnetic field components given by Eq. (3.4) and (3.5) can be calculated as: $\mathbf{s} = \Psi^\dagger \hat{\mathbf{S}} \Psi$, where $\mathbf{S}$, the Pauli spin matrices, are given by:

$$\hat{\mathbf{S}}_{\mathbf{x}} = (-i) \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{pmatrix}, \hat{\mathbf{S}}_{\mathbf{y}} = (-i) \begin{pmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \hat{\mathbf{S}}_{\mathbf{z}} = (-i) \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (3.6)$$

Spin components associated with electric ($\mathbf{s}_e$) and magnetic ($\mathbf{s}_m$) field are given by:

$$\mathbf{s}_e = A(\sigma \frac{k_x}{k} \hat{\mathbf{x}} - \eta \frac{k_y}{k} \hat{\mathbf{y}} + (1 + \tau) \frac{k_x k_y}{k^2} \hat{\mathbf{z}}) \quad (3.7)$$

$$\mathbf{s}_m = A(\sigma \frac{k_x}{k} \hat{\mathbf{x}} + \eta \frac{k_y}{k} \hat{\mathbf{y}} + (1 - \tau) \frac{k_x k_y}{k^2} \hat{\mathbf{z}}) \quad (3.8)$$

here, A is a constant. Thus, the expression for total spin density $\mathbf{s} = \mathbf{s}_e + \mathbf{s}_m$ will be:

$$\mathbf{s} \propto 2\sigma \frac{k_x}{k} \hat{\mathbf{x}} + 2\frac{k_x k_y}{k^2} \hat{\mathbf{z}} \quad (3.9)$$

The expression (Eq. (3.9)) suggests that, for an evanescent wave propagating along x and decaying along $y > 0$ direction, the spin component parallel to the propagation direction (s_x) is dependent on the helicity (σ), while the transverse spin along z direction, s_z , depends on both propagation (k_x) and decay wave-vector (k_y) components of the evanescent wave. The expression suggests that, for a given $k_x > 0$ direction, the spin of the evanescent wave decaying in the direction of $k_y > 0$ has opposite handedness with respect to that of $k_y < 0$, resulting in spin-momentum locking of SPP evanescent fields. It must be noted that the transverse spin of the SPPs can be quantified in the far-field through measurement of the third Stokes parameter (s_3) since $s_3 \propto s_z$. The formulation closely follows the work by K. Bliokh et al.[108].

3.4 Experimental implementation of the concept: For Leaky mode of silver nanowire

Chemically synthesized AgNWs having pentagonal cross-section with average diameter 350 nm and length $\sim 30 \mu\text{m}$ are dropcasted on to a glass substrate (refractive index = 1.518). SPPs in the AgNW is generated by illuminating one end of the NW with a focused linearly polarized Gaussian beam with 100×0.95 NA objective lens at wavelength $\lambda = 633$ nm. High NA excitation of the NW end with polarisation along the long axis (x axis) of the NW ensures satisfying of the SPP momentum matching conditions and hence easier generation of the NW SPP modes. Elastic scattered light is collected using a 100×1.49 NA objective lens in forward scattering configuration. The real plane and FP intensity distribution of collected light is projected on to a CCD using relay optics and the polarisation is analysed by placing a combination of quarter wave-plate and an analyser in the detection path (Optical set-up given in Fig. 2.3).

At the excitation wavelength, AgNW used for experiment supports one bound and two leaky mode. As discussed in chapter 1, evanescent NF due of leaky SPP modes are confined around the upper vertices of the NW and have refractive index smaller than the glass substrate, allowing for their conversion into propagating waves at the air-glass interface. Fig. 3.3(a) shows optical bright field image of AgNW placed on a glass substrate. Upon excitation at one end, bound and leaky mode propagating along the length can be visualised using far-field real plane imaging (Fig. 3.3(b) and (c)). As can be seen that bound mode (Fig. 3.3(b)) does not radiate during propagation and only converts to photons at the other end due to scattering whereas leaky mode can be seen radiating photons during propagation (Fig. 3.3(c)) along the length of NW.

Thus, the far-field polarisation analysis of the leaky SPP modes allows the investigation of the properties of the evanescent field. Therefore, for experimentally measuring s_z for evanescent SPP waves, we will only focus on leaky modes supported by probed AgNW.

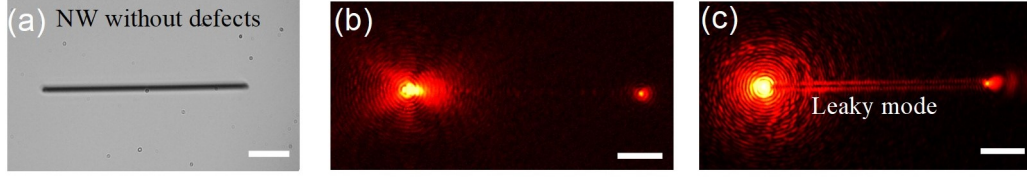


FIGURE 3.3: (a) Optical bright field image of an AgNW without any defects on the surface. (b) and (c) Real-plane intensity distribution of excited bound plasmon mode (BPM) and leaky plasmon mode (LPM) of the AgNW by illuminating the one end of the NW with laser wavelength 633 nm polarised along the length of AgNW.

3.4.1 Mode analysis of the experimentally excited leaky mode

We start with experimental measurement of real plane intensity distribution (I) of a leaky SPP mode excited in an AgNW as shown in Fig. 3.4(a). The characteristic leaky SPP mode signature can be identified as two luminous lines in $y > 0$ and $y < 0$ region along x axis (NW long axis, excitation point being the origin). The intensity distribution of the SPP mode exhibits symmetric distribution about x axis. The corresponding FP intensity distribution is shown in Fig. 3.4(b). The symmetric bright line along k_y/k_0 axis at a positive value of k_x/k_0 in the super-critical region ($NA > 1$) represents the characteristic wave-vector property of the leaky SPP mode [25].

Excited leaky SPP mode property ($k = k_r + ik_i$) can be quantified by analyzing the Fig. 3.4(b). k_r represents the real part of the mode refractive index which can be directly measured by taking the intensity cross-cut along k_x/k_0 axis at $k_y/k_0 = 0$. It can be seen that intensity is maximum at $k_x/k_0 = 1.11$ (k_r) (Fig. 3.4(d)). The intensity distribution of the bright line along k_y/k_0 axis at a fixed positive value of $k_x/k_0 = 1.11$ indicates the confinement and decay of the mode along y axis and propagation along x axis in the real plane. White solid circle in FP represents the collection limit of the objective lens whereas the inner white circle indicates the region upto $NA=1$. The black disk at the center of FP blocks the unscattered wave-vectors lying within inner white circle. It must be noted that the electric fields of the SPP mode also undergo exponential decay along x axis due to propagation losses, dictated by the imaginary part of mode refractive index. k_i can also be calculated by finding out the propagation length ($L = \frac{\lambda}{4\pi k_i}$) of the SPP mode, obtained by investigating the intensity profile (I) of the leaky SPP mode in real plane along x axis. Fig. 3.4(c) shows the corresponding plot of $\ln(I)$ as a function of distance from the excitation point along x axis for the two luminous lines in Fig.3.4(a). The intensity distribution is fitted with a linear equation (solid purple line) $\ln(I) = (-\frac{1}{L})x + 2\ln(A)$, where L represents the propagation length and A is a fitting parameter. The value of the propagation length (L) from the fitting equation is found to be $L \approx 12\mu\text{m}$.

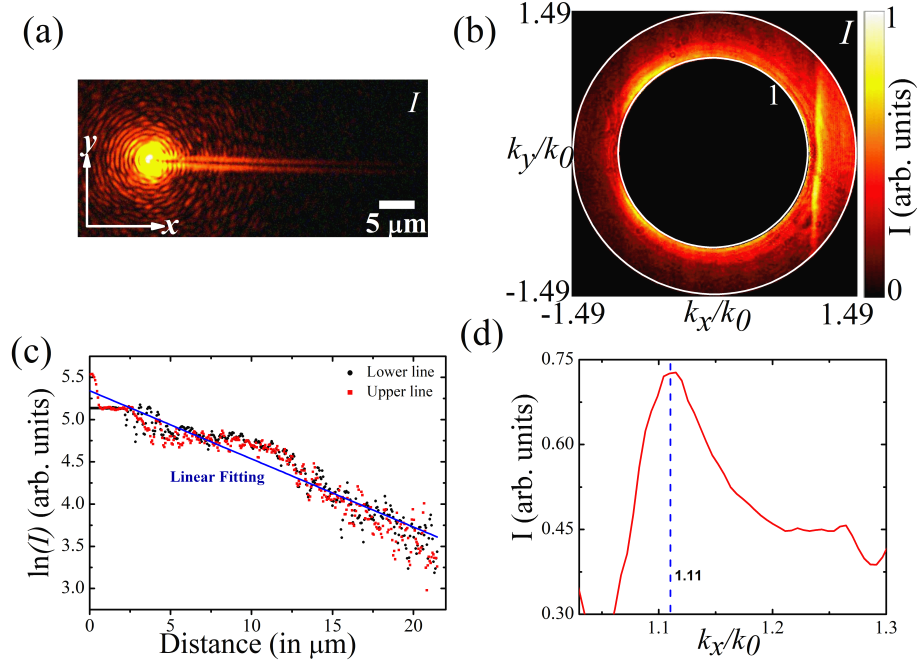


FIGURE 3.4: (a) Real plane intensity distribution of leaky SPP mode excited in an AgNW at $\lambda = 633$ nm. Corresponding FP intensity distribution of the mode is shown in (b). (c) Variation of natural logarithm of the Intensity distribution with the distance along the length of NW for upper (red points) and lower (blue points) luminous lines of the mode shown in (a). Solid purple line indicate the linear fit for the intensity distribution. (d) Intensity profile at $k_y/k_0 = 0$ and along k_x/k_0 axis of the FP image shown in (b).

3.4.2 Transverse Spin density measurement of excited leaky mode

We now investigate the LCP (I_+) and RCP (I_-) components of the NW SPP mode and compare the corresponding real plane and FP intensity distribution with that of the total intensity (I). In contrast to the symmetric intensity distribution shown in Fig. 3.5(a) (micrograph of the NW shown in inset of Fig. 3.5(a)), the real plane I_+ and I_- components of SPP mode as shown in Fig. 3.5(c) exhibit bias along $y > 0$ and $y < 0$ luminous lines respectively, as shown by the dashed white arrows. Correspondingly, the characteristic SPP mode line in FP intensity distribution of I_+ and I_- components shown in Fig. 3.5(d) have bias along $k_y/k_0 > 0$ and $k_y/k_0 < 0$ respectively, shown by the solid white arrows. The differential distribution of I_+ and I_- components both in real plane and FP indicates the existence of partial circular polarisation of the SPP field. Thus, the magnitude of the transverse spin (s_3) in the real plane and consequently in the FP can be calculated by obtaining $s_3 \propto I_+ - I_-$. The real plane distribution of s_3 of the SPP mode obtained from the experimental data is shown in Fig. 3.5(e). The corresponding FP distribution is given by Fig. 3.5(f). The experimentally measured intensity values are normalized with respect to the maximum of I .

The existence of s_3 of the leaky SPP mode of the AgNW can be well understood from Eq. 3.9. The handedness of the spin as well as its emission direction gets dictated by the propagation (k_x/k_0) and the decay wave-vector (k_y/k_0). For the SPP mode under study, the propagation

direction ($k_x/k_0 > 0$ direction) is fixed along the long axis of the NW (x axis). However, the decay wave-vector component (k_y/k_0) changes its sign for upper luminous line ($k_y/k_0 > 0$ for $y > 0$) with respect to that of lower luminous line ($k_y/k_0 < 0$ for $y < 0$). This results in $s_3 > 0$ for upper luminous line and $s_3 < 0$ for lower luminous line, i.e., opposite handedness of the transverse spin of the evanescent SPP mode decaying along opposite direction for a fixed propagation direction. The explicit dependence of the transverse spin handedness of the SPP mode excited in the AgNW on the wave-vector components indicates experimental observation of spin-momentum locking of the evanescent waves.

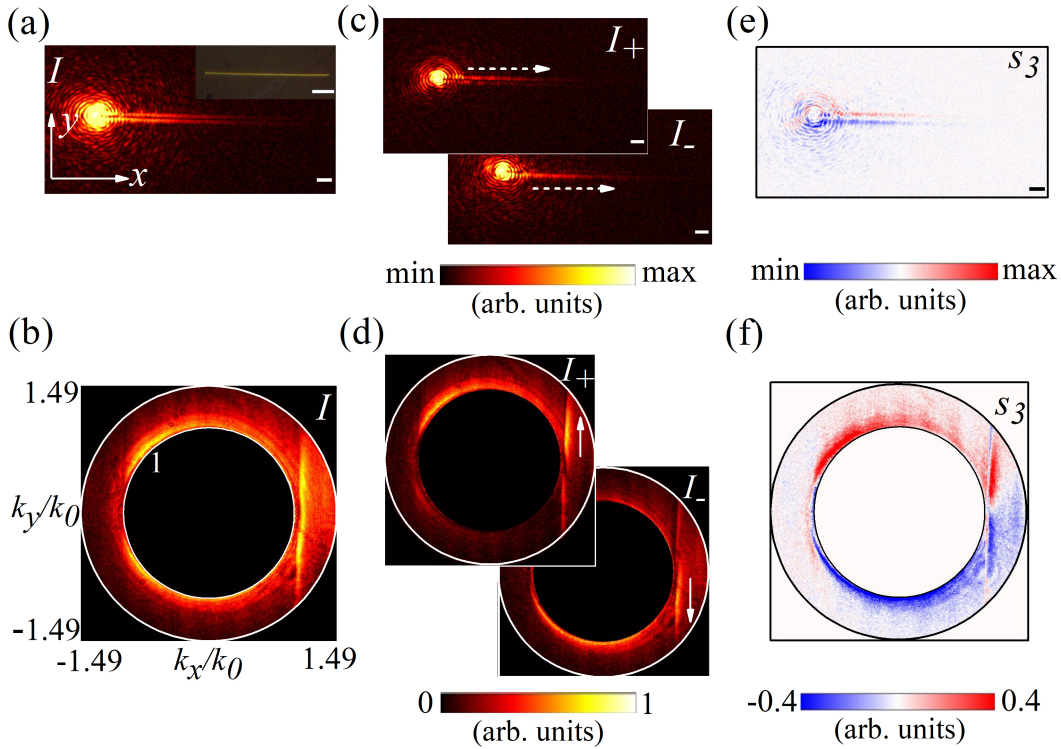


FIGURE 3.5: (a) Experimentally measured real plane and the corresponding (b) Fourier plane (FP) intensity distribution of total field (I) of the SPP mode excited in the AgNW shown in the inset of (a). Inner and outer white circle in (b) represents collection limit of the objective lens and the region upto NA=1. A black disk at the center of (b) blocks the unscattered incident field within the inner white circle. Real plane intensity distribution corresponding to LCP (I_+) and RCP (I_-) analyzed components of the total intensity (I) is shown in (c). White dashed arrows indicate the bias of intensity distribution of the SPP mode. (d) The corresponding FP intensity distribution of I_+ and I_- components, where the white arrows indicate the bias of the SPP mode line. (e) The real plane and (f) FP transverse spin density of the SPP field. The scale bar is 5 μm .

3.4.3 Numerical calculations for transverse spin density measurement of excited leaky mode

The experimental results have been corroborated with full wave three-dimensional finite element method (FEM) calculations (COMSOL). AgNW is mimicked by a geometry having pentagonal

cross-section of diameter 350 nm and length 14 μm elongated along x axis, with its refractive index being set to that of Ag at 633 nm wavelength. It is placed parallel to x - y plane on a cuboid geometry mimicking a glass substrate with refractive index 1.518. Similar to the experimental configuration for excitation of SPPs, one end of the NW is illuminated with Gaussian beam at 633 nm wavelength with polarisation along x axis and the scattered field is calculated. The calculated NF electric field profiles were projected to the far-field by employing reciprocity arguments [142], since the plasmonic nano-structure interacts more strongly with the electric field of the incident electromagnetic field.

Numerically calculated intensity distribution corresponding to total field (I) due to leaky SPP mode in the longitudinal plane (x - y plane at $z = 196$ nm) is shown in Fig. 3.6(a). The plane intersects the upper vertices of the NW, as indicated by the dashed white line in the inset. The inset shows the field distribution in the transverse plane (y - z plane). The intensity distribution indicates symmetric distribution of the generated SPP field about x axis, similar to that shown in Fig. 3.5(a). Correspondingly, the SPP mode line in the FP intensity distribution shown in Fig. 3.6(b) exhibits symmetric intensity distribution along k_y/k_0 at a fixed k_x/k_0 value. For better comparison with the experimental results, the incident field wave-vectors upto NA=1 has been rejected in FP intensity distribution by inserting a back disk with diameter of NA=1. Along with the SPP mode line, a bright arc near the boundary of NA=1.49 and fringe pattern are also visible in the FP intensity distribution. These well studied signatures in FP distribution can be attributed to the excited bound mode of AgNW. The bright arc can be understood as the truncated Fourier transform of an excited bound mode due to the finite length of the AgNW, whereas fringe pattern represents Gibbs oscillations which originates when the length of the AgNW is comparable or shorter than the propagation length of the SPP mode [36, 143]. For the current study, the main region of interest lies in the modal signature of the Leaky SPP mode.

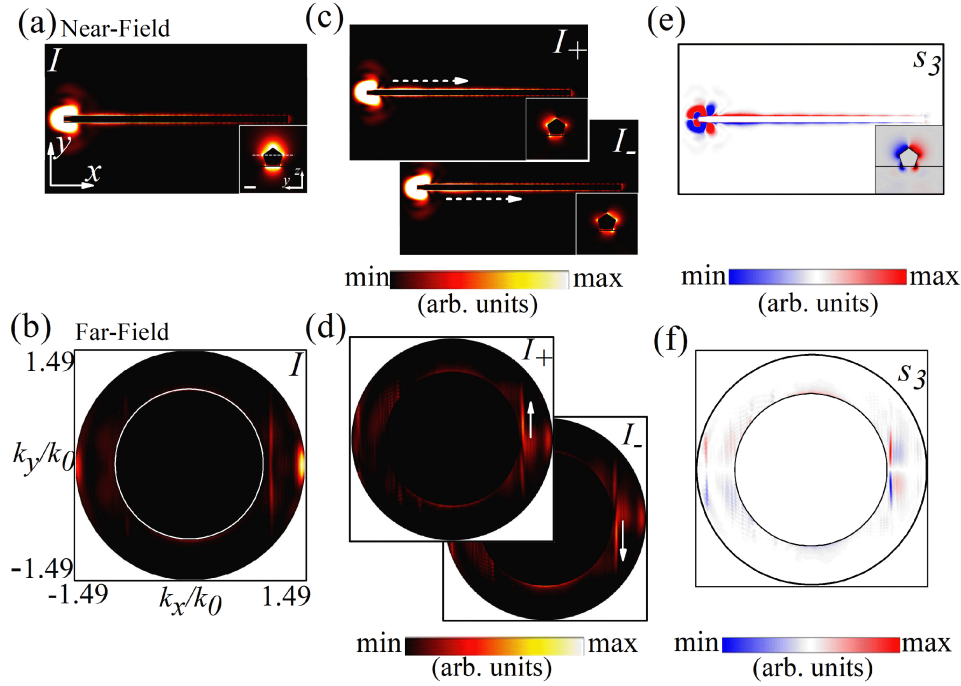


FIGURE 3.6: (a) Numerically calculated intensity distribution of the SPP mode in the real plane (x - y plane at $z = 196$ nm, as indicated by white dashed line in the inset) is shown in (a) and corresponding near-field of the SPP at y - z plane is given in the inset. (b) The corresponding FP intensity distribution. (c) Real plane intensity distribution of the SPP mode corresponding to I_+ and I_- components and corresponding y - z plane near-field distribution shown in the insets. White dashed arrows indicate the bias of intensity distribution of the SPP mode. (d) FP intensity distribution of I_+ and I_- components where the white arrows indicate the bias of the SPP mode line. (e) The real plane and (f) FP transverse spin density of the SPPs field. The transverse spin distribution in the y - z plane is shown in inset of (e).

Numerically calculated intensity distribution in the x - y plane corresponding to I_+ and I_- components of the total field (I) is shown in Fig. 3.6(c). As in the experimentally measured case (Fig. 3.5(c)), the SPP mode intensity distribution of I_+ and I_- exhibit bias along $y > 0$ and $y < 0$ luminous lines respectively, indicated by the dashed white arrows. The intensity distribution for the SPP field at the NW edges in the y - z plane for I_+ and I_- components shown in the insets exhibit equivalent bias. Correspondingly, the SPP mode line in the normalised FP intensity distributions of I_+ and I_- components exhibit bias along $k_y/k_0 > 0$ and $k_y/k_0 < 0$ respectively, as shown by the solid white arrows in Fig. 3.6(d). The opposite bias in the intensity distribution corresponding to I_+ and I_- components both in x - y plane and FP intensity distribution indicates presence of spin, which is further quantified by $s_3 \propto I_+ - I_-$. Fig. 3.6(e) represents the x - y plane s_3 distribution (y - z plane shown in the inset) and the corresponding normalised FP intensity distribution is given in Fig. 3.6(f). The numerically calculated intensity distributions corroborate our experimental observation of spin-momentum locking. The insets of the Fig. 3.6(e) also show the existence of transverse spin in the bound mode of the AgNW.

Since, this phenomenon stems from the evanescent nature of SPP fields, both bound and leaky SPP modes supported by AgNW exhibits spin-momentum locking.

To further confirm spin-momentum locking, we numerically calculate the intensity distributions of SPP mode when the propagation direction is reversed ($k_x/k_y < 0$) by changing the excitation end of the NW (Fig. 3.7). Since the handedness of the transverse spin of the SPP mode is dictated by the wave-vector direction, reversing the SPP propagation direction ($k_x/k_0 < 0$) results in the inversion of intensity distribution corresponding to I_+ and I_- components with respect to that of $k_x/k_0 > 0$ case. Consequently, the handedness of the transverse spin of the SPPs decaying along $k_y/k_0 > 0$ (for $y > 0$ luminous line) and $k_y/k_0 < 0$ (for $y < 0$ luminous line) reverses.

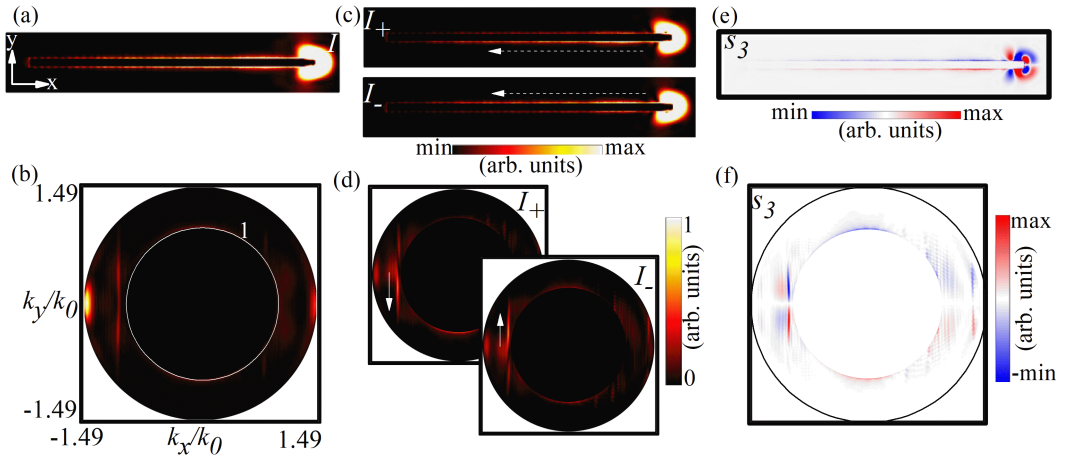


FIGURE 3.7: (a) Numerically calculated intensity distribution of the SPP mode in the real plane (x - y plane at $z = 196$ nm) is shown in (a). (b) The corresponding FP intensity distribution. (c) Real plane intensity distribution of the SPP mode corresponding to I_+ and I_- components. Dashed white arrows indicate the bias of intensity distribution of the SPP mode. (d) FP intensity distribution of I_+ and I_- components where the solid white arrows indicate the bias of the SPP mode line. (e) The real plane and (f) FP transverse spin density of the SPPs field.

3.5 Conclusion

To summarize, we investigate the transverse spin (s_z) of SPPs propagating along x axis in a quasi-one-dimensional AgNW by analyzing the circular polarisation state of the collected evanescent mode signal through a high NA objective lens. Both experimentally measured and numerically calculated real plane and FP field distribution corresponding to LCP and RCP components of the total field exhibit biasing. Further, the biasing of the mode signal inverts for opposite circular polarisation states indicating existence of spin-momentum locking of the evanescent wave. The existence of the transverse spin as well as the spin-momentum locking phenomena can be attributed to the decay of evanescent SPP field in the longitudinal plane (x - y plane). Our results exhibit a direct and non-invasive measurement of the spin momentum locking as well as the corresponding transverse spin density and bypasses the complexity of fabrication based

techniques [144, 145] or near-field nano-probing methods [109, 125]. The results add to the emerging study of SOI due to existence of spin components in non-paraxial fields, specifically in evanescent waves. Additionally, the SOI with an AgNW will find relevance in various chip-scale nano-photonic device applications[114].

Chapter 4

Sub-wavelength channeling of whispering gallery modes into silver nanowire as plasmon polaritons

Combining plasmonic and dielectric photonic structures can offer interesting opportunities in hybrid nanophotonics [146–148]. This chapter shows how plasmonic silver nanowires (AgNW) combined with fluorescent dielectric microsphere (μ S) can be harnessed to realize a directional source of whispering gallery modes (WGMs). We study subwavelength propagation of μ S's WGMs mediated via surface plasmon polaritons (SPPs) in an AgNW. Given that the discussed geometry is self-assembled from a solution-phase, our results will find relevance in WGM-based soft-photonics platforms including miniaturized optical resonators and couplers. The chapter is an adaptation of the research article "Mater. Res. Bull. 142 111412 (2021)".

4.1 Introduction

In the previous chapters we have seen how metallic nanostructures support surface plasmons, which lead to field enhancement at the surface of metallic nanostructures [1–3]. Although, metallic nanostructures can focus and channel light at sub-wavelength scale, they suffer huge losses at optical frequencies [149]. Certain dielectric cavities on the other hand, facilitate high quality factor WGMs, which have been utilized for various applications such as lasing [62], biochemical sensors [59] and curved light beams [150]. However, these dielectric structures are of the scale of μ m and can not support subwavelength propagation of light, which is not ideal for device related applications. Moreover, isotropic emission results in the low collection efficiency and inefficient coupling at sub-wavelength scales.

Coupling chemically prepared single crystalline AgNW to a dielectric microstructures opens up the possibility of waveguiding WGMs at sub-wavelength scale [53]. Further, light coupled at one end of the metallic NW out-couple directionally from the other end or at any discontinuity along the NW [27, 40]. This suggest that coupled WGMs could be out-coupled directionally. This hybrid nanophotonic structure would overcome the losses associated with metals, low coupling and impossible subwavelength propagation of high quality factor WGMs of dielectric microstructures.

Among all the dielectric structures supporting WGMs like micro-rings [151], toroids [152], micro-disks [153], dielectric μ S [154–156] have gained a lot of interest due to the ease in the fabrication. A large number of the studies have been focused on examining spectral and polarisation signatures of these modes [154, 157]. Wavevectors of WGMs emission, which is crucial for device related application is still relatively less explored [158, 159]. As discussed earlier, WGMs emission from an isolated dielectric μ S are isotropic in nature because of the symmetry of dielectric cavities. Isotropic emission results in the low collection efficiency and inefficient coupling at sub-wavelength scales. In the past, dielectric μ S have been coupled to dielectric waveguides for evanescent excitation of WGMs [160, 161]. However, diffraction limited waveguides cannot support sub-wavelength propagation of WGMs and the emission from these coupled structures is non-directional in nature. Motivated by this, we utilize a hybrid, self-assembled AgNW- μ S junction (Fig. 4.1) for sub-wavelength propagation of μ S's WGMs and simultaneously tuning the directionality.

4.2 Experimental schematic of the system

AgNWs with average diameter ~ 350 nm are chemically prepared using polyol process and cleaned by centrifuging in acetone followed by ethanol [162, 163]. After cleaning, NWs are diluted in Ethanol. As prepared NWs ($7 \mu\text{l}$ solution) are dropcasted on glass substrate. Before completely drying, we disperse $7 \mu\text{l}$ solution of Nile-blue dye coated SiO_2 μ Ss (brought from microspheres-nanospheres with diameter ($3 \mu\text{m}$)) over the substrate. After drying, the sample contains capillary force assisted self-assembled AgNW- μ S geometries [49, 53].

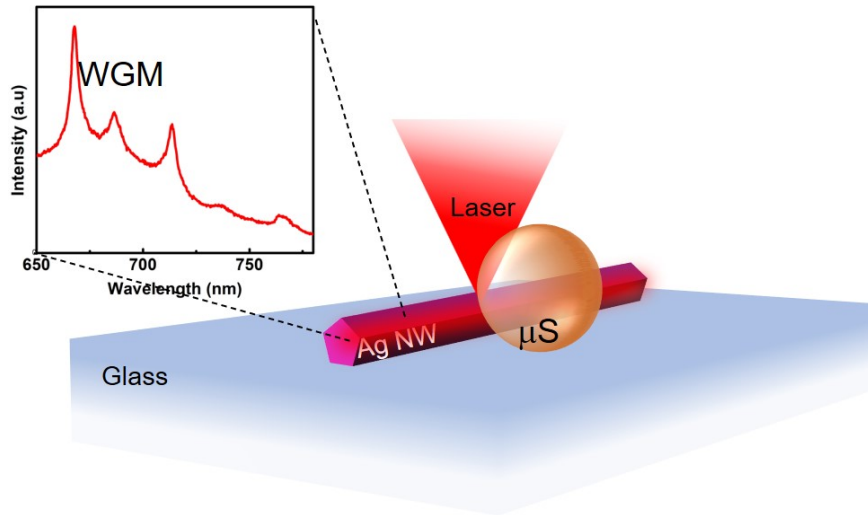


FIGURE 4.1: Architecture of the system. A Nile-blue dye coated SiO_2 μ S is assembled near plasmonic AgNW using self-assembly methods. Inset shows spectral signatures of WGMs propagating as SPPs excited in AgNW.

It is noticed that the position where μ S will couple to AgNW along the length of NW is not controllable using self-assembly methods. However, self-assembled structures are easy to prepare and can be found in large numbers in a single sample. The scanning electron micrograph

(SEM) image of one such AgNW- μ S junction and optical bright field images of many junctions found in the same sample is given in Fig. 4.2.

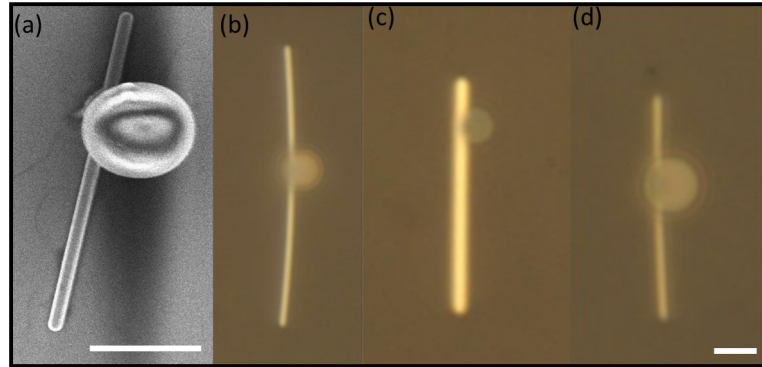


FIGURE 4.2: (a) SEM image of one AgNW- μ S junction on a glass substrate (b)-(d) Optical bright field images of four junctions found in the same sample showing reproducibility and different positions where μ S is attached to AgNW along the length of NW.

4.3 Optical set-up: Back scattering geomtery for inelastic emission

The optical set-up used for spectral and wavevector studies for WGMs is shown in Fig. 4.3(a). We utilise the backscattered geometry, the AgNW- μ S is excited with 100x 1.40 oil immersion lens and emission is collected back from the same objective lens. High NA objective lens ensures maximum excitation and collection efficiency. Given that WGMs are inelastic emission from μ S, studies of WGMs would require spectrometer and EMCCD for spectroscopy and imaging. In the imaging channel we implement Fourier plane (FP) imaging in both CCD (for elastic emission (633 nm)) and EMCCD (for inelastic scattering) path as described in chapter 2. For spectroscopy, emission is sent to an andor spectrometer with 300 lines/mm grating.

If we incident light at any discontinuity or scatterer along the length of NW, some of the scattered wavevectors satisfy the momentum matching condition and lanuch plasmon into the AgNW. For AgNW- μ S system, μ S acts as a scatterer to couple light into the NW plasmons (Fig. 4.3 (b)). These propagating plasmons travel along the length of AgNW and out-couple as free photons at both the ends of NW which can be seen from the elastic scattering image of AgNW- μ S system in the Fig. 4.3(c).

Since Nile blue molecules coated on the μ S is fluorescent around excitation laser, the fluorescence of the molecules also gets excited at the junction which couples to the WGMs of the μ S. Upon excitation of the junction, inelastic emission at the junction and at the distal ends of AgNW can be seen in the inelastic scattering image of the AgNW- μ S system (Fig. 4.3(d)).

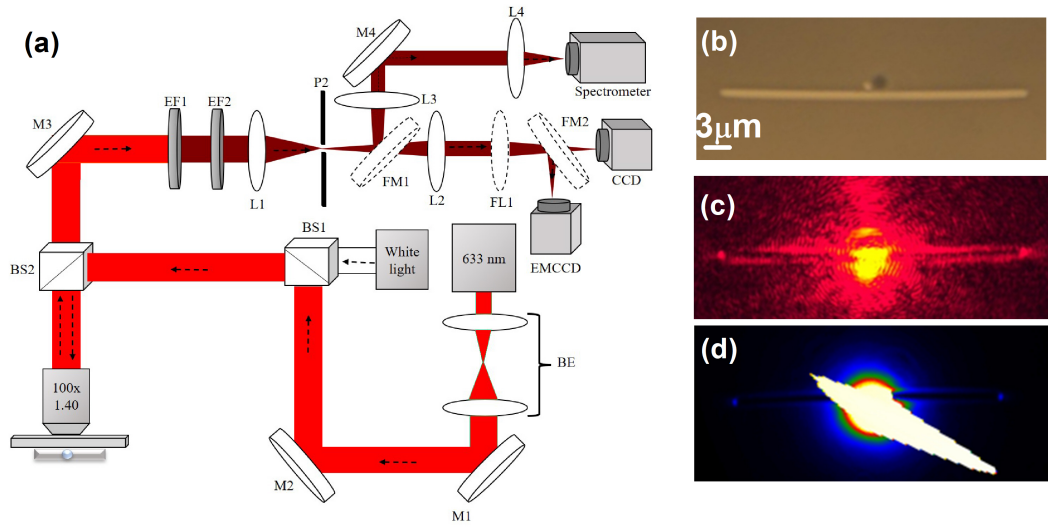


FIGURE 4.3: (a) Optical set-up used for spectral and wavevector studies for WGMs (b) Optical bright field AgNW- μ S system on glass substrate. (c) Real-plane elastic scattering image of the system upon the excitation of the junction using 633 nm laser wavelength. SPPs propagating along the length and outcoupling at the distal end is clearly visible. (d) Inelastic real plane image of the system showing fluorescence mediated WGMs excited at the junction and their out-coupling at the NW ends. Here, BS1-BS2 are beam splitters, M1-M4 are mirrors, L1-L4 are lens, FL1 is flip lens, FM1-FM2 are flip mirrors, P2 is pin-hole and EF1-EF2 are 633 edge filters to block the excitation.

4.4 Spectral analysis of fluorescence emission coupled to WGMs

Inelastic emission at the junction and distal end of NW is clearly visible in inelastic scattering image of AgNW- μ S system. For the spectral study of the inelastic emission, junction and distal end are spatially filtered using a pinhole (P_2) and the collected light is projected to the spectrometer after rejecting elastically scattered light. The black solid and red dashed curves are spectra collected from the junction and NW end respectively (Fig. 4.4(a)). Both the spectra are collected for different exposure time as the intensity of the emission is different at both spots.

Spectra collected at the junction, shows WGMs of the μ S coupled to fluorescence of the Nile blue molecules. WGMs are labelled using Mie theory as transverse electric (TE) and transverse magnetic (TM) based on polarisation of the mode. Modes (TE/TM l, n) are identified using three quantum numbers n, l and m . n , radial quantum number quantifies the intensity maxima along the radius of the μ S ($n=1$ for WGMs). l , orbital quantum number represents the number of halves of the intensity maxima along the circumference of the μ S. Projection of the orbital quantum number on the quantization axis is called azimuthal quantum number m . We simulate the near-field of a particular mode observed experimentally using COMSOL (Fig. 1.5(c)) and calculate the intensity maximas along the circumference for calculating 'l' to represent the mode. We also calculate the WGMs of μ S with diameter 3 μ m in air using Mie scattering for a refractive

index of 1.45 (computationally) [164] and match with WGMs peaks observed experimentally for an isolated μ S placed on a glass substrate (black and red curve in Fig. 4.4(b)). We observe slight difference in the peak positions of the isolated μ S and μ S placed on the glass substrate is because of the interaction of the μ S with the substrate which causes a red shift in the spectrum [165].

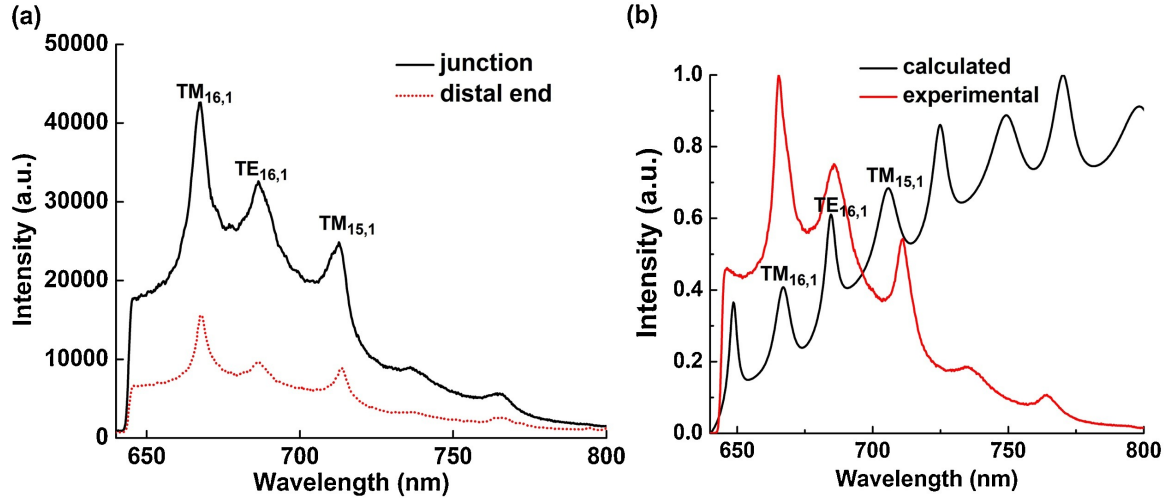


FIGURE 4.4: Spectral signatures of whispering gallery modes. (a) WGMs of a μ S coupled to NW. Black and red curves show the spectral signatures of the emission collected from the AgNW- μ S junction and NW end respectively. (b) WGMs of an isolated μ S. Red curve shows the experimentally obtained WGMs of an isolated dye coated μ S placed on a glass substrate. Black curve shows the calculated WGMs of an isolated μ S in a medium of refractive index 1.

It is interesting to note that the spectrum collected from one of the distal ends of the AgNW also show sharp resonances where the peak positions represents the TE and TM polarized WGMs of the μ S. This suggests that WGMs of the μ S excited at the junction couple to the NW plasmons and out-couple at the NW end.

4.5 Directionality of remotely collected WGMs: Fourier plane imaging

Spectral analysis confirms that WGMs of the μ S coupled to a AgNW can be collected remotely at the NW end. The next step is to study the directionality of the WGMs wavevectors at the distal end of NW. For this, we perform FP imaging to quantify the directionality of emission wavevectors in terms of radial and azimuthal angles. The FP image of the inelastic emission from the spatially filtered distal end of the NW is shown in the Fig. 4.5(c). It is evident that out-coupled WGMs wavevectors are directional in nature. For the qualitative analysis, we compare directionality of the WGMs wavevectors out-coupled at the NW end with the WGMs wavevectors of an isolated dielectric μ S of same size placed on a glass substrate.

Fig. 4.5(a) (i) and a (ii) show the bright field and inelastic scattering image of the spatially filtered distal end of NW coupled to a μ S upon excitation of the junction. Similarly, Fig. 4.5(b)

(i) and (ii) show the bright field and inelastic scattering image of an excited isolated μS placed on a glass substrate. The FP images shown in Fig. 4.5(c) and (d) correspond to the emission shown in Fig. 4.5(a)-(ii) and 4.5(b)-(ii) respectively. Intensity cross-cut along white dotted line, in Fig. 4.5(c), shows radial angle distribution of the WGMs emission at the NW end and reveals a sharp emission near the critical angle of glass-air interface. For the azimuthal spreading of the emission from the NW end, polar plot of intensity along the circumference of the circle at critical angle is plotted in Fig. 4.5(f). The emission covers very narrow range of azimuthal angles.

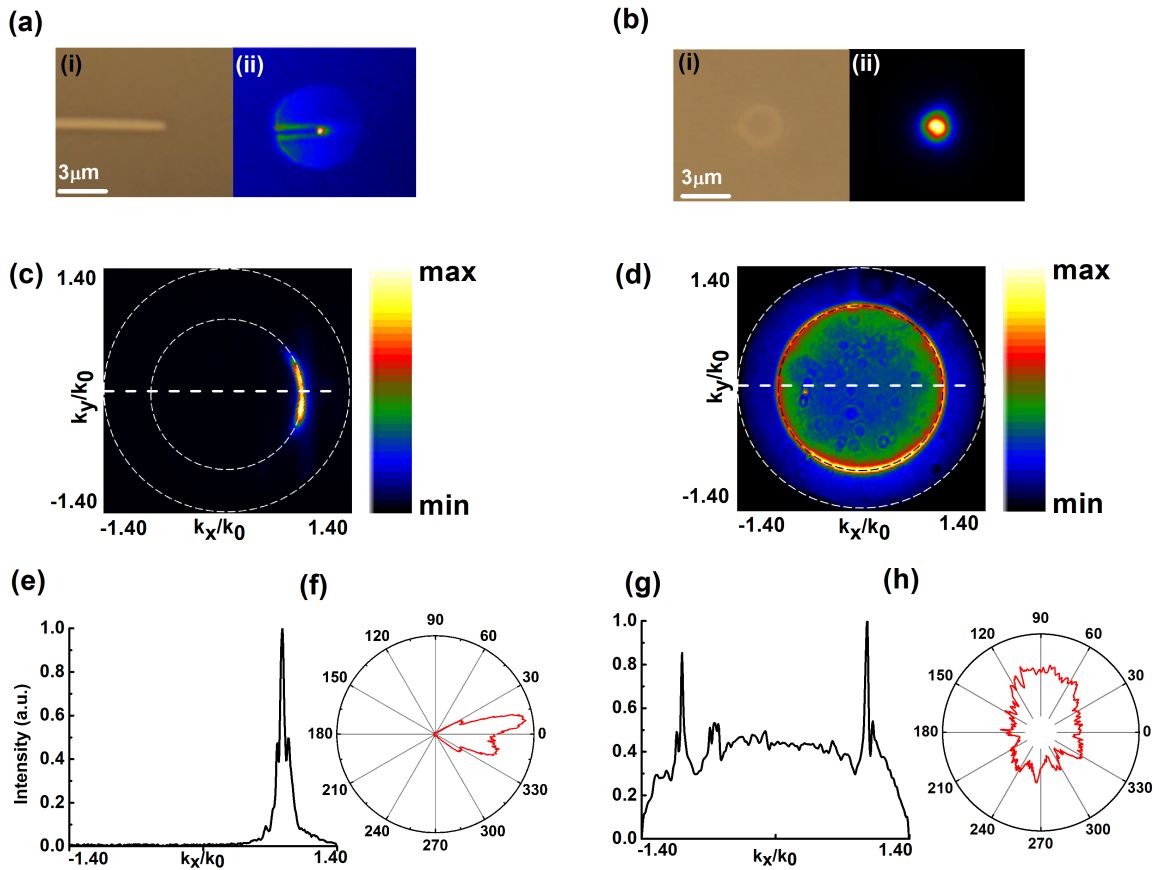


FIGURE 4.5: WGMs wavevector comparison of emission from NW end with the emission from isolated μS . (a) (i) Bright field (ii) inelastic scattering images of spatially filtered NW end. (c) FP image of the emission collected from distal end of NW shown in (a) (ii). (e) Intensity cross-cut along the white dotted line shown in (c) representing out-coupled wavevectors near the glass-air critical angle. (f) Azimuthal intensity distribution along the inner circle in (c) at a constant radial angle. (b) (i) Bright field (ii) inelastic scattering images of a molecule coated μS placed on a glass substrate. (d) FP image of inelastic emission from μS . (g) Intensity cross-cuts along the white dotted line shown in (d), (f) azimuthal intensity distribution along the inner circle in (d) at a constant radial angle.

4.6 Selectively probing the directional WGMs at NW ends

Inelastic scattering image from the AgNW- μ S system (Fig. 4.6(a) shows emission from both ends of NW, which can be used to get directional WGMs in different directions. For this, we selectively probe the directionality of emission from both the ends. Ends of the NW are marked as end 1 and end 2, visible in the optical bright field image of AgNW- μ S system in Fig. 4.6. Selectively, each end of the NW is spatially filtered using a pinhole and projected to a spectrometer for spectral analysis. Black (solid) and red (dashed) curves in Fig. 4.6(b) show the spectra collected from end 2 and end 1 respectively after rejecting the elastically scattered light. The relatively higher intensity of end 1 in comparison to end 2 can be attributed to different distance of both ends from the junction. Spectra confirms out-coupling of WGMs of the μ S coupled to AgNW through both the ends. The FP images of emission from end 1 and end 2 are shown in Fig. 4.6(c) and (d) respectively. The emission covers a small range of both radial and azimuthal angles and can be tuned in either of the directions along the NW depending on the AgNW end selected.

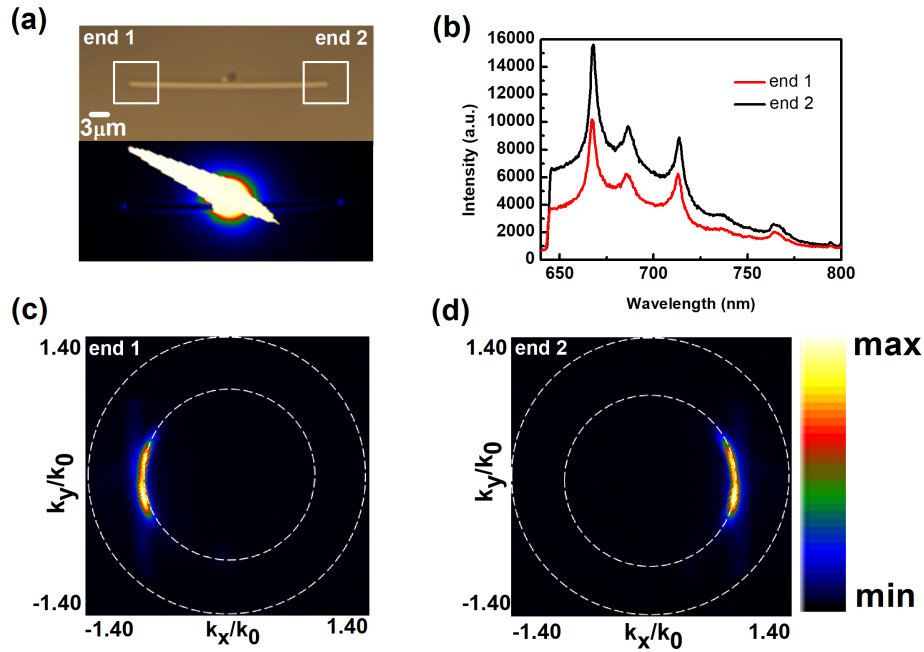


FIGURE 4.6: FP imaging of WGMs wavevectors from both the ends of NW. (a) Bright field and inelastic scattering images showing the WGMs emission at the excitation point as well as at both ends of AgNW upon excitation of the junction. (b) Spectral signatures of the emission at end 1 and end 2 of the AgNW as labelled in (a) with white square boxes. Red (dashed) and black (solid) curves show the spectra collected individually from spatially filtered end 1 and end 2 respectively. FP images of the emission from (c) end 1 and (d) end 2.

4.7 Coupling of WGMs into nanowire mode

To understand the coupling of these WGMs into AgNW, we perform plasmon leakage radiation microscopy [166] on the emission from AgNW- μ S system without any spatial filtering. Fig. 4.7(a) shows the optical bright field image of the AgNW- μ S system in transmission mode. The AgNW- μ S is excited with a 633 nm laser polarized along the junction using 100x, 0.95 objective lens and the forward scattered light is collected using 100x, 1.49 oil immersion objective lens. Elastic scattering image of the AgNW- μ S system in Fig. 4.7(b) shows the emission at the junction and at the distal end of NW. Along with the emission, leaky mode of the NW at excitation wavelength in bright field image can also be seen along the length of the NW. Fig. 4.7(c) shows the spectral signatures of the emission from the AgNW- μ S system after rejecting the excitation wavelength. The emission is indeed WGMs of the μ S coupled to the fluorescence of Nile blue molecules.

This inelastic emission is sent to EMCCD for leakage radiation microscopy without any spatial filtering, FP image is shown in Fig. 4.7(d). FP image shows that the majority of the emission is near the air-glass critical angle (similar to an isolated μ S). In addition, two straight lines along k_y/k_0 at constant values of k_x/k_0 are also prominent. As also discussed in chapter 3, guiding inelastically scattered light (WGMs mediated via fluorescence). This confirms the coupling of WGMs of μ S into NW plasmons.

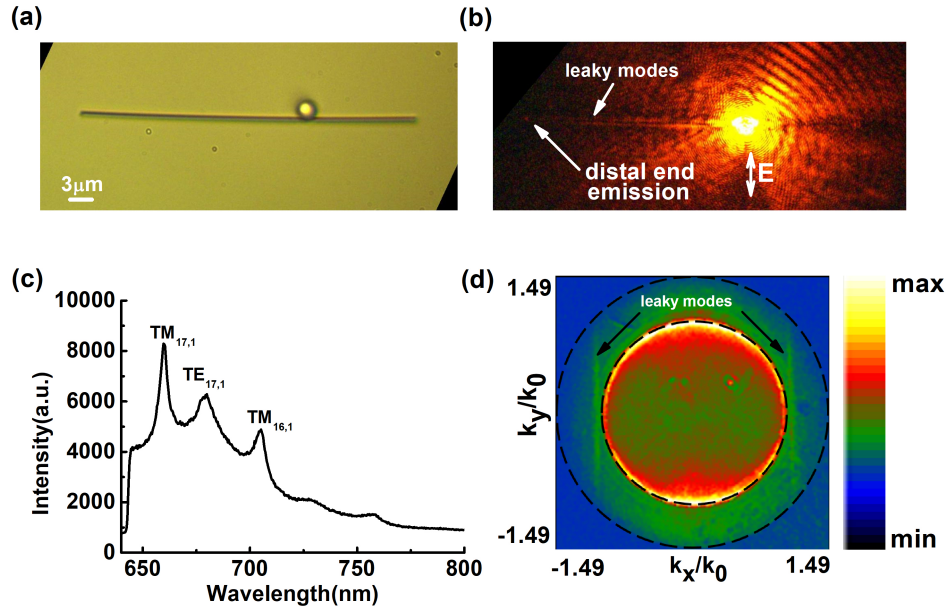


FIGURE 4.7: Spectral and wavevector analysis of WGMs of dielectric μ S coupled to NW plasmons. (a) Bright-field image of AgNW- μ S system in transmission mode where μ S of diameter 3 μ m is coupled to a ≈ 350 nm thick NW. (b) Elastic scattering image of the system upon exciting the AgNW- μ S junction with 633 nm wavelength laser. (c) Spectral signatures of emission showing WGMs of μ S riding over the fluorescence. (d) FP image of emission from the full system of NW coupled to the μ S. Two leaky modes in the FP image represent the coupling of WGMs to the NW plasmons propagating in opposite directions.

4.8 Conclusion

We show sub-wavelength propagation and directional out-coupling of WGMs of a fluorescent silica μ S resonator mediated via plasmon polaritons in a single crystalline AgNW. Fluorescent spectral signatures of emission from the NW ends confirm efficient guiding of WGMs via NW plasmons. By employing FP optical microscopy, we reveal and quantify the directional fluorescence emission of WGMs from the ends of the NW. To understand the mechanism behind the directional emission of WGMs from NW ends, Leakage radiation microscopy is utilised. It is found that WGMs of μ S couple to the NW as propagating modes and out-couples from the NW end. The emission is directional in nature and spans a very narrow range of radial and azimuthal angles making the system a directional hybrid antenna. We also show the control on the directional wavevectors depending on the NW end used for WGMs out-coupling.

Chapter 5

Mapping 1-D nanocavities using light scattering from molecular monolayers

In the previous chapters, we have discussed the confinement and enhancement of electromagnetic field on the surface of metallic nanostructures intensely focused on silver nanowires (Ag-NWs). However, it has been shown that the plasmonic nanocavities offer much more confined and enhanced field (~ 2 nm) inside the gap between two nanostructures. Motivated by this, in the following two chapters, we study Nanowire over mirror (NWoM) nanocavities in details.

In this chapter, we map the spatial inhomogeneities inside the nanogap between two metallic nanostructures which are often inaccessible in experimental characterisation. Here we overcome this challenge by mapping the localised plasmons which are highly-sensitive to surface inhomogeneous and defects, in micron-long plasmonic nanocavities using a NWoM geometry. We study the polarized gap plasmon modes supported by NWoM by analysing the dark-field (DF) scattering spectrum and correlate this with polarisation-resolved surface enhanced Raman scattering (SERS) from molecules inside the NWoM nanogap. The spectral wandering of nanocavity modes at different spatial positions along the nanowire (NW) are correlated to SERS intensities. These correlations reveal non-uniformities of the local environment and track the sub-nm spatial changes inside the elongated nanogap along the length of the NW. The work presented in this chapter is performed at Nanophotonics group, University of Cambridge with Prof. Jeremy Baumberg.

5.1 Plasmonic silver nanowire over mirror nanocavity

Plasmonic nanocavities support gap plasmon modes which offer confined and enhanced field inside the nanogap owing to the hybridization of plasmons [167, 168]. The quality factor 'Q' associated with gap plasmon modes are really low (below 100) due to losses in metals in comparison to dielectric optical cavities ($\sim 10^9$) [12, 169, 170]. However plasmon mode facilitate ultra small mode volume ' V_{eff} ' (below 10^{-3}), which increases the Purcell factor (rate of spontaneous emission from emitter inside the cavity, $F_p \propto Q/V_{eff}$) [77, 171]. In addition to large enhancement of Purcell factor, strong optical fields inside the nanogap offers many photonic applications such as increased molecular emission (SERS and fluorescence) from the cavity [71, 172], non-linear optical responses [173], strong coupling of light-matter [72, 174].

Of all nanocavities, metallic nanostructure over Au mirror has gained particular importance due to their ease of fabrication and reproducible nanogap ($\sim 1\text{nm}$) [172]. However, this limits ability to look into the nanogaps and map the spatial inhomogeneities. Quasi one-dimensional silver nanowire (AgNW) is an important geometry with extended nanogap along the length of NW with directional surface plasmon polaritons (SPP) waveguiding and localized electromagnetic hot-spots along the length of AgNW [28]. Specifically, chemically prepared AgNW are desired for applications due to ease of fabrication and single crystalline nature [163, 175]. However, AgNW also supports surface non-uniformities and defects due to unreacted silver nanoparticles and non-uniform coating of Polyvinylpyrrolidone (PVP) which acts as a capping agent during chemical synthesis [162]. Of late, gap plasmon modes supported by NWoM geometry have been shown to be extremely sensitive to the local environment change like refractive index and gap thickness of the nanocavity [76, 176]. Mapping gap plasmon modes for NWoM geometry along the long length allows the probing of different types of inhomogeneities from the lower facet in the near-field along their 1-D plasmonic nanogap.

Motivated by this, here we study the plasmon modes supported by AgNWs elongated along y -axis placed on a template stripped Au film (Fig. 5.1(a)) with self-assembled monolayer (SAM) of Biphenyl-4-thiol (BPT) molecules (Fig. 5.1(c)). A SAM of BPT molecules forms onto the Au mirror in an easily reproducible method. For SAM formation template stripped Au substrate was immersed in $1\text{ }\mu\text{l}$ solution of BPT in ethanol for 24 hr. After 24 hr, substrate is removed from BPT solution and washed with ethanol to remove excess molecules. $5\text{ }\mu\text{l}$ solution of AgNWs is drop-casted on the SAM formulated Au substrate and dried with nitrogen gun.

AgNWs used for the studies are chemically synthesised using polyol process with characteristic radius ' R ' [163]. Cross-sectional schematic of one such AgNW with characteristic PVP coating placed on a mirror is shown in Fig. 5.1(b). PVP coating and BPT monolayer on mirror together forms the nanogap ' d ' of $< 5\text{nm}$ between the AgNW and Au film. The scanning tunneling microscope (STM) and DF image reveal single-crystalline nature and sharp edges of AgNW with pentagonal cross-section (Fig. 5.1(d) and (e)). From analysing these STMs, the facets are extremely smooth, consistent in size, and with uniform edge sharpness, which should thus create nanocavities with extremely precise spectral characteristics.

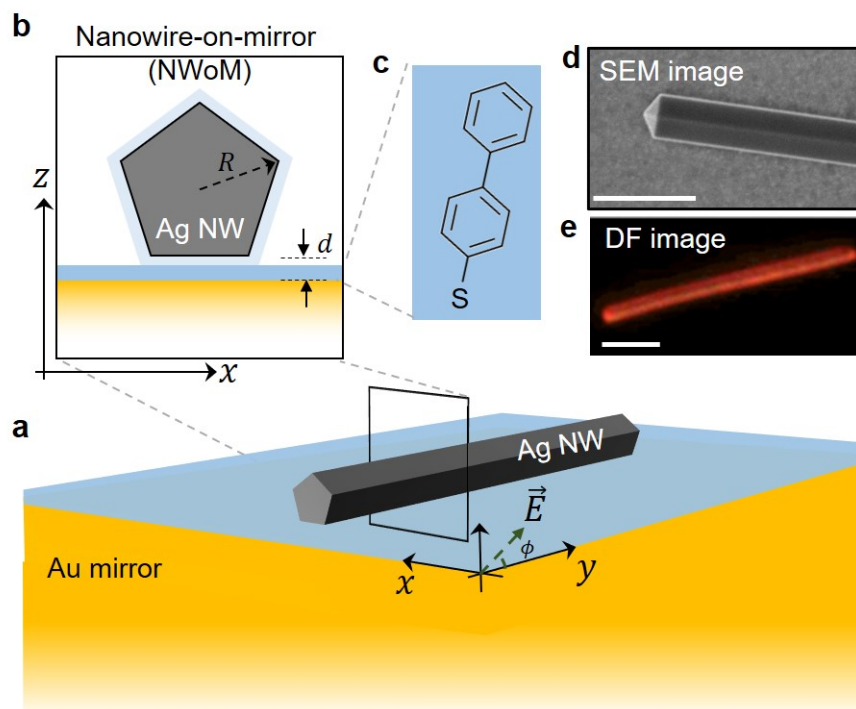


FIGURE 5.1: (a) Schematic of the chemically prepared AgNW extending along the y direction on a template stripped Au mirror. (b) Diagrammatic Cross-section view of the AgNW with characteristic 5 nm thick PVP coating placed on a BPT molecular assembled Au mirror. PVP along with BPT acts scaffolds the nanogap (d) between the AgNW and Au mirror. (c) Chemical structure of BPT molecule. (d) SEM image, with scale bar of $1\ \mu\text{m}$ (e) DF scattering image of the NWoM with scale bar of 100 nm.

5.2 Gap plasmon modes supported by nanowire over mirror nanocavity

The NWoM geometry is illuminated with white light in a DF configuration to understand the nanocavity modes from the polarimetry of scattered light (optical set-up in Fig. 2.11). The DF scattered light is resolved along the in-plane polarisation angle (ϕ) defined as the angle between the analyser axis and long-axis of AgNW (y -axis) (Fig. 5.1(a)). The spectra reveal the localised spectrally-narrow resonances when analysed perpendicular to the NW direction (x -axis, $\phi = 90^\circ$) (Fig. 5.2(b)). Two characteristic modes are observed labelled as $(1x)$ and $(2x)$. Contrary to broadband propagating modes, when analysing along the length of AgNW (y -axis, $\phi = 0^\circ$). The polarisation resolved DF scattering image (Fig. 5.2 (a) and (b)) and spectra for $\phi = 0^\circ, 90^\circ$ (Fig. 5.2(c)) showing polarisation sensitivity of gap plasmon modes supported by NWoM.

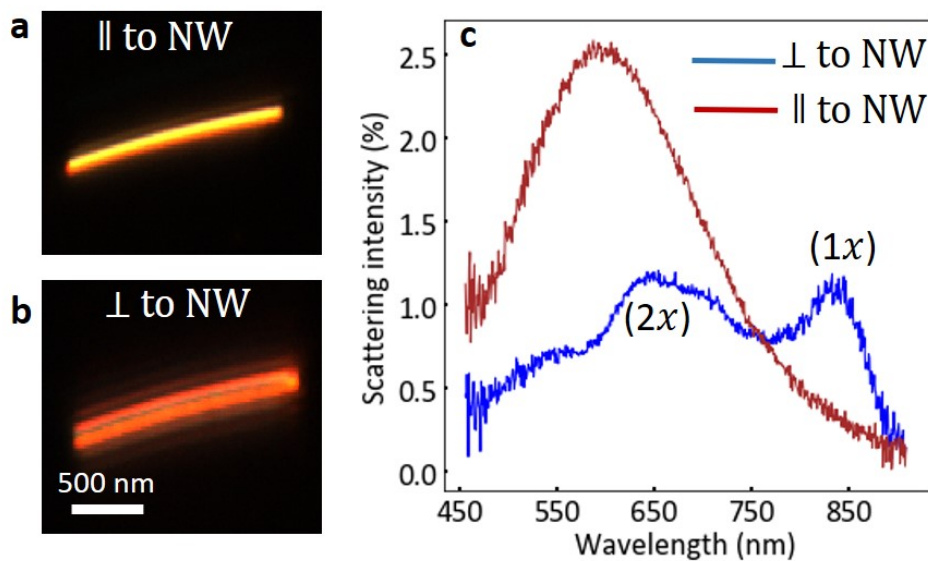


FIGURE 5.2: (a) DF scattering image of AgNW with polarisation angle (a) $\phi = 0^\circ$ (b) $\phi = 90^\circ$. (c) DF scattering spectra for polarisation angle $\phi = 0^\circ$ (dark-red) and $\phi = 90^\circ$ (blue curve). (1x) and (2x) modes are visible upon analysing perpendicular to AgNW.

5.2.1 Numerical simulations for gap modes

Lumerical FDTD Solutions v8.12 was used for 2-D simulations of scattering cross-section from NWoM system. A Schematic of the simulated NWoM geometry is shown in Fig. 5.3(a). AgNW is modelled using a pentagon geometry having refractive index set to silver material. A rectangular geometry with thickness of 500 nm and refractive index of Au material was formed to mimic the Au substrate. A varying nanogap ($d = 5$ and 3 nm) between the pentagon geometry and Au mirror with refractive index of 1.4 acts together as PVP coating and BPT molecular layer in experiments. Full geometry is excited using a total field scattered field source. The meshing size of whole geometry is set to 3 nm for both x and z -axis. The nanogap (along z -axis) is meshed differently using 0.5 nm and 1 nm meshing size for nanogap along the perpendicular direction and along the NW length respectively. The scattering cross-section module was used to calculate the scattering cross-section from the geometry.

Four cases for calculating scattering cross-section for NWoM geometry (Fig. 5.3) are simulated –

- i $\vec{k}$ along z -axis and $\vec{E}$ along x -axis – Incident wave-vector normal to NWoM with electric field vector perpendicular to AgNW.
- ii $\vec{k}$ along z -axis and $\vec{E}$ along y -axis- Incident wave-vector normal to NWoM with electric field along the long axis of AgNW.
- iii $\vec{k}$ along x -axis and $\vec{E}$ along z -axis- Incident wave-vector at high angle as experimental configuration of DF scattering with electric field along perpendicular to AgNW.

- iv $\vec{k}$ along x -axis and $\vec{E}$ along y -axis- Incident wave-vector at high angle as DF scattering with electric field along the long axis of AgNW.

Schematic of (i) and (ii) are shown in dashed black rectangular region as (a) and (b). (iii) and (iv) are shown in red dashed rectangular region as (c) and (d) respectively (Fig. 5.3). Scattering cross-section obtained for four configurations show that $\vec{k}$ along x -axis and $\vec{E}$ along z -axis shows two narrow gap plasmon modes and is closest to the experimental configuration. Hence-fourth, all the simulation results presented for cavity plasmon modes are simulated using configuration (c).

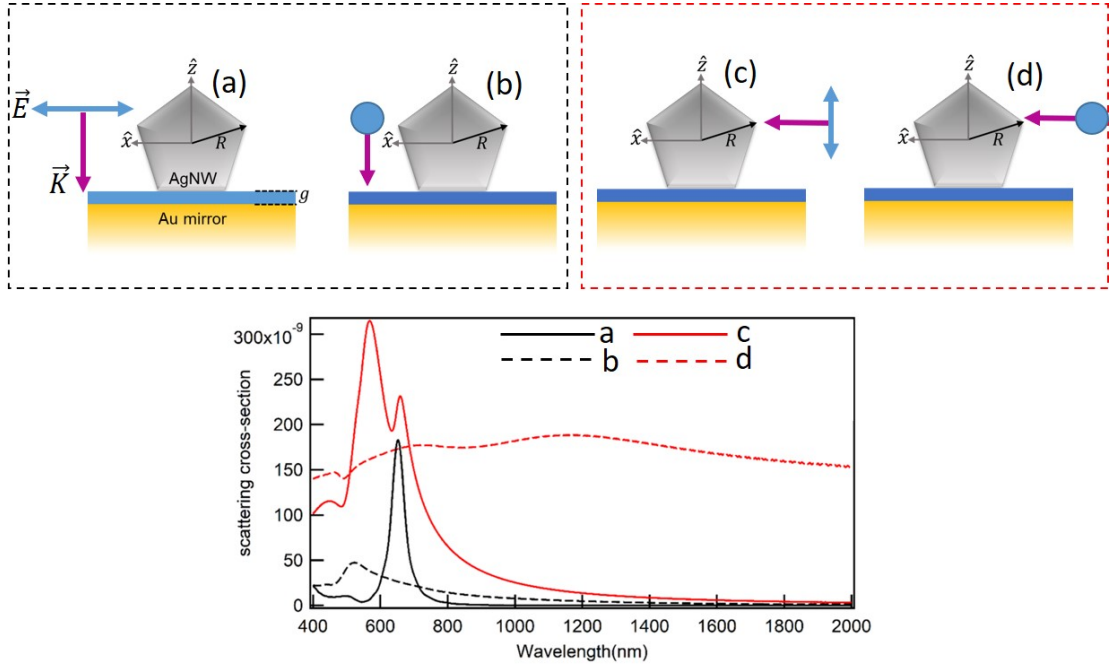


FIGURE 5.3: Upper Panel: Schematic of the four possible configurations with different directions of $\vec{k}$ and $\vec{E}$ for NWoM geometry while calculating scattering cross-section using 2-D ftdt calculation. AgNW is modelled as a pentagonal geometry with refractive index set to silver placed on a rectangular geometry with gold refractive index. The nanogap ($d=5\text{nm}$) has been set to have refractive index ($n=1.4$). The incident wave-vector $\vec{k}$ and electric field $\vec{E}$ of a total field scattered field source are shown as purple and blue colour respectively. Lower panel shows scattering cross-sections corresponding to four configurations shown in the schematic.

5.2.2 Estimation of gap thickness for NWoM system using numerical simulations

We correlate numerically calculated scattering cross-section with experimentally measured localised spectrally-narrow resonances when analysed perpendicular to the NW direction (x -axis, $\phi=90^\circ$) (Fig. 5.4(b)). Two characteristic modes (1x) and (2x) as discussed earlier are observed.

The analysis of near-electric field profiles (E_z) for an AgNW with $R=30\text{ nm}$ (Fig. 5.4(a)) for these two modes show confined fields inside the nanogap between AgNW and Au mirror, representing the gap plasmon modes of the NWoM geometry (Fig. 5.4(c)). For the (1x) mode at longer wavelength the electric field exhibit node at the centre of the facet width, whereas the

(2x) mode at lower resonance wavelength has intensity maxima across the facet width. The (1x) and (2x) represent the number of nodes along x -direction of the AgNW. The extracted near-field line profile along x -axis for both modes are given in Fig. 5.5.

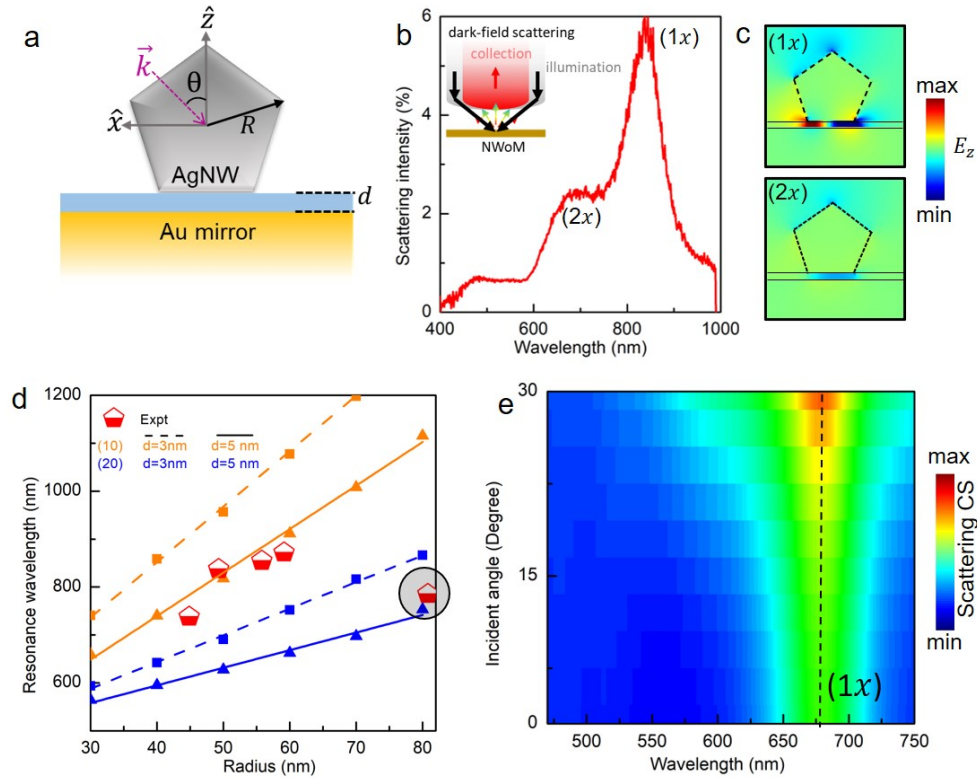


FIGURE 5.4: (a) Schematic for NWoM geometry used for in 2D-FDTD simulations. The geometry is excited with a broad wavelength plane wave source with incident wave-vector at an angle (θ) with respect to z -axis. (b) Experimentally obtained DF scattering spectra of NWoM geometry when polarisation-analysed along x -direction ($\phi = 90^\circ$) showing two plasmon modes termed as (1x) and (2x). The inset shows DF illumination scheme. (c) Simulated near-electric field along the perpendicular direction (E_z) for (1x) and (2x) plasmon modes with incident wave along x -axis (d) Orange and blue curve for simulated (1x) and (2x) resonance wavelengths as a function of AgNW radius ' R ' (dashed and solid line for $d=3$ and 5 nm) respectively. The red bullet points show experimentally obtained resonance positions of (1x) mode as a function of R . (e) Simulated (1x) mode resonance wavelength as a function of incident angle (θ).

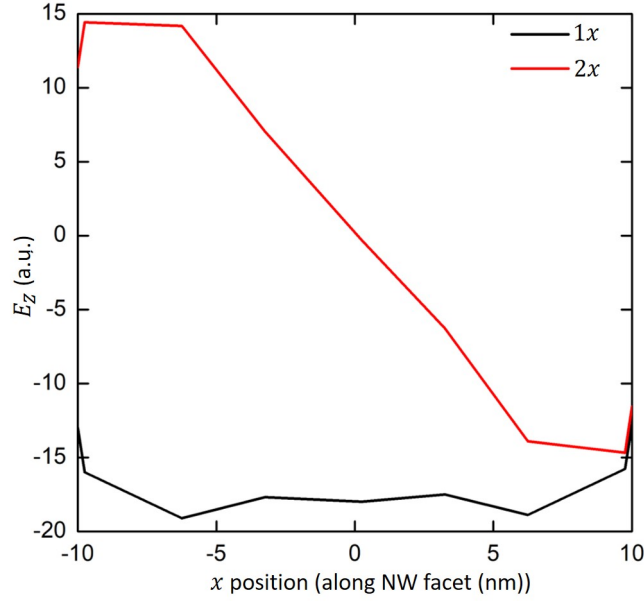


FIGURE 5.5: Line profile of simulated field component E_z (perpendicular to AgNW elongated along y -axis) along the facet width of AgNW (x -axis) for $(1x)$ and $(2x)$ plasmon modes in red and black curve respectively.

The confined near-field nature of these modes implies the tuning of the resonance positions with R and d . The resonance tuning of $(1x)$ and $(2x)$ as a function of R for $d=5$ nm and $d=3$ nm is given in Fig. 5.4(d). The orange and blue curve show the $(1x)$ and $(2x)$ resonance positions as a function of R for $d=3$ nm (dashed lines) and $d=5$ nm (solid lines) respectively, calculated in simulations. As predicted from the change in capacitance of the gap modes, $(1x)$ and $(2x)$ modes redshift as gap thickness decreases [177] and consistent with simulations. It is also clear that for both d values as R increases, $(1x)$ and $(2x)$ modes follow the characteristic redshift, making it hard to disentangle the individual effects.

For an estimation of the gap thickness of NWoM geometry used for experiments, we experimentally obtain R from SEM images and $(1x)$ mode positions from DF scattering and append those points to graph in Fig. 5.4(d). The $(1x)$ mode positions of five such NWoMs as a function of AgNW radius obtained from SEM are shown as red bullet points on the graph. The experimentally obtained $(1x)$ resonance wavelengths are very close to simulated resonance positions for $d=5 \pm 0.6$ nm, expected from the PVP and BPT thicknesses. The $(1x)$ mode for $R=80$ nm modes lies at higher wavelength (~ 1100 nm, solid orange curve) which is out of the detection limit for our fibre-coupled spectrometer. The resonance peak recorded in the DF spectrum (circled point, Fig. 5.4(d)) is the $(2x)$ mode which matches pretty well with the simulated mode position for this $(2x)$ mode and using $d=5$ nm.

The direct comparison of simulations to experiments on mode position is valid here, even though illumination conditions are different. This is because the $(1x)$ and $(2x)$ mode are highly localised and do not exhibit dispersion of mode positions with changing illumination directions ($\vec{k}$). We confirm this with simulations of different $\vec{k}$ illumination (θ in Fig. 5.4(a)) and $(1x)$ resonance wavelength remain unchanged (Fig. 5.4(e)).

We also performed 3-D simulations for 10 μm long AgNW with radius $R=30$ nm. Same $(1x)$ and $(2x)$ mode appear with no additional modes in scattering cross-section. As can be seen that relative position of both modes are shift by few nm which can be attributed to the poor meshing of the nanogap due to computational size limitations. However, the convergence of simulations for high angle illuminations remains challenging given the computational limitation with narrow gaps and large simulation volume (Fig. 5.6).

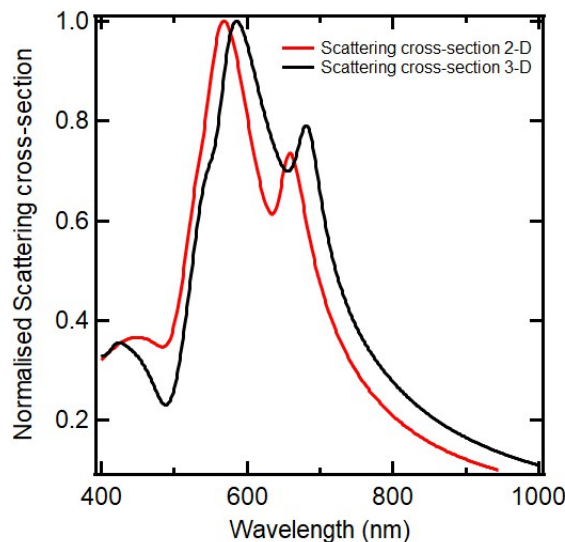


FIGURE 5.6: Normalised scattering cross-section for AgNW ($R=30$ nm) obtained using 3-D (black curve) and 2-D FDTD simulation (red curve).

5.3 Polarimetry of gap plasmon modes and SERS

Confined $(1x)$ and $(2x)$ modes allow for SERS from BPT molecules sandwiched inside NWoM nanocavity. Fig. 5.7(a) shows two simulated near-electric field profiles (E_z) for NWoM with $R=45$ nm at the excitation wavelength ($\lambda=633$ nm) and wavelength corresponding to the most intense SERS peak for BPT molecules ($\lambda=710$ nm at 1585 cm^{-1}). Given that field is confined inside the nanogap at both excitation and SERS wavelengths, BPT provides robust and strong SERS signals from the nanocavity.

SERS spectra for two polarisation axes of analyser corresponding to $\phi=90^\circ$ (blue curve) and $\phi=0^\circ$ (red curve) respectively are plotted in Fig. 5.7(b). Three characteristic SERS peaks from BPT molecules at 1080 cm^{-1} (C–H rocking mode), 1256 cm^{-1} and 1586 cm^{-1} (two in-plane stretching of benzene rings) are clearly visible in the spectra with the most intense peak at 1586 cm^{-1} [178]. Both DF, SERS intensities are polarised along $\phi=90^\circ$ (perpendicular to AgNW) with minimal intensity counts along $\phi=0^\circ$ (along the AgNW axis). Complete polarisation resolved DF scattering intensity is plotted as a function of wavelength (λ (nm) along x -axis) and ϕ (in $^\circ$) along y -axis) (Fig. 5.7(c)). SERS intensity as function of Raman shift (in cm^{-1}) and ϕ (in $^\circ$) is shown in Fig. 5.7(d). It can be seen that both SERS intensity and plasmon modes are polarised perpendicular to long-axis of AgNW. The narrow gap plasmon modes are visible

for a range of ϕ angles, specifically when analyser axis is closer to the angles perpendicular to the NW. Correspondingly, SERS signal is also maximum for the same range of angles.

It should be noted that the Stokes background in SERS spectra is also polarised as the SERS emission. For a better understanding, a polar plot of DF intensity for (1x) mode, SERS and SERS background counts at 1585 cm^{-1} as a function of analyser angle is shown in Fig. 5.7(e). DF, SERS and SERS background intensity counts are maximum along the perpendicular direction from the AgNW long axis. It can be concluded that both SERS from the molecules inside the NWoM nanocavity and SERS background outcouple into the far-field by coupling to the gap plasmon modes with the same polarisation signatures.

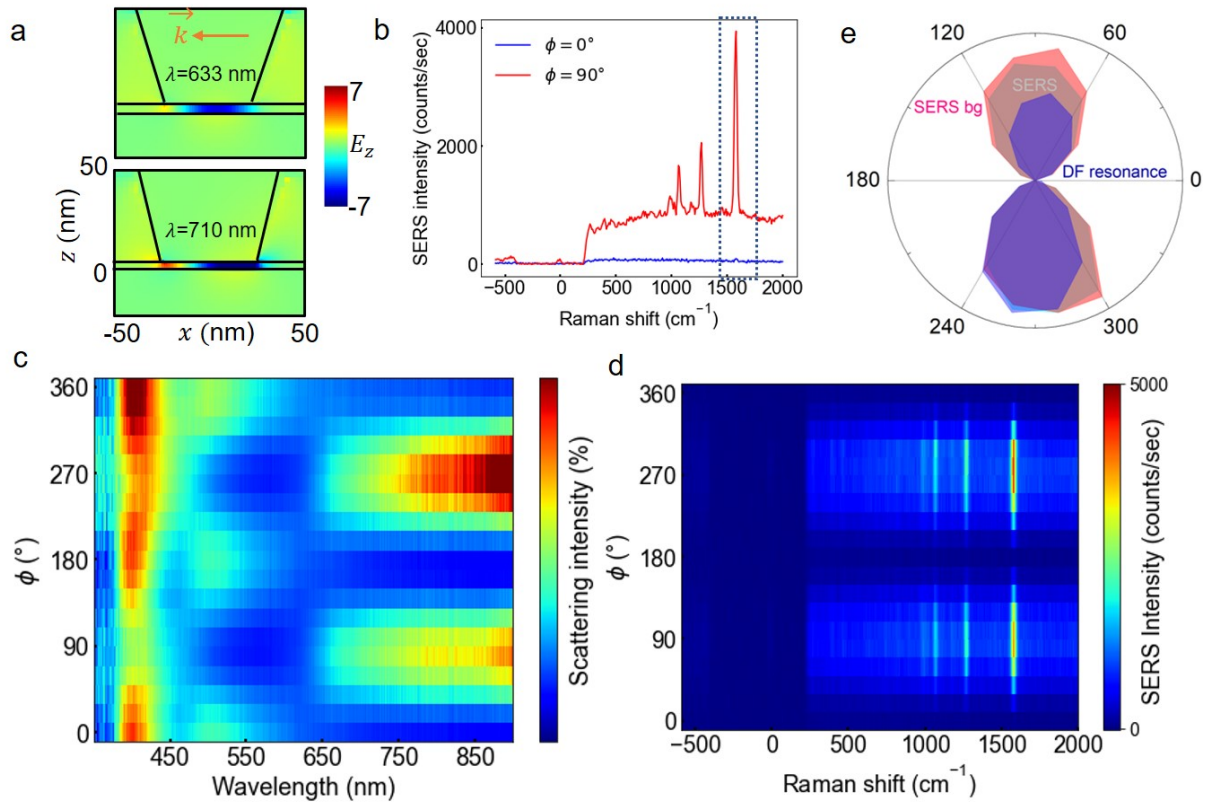


FIGURE 5.7: (a) Simulated near-electric field (E_z) profiles for NWoM with $R=45\text{ nm}$ at the excitation wavelength (633 nm) and at wavelength corresponding to the most intense SERS peak of BPT molecules (at 705nm, 1585 cm^{-1}). (b) SERS intensity plotted as a function of Raman shift for two analyser angles corresponding to $\phi=0^\circ$ (red curve) and $\phi=90^\circ$ (blue curve). (c) DF scattering intensity as a function of wavelength (in nm) (d) SERS as a function of Raman shift (in cm^{-1}) for different analyser angles ranging from 0 cm^{-1} to 360 cm^{-1} . (e) Polar plot of DF (orange) scattering intensity of (1x) mode, SERS (blue) and SERS background (light yellow) intensities at 1585 cm^{-1} as a function of analyser angle.

5.4 Mapping gap plasmon modes along the 1-D extended plasmonic nanocavity

Having understood the modes and polarisation properties we focus on mapping the modes along the 1-D plasmonic nanocavity. Any defects or sub-nanometre spatial variations in nanocavity will change scattering in SERS intensities, so we perform correlated SERS and DF measurements on a single NWoM system. For all measurements the analyser is placed at $\phi = 90^\circ$ for maximum intensities. We map the SERS and DF at 12 different points along the length of the NWoM (Fig. 5.8(a) and (b)), with resolutions limited by the $\sim 0.5 \mu\text{m}$ diffraction limited spot of collection fibre and laser excitation. The Vertical axis in Fig. 5.8(a) and (b) represents the position along the AgNW (in μm) where DF and SERS measurements are recorded.

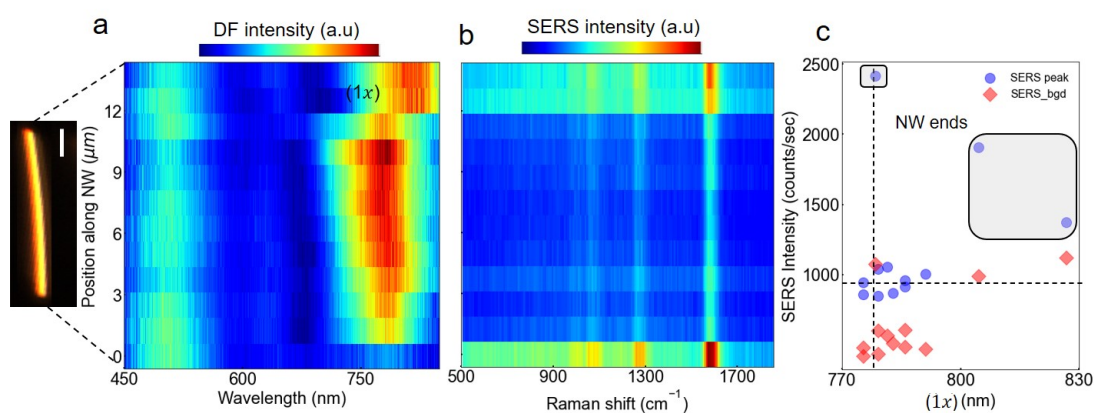


FIGURE 5.8: (a) DF scattering intensity vs wavelength (in nm) along the NW. Inset: DF scattering image with scale bar=100 nm of NWoM system. (b) SERS intensity vs Raman shift (cm^{-1}) for different positions along the length of AgNW. (c) SERS peak intensity and SERS background at Raman wavelength (1586 cm^{-1}) as a function of (1x) resonance position (in nm) along the length of AgNW. Black region showing SERS intensities at NW ends.

In DF scattering maps (1x), the mode resonance positions fluctuate along the length of nanocavity. This arises from the non-uniformity of the extended gap contents (Fig. 5.8(a)) with the mean peak centred at 778 nm, so that correspondingly fluctuations in SERS are also observed. We correlate these non-uniformities inside the nanogap to the SERS intensities from the nanocavity (Fig. 5.8(b)). Dashed black lines along x and y axis show the average resonance position of (1x) mode at 778 nm and corresponding SERS intensity of 1000 counts/sec from the NWoM nanocavity. We note two different kinds of variations, which here are classified as NW ends and non-uniformities.

At the ends of the AgNW strong redshifts of the (1x) mode is observed. It has been reported that synthesised AgNWs with regular pentagonal geometry possess tapered cross-sections at the wire ends along with the wires having regular pentagon geometry depending on the molar ratio of silver nitrate and PVP used during the polyol synthesis [162]. SEM images of AgNWs with tapered and regular pentagonal cross-section from the same sample are shown in Fig. 5.9. Note that we do not observe the redshift at one or both end of AgNW for every NWoM system,

indicating different geometrical termination for different NWs. Fig. 5.10 shows the DF and SERS correlation along the length of a different NW not showing redshift for (1x) mode position at the end of NW.

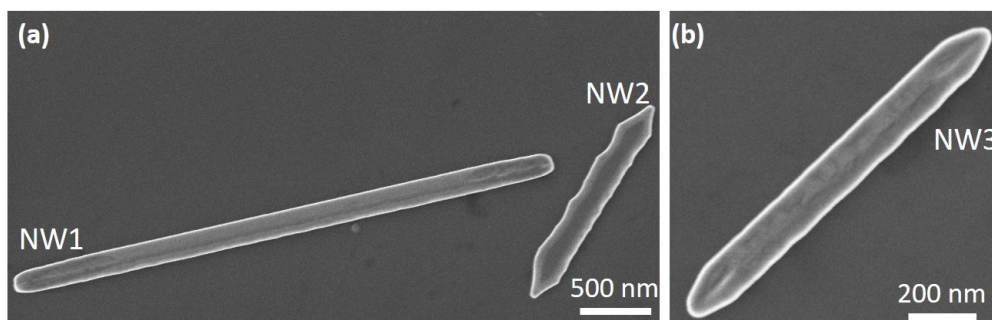


FIGURE 5.9: (a) SEM images of two AgNWs within the same solution showing different cross-sections. NW1 having regular pentagon whereas NW2 having tapered cross-section. NW2 also show non-uniform coating of PVP at the surface of NW. (b) SEM image of NW3 having tapered cross-section however uniform coating of PVP at the surface.

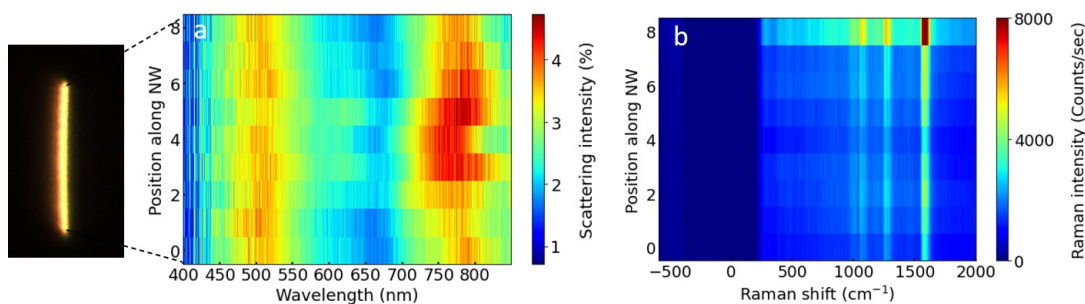


FIGURE 5.10: (a) DF scattering intensity vs wavelength (in nm) along the NW. Inset: DF scattering image of NWoM system. (b) SERS intensity vs Raman shift (cm^{-1}) for different positions along the length of AgNW.

Along the length of the AgNW, we observe spectral wandering of the (1x) resonance position by ± 10 nm from the average resonance wavelength of 778 nm. This is accounted for by surface non-uniformities and defects due to unreacted silver nanoparticles in solution or non-uniform coating of polyvinylpyrrolidone (PVP). These surface non-uniformities result in non-uniform near-fields, since they are enhanced in the 1-D nanogap cavity, with for gaps < 5 nm, are very sensitive to the gap contents. This is also reflected in SERS intensities. While it is hard to see how the nanogap spacing itself can vary given the mechanical strength of the nanowires, it is likely that the PVP thickness spanning this gap can vary (either in thickness or in density). Simulations show that this would account for the observed mode spectral variations. This also accounts for a weak dependence of DF to the SERS intensity of BPT molecules assembled on the Au mirror with the (1x) spectral position (Fig. 5.8(c)). The lack, having of systematic weaker influence on the SERS from the PVP inhomogeneities on at the AgNW surface suggests that in/out coupling, which is dependent on detuning of the laser and SERS from the resonant mode, does not dominate the signal variations observed.

5.5 Conclusion

In conclusion we show that mapping of polarisation resolved DF and SERS measurement can be used as a tool to reveal the spatial changes of the nm scale inside the nanogap. We correlate these spatial changes to resultant SERS signal variation inside the extended nanogap between the AgNW and Au mirror. We are able to track the SERS signal variation at the scale of < 3 nm change inside the nanogap for NWoM system. SERS signal from different positions of nanocavity increases significantly when the mode redshifts (>50 nm) inside the nanogap.

The crucial aspect of non-uniformity of surface coating which affects localized plasmonic modes along the nanocavity which is usually neglected however plays a significant role. Our results would provide insight to characterization of the non-uniformities of surface using far-field scattering which will impact on cavity enhanced molecular emission, spin-orbit interaction, optical antenna and waveguiding.

Chapter 6

Non-reversible local structural change inside 1-D extended nanogap

In this chapter, we observe local morphological changes on the surface of silver nanowire (AgNW) placed on a gold (Au) mirror forming nanowire over mirror (NWoM) nanocavity. These atomic scale structural changes are created by purely optical means using high power laser excitation and detected by recording millisecond time evolution of surface enhanced Raman scattering (SERS) from the molecules sandwiched inside the nanocavity. The work presented in this chapter is performed at Nanophotonics group, University of Cambridge with Prof. Jeremy Baumberg.

6.1 Introduction

The atomic scale restructuring or morphological changes on the surface of metal nanostructures are very important for understanding catalysis [179–181], molecular electronics [182] and interfacial effects for enhanced surface chemistry [183, 184]. Traditionally techniques such as scanning tunneling microscopy [185], transmission electron microscopy [186] are utilised for atomic scale mapping at low temperatures. However it is not possible to use these techniques at room temperature in ambient conditions.

Recently, there have been studies on atomic-scale surface protrusions of a faceted Au nanoparticle placed on a mirror (NPoM) [82, 88]. These protrusions have been induced and detected optically by laser excitation, however are known to be transient in nature with no long term changes on the surface of metal nanostructures. The ability to create local atomic scale non-reversible changes to modify surface morphology of the metallic nanostructures using non-invasive tools at room temperature is still lacking.

We show non-reversible structural changes on the surface of chemically prepared AgNW created by purely optical means using excitation of high power laser beam. We utilise NWoM to provide strong field confinement (plasmonic hot-spot) inside the extended gap along the length of NW [33, 76, 187] which induce surface protrusions on the surface of AgNW. We show that these atomic scale protrusions are locally excited at specific excitation spot along the length of NW. These morphological changes would change near-field inside the extended nanogap which is detected by millisecond time evolution of surface enhanced Raman scattering (SERS) intensity from molecules sandwiched inside the nanocavity. Along with the SERS, we study

Dark-field (DF) scattering spectrum to correlate changes to gap thickness which would be evident in DF (1 x) cavity mode resonance position for NWoM nanocavity. The nanogap thickness reduction (redshift of resonance position of the order of 3 nm) is reported and confirmed that these protrusions are stable and non-reversible in nature. Presented findings could pave the way towards an atomic scale lithography for plasmonic nanostructures using metallic nanocavities.

6.2 NWoM nanocavity assembly and millisecond SERS evolution from nanocavity

NWoM assembly process with a molecular layer placed inside the nanocavity follows the same procedure as described in previous chapter. A chemically prepared AgNW with characteristic Polyvinylpyrrolidone (PVP) coating having pentagon cross-section [163] and radius ' R ' is placed on a template stripped Au mirror forming NWoM nanocavity. A monolayer of Biphenyl-4-thiol (BPT) molecules self-assembled onto the mirror together with PVP forms the nanogap ' d ' for the nanocavity. Cross-sectional schematic of one such NWoM nanocavity with chemical structure of gap contents BPT and PVP molecule are shown in Fig. 6.1(a).

Electric near-field profiles for Gaussian wave excitation ($\lambda = 632.8$ nm) are simulated using 2-D finite difference time domain (FDTD) for an AgNW ($R = 40$ nm) elongated along y axis placed on a mirror with nanogap ' $d = 5$ nm' (Fig. 6.1(a)). Profiles show strong field confinement inside the nanogap along z -direction (Fig. 6.1(d)). Coupling into this field would result in good and robust SERS signal from BPT molecules placed inside the NWoM nanocavity. High SERS intensity would enable us to watch millisecond time dynamics of the signal with good signal to noise ratio during continuous laser exposure [88].

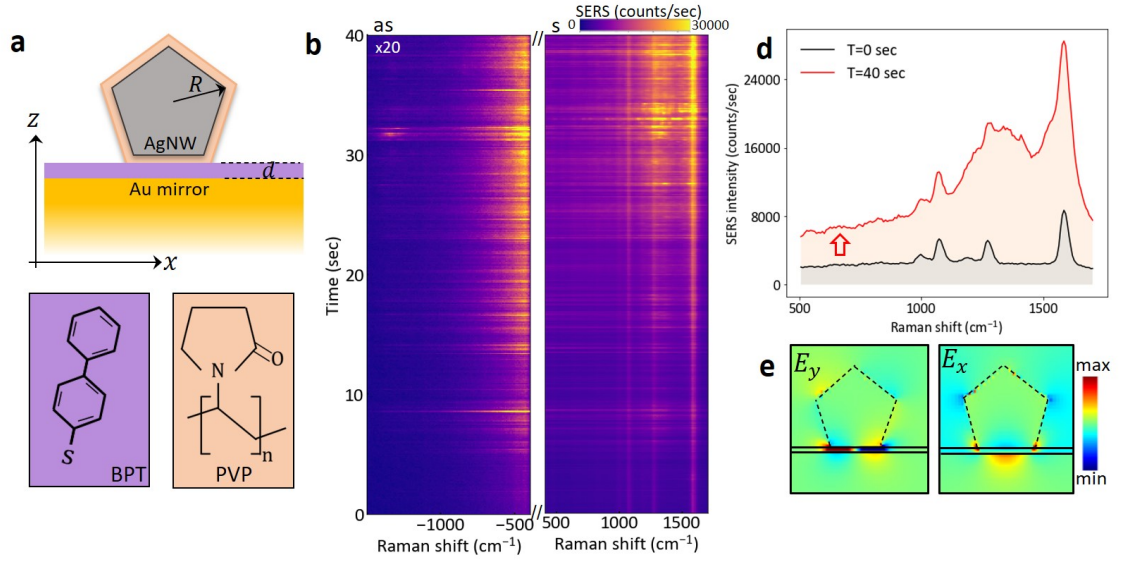


FIGURE 6.1: (a) Cross-sectional schematic of AgNW extended along y -axis placed on a template stripped Au mirror. Characteristic PVP coating on AgNW and self-assembled monolayer of BPT molecules on the mirror together forms the nanogap ' d ' between the silver nanowire and mirror. Inset: Chemical structure of the gap contents BPT and PVP. (b) SERS (stokes ' s ' and anti-stokes ' as ') time trace for BPT molecules when NWoM nanocavity is excited with 633 nm laser polarised perpendicular to the AgNW (along x -axis). Colorbar (counts/sec) shows increasing SERS intensity as a function of time. (c) SERS intensity plotted as a function of Raman shift (in cm^{-1}) at $t=0$ sec (black curve) and $t=40$ sec (red curve). (d) Simulated near-field profile of Electric field E_z and E_x for NWoM nanocavity ($R=40$ nm and $d=5$ nm) excited using a gaussian field with 633 nm wavelength polarised perpendicular to AgNW (x -direction).

NWoM geometry is illuminated with a diffraction limited spot of $\lambda=632.8$ nm using 100x 0.9 objective lens and scattered light from the geometry is collected using back-scattered geometry (Fig. 2.11). The polarisation of the excitation is kept along the perpendicular direction to AgNW (x -direction) for maximum field confinement inside the nanogap. For continuous laser exposure (Power $P=2.5$ mw) for time $t=40$ sec at the excitation spot along the length of NW, SERS time trace is recorded by taking 400 SERS spectra for 0.1 sec acquisition time for each spectrum. Time trace for stokes (s) and anti-stokes (as) SERS intensities from BPT molecules inside the nanogap as a function of Raman shift (in cm^{-1}) is shown in Fig. 6.1(b) where colorbar represents SERS intensity in counts/sec. The anti-stokes intensities are multiplied by a factor of 20 for representation on the same scale as stokes intensities. Three prominent characteristic BPT SERS lines at 1080 cm^{-1} (C–H rocking mode), 1256 cm^{-1} and 1586 cm^{-1} (two in-plane stretching of benzene rings) are clearly visible in each spectrum. It is to note that during the time trace SERS intensity for each spectrum is increasing with time. SERS spectra as a function of Raman shift for time $t=0$ sec (black curve) and $t=40$ sec (red curve) (Fig. 6.1(d)) show the SERS signal at 1586 cm^{-1} Raman peak and as well as background (red arrow) evolution with intensity increment of more than 200%.

6.3 Power dependence of SERS evolution and correlation with cavity plasmon mode

Observed increment of SERS signal from NWoM nanocavity should relate to the enhanced near-field ($\vec{E}_{max}$) inside the nanogap. As reported previously for metal-insulator-metal (MIM) nanocavities [188], ($\vec{E}_{max}$) inside the gap with thickness ' d ' and effective refractive index ' n_g ' is given by [172]

$$\frac{E_{max}^2}{E_0^2} \propto \frac{n_g R^2}{d^2} \quad (6.1)$$

here, E_0 is the incident electric field and R is the radius of the metallic nanostructure placed on a mirror forming MIM nanocavity. In our case, the required change of the refractive index for this 200% increased SERS signal would be huge. Since, the radius of the NW is fixed, there is a possibility of diffusion of Ag atoms near the hot-spot during the high-power laser exposure which decrease the nanogap to account for the increased near-field. These type of diffusion of surface atoms at room temperature although transient are reported in the past for NPoM nanocavities [88].

However, if these atomic scale changes are optically generated due to laser exposure, there should be dependence on the incident laser power (energy barrier for surface atoms to diffuse). Along with the power dependence, cavity plasmon mode should show redshift in DF scattering spectra. (1x) gap plasmon mode for NWoM nanocavity in DF scattering spectra has been shown to be extremely sensitive to the local changes inside the nanogap. It has been shown in the previous chapter that mode redshifts as the gap decreases (Chapter 5).

Extended gap along the length of NW allows us to probe four different locations along the length of same AgNW with four different laser power ($P = 0.5 - 2.0$ mw) for $t = 50$ sec. At each location SERS time trace (Fig. 6.2(a)-(d)) is recorded by taking 500 SERS spectra for 0.1 sec acquisition time. For $P = 0.5$ mw, SERS time trace (Fig. 6.2(a)) shows the constant SERS intensity as a function of time, which suggests no changes inside the gap or protrusions on NW surface. We also record the DF scattering spectra from the cavity before and after SERS time traces. At this power, (1x) gap plasmon mode resonance position marked by dotted black line in DF scattering spectrum (Fig. 6.2(i)) does not change from $t = 0$ sec (blue curve) and $t = 50$ sec (red curve).

For higher powers, SERS time traces and DF scattering spectra are given in Fig. 6.2(b) and (ii) for $P = 1.0$ mw, Fig. 6.2(c) and (iii) for $P = 1.5$ mw, Fig. 6.2(d) and (iv) for $P = 2.0$ mW respectively. It can be seen that SERS signal intensity increases with time and correspondingly (1x) plasmon mode also redshifts. White arrows in SERS time trace represent time t , where SERS intensity counts are increased by a factor of 2 in comparison to SERS counts at $t = 0$ sec ($SERS(t) = 2SERS(0)$). The positions of the white arrows from Fig. 6.2(b)-(d) as laser power is increased indicate that high laser power results in increased rate of SERS enhancement from NWoM nanocavity. Similarly, redshift in the (1x) resonance position also increases as a function of laser power (Fig. 6.2(i)-(iv)) which can be seen from the black arrows showing the redshift

of the NWoM cavity mode.

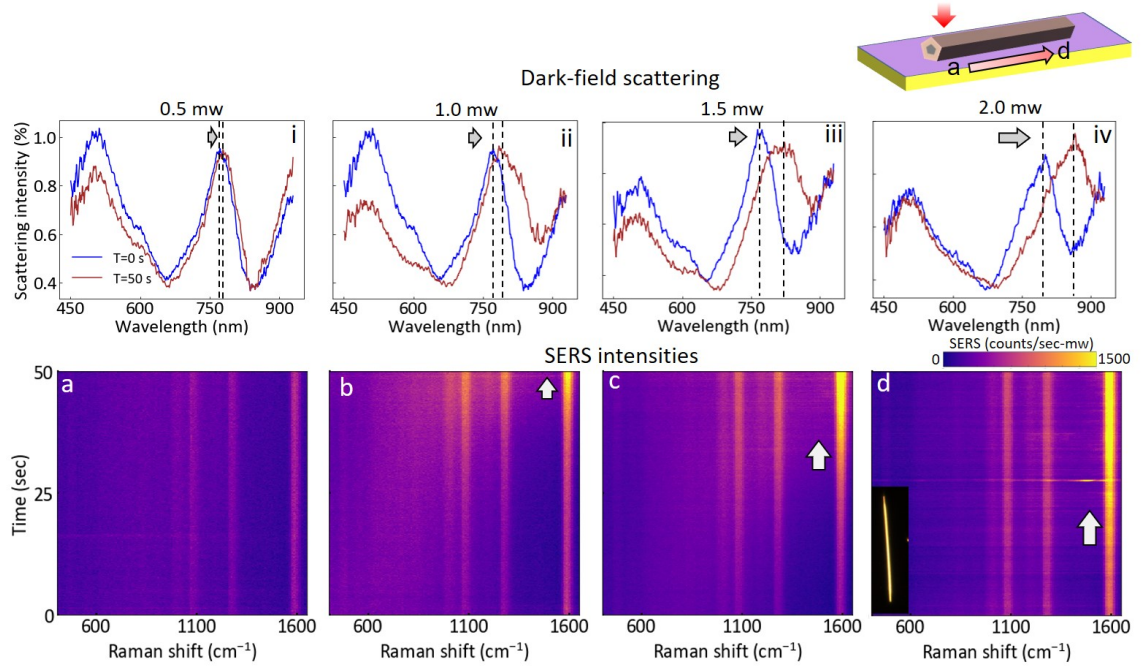


FIGURE 6.2: SERS time trace from four different locations along the length of AgNW where NWoM cavity is excited with (a) 0.5 mW (b) 1.0 mW (c) 1.5 mW and (d) 2.0 mW incident laser power. Colorbar is in counts/mW-sec. White arrows represent the spectra at time t , where SERS intensity counts at 1586 cm^{-1} are increased by a factor of 2 in comparison to SERS counts at $t=0 \text{ sec}$ ($\text{SERS}(t)=2*\text{SERS}(0)$). Inset: Optical image of NWoM system used for measurements. DF scattering spectra at the same four locations recorded for (e) 0.5 mW (f) 1.0 mW (g) 1.5 mW (h) 2.0 mW incident laser power. Black dotted lines show the resonance position of NWoM nanocavity mode before and after the SERS time trace. Black arrow shows redshift of NWoM mode from $t=0 \text{ sec}$ (blue curve) to $t=50 \text{ sec}$ (red curve).

For a quantitative measurement at each incident power, average SERS background (Fig. 6.3(a)) and peak intensity counts (Fig. 6.3(b)) at 1586 cm^{-1} are plotted as a function of time. Excluding $P=0.5 \text{ mW}$ (blue curve), for $P=1.0 \text{ mW}$ (magenta curve), 1.5 mW (yellow curve) and 2.0 mW (cyan curve) both SERS background and SERS peak can be seen increasing with time. This power threshold ($P=1 \text{ mW}$ for shown NWoM system) for SERS increment is found to vary between $0.5 - 1 \text{ mW}$ for different NWoM systems.

(1x) cavity mode resonance position before (red pentagon bullet point) and after (yellow pentagon bullet points) the SERS time trace at four locations as a function of power are plotted in Fig. 6.3(c). Similar to SERS intensity, redshift of the mode position can be seen increasing as power increases with redshift $> 60 \text{ nm}$ at $P=2.0 \text{ mW}$. To estimate the gap thickness change to account for this large redshift, we calculate the scattering cross-section for NW with $R=40 \text{ nm}$ placed on Au mirror using 2-D finite difference time domain simulations (blue squares). Calculated resonance position of (1x) mode matches well with the experimentally obtained resonance position for $d=5 \text{ nm}$ at $P=0.5 \text{ mW}$. It is to note that experimentally obtained resonance position for $P=2.0 \text{ mW}$ after the SERS time trace is closer to the calculated resonance position

corresponding to $d = 3$ nm. This data strongly suggests that local morphological modifications in the gap thickness (~ 2 nm) are dependent on the power of incident light.

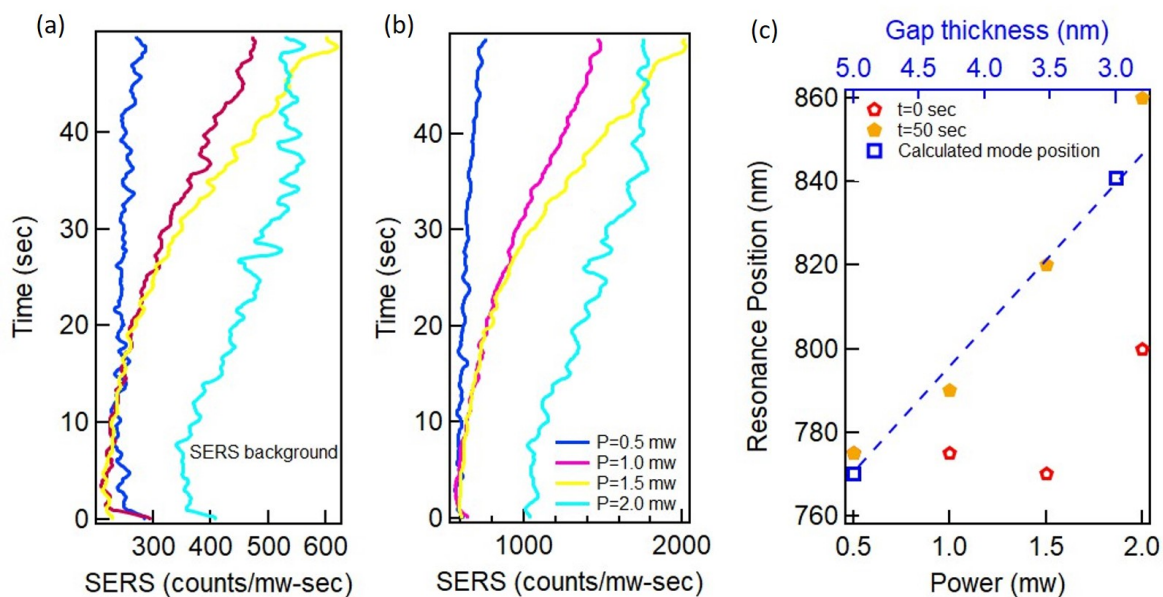


FIGURE 6.3: (a) Average SERS background (b) SERS peak intensity counts at 1586 cm^{-1} as a function of time for during SERS time trace for $P = 0.5$ mw (blue), $P = 1.0$ mw (magenta), $P = 1.5$ mw (yellow), $P = 2.0$ mw (cyan) respectively. (c) $(1x)$ mode resonance position before (red bullet points) and after (yellow bullet points) SERS time trace at four different points along the NWoM nanocavity as a function of incident power (mw). Blue square points show the calculated resonance positions of the $(1x)$ mode for NWoM system as a function of gap thickness using 2-D FDTD simulations.

To further investigate the scale of this local modification of the gap size along the length of NWoM nanocavity, a specific location (approximately middle position) along the length of AgNW is excited with laser power $P = 2.5$ mw. SERS time trace is recorded to ensure the local structural changes by increment in SERS intensity. SERS intensity from different position of the AgNW (at $P = 1$ mw) are compared before and after making these local changes at the specific location along the length of AgNW.

SERS spectra from 7 different positions along the length of AgNW with laser power $P = 1.0$ mw (below the threshold) shows constant average SERS intensity from all the positions (Fig. 6.4(a)). Specific location along the length of AgNW is excited with laser power $P = 2.5$ mw for time $t = 50$ sec. Increasing SERS signal with time (Fig. 6.4(b)) ensures local modifications inside the gap. Colorbar shows the time ($t = 0$ -50 sec) where each SERS spectrum is collected with acquisition time of 0.1 sec. The SERS spectra are again collected from different position along NWoM nanocavity (Fig. 6.4(c)). It can be seen that SERS spectra collected from near the middle position still shows high SERS intensity in comparison to other positions. This implies that local structural changes inside the cavity are non-reversible and locally excited at the excitation spot.

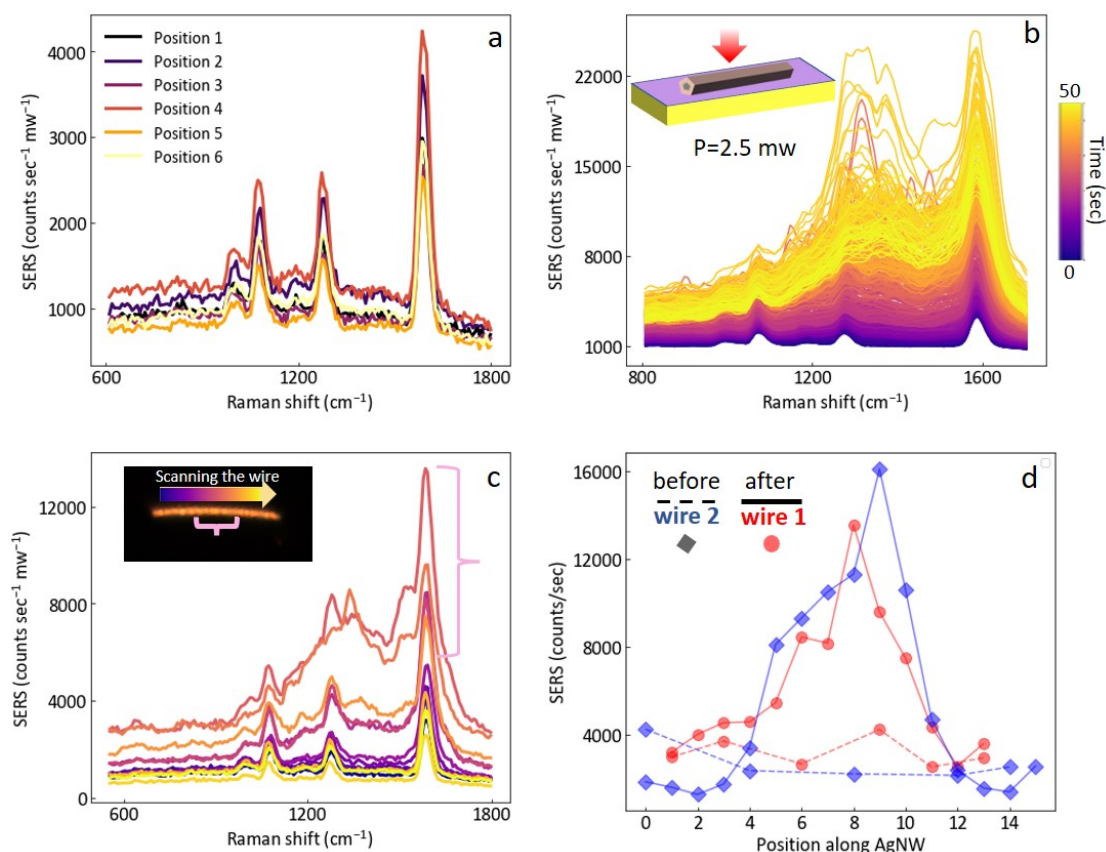


FIGURE 6.4: (a) SERS spectrum from different positions along the length of AgNW for a fixed laser power $P=1$ mw. (b) SERS spectra as a function of Raman shift (cm^{-1}) upon the excitation of middle position with a laser Power= 2.5 mw. Colorbar represent the time evolution of 500 different SERS spectrum during the laser exposure. (c) Scanning the SERS signal from NWoM nanocavity after the time trace at the middle position. SERS spectrum from different positions along the length of AgNW for a fixed laser power= 1mw. Optical image of NWoM system shown in the inset of Fig. 6.3(c). (d) Average SERS intensity from different position along NWoM before (dotted line) and after (solid) the middle position SERS time trace for two NWs (NW1 in red curve and NW2 in blue curve).

6.4 Calculation of NWoM nanocavity temperature

Our data strongly supports that enhanced SERS emission from the nanocavity is due to the diffusion of the Ag atoms inside the nanogap creating local morphological changes set by the incident laser beam. However, we have to exclude other possibilities such as melting of PVP coating on AgNW or reorganisation and binding of PVP polymer molecules with Ag atoms inside the nanogap during laser exposure [189, 190]. While the first possibility would lead to the SERS enhancement but as discussed earlier it would not be able to explain the large redshift in DF scattering spectra before and after the SERS time trace. The other possibility however would require the near-field scanning of the nanogap between AgNW and mirror which is very

difficult to achieve. However, an idea about the local temperature inside the gap would help us eliminate the role of heat in SERS enhancement.

For an estimation of the temperature, we utilise Raman thermometry of plasmonic nanostructures [191]. One of the method determines local temperature experienced by molecules by taking the ratio of anti-stokes and stokes SERS peak intensities [192, 193]. However, this method does not provide the temperature of the plasmonic nanostructure and requires additional calibration methods. It has been shown that anti-stokes SERS background intensity exhibits exponential decay given by the thermal distribution of electron-hole pairs in metals with occupancy ' n ' given by [194, 195]:

$$n = \frac{1}{\exp(\frac{-\Delta E}{k_B T}) - 1} \quad (6.2)$$

here, ΔE is the energy difference between the excitation laser and inelastically scattered light, k_B is the Boltzmann constant and T is the temperature of the system.

The strong dependence on temperature provides a non-invasive tool for measuring temperature of plasmonic nanostructures using anti-stokes SERS exponential decay at a particular temperature ' T ' [196, 197]. This equation can be modified to get rid of wavelength dependent scattering due to plasmon resonances of NWs in wavelength range of interest [198]. Normalisation of the anti-stokes intensity ($I(\Delta E)_{Au}$) at a particular temperature ' T_{Au} ' with intensity ($I(\Delta E)_0$) at room temperature (T_0) can be given as

$$\frac{I(\Delta E)_{Au}}{I(\Delta E)_0} = \frac{\exp(\frac{-\Delta E}{k_B T_0}) - 1}{\exp(\frac{-\Delta E}{k_B T_{Au}}) - 1} \quad (6.3)$$

By taking the ratio of intensities at anti-stokes wavelength at a given time with intensities at room temperature and fitting the above equation provides T_{Au} for NWoM nanocavity. For our experiment, anti-stokes time trace for a laser excitation of $P = 2.5$ mw for NWoM nanocavity is given in Fig. 6.5(a) and the calculated temperatures for each SERS spectra in the time trace as a function of time is given in Fig. 6.5(b). It can be seen from the graph that average temperature value of the NWoM system does not exceed beyond 300K. The calculated values of temperatures are not high enough to melt the PVP coating on AgNW.

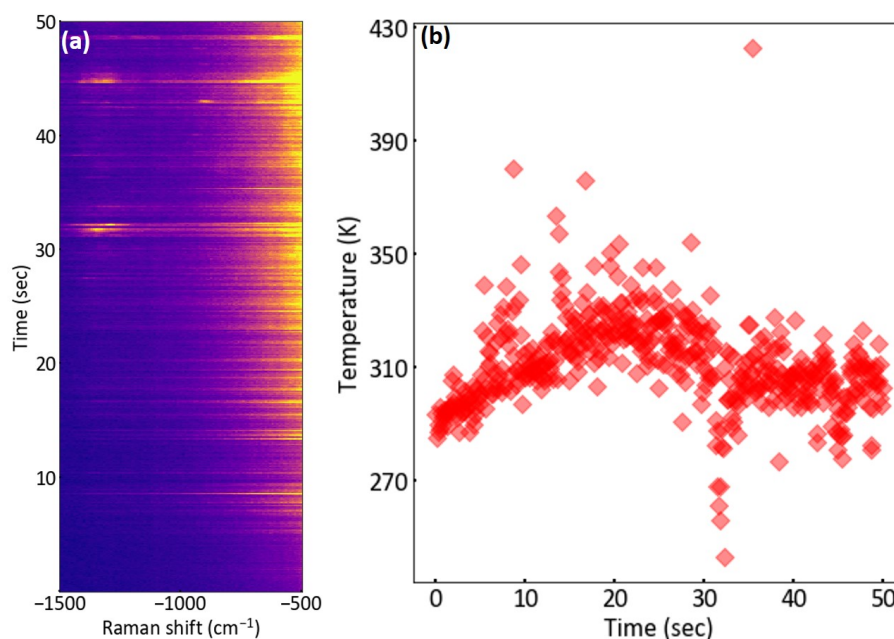


FIGURE 6.5: (a) SERS anti-stokes time trace for laser power $P = 2.5$ mw at a fixed location along the NWoM nanocavity. (b) Calculated temperature (in kelvin) of the NWoM system from the anti-stokes SERS spectra as a function of time.

6.5 Dual laser excitation for NWoM nanocavity

It is also important to confirm that structural changes which result in high SERS intensity from NWoM nanocavity are due to atoms diffusing from AgNW not from template stripped Au mirror. To confirm, NWoM nanocavity is excited with two laser wavelengths ($\lambda = 632.8$ nm, 785 nm) simultaneously at the same location (Fig. 6.6(a)). A low power $\lambda = 785$ nm laser excites the NWoM system to act as a probe beam to scan the changes made by a high laser power ($P = 2.5$ mw) of $\lambda = 632.8$ nm.

SERS time trace is collected for a total of $t = 50$ sec. BPT SERS from $\lambda = 632.8$ nm (red curve) and $\lambda = 785$ nm (purple curve) at time $t = 0$ sec (Fig. 6.6(b)) shows high SERS intensity for $\lambda = 632.8$ nm. This can be attributed to low power and poor collection efficiency of the detector at the wavelengths corresponding SERS lines for $\lambda = 785$ nm excitation. Fig. 6.6(c) shows the BPT SERS from $\lambda = 632.8$ nm (red curve) and $\lambda = 785$ nm (purple curve) at time $t = 50$ sec. Increased and consistent three SERS intensity for SERS lines from both the $\lambda = 632.8$, 785 nm excitation can be seen at $t = 50$ sec. One additional peak is observed around 1330 cm^{-1} for 632.8 nm excitation which can be attributed to breathing mode of pyrrole ring for C-H stretching in PVP. It can be seen that the molecules are still attached to Au mirror and thus providing consistent SERS from the nanocavity.

Fig. 6.6(d) shows full SERS spectrum collected at $t = 0$ sec (purple curve) and $t = 50$ sec (red curve). For $t = 0$ sec, 632.8 nm SERS lines are more intense than 785 nm SERS lines as already discussed. 632.8 nm laser act as a pump beam to create the local morphological changes as can be seen from the more than 200% change in the SERS intensity. It is interesting that with

low powers, SERS intensity for 785 nm also increases. This reconfirms that structural changes results in reduced gap thickness and enhanced near-field which can be probed by using a low laser power excitation. Molecules are still attached to the Au mirror throughout this process.

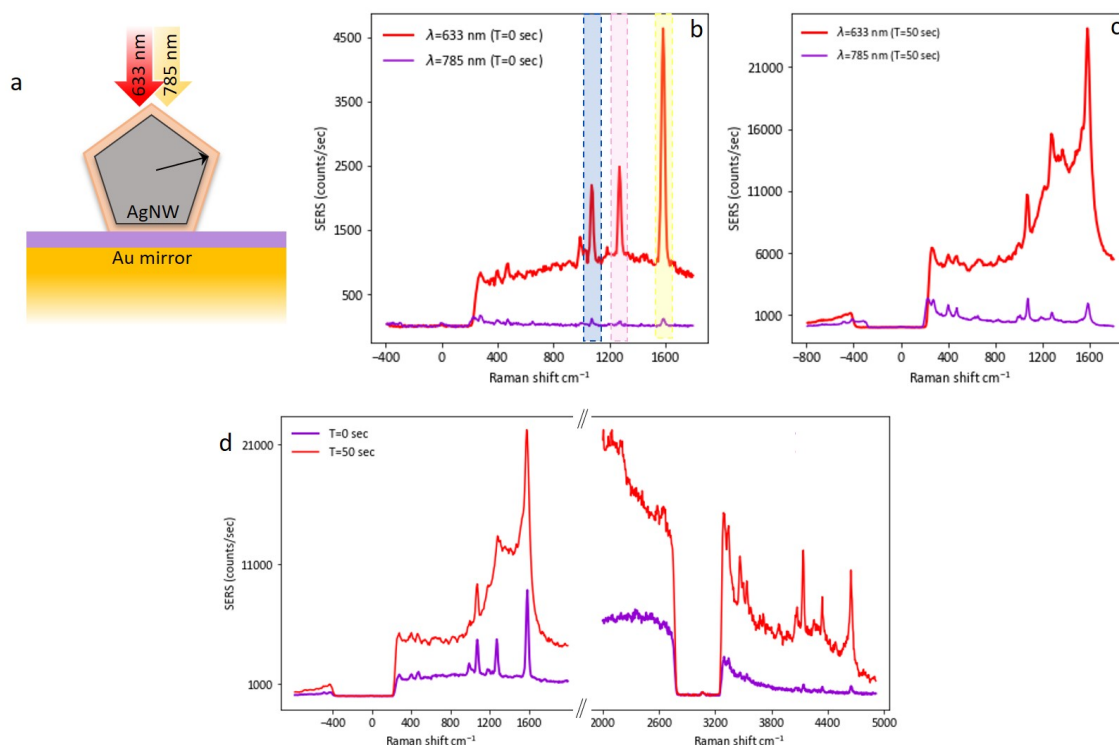


FIGURE 6.6: (a) Schematic of NWoM nanocavity with dual wavelength excitation. Two lasers with high power ($P = 2.5$ mw) 632.8 nm laser wavelength and low power 785 nm laser wavelength are exciting the NWoM system using the same objective lens in upright microscope configuration. (b) SERS spectrum collected at time ($t = 0$ sec) showing SERS lines with $\lambda = 632.8$ nm (red curve) and with $\lambda = 785$ nm (purple curve). (c) SERS spectrum collected at time ($t = 50$ sec) showing SERS lines with $\lambda = 632.8$ nm (red curve) and with $\lambda = 785$ nm (purple curve). (d) SERS with full wavelength range at $t = 0$ sec (purple) and $t = 50$ sec (red curve).

6.6 Conclusion

In conclusion, we report the increasing molecular emission as a function of time upon excitation with high laser power from the NWoM nanocavity. Power dependence and simultaneous DF scattering measurements indicate a power threshold for the incident laser to observe such enhanced emission from the nanocavity. This suggests local structural changes inside the nanogap originated optically which decreases the gap thickness. Varying gap thickness would result in changed near-field strength inside the cavity which is evident in varying SERS intensity as a function of time. Furthermore, we measure temperature of the system using anti-stokes Raman thermometry to rule out the role of heat generated at these laser powers inside the nanogap to melt the PVP coating and produce high SERS intensities. It is found out that temperature increase inside the nanogap is not sufficient for PVP to melt and ensures that local atomic scale

changes originated by purely optical means. Our results indicate the possibility of controlled atomic scale structural change on the surface of plasmonic AgNW in ambient conditions at room temperature.

Chapter 7

Conclusions and Future Directions

In conclusion, this thesis focuses on understanding the subwavelength propagation and confinement of light in plasmonic silver nanowire (AgNW). Upon excitation with light at one end, surface plasmon polaritons (SPPs) waveguiding and directional out-coupling at the other end, makes AgNW ideal for energy transport beyond diffraction limit to act as an optical antenna for nanophotonic devices. We intensely study the transverse spin and associated spin-momentum locking of SPPs excited in AgNW. Although chemically prepared AgNWs (used for experiments) with pentagonal cross-section, single crystalline nature and smooth facets supports low surface scattering losses during SPP propagation, the inherent losses associated with metal absorption limits their practical applications. We further show that coupling AgNW with a dielectric microsphere (μ S) could act as a hybrid metallo-dielectric optical antenna to repress the losses associated with metallic nanostructures. A self-assembled AgNW- μ S antenna could channel high quality factor modes supported by dielectric μ S into AgNW through SPPs overcoming the challenge of mode confinement at subwavelength scale. All experiments are performed on a home-built dual channel microscope with both forward and backward far-field scattering in real and Fourier plane imaging/spectroscopy. Next, confinement of light has been pushed from the surface of the AgNW to few nm (upto 5 nm) inside the gap between NW and mirror using NW over mirror (NWoM) nanocavities. Polarisation of the plasmon modes supported by the NWoM nanocavity and their correlation with the molecular emission from molecules sandwiched inside the cavity is studied. Lastly, we explore the possibility of atomic scale lithography on the surface of AgNW at room temperature in ambient conditions using NWoM nanocavity.

Our study would play an important role in understanding the plasmon propagation in AgNW and cavity electrodynamics for NWoM nanocavities. AgNWs have been utilised for various applications such as strong coupling, non-linear optics, single photon sources and many more. We anticipate that our study would add to more complete description and fundamental understanding of these effects, specifically emerging spin-hall effect in light due to transverse spin. Additionally, we hope our work on hybrid metallo-dielectric optical antennas will find relevance in soft-photonic platforms including miniaturized optical resonators and couplers.

In the following, I present a chapter-wise brief summary of the work and discuss future directions.

Transverse spin and associated spin-momentum locking of plasmon polaritons in a single crystalline silver nanowire

In chapter 3, we report an experimental observation of the transverse spin and associated spin-momentum locking of SPPs excited in a plasmonic single crystalline AgNW. In contrast to the SPPs excited in metal films, the electromagnetic field components of the evanescent SPP mode propagating along the long axis of the NW can decay along two longitudinal planes, resulting in two orthogonal transverse spin components. Analysis of the opposite circular polarisation components of the decaying SPP mode signal in the longitudinal plane reveals spin dependent biasing of the signal and hence the existence of transverse spin component. The corresponding transverse spin density in the Fourier plane reveals spin-momentum locking, where the helicity of the spin is dictated by the wave-vector components of the SPP evanescent wave. The results are corroborated with three-dimensional numerical calculations.

Future direction:

Leaky plasmon mode of AgNW provides the platform to probe optical spins in evanescent SPP waves using far-field imaging methods. It is really interesting that the spin has opposite helicity dictated by the SPPs wavevector's decay direction. This opens up a lot of interesting ideas and areas to be explored.

- The spin-momentum locking can be further explored for a complex network of AgNWs where directional spin coupling depending on SPP propagation and decay wavevector could lead to miniaturised photonics logic gates for optical spins.
- NWs with average diameter > 300 nm supports two leaky plasmon modes. Simultaneously exciting these two modes lead to helical wave pattern along the length of AgNW. The helicity of SPPs would lead to helical optical spins excited in AgNW. It would be really interesting to coat AgNW with chiral molecules and study their interaction with these helical spins propagating in AgNW. As a proof of principle, we investigate nanowire-nanoparticle (NW-NP) junction. We couple a single NP to a thick NW using self-assembly processes and excite the NW-NP junction. Excitation at the hot-spot (NW-NP junction) ensures the simultaneous excitation of two leaky plasmon modes supported by AgNW [36]. Fig. 7.1(a) shows the optical bright field image of the NW-NP junction where AgNW with average diameter 350 nm is coupled to a NP of 400 nm diameter. Real plane elastic scattering image (Fig. 7.1(b)) shows the helical SPPs propagating in AgNW upon excitation of the junction with $\lambda = 632.8$ nm laser. Interestingly, upon measuring the transverse spin (S_3) the helical pattern of SPPs optical spin propagating towards either end of NW from junction can be seen (Fig. 7.1(c)). In continuation along the same lines, we can also coat the molecules on the NP and investigate the interaction of molecular emission excited at the junction and optical spins of helical SPPs.

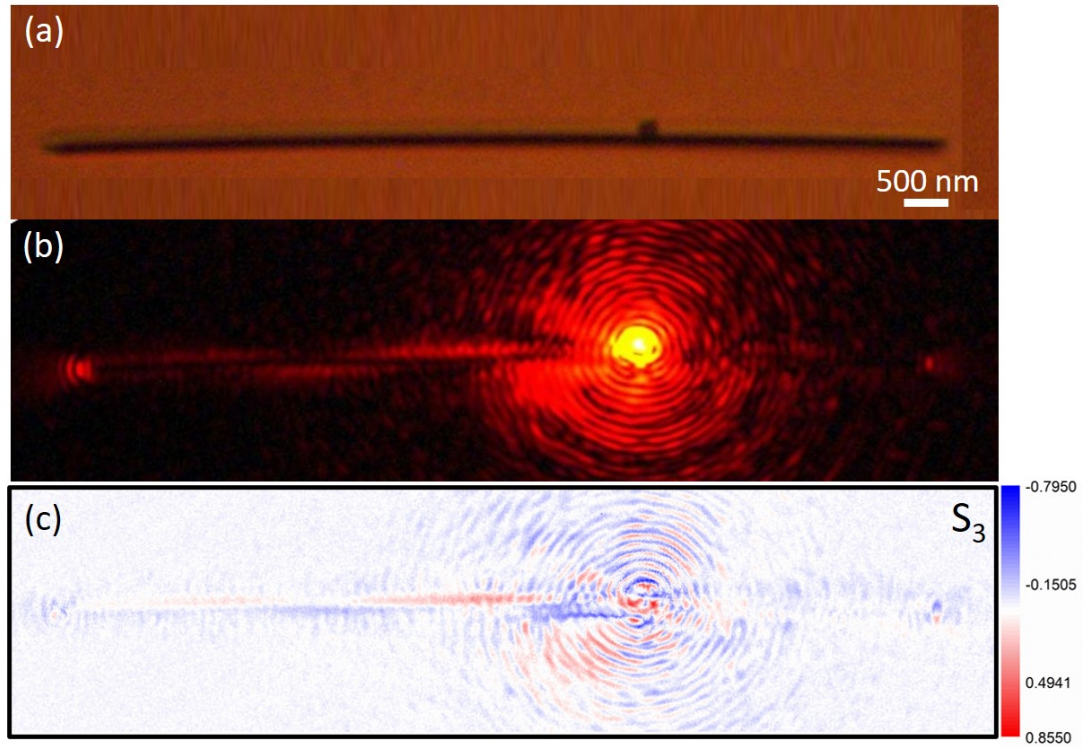


FIGURE 7.1: (a) Optical bright field image of the nanowire-nanoparticle (NW-NP) geometry where AgNW with average diameter 350 nm is coupled to a NP of 400 nm diameter using self-assembly processes. (b) Real-plane elastic scattering image of the NW-NP geometry upon exciting the junction with $\lambda = 632.8$ nm laser polarised along the junction for maximum coupling. (c) Transverse spin density in real-plane imaging for NW-NP system

- Confined and enhanced field at NW-NP junction also opens up the possibility for studying non-linear emission such as second harmonic generation of metallic nanostructures. Here we provide preliminary results where a NW-NP junction is excited with 810 nm wavelength femtosecond laser using 100x 1.49 objective lens. We collect the back-scattered light using same objective lens. After rejecting the elastically scattered light using two edge filters in the path, we utilise a 405 nm laser line filter just before the spectrometer to only study the SHG signal from the junction. Fig. 7.2 shows the SHG signal from the junction in both air and water medium. It can be seen that we are able to collect SHG intensity counts for both the medium.

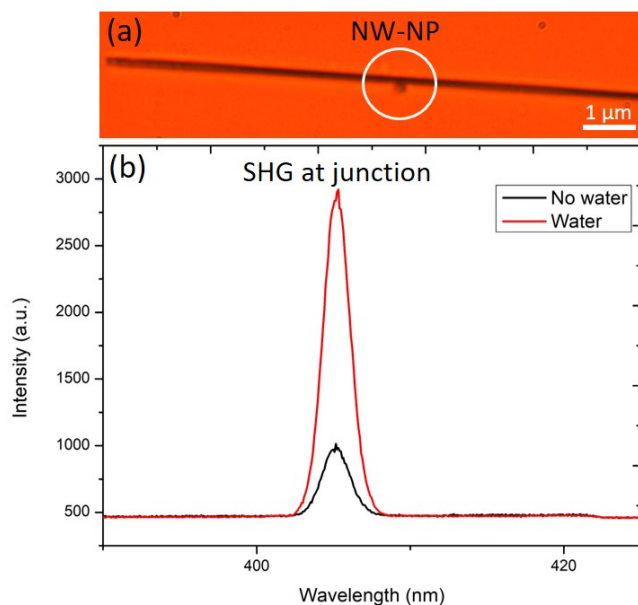


FIGURE 7.2: (a) Optical bright field image of the nanowire-nanoparticle (NW-NP) geometry where AgNW with average diameter 350 nm is coupled to a NP of 400 nm diameter using self-assembly processes. (b) SHG signal from the NW-NP junction suspended in air (red curve) and water (black curve).

Sub-wavelength channeling of whispering gallery modes into silver nanowire as plasmon polaritons

In chapter 4, we report sub-wavelength propagation and directional out-coupling of whispering gallery modes (WGMs) of a fluorescent silica μ S resonator mediated via plasmon polaritons in a single crystalline AgNW. Fluorescent spectral signatures of emission from the NW ends confirm efficient guiding of WGMs via NW plasmons. By employing Fourier plane optical microscopy, we reveal and quantify the directional fluorescence emission coupled with WGMs from the ends of the NW.

Future direction:

- For the potential applications of AgNW- μ S geometry as an hybrid optical antenna, miniaturized optical resonators and couplers, it is important to have full control over the assembly process for this hybrid structure. As mentioned in chapter 4, geometry is prepared using self-assembly processes, however we do not have control over the the position of μ S along the length of NW forming the AgNW- μ S junction [49]. There have been reports on the capillary force calculation for geometry such as NW-NP junction, similar calculations for AgNW- μ S geometry would ensure a complete reproduction and control over the assembly processes.
- Along the similar lines, it would be advantageous to utilise optical trapping to form AgNW- μ S junction. It would require a high power laser to trap dielectric μ S [199, 200]

and move the μS closer to the AgNWs resting on the substrate. This method although a little complex than self-assembly would provide us complete freedom to place the μS anywhere along the length of NW. Moreover, we can also perform a systematic study on the distance variation between AgNW and μS at the junction to the coupling of WGMs into NW SPPs.

- Two leaky plasmon mode channeling WGMs towards both the ends of NW are clearly visible in the Fourier plane imaging. We can measure the transverse spin for these leaky modes and study the optical spins generated in dielectric resonator mode due to coupling into NW.

Mapping 1-D nanocavities using light scattering from molecular monolayers

In chapter 5, we study the polarisation resolved cavity plasmon modes for NWoM nanocavity. We show that we can reveal non-uniformities inside the nanogap by mapping the resonance position of $(1x)$ cavity mode along the extended gap. Further we study the correlation of these non-uniformities with the molecular emission from the BPT molecular mono-layer sandwiched inside the nanocavity.

Future direction:

Recently, metallic nanocavities such as nanoparticle over a resonator (NPoR) has been used as an efficient mid-infra red detector at room temperature in ambient conditions [73]. However, the resonator requires complex fabrication techniques and there is no control over the assembly process of NP over the resonator. The experimental results along with the simulations for the cavity plasmon modes presented in this chapter opens up the possibility for mid-infra red (MIR) gap plasmon modes supported by the NWoM nanocavity. It has been shown that the cavity mode redshifts as the diameter of NW increases. This could potentially replace NPoR with a single thick AgNW plasmonic structure placed on a mirror without the need for any complex fabrication techniques.

As a starting evidence, we report the reflectivity measurement at MIR wavelengths using Fourier transform infrared spectroscopy (FTIR) [201] for NWoM geometry. Schematic of the NWoM geometry with AgNW placed on a Au mirror is shown in Fig. 7.3(a). It is clear from the FTIR data, that NWoM system supports MIR resonances (clear dips in the spectra, Fig. 7.3(b)). However, it is not found in every NWoM system measured. A systematic study on the resonance dependence on NW diameter and length can be very useful for this purpose.

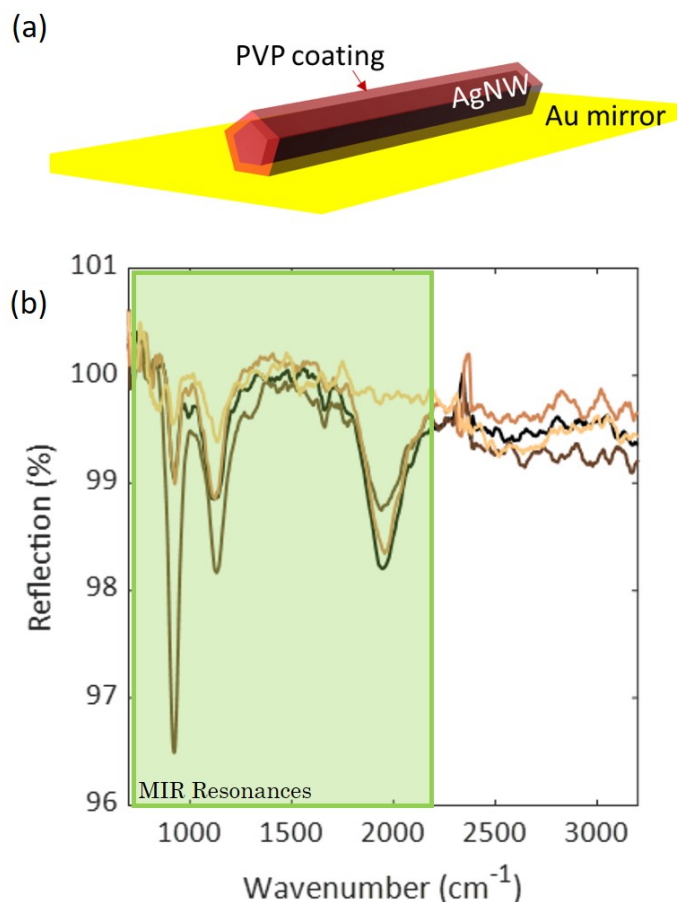


FIGURE 7.3: (a) Schematic of NWoM system where a thick NW (diameter > 250 nm) is placed on top of a template stripped Au mirror. Characteristic regular pentagon cross-section and PVP coating which acts as a capping agent during chemical synthesis of AgNW is shown in the Figure. (b) FTIR spectra for the NWoM system showing mid-infra red resonances at high wavenumbers (cm^{-1}).

Non-reversible nm-scale local structural change inside 1-D extended nanogap

In chapter 6, we have reported non-reversible local morphological changes inside the nanogap for NWoM nanocavity created by purely optical means using high laser power excitation. We detect these changes by watching the millisecond time evolution of the SERS signal from the molecular layer inside the nanogap. Increasing SERS signal with time along with the redshift of the $(1x)$ cavity plasmon mode of NWoM nanocavity ensure the structural changes inside the nanogap.

Future direction:

- As discussed in the chapter, It is important to rule out the possibility of PVP polymer reorganisation with molecular layer inside the nanogap to produce approximately 200% increase in SERS signal with time. For this, a near-field scanning to reveal the atomic

facet of the NW after the laser exposure is essential. For this, experimental techniques such as focussed ion beam where we can excite a specific point along the length with high power, and investigate the cross-section of NW at that location would be very useful.

- In general, NWoM geometry with extended gap can be utilised to watch real-time dynamics of biological molecules such as lipids and proteins placed inside the nanocavity. Extended hot-spot along the length of NW, would give access to probe the molecular dynamics such as diffusion, binding which very important for medical application using far-field spectroscopic techniques [202]. Fig. 7.4 shows the schematic of the proposed geometry to probe the lipid bilayer sandwiched inside the nanocavity. We can study binding and diffusion by recording SERS spectra from the NWoM nanocavity and observing SERS lines.

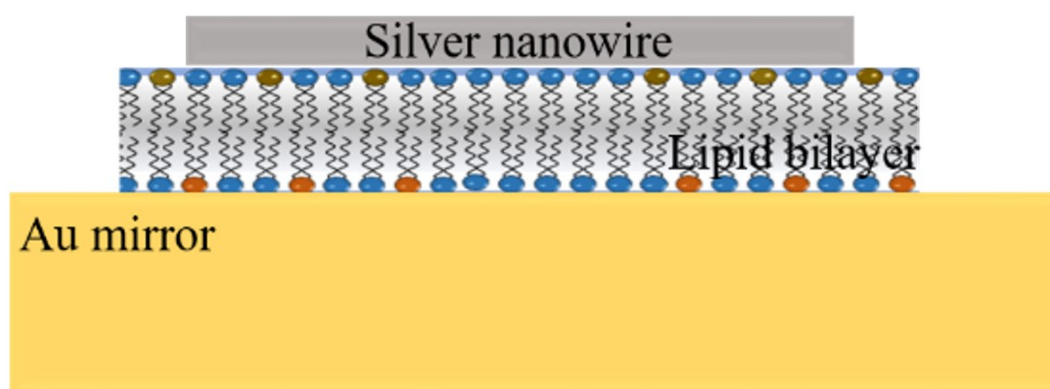


FIGURE 7.4: Schematic of NWoM system assembled with lipid bilayers inside the naogap.

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