
Localized Optical-fields and Directional Far-field Emission From Plasmonic Nanojunctions

A thesis

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

by

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PUNE

CERTIFICATE

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Abstract

The coupled oscillations of free electrons and the optical waves at the metal-dielectric interfaces are known as surface plasmons. This kind of light-matter interaction in plasmonic nanostructures has made it possible to realize the concept of optical antennae. These are the devices which can work as a transducer between free radiation and localized source. An optical antenna can be characterized by two main properties: a) ability to localize optical fields to sub-wavelength scales and b) the ability to spatially redirect the near-field emissions. Localization of fields is important for obtaining enhanced interactions with nearby molecules; whereas, defined directionality is useful to increase detection efficiency. Here in this thesis, we will present how the two fundamental excitations of surface plasmons i.e., (i) localized surface plasmon (LSP) and (ii) propagating surface plasmon polaritons (SPP) can be utilized to obtain field localization and well defined directional emission at plasmonic nanojunctions, which in turn work as optical antennae.

First, we shall present how the LSP mediated field localization at the junction of a Palladium (Pd) bridged gold (Au) nanocylinder dimer can be tuned by varying the geometrical parameters of the system and how this geometry can be used for efficient hydrogen detection.

Next, we will present how the propagating SPP in silver (Ag) nanowire (NW), generated due to terminal optical excitation of the wire; can lead to field localization at a serially-coupled Ag NW- dimer junction or a NW-nanoparticle junction which is spatially separated from the excitation point. We will also show that the efficient SPP waveguiding through the NW results in directional scattering of light at the coupled NW dimer junction. Furthermore, we will show how these phenomena can be employed to remotely excite molecules placed at the junctions and influence directional emission from them.

List of Publications

Included in thesis:

- Palladium bridged gold nanocylinder dimer: Plasmonic properties and hydrogen sensitivity; **Arindam Dasgupta** and G.V. Pavan Kumar, *Applied Optics*, 51, 1688-1693(2012). (Chosen for Virtual Journal for Biomedical Optics Vol. 7, Iss. 6)
- Dual-Path Remote-Excitation Surface Enhanced Raman Microscopy with Plasmonic Nanowire Dimer; **Arindam Dasgupta**, Danveer Singh and G. V. Pavan Kumar, *Applied Physics Letters*, 103, 151114 (2013).
- Remote-Excitation Surface Enhanced Raman Scattering with Counter-Propagating Plasmons: Silver Nanowire-Nanoparticle System; **Arindam Dasgupta**, Danveer Singh, Shreyash Tandon, Ravi P.N. Tripathi and G. V. Pavan Kumar, *Journal of Nanophotonics*, 8(1), 083899 (2014).
- Directional fluorescence mediated by chemically-prepared plasmonic nanowire dimers; **Arindam Dasgupta**, Danveer Singh, Ravi P. N. Tripathi and G. V. Pavan Kumar. *Manuscript under review*

Not included in thesis:

- Mapping of Electro-catalytic Sites on Single Strand of Carbon Fiber Using Scanning Electrochemical Microscopy (SECM); Vrushali Joshi, Santosh Haram, **Arindam Dasgupta** and G.V. Pavan Kumar, *Journal of Physical Chemistry C*, 116, 9703-9708 (2012).
- Microsphere-coupled organic waveguide: preparation, remote excitation of whispering gallery modes and waveguiding property, Rohit Chikkaraddy, **Arindam Dasgupta**, S. Dutta Gupta, G. V. Pavan Kumar, *Applied Physics Letters*, 103, 031112 (2013).
- Subwavelength propagation and localization of light using surface plasmons: A brief perspective; G. V. Pavan Kumar, Danveer Singh, Partha Pratim Patra and

Arindam Dasgupta, *Pramana - Journal of Physics* (invited review article, NLS-21 issue), 82, 59-70 (2014).

- Plasmo-fluidic Single-Molecule Surface Enhanced Raman Scattering from Dynamic Assembly of Plasmonic Nanoparticles; Partha P. Patra, Rohit Chikkaraddy, Ravi P.N. Tripathi, **Arindam Dasgupta** and G.V. Pavan Kumar, *Nature Communications*, 5, 4357 (2014).
- Directional Out-Coupling of light from Plasmonic Nanowire-Nanoparticle Junction; Danveer Singh, **Arindam Dasgupta**, Aswathy V.G., Ravi P.N. Tripathi, G. V. Pavan Kumar, *Optics Letters*, 40, 1006-1009 (2015).
- Directional emission of light from organic exciton-polariton mesowire in active and passive regimes; Ravi P.N. Tripathi, **Arindam Dasgupta**, Rohit Chikkaraddy, Partha P. Patra, Adarsh Vasista and G.V. Pavan Kumar, *Manuscript under review*.

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Dedicated to my mother...

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¹Results published as full article in *Applied Optics*, Vol 51, pp 1688-1693, 2012.

²Results published as full article in *Applied Optics*, Vol 51, pp1688-1693, 2012.

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⁵Manuscript under review.

⁶Manuscript under review.

Chapter 1

Introduction

Plasmonics is promising and rapidly expanding field of science that exploits the unique optical properties of metallic nanostructures to manipulate optical fields at sub-wavelength scales. Such manipulation is derived from the ability of metallic nanostructures to sustain coupled electron oscillation with optical fields, known as surface plasmons which lead to confinement fields at the metallic surfaces. In addition to confinement, the optical fields can be propagated through extended nanostructures which depend upon propagating surface plasmon polaritons (SPP) waves[1, 2].

At present, the plasmonic research enables the realization of various fundamental applications including plasmonic devices and miniaturization of optical components in an electronic device to sub-100 nm length-scale[3–7]. Despite the presence of heating loss in metals, plasmonics have various useful functionalities. One such useful function is the ability to concentrate optical fields to sub-wavelength volume and/or produce highly localized intensity. This field concentration volume can be much smaller than the classical diffraction limit of electromagnetic wave i.e., less than half the wavelength ($< \lambda/2$) of the excitation field. Also the mode volume (ν_m) supported by a plasmonic resonator can be lower than the $(\lambda/2)^3$ limit in case of dielectric resonators[8, 9]. These properties have been harnessed to build applications based on enhanced light matter interaction such as enhanced molecular spectroscopy techniques[10–14], highly sensitive bio and molecular detection[5, 15–17], sub-diffraction limit resolution microscopy techniques[18, 19], miniaturized plasmonic nanolasers[20–22] etc.

Apart from this, if a light emitter such as a fluorescent molecule or quantum dot is placed in the vicinity of a plasmonic nanostructure, the interaction between emitted light and the plasmon modes of the the system influence the optical properties of the emitter in many ways. For example, fluorescence cross-section and lifetime can be altered, emission spectra can be reshaped or most importantly emission can be spatially redirected[23–27]. This phenomenon has been utilized to enhance detection efficiencies in molecular spectroscopy techniques[28], photo-detectors[29–31] and for building communication devices

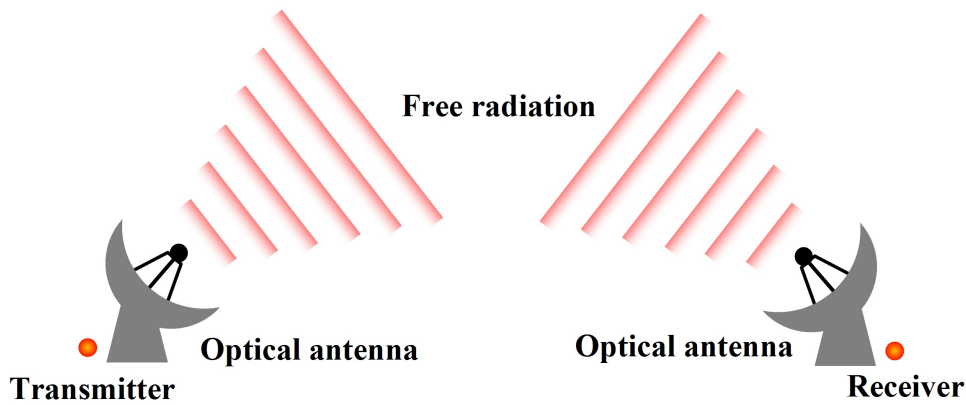


FIGURE 1.1: Schematic showing working principle of an optical antenna

Such interesting properties of plasmonic nanomaterials open up the possibility of utilizing it as a communicator between a localized source of nanoscale dimensions and free optical radiations; which originates the idea of an exceptional optical device called optical antenna[32, 33]. In this thesis, we mainly investigate various plasmonic nano-junctions for their antenna like behaviour: field localization and spatial redirection of farfield emission. Therefore, to put the content of this thesis in a wider and clearer perspective; we start with a short introduction to the concept of optical antenna.

1.1 Optical antenna

Electromagnetic antenna is a well established concept in the field of radio-wave and micro-wave communication technology which enabled the realization of cellular phones, televisions etc. There, the antennae are predominantly used to manipulate electromagnetic fields at sub-wavelength scale and interface it efficiently between radiation and localized field. Basically, these antennae work as electrical devices which convert electrical power to free radiation and vice-versa[34]. Exploring the ways to incorporate radio-wave and microwave antennae theories into optical frequency regime is main reason behind the origination of the term optical antenna. These are the devices which are used to optimize the energy transfer between a localized source (transmitter) or a receiver and free radiation[32, 33, 35]. the main objectives of an optical antenna can be two fold:

- a) It can be used to collect the photons emitted from a localized source behaving as a transmitter, to direct it in a specified direction as freely propagating waves (figure 1.1).

- b) It can also be used to enhance the energy transfer from free radiation fields to a nanoscale emitter, acting as receiver (figure 1.1).

Therefore, unlike the radio-wave antenna, the optical antenna is simply not a resonator or a strong scatterer. Instead, it works as a transducer between free radiation and localized source. The degree of localization and magnitude of transduced energy define the efficiency of an optical antenna.

Antenna parameters: The main objective of introduction of the transmitting antenna is to enhance the transmission efficiency [32, 33]. This can be achieved if more of the energy from the transmitter is radiated as free propagating waves. This parameter is called *antenna efficiency* ϵ_{rad} and mainly governed by the losses at the antenna.

$$\epsilon_{rad} = \frac{P_{rad}}{P} = \frac{P_{rad}}{P_{rad} + P_{loss}} \quad (\text{Eq 1.1})$$

where P is the total power collected by the antenna, P_{rad} is the radiated power and P_{loss} is the power dissipated through absorption in the antenna.

The transmission can also be improved by directing majority of the radiated energy towards a specific direction. This is known as directivity of the antenna.

$$D(\theta, \phi) = \frac{4\pi}{P_{rad}} p(\theta, \phi) \quad (\text{Eq 1.2})$$

where θ and ϕ represent the angular radiation directions and $p(\theta, \phi)$ is the angular power density.

Combination of antenna efficiency and the directivity is referred as the antenna gain:

$$G = \epsilon_{rad} D \quad (\text{Eq 1.3})$$

By reciprocity, it can be said the afore-mentioned transmitting antenna can also work as receiving antenna (figure 1.1)[32, 33, 36]. This can be achieved by interchanging the fields and sources in figure 1.1. Now, antenna efficiency will define the amount of energy that is being delivered to the receiver which mainly represents the ability of the antenna to localize field to receiver's site. Directivity will stand for the radiation directions from which the radiation can be collected by the antenna.

1.2 Plasmonics: the route to realize optical antenna

Although, the classical antennas found widespread use in astronomy and telecommunication industry, the optical counter-part had not found technological applications for a

very long time due to its small size requirements. The dimension of an element in radio-wave antenna is of the order of the radiation wavelength, whereas in case of optical antennae, this characteristic dimension is reduced down to few tens of nanometers[35, 37]. This requires very high accuracy in nanofabrication of the scale of few nanometers which has been a major hindrance for a long time. However, in recent years, the development of highly improved nanofabrication tools have made these length scales accessible. These antennae can now be fabricated using highly modernized top-down fabrication systems such as focused Ion beam milling[38–40] and electron beam lithography[41–44] or by using different bottom-up chemical synthesis methods[45–48]. Once the fabrication tools were available, next job was to fabricate plasmonic nanoarchitectures which in turn can work as optical antennae.

Recent research on optical properties of wide variety of metallic nanostructures indicate that the structures come in two varieties: resonant and non-resonant. The behaviour of the resonant structures are influenced by localized surface plasmons (LSP) whereas in case of non-resonant antenna structures, the optical properties are mostly driven by surface plasmon polaritons (SPP)[1, 2, 8, 43, 49]. In following sections, we will give a brief discussion on two kinds of surface plasmons i.e., localized surface plasmons (LSP) and surface plasmon polaritons (SPP) which can be utilized to design optical antennae with specific optical characteristics. In the process, we will also briefly review some of the earlier works on plasmonic optical antennae.

1.2.1 Localized surface plasmons

This kind of resonant electromagnetic behaviour occurs in noble metal nanoparticles due to resonant oscillation of conduction electrons within small particle volume[1, 2, 50]. Simplest of these particles is a nanosphere. A schematic representation of LSP resonance in case of a metallic nanosphere is shown in figure 1.2. For a particle of diameter $d \ll \lambda$, the conduction electrons are driven into oscillation in phase with the incident light of wavelength λ . This leads to a build-up of polarization charges across the particle surface which means the opposite charges get accumulated at opposite sides of the sphere. The Coulomb interaction between these different charges provides a restoring force, leading to a natural frequency of oscillation. When the excitation light has the frequency same as the natural oscillation of conduction electrons, energy is coupled into LSP modes. In this particular case (figure 1.2), it is a dipolar LSP mode where the response of the electrons show a $\pi/2$ phase lag with the driving optical field. Therefore, when energy is coupled into LSP, a resonantly enhanced homogeneous field is built-up inside the particle which provides a strongly enhanced dipolar field outside the particle at its immediate vicinity. This leads to enhanced absorption and scattering

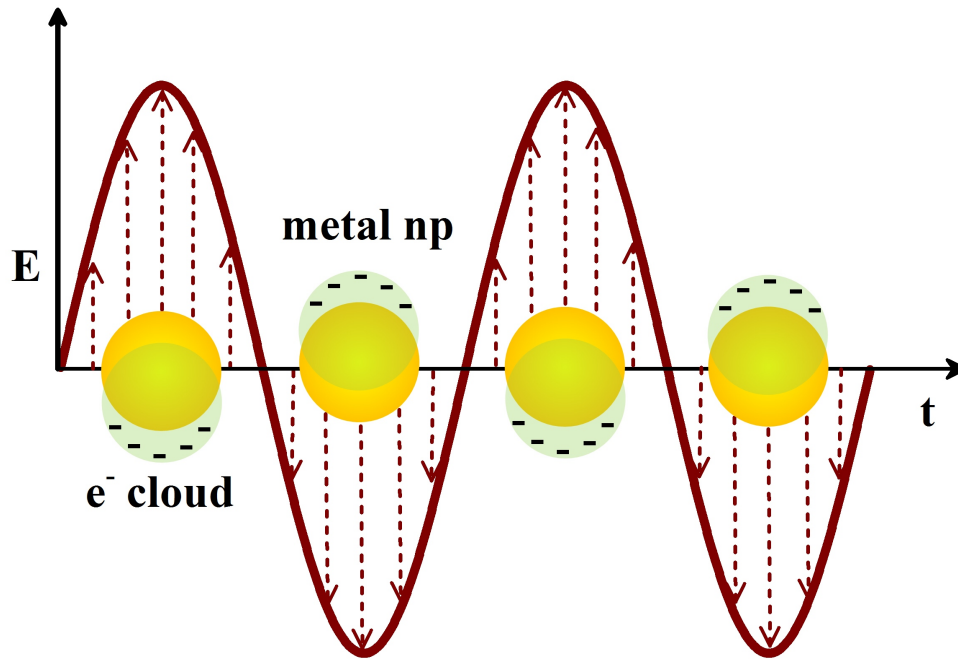


FIGURE 1.2: Schematic showing localized surface plasmons in metallic nanosphere

cross-section for electromagnetic waves, known as localized surface plasmon resonance (LSPR)[1, 2, 49]. This enhanced near-field is at the heart of most promising applications in plasmonics. For larger particles and particles of different shapes, the retardation effect can change and hence higher order plasmon modes can also occur[51–54].

1.2.2 Surface plasmon polaritons

The enhanced near-field generation due to coherent oscillations of electrons is not only limited to metallic nanoparticles, but can also be present at planar interfaces between metal and dielectric. This type of coupled electromagnetic behaviour gives rise to surface plasmon modes which can propagate along the metal-dielectric interface and are known as surface plasmon polaritons (SPP)[1, 2, 55, 56]. These can easily be thought of as surface electromagnetic waves which are confined to propagate along the metal-dielectric interfaces and their field strengths decay exponentially in both mediums[57] (figure 1.3a and b). The most interesting property of this interaction is; the momentum of the SP modes $\hbar k_{sp}$ is greater than that of a free space photon of same frequency, $\hbar k_0$ ($k_0 = \omega/c$ is the free space wavevector). By solving Maxwell's equations under appropriate boundary conditions, we obtain the SPP dispersion relation which shows

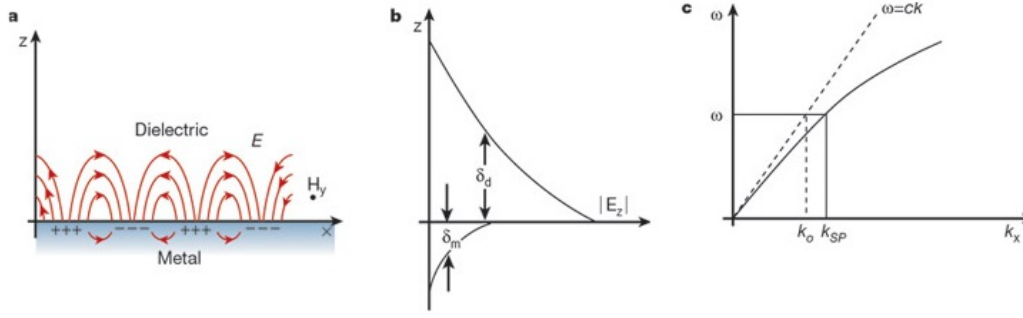


FIGURE 1.3: a) SPP in plane metal dielectric interface has combined electromagnetic wave and surface charge character. b) Field associated with SPP in the perpendicular is evanescent in both metal and dielectric. δ_m and δ_d are corresponding decay lengths c) The dispersion curve of SPP modes.[53]

the frequency dependence of the SP wavevectors[1, 2, 57].

$$k_{sp} = k_0 \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}} \quad (\text{Eq 1.4})$$

where ϵ_m and ϵ_d are frequency dependent permittivity of the metal and dielectric. Now, for SPP to be possible, the frequency dependent permittivity ϵ_m and ϵ_d must have opposite sign which is satisfied as for metal ϵ_m is both negative and complex. As can be seen in figure 1.3c, the dispersion curve of SPs always lie to the right of the dielectric light line, approaching to a maximum value $\omega_{sp} = \omega_p / \sqrt{1 + \epsilon_d}$ for large wavevectors. Here ω_p signifies the bulk plasma frequency of the metal. The extra momentum of the SPP modes is associated with binding of charges to the metal surfaces. As a consequence of this bound and non-radiative nature of the SPs, the field in perpendicular direction to the metal surface is said to be evanescent in nature.

As the SP momentum is always greater than light for same frequency, it is not possible to excite SPP using light. Therefore, in order to use light to excite SPPs this momentum mismatch has to be bridged[1, 2, 57]. There are three main techniques by which the extra momentum can be provided to light.

- i. **grating coupling:** In this configuration SPP is excited by light via a grating coupler. If the grating constant is b , then the wavevector of light is increased by a factor $2\pi/b$ [57] (figure 1.4a). Therefore, the SPP dispersion relation can be matched with a component of light vector along the metal surface by the following equation,

$$k_{sp} = k_0 \sin \theta_0 + \frac{2\pi}{b} \quad (\text{Eq 1.5})$$

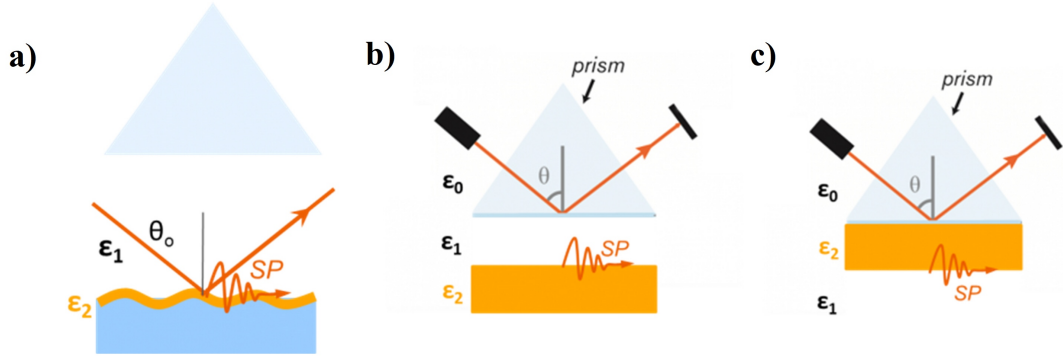


FIGURE 1.4: Schematic for SPP excitation using light: a)Grating coupling, b)Otto configuration, b)Kretschman configuration.[58]

where, θ_0 is the light incidence angle.

ii Prism coupling:

Otto configuration: In this configuration (figure 1.4b), the light line in dispersion curve is lowered by a factor $\sqrt{\epsilon_0}$ by making it travel through a high refractive index medium, having dielectric constant ϵ_0 [1, 2, 55, 57]. This can be done making the light undergo total internal reflection (TIR) at glass-air interface to generate evanescent waves which penetrate upto the metal-air interface to generate plasmons. Here the resonance condition is defined by,

$$k_{sp} = nk_0 \sin \theta_0 \quad (\text{Eq 1.6})$$

Kretschman configuration: Here, the metal film is directly formed on the glass substrate. The thickness of the film needs to be lower than the skin-depth for SPP to happen. The evanescent field in this case penetrate through the metal to generate SPP at the metal-air interface[1, 2, 55, 57] (figure 1.4c). Resonance condition is again given by,

$$k_{sp} = nk_0 \sin \theta_0 \quad (\text{Eq 1.7})$$

iii **Defects on a film:** Another way to generate SPP in metal films is to scatter light at a defect on a plane film. The local symmetry breaking at the defect site provides the extra momentum to the scattered light, required to generate SPP in the film[57].

1.3 Examples and applications

As discussed earlier, the main objective of an optical antenna is either to localize field or to redirect the radiation from a localized source. In this section, we will discuss how different kinds of surface plasmons in plasmonic antennae i.e., LSP and SPP have been utilized to build useful applications. First we shall discuss about applications based on field localizations.

1.3.1 Field localizations

The most useful application of local field enhancement near the plasmonic nanostructures due to LSP resonance and SPP modes is surface enhanced molecular spectroscopy techniques for molecular sensing. When a molecule is placed in the localized fields associated with the plasmonic nanostructures, its optical responses get highly enhanced. This has been the key behind the development of surface enhanced Raman spectroscopy (SERS)[59–63], surface enhanced fluorescence (SEF)[64–66] and surface enhanced infra-red spectroscopy (SEIRS)[67] etc. Such local field enhancements can further be improved by focusing the field to sub-wavelength volumes. This can be done by keeping the particles very close to each other, where the LSPs in the particles couple with each other to create highly localized fields at the inter-particle gaps[59, 60, 68]. These sites are known as electromagnetic hotspots. The field enhancements obtained at hotspots formed in case of nanoparticle aggregates and assemblies are found to be high enough to realize single molecule detection[68–72]. In addition to that, LSPs in metal nanoparticles can be used for nanofocusing by adopting many simple strategies such as nanofocusing of LSP resonances within a chain of coupled metal particles of decreasing sizes in case of self similar nanoparticle assembly (figure 1.5a)[73–75] or close to triangular nanotip[76]. SPPs in nanostructures can also be utilized, like in case of a tapered plasmonic waveguide or a nanoparticle junction on a plasmonic nanowire waveguide (figure 1.5b) where the SPP modes are focused at the tip or at the particle junction respectively to create field localizations[77, 78].

The nearfield of plasmonic nanostructure is extremely sensitive to the surrounding dielectric medium. Therefore, slight change in the surrounding medium induces a change in the scattering and absorption cross-section and thereby in LSP resonance of the nanostructure[1, 2]. This phenomenon has been widely used to develop several plasmonic sensing devices[81, 82]. Figure 1.5c shows a similar plasmonic sensor developed for hydrogen sensing. It consisted of a Au nanotriangle and a Pd nanodisc. The disc is placed very close to the nanotriangle where there is a significant field enhancement and high density of optical states. Now, for different partial pressure of

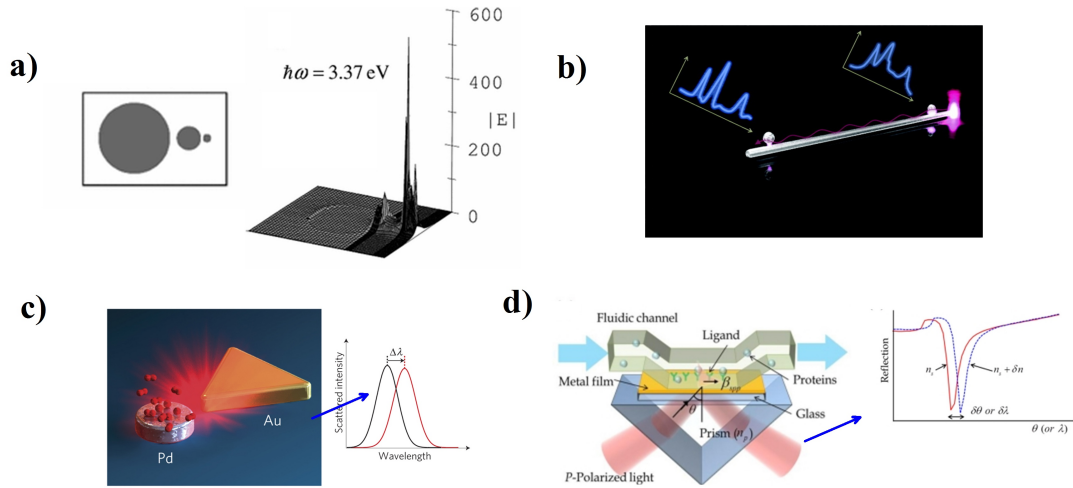


FIGURE 1.5: a) Nanofocusing of LSP resonances through a self-similar chain of metallic nano particles[73]. b) Nano focusing of SPP modes in a silver nanowire to a nanowire- nanoparticle junction[77]. c) A hydrogen sensor based on resonant scattering of Au nanotriangle. Different hydrogen pressure leads to shift in the scattering spectrum[79]. d) A Protein density sensor based on Kretschmann configuration based SPP mode excitation. Change in protein density leads to a shift in the SPP coupling angle[80].

H_2 in the atmosphere, different proportion of it will be adsorbed by the Pd disc which will change the dielectric constant of Pd. This induces a spectral shift in the LSP resonance. Therefore, the scattering spectra of the system can be used to effectively sense the H_2 in the atmosphere. SPP based sensing is also well-known[79]. Sensing devices can also be built with structures which support SPP. As the SPP modes are confined to the metal-dielectric interface, slight change in the dielectric medium gets reflected in the SPP behaviour[1, 2, 56]. Figure 1.5c shows a Kretschman configuration density sensors, where the density change in the dielectric medium changes the resonance in the SPP coupling angle[17, 80]. This type of system has also been used for probing the change in protein densities. Apart from these, field localization to subwavelength scales has been utilized to beat diffraction limit in optical microscopes [9, 18, 19] and photolithography techniques[83, 84]. It has also been utilized to build laser cavities with very low mode volumes[20, 22].

1.3.2 Directional emission

In typical experiment for dipolar emission from molecules, the collected radiation from a randomly oriented population of molecules is isotropic in nature. Even for oriented

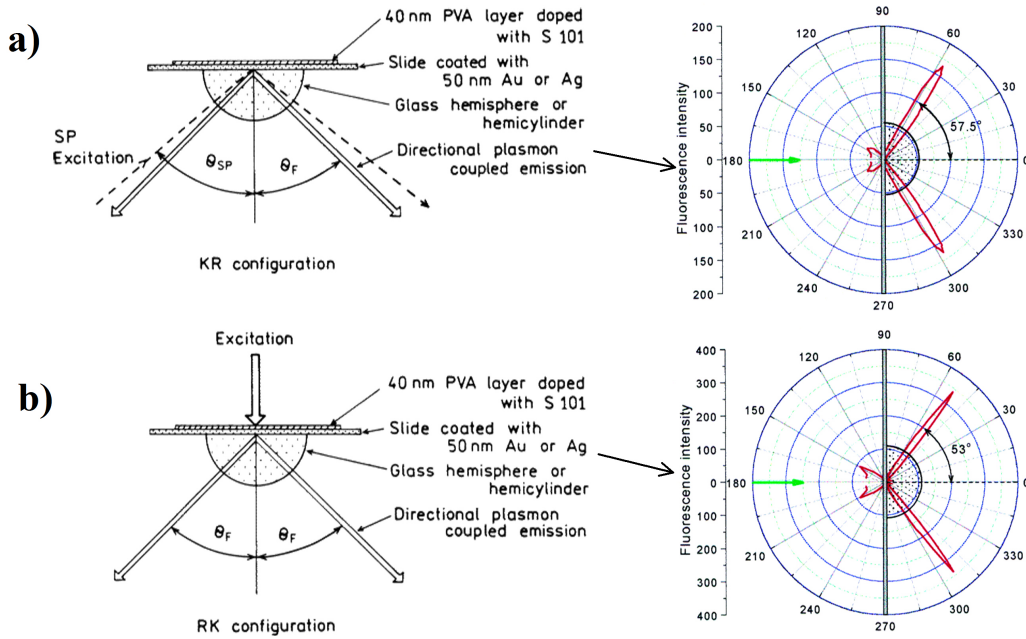


FIGURE 1.6: Directional fluorescence emission in case of surface plasmon coupled emission when molecules are coated on gold thin film: a)Kretschmann (KR) configuration excitation and corresponding radiation pattern. b)Reverse Kretschmann (RK) configuration excitation and corresponding radiation pattern.[85]

molecules excited with polarized light, the emission is nearly isotropic. As a result, the detection efficiency of the molecule is limited by the highest angle of light collection possible. But if molecules are placed close to a metallic nanostructure, their emission can be spatially redirected to specific directions governed by the nanostructure. This does not happen due to reflection of emission from the metallic surface but happens due to the interaction of molecular dipole oscillation with the oscillations of free electrons in metal and their directed emission. In these cases, the plasmons in metal couple with fluorophores to form plasmaphores which radiate in a direction governed by the plasmon modes. The spatial redirection of the emission is advantageous because the detection efficiency can be highly enhanced by placing a detector along the emission direction[26, 28, 86]. Apart from enhancing detection efficiency, the directional emission from metallic nanostructures can also be utilized for designing optical communication between the components of a nanophotonic device[86, 87]. Furthermore, coupling of single emitters with metallic nanostructures has drawn much interest for designing directional single photon sources which can be utilized for designing quantum computational devices[88–90].

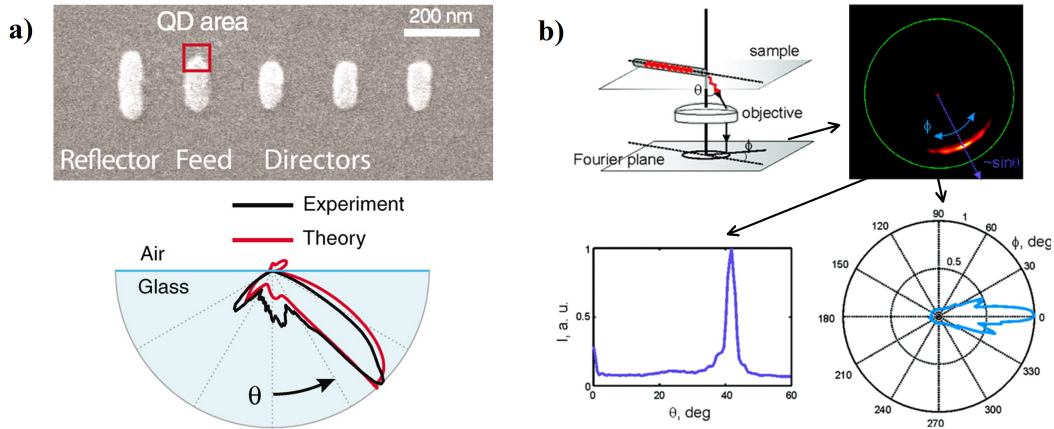


FIGURE 1.7: Directional emission from plasmonic nanostructure: a) LSPR based directional emission from an optical Yagi-Uda antenna.[86] b) Propagating SPP based directional emission from silver nanowire terminals[91].

The most common application of such directional emission is surface plasmon coupled emission (SPCE) (figure 1.6) where the fluorophores are placed very close to metal thin film. Here the emission from the molecules couple to the SPP modes in thin film to exhibit unidirectional emission governed by the SPP radiation angle[26, 28, 85, 92]. LSPs in nanostructures have also been utilized to obtain directional emission. Figure 1.7a shows an example of an optical Yagi-Uda antenna where a quantum dot was coupled to the feed of the antenna. When the quantum dot emission was in resonance with the feed element of the antenna, the resulting quantum dot emission was strongly polarized and highly directed into a narrow forward angular cone[86, 93]. A variety of nano-architectures have been studied in the context of directional optical antennas that include dipole antenna, patch-antenna[88, 94], hetero-dimer antenna[95, 96], tip-on-an-aperture antenna[97], Groove-nanoaperture antenna [98], phase-antenna, v-shape antenna[99, 100] etc. Each of these nanofabricated antennae has a well-defined light directivity depending upon the base structures, which is mainly governed by the LSPR of the antenna element[98]. Therefore, the response of these LSP based nanostructures are narrowband and limited by their LSPR bandwidth.

In contrast to LSP response, SPP is broadband response, therefore structures where the main characteristics are defined by the SPP modes give a broadband response. One such example is plasmonic nanowire waveguide where efficient SPP waveguiding[101] through the structure results in a polarized unidirectional emission[91] from the wire termination along the SPP propagation direction i.e., along the axis of the wire (figure

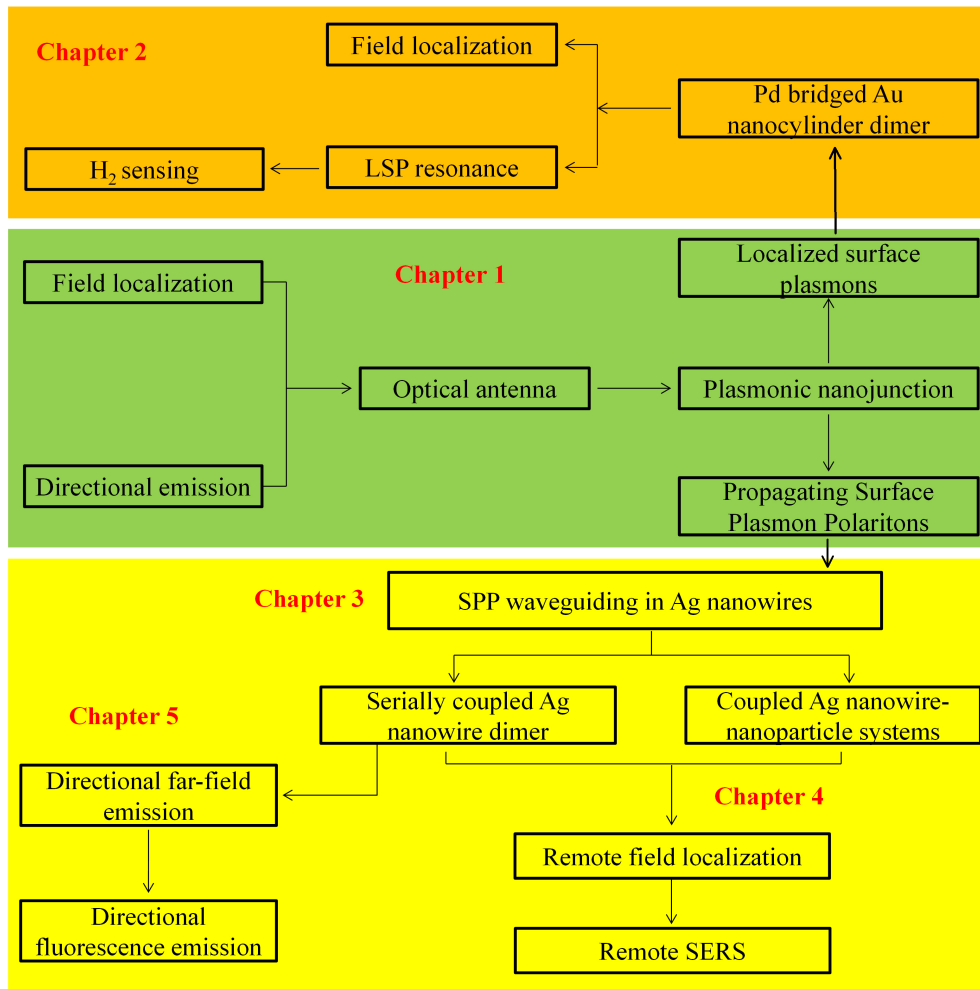


FIGURE 1.8: Schematic representation of the outline of the thesis

1.7b).

1.4 Scope and outline of this thesis

As discussed earlier in section 1.3.1 the junctions between two plasmonic nanostructures are the places where we obtain very high density of optical states. The research works presented in this thesis mainly address how to obtain different kinds of field localizations and directional emissions from plasmonic nanostructure junctions which points towards their capability of working as optical antennae. The content of the thesis can be divided into two parts depending upon which type of surface plasmon excitation (LSP or SPP) is being utilized to obtain these special properties. Specific applications

in both areas have been addressed in this thesis. For a clear overview, the basic structure of the thesis has been schematically illustrated in figure 1.8. Below we elaborate the whole content:

Chapter 2: In this chapter, we present our work on a type of plasmonic junction which supports localized surface plasmons: Palladium (Pd) bridged gold (Au) nanocylinder dimer. Before presenting the results, we briefly discuss different kinds of LSP modes which can occur in an Au nanocylinder and how these modes get modified upon introduction of another nanocylinder in the close vicinity. Then the actual results contain the mode modification and field localization resulting from the introduction of Pd bridge between the two cylinders. We also present how the LSP resonances can be tuned by varying the geometrical parameters (length and width) of the Pd bridge. Furthermore, we show how this nanojunction can be utilized for nanooptical hydrogen sensing.

Chapter 3: From here on, we mainly focus on plasmonic nanowire geometries: a) serially coupled Silver (Ag) nanowire (NW) dimer and b) Ag nanowire-nanoparticle (NW-NP) systems. These support SPPs for propagation of optical fields while being confined within the nanostructure. Hence, in this chapter we give a small discussion and theoretical background for identifying different SPP modes supported by a plasmonic nanowire. Then, we briefly discuss how SPPs can be generated in those silver nanowire systems to obtain subwavelength propagation towards the Ag NW dimer junctions and the Ag NW-NP junctions.

Chapter 4: The main focus of this chapter is on how to obtain remote optical field localization at the Ag NW dimer junctions and Ag NW-NP junctions. We utilize this field localization to remotely excite surface enhanced Raman scattering (SERS) from molecules placed in the vicinity of these junctions. Before presenting the actual experimental results, we provide a discussion on remote excitation SERS and its applications. Then we describe the specialized Raman microscope capable of providing laser excitations at two spatially separated points (dual excitation) and spatially filtered collection, which we built exclusively for the experimental studies. Then we show that the free ends of both nanowire geometries provide two excitation channels to excite SERS from the molecules placed at the junction and both the ends can be used simultaneously to obtain remote excitation SERS. Here, we emphasize that if total excitation power is kept constant, dual excitation gives greater SERS enhancement compared to single end excitation. This can be attributed to inphase bonding of SPP modes at the junction. We end the chapter by presenting the results on how the SERS enhancement in case of dual excitation for both nanowire geometries can be modulated by varying the excitation light polarizations. We corroborate all experimental results with 3 dimensional (3D) finite difference time domain (FDTD) method.

Chapter 5: Once we show how the field can be localized at the junction of an Ag NW dimer, we focus on the directionality of the out-coupled light. For that, we need to image the back focal plane (BFP) of the microscope objective lens which provides Fourier transformed image. Therefore, we start this chapter by discussing the basics of BFP imaging methods. Then we describe the specially designed BFP imaging microscope with dual excitation and spatial filtering capability, used for the experimental studies. We show how far-field radiation of the out-coupled light from the junction of the coupled Ag NW dimer can be engineered upon single and dual excitation of the termini of the dimer. Here, we emphasize that the efficient wave guiding of SPP modes in the Ag NW structures is the main reason behind obtaining directional emission from the junction. Then we discuss different strategies for manipulating the radiation direction of the emitted photons from the junction. Which is followed by the presentation on how secondary emission for example fluorescence of the molecules placed at the junctions can be spatially redirected using these nanowire architectures. We also verify all the experimental results with 3D-FDTD calculations. At the very end of the chapter, we again emphasize on the fact that these Ag NW dimers can be utilized for both field localization and directional far-field emission; hence these are the excellent candidate for realization of optical antennas.

Chapter 6: Here, we mainly provide the future directions of the presented work in the thesis. One of these is the projection of back focal plane image directly on the spectrometer. This will allow us to do energy momentum spectroscopy. Here we present preliminary results on how we have built an energy momentum spectroscopy system and how to collect energy momentum spectra using it. These experiments will allow us to detect how different parts of the visible light can be spatially redirected using the optical antennae presented in the thesis. To end the chapter and hence the thesis, we draw a general conclusion on all the results presented in this thesis.

Chapter 2

Conductively Coupled Plasmonic Nanoparticle Dimers

Localized surface plasmon resonances (LSPR) in metal nanoparticles have been studied extensively for many years due to their unusual optical effects. The resonant oscillation of free conduction electrons of such particles with the incident photons lead to selective absorption and scattering of optical energies. The LSPR spectrum of a metallic nanoparticle strongly depends on the shape, size, particle composition and the local environment[1, 2]. Apart from these, LSPR of a metallic nanoparticle is very sensitive to the presence of a nearby nanoparticle. If two particles placed in close proximity, the light induced dipole moment of both the nanoparticles couple with each other which leads to a dramatic change in the absorption and scattering spectra of the system[102]. In addition to that, under certain circumstances, enormous electric field can be localized at the gap by exciting the nanoparticle dimer with an external electromagnetic radiation. Such nanoparticle dimer junction constitutes electromagnetic hotspot which is very sensitive to the chemical and physical environment[1, 2, 102]. This enormous localization of the electric field has been harnessed for enhanced molecular spectroscopy, single molecule detection[69–72, 103], refractive index sensing[5], and for developing plasmonic switching devices[104]. The coupling of the plasmon modes in a nanoparticle dimer can be controlled by filling the gap with specific nanomaterials. The bridging between two nanoparticles gives rise to new plasmon resonances which in turn has effects on the scattering and absorption spectra. Bridged nanoparticle dimers are very important in context of optical nanoantennas, where the sensitivity, bandwidth, and efficiency of the antenna can be tuned by the loading parameters and can be utilized as optical sensors[105–108]. Apart from reducing the detector size, such sub-wavelength individual nanostructure based sensors have the added advantage to overcome statistical averaging effects of a conventional macro-detector. Therefore, study of coupled nanoparticle dimers is very important for building ultrasensitive photonic devices with very high optical throughput. Here in this chapter, we will mainly present:

- i. How a conductive bridge of palladium (Pd) between a plasmonic nanocylinder dimer give rise to new plasmon resonances which changes the far field scattering spectra of the system.
- ii. How these resonances can be tuned by varying the width and length of the Pd bridge.
- iii. How this system can be utilized for optical hydrogen sensing.

Before I get into the aforementioned work, I shall discuss scattering characteristics of a single isolated nanoparticle and nanoparticle dimers.

2.1 Calculation OF Scattering and Absorption Spectra

The use of LSPR of metallic nanoparticles dates back to Roman times and the best known example of that is the Lycurgus cup, which looks greenish when seen in reflected light but appears red while viewed in transmitted light. This unusual optical effect is due to the presence of gold nanoparticles in the glass goblet which selectively absorb and scatter blue and green light. This was first explained by Gustav Mie who provided a detailed numerical solution for the absorption and scattering radiation by a metallic sphere of any size[109]. The provided theory is able to explain the resonance associated with conduction electrons in small metallic nanospheres and can be extended to calculate scattering spectra of other simple structures like nanocylinder, core-shell particles and nanorods. To predict the LSPR spectra of an arbitrarily shaped structures and array of nanoparticles many computational methods have also been developed in recent times. Discrete dipole approximation (DDA)[110], Boundary element method (BEM)[111–113], Finite element method (FEM)[114–116], Finite difference time domain (FDTD)[117–119] method are some of them. All these computational methods are used to solve Maxwell's equations to accurately predict the optical properties of nanoscale plasmonic systems. Here in this thesis, we have mainly used FEM and FDTD for computing the optical properties of the systems presented.

2.2 Scattering and absorption by a single isolated nanosphere and nanocylinder

The extinction cross-section C_{ext} of a plasmonic nanosphere of radius R , embedded in a non-absorbing medium of dielectric constant ε_i , can be calculated using Mie scattering

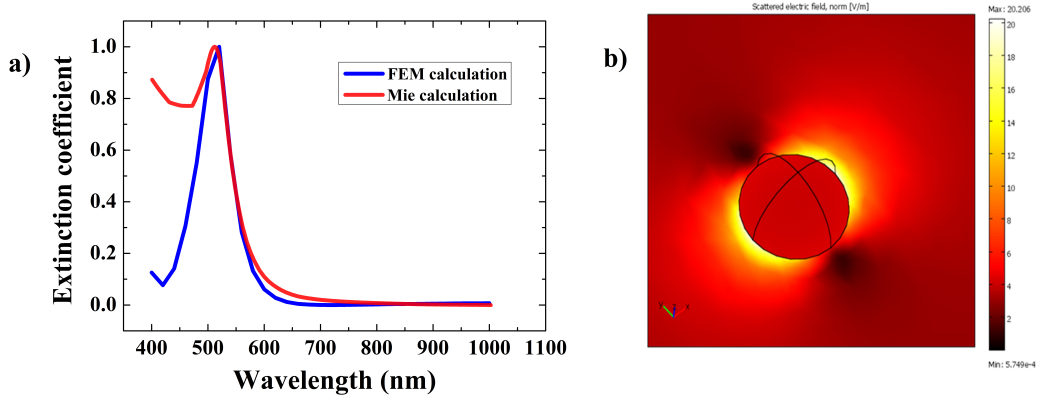


FIGURE 2.1: a) Extinction spectra of a 30nm radius Au nanosphere obtained by Mie theory (red) and 3D-FEM (blue) calculation. b) Near-field map at at xy plane at the middle of the sphere.

theory as[50, 120, 121],

$$C_{ext} = \frac{2\pi}{k^2} \sum_{n=1}^{\infty} (2n+1) \text{Re}(a_n + b_n) \quad (\text{Eq 2.1})$$

Where $k = 2\pi\sqrt{\epsilon_i}/\lambda$ while a_n and b_n are scattering coefficients expressed in terms of radius R of the nanosphere and wavelength λ as Ricatti-Bessel functions. Let us assume the case where the plasmonic nanosphere has wavelength dependent dielectric constant $\epsilon_m = \epsilon' + \epsilon''$ where ϵ' and ϵ'' are real and imaginary parts of the dielectric constant. Now for the case $R \ll \lambda$, the equation Eq 2.1 can be simplified to

$$C_{ext} = \frac{24\pi^2 R^3 \epsilon_i^{3/2}}{\lambda} \frac{\epsilon''}{(\epsilon' + 2\epsilon_i)^2 + \epsilon''^2} \quad (\text{Eq 2.2})$$

The λ at which the resonance condition $\epsilon' = -2\epsilon_i$ is satisfied, that light is strongly absorbed by the particle.

The red spectrum in figure 2.1a shows the Mie theory calculated LSPR spectrum of a 30 nm radius gold (Au) nanosphere and blue spectrum in figure 2.1a is the LSPR spectrum of the same nanosphere obtained by FEM calculation¹. Figure 2.1b shows the nearfield map of the particle at x-y plane for 520nm plane wave excitation when incident polarization was along x axis and k vector was along z direction. The LSPR spectrum for spherical nanoparticle has no dependence on the polarization of incident optical field due to its spherical symmetry.

In case of nanocylinder, the spherical symmetry is broken in one of the dimensions

¹For details of FEM calculation, see **appendix A**

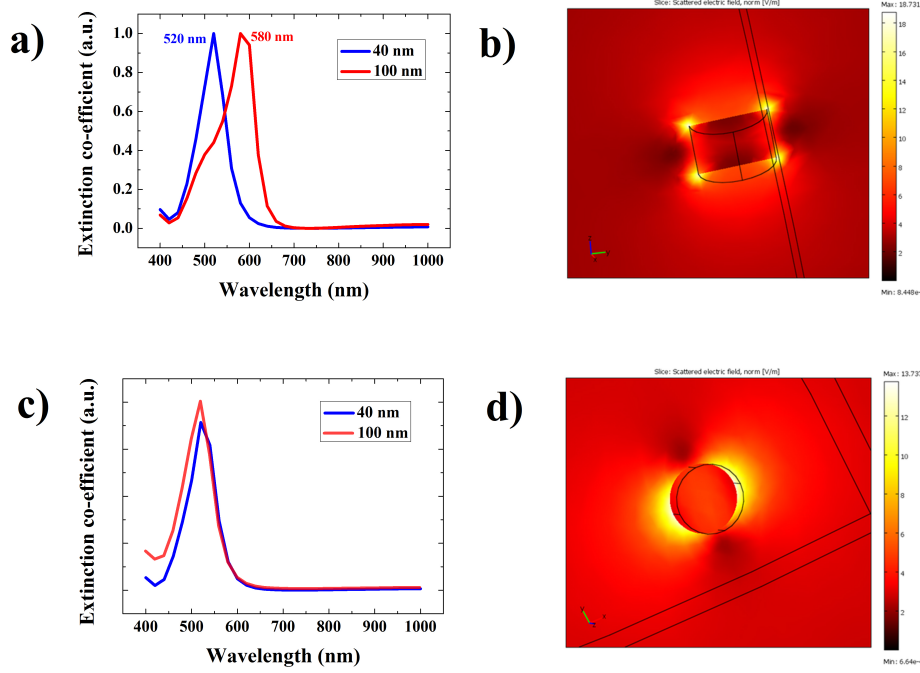


FIGURE 2.2: a) extinction spectra of 30nm radius, 40 nm (blue curve) long and 30nm radius, 100nm (red curve) long nanocylinder when the incident polarization along the length of the cylinder (z axis). b) near field map of 40nm long cylinder at Y-Z plane for same polarization. c) extinction spectra for 40nm (blue curve) and 100nm (red curve) when the incident polarization was along the radius of cross-section (x axis). d) near field map at X-Y plane for 40 nm long cylinder for same polarization.

and new LSPR modes arise depending on the incident polarization. The shape effect can be addressed by treating the cylinder as an ellipsoid. For a cylinder of aspect ratio $A=a/b$ where a is the cylinder length and b is the diameter of the cross section, the extinction cross-section can be expressed analytically within the dipole approximation[122];

$$C_{ext} = \frac{2\pi V \varepsilon_i^{3/2}}{3\lambda} \sum_j \frac{(1/L_j^2 \varepsilon'')}{(\varepsilon' + \frac{1-L_j}{L_j} \varepsilon_i) + \varepsilon''^2} \quad (\text{Eq 2.3})$$

Here, L_j ($j=a,b$) is the depolarization factors of the nanorod. If the aspect ratio of the nanorod is given as $A = a/b$, then the depolarization factors are given by,

$$L_a = \frac{1-e^2}{e^2} \left[\frac{1}{2e} \ln\left(\frac{1+e}{1-e}\right) - 1 \right] \quad (\text{Eq 2.4})$$

$$L_b = \frac{1 - L_a}{2} \quad (\text{Eq 2.5})$$

where $e = \sqrt{1 - \frac{1}{A^2}}$ is the ellipticity of the cylinder.

We numerically calculated the extinction spectra of gold nanocylinder of radius 30nm, length 40nm and radius 30nm, length 100nm using 3D FEM. Now, from the spectra presented in figure 2.2, it can be clearly seen that the polarization independence in case of sphere is now lifted. The LSPR for a cylinder now splits into one longitudinal mode and two degenerate transverse modes. The longitudinal mode occurs when the incident polarization is along the length of the nanocylinder and corresponds to the oscillation of free electrons along the long axis. This mode is strongly dependent on the aspect ratio A of the nanocylinder. As aspect ratio increases the mode is red shifted. On the other hand, the transverse mode corresponds to the excitation with incident polarization along the perpendicular the long axis. This mode more or less holds the position as aspect ratio increases. Red and blue spectra in Figure 2.2a corresponds to longitudinal LSPR mode of nanocylinders of length 40nm and 100nm. Red and blue spectra in figure 2.2c represent the transverse modes for same cylinders respectively. Figure 2.2b and d are the nearfield maps around the cylinder of 40nm length when the incident polarization was along and perpendicular to the long axis of the nanocylinder.

2.3 Light scattering by plasmonic nanocylinder dimer

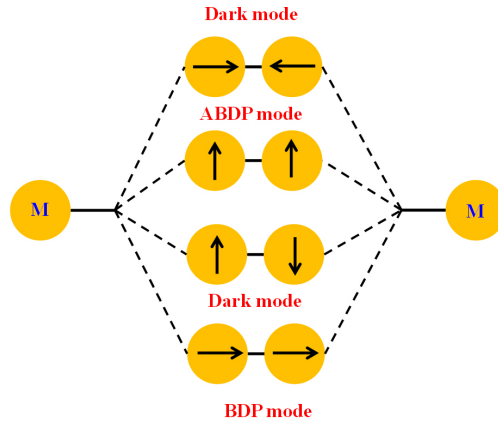


FIGURE 2.3: Hybridization of plasmon modes in case of metal nanoparticle dimers.

In the preceding sections, we presented how the optical properties of single nanostructure depend sensitively on its size, shape and incident light polarization. In this section, we will discuss the LSPR modes of two metallic nanoparticles couple with each other when they are placed in close vicinity of each other. By close vicinity, we mean the distance between two particles are greater than 0.3nm (quantum regime) but less than twice the diameter of the particles[123]. In this region, the plasmon modes in each particle interact with each other to give rise to completely new plasmon resonances. The occurrence of these new modes can be explained by the hybridization of the plasmon modes in both particles where the modes can hybridize either in phase or out of phase (figure 2.3)[102, 124–127]. When the incident light is polarized along the inter particle axis, the in-phase hybridization happens in a way analogous to bonding interactions. The attractive nature of the interaction between the induced charges in the particles at the junction results in a red-shift in the LSPR spectrum and the resonance is known as bonding dimer plasmon (BDP) mode. The out-of-phase interaction is optically forbidden in case of homodimers as the induced dipole moment in the particles cancels out for being equal and oppositely oriented. For the case of transverse polarization, the in-phase coupling results in an anti-bonding interaction. the repulsive force between the particles in this case result in a slight blue shift in the LSPR resonance observed in case of a monomer. This resonance is known as anti-bonding dimer plasmon (ABDP) mode.

We numerically simulated the electric-field and extinction spectrum of a gold nanocylinder dimer where each particle were of 30nm radius and 40nm long. The gap between two particles was of 10nm. Figure 2.4a shows the extinction spectra for two incident polarizations. Blue curve represents the extinction spectrum of the system when incident polarization was perpendicular to the long axis of the dimer where the resonance peak occurs at 520nm. This is similar to a transverse mode of a single nanocylinder of same dimension (see figure 2.2). Figure 2.4b is the near-field map for same incident polarization at the cross-section plane of the cylinder. When the incident polarization was along the long axis of the dimer, we see a red shift in the resonance peak (see red curve in figure 2.4a). As can be seen from the near field map in figure 2.4c, the electric-field at the junction in this case was far more (61V/m compared to 12V/m). Therefore in case of dimer, the degeneracy in the transverse mode is lifted and two new modes in form of ABDP and BDP occur. It is well known that for parallel polarization the junction electric field can be further increased by decreasing the gap distance. If the gap size is decreased, the red shift in BDP mode can be more and at gap sizes less than 5nm, higher order plasmon modes can arise in the extinction spectra.

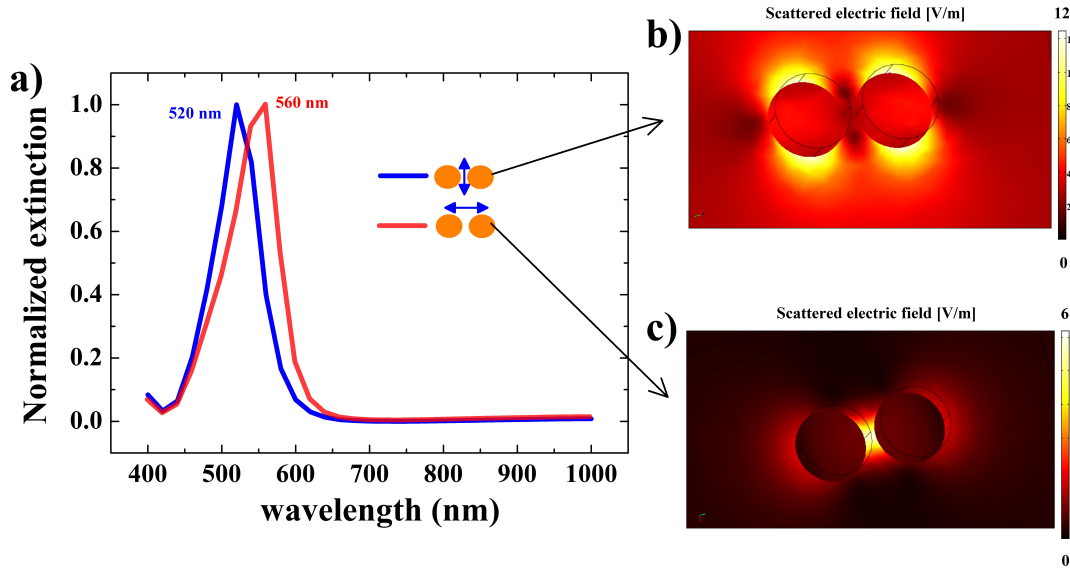


FIGURE 2.4: a) extinction spectra of a dimer of two 30nm radius, 40 nm (blue curve) long. Red and blue curves represent extinction spectrum when incident polarization was perpendicular and parallel to the long axis of the dimer. b) Near field map at cross section plane for perpendicular polarization excitation. c) Near field map at cross section plane for parallel polarization excitation.

2.4 Palladium bridged gold nanocylinder dimer as tunable plasmonic substrate²

Until now, we have discussed the influence of the presence of a nearby nanocylinder on the scattering spectra and near field of nanocylinder. In this section, we will present how a conductive bridge of palladium between two gold nanocylinder can influence the extinction spectra and near field of the dimer [128]. Furthermore, we will present how the LSPR of the system can be tuned by changing the dimension of the Pd bridge.

2.4.1 Simulation Geometry

Figure 2.5 shows the geometry, considered for the study. The radius of the each nanocylinder was 50nm. The gap between the two nanocylinders was filled with Pd. We used 2-dimensional finite element method (2D-FEM) to numerically calculate the SPR spectra and near field optical profile of the system. As the simulations were performed in a 2D environment, therefore the geometry can be considered as a cross-section of an infinitely long geometry. The width (w) and the length (l) of the Pd bridge between the

²Results published as full article in *Applied Optics*, Vol 51, pp 1688-1693, 2012.

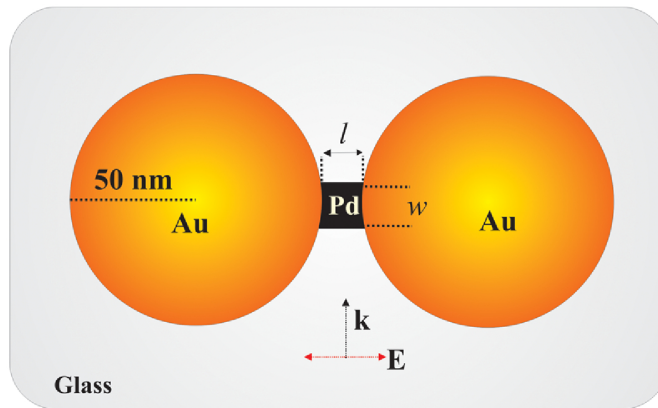


FIGURE 2.5: Geometry of the Pd bridged Au nanocylinder dimer, used in the simulation. Radius of each Au nanocylinder $r=50\text{nm}$; refractive index $n=1.5$; l and w are variable length and width of the Pd bridge. The arrows E and k represent electric field polarization and propagation direction of the incident electromagnetic field.

Au nanocylinder dimer were variable parameters in the simulation. The whole geometry was embedded in glass and refractive index of the glass medium was considered 1.5. The wavelength dependent dielectric constant of the Au was taken from the experimental values provided by Johnson and Christy[129]. The frequency dependent dielectric constant of Pd was taken from experimental values provided by Vargas et al[130]. The system was excited with incident polarization along the Pd bridge and the k vector perpendicular to that as shown in figure 2.5.

2.4.2 Extinction properties of the geometry

First, we have considered a bridged gold nanocylinder dimer where the conductive Pd bridge is 5nm long and 20 nm wide and compared the extinction spectrum of this arrangement with the extinction spectrum of an Au nanocylinder dimer without any conductive bridging. The incident polarization in both the cases was kept along the interparticle axis. The extinction spectrum of the conventional Au nanocylinder dimer is shown as the black curve in figure 2.6a. This spectrum has a peak at 598nm. This peak is assigned to bonding dimer plasmon (BDP) mode originating from the interaction of the plasmon modes of two nanoparticles in close proximity. This mode corresponds to in-phase surface charge oscillation in both particles along the dimer axis and is dipolar in nature. When the Pd bridge between two nanocylinders was introduced, two distinct plasmon modes at 839nm and 578nm were observed in the far-field extinction spectrum (see red curve in figure 2.6a). The new resonance at 839nm originates due to charge

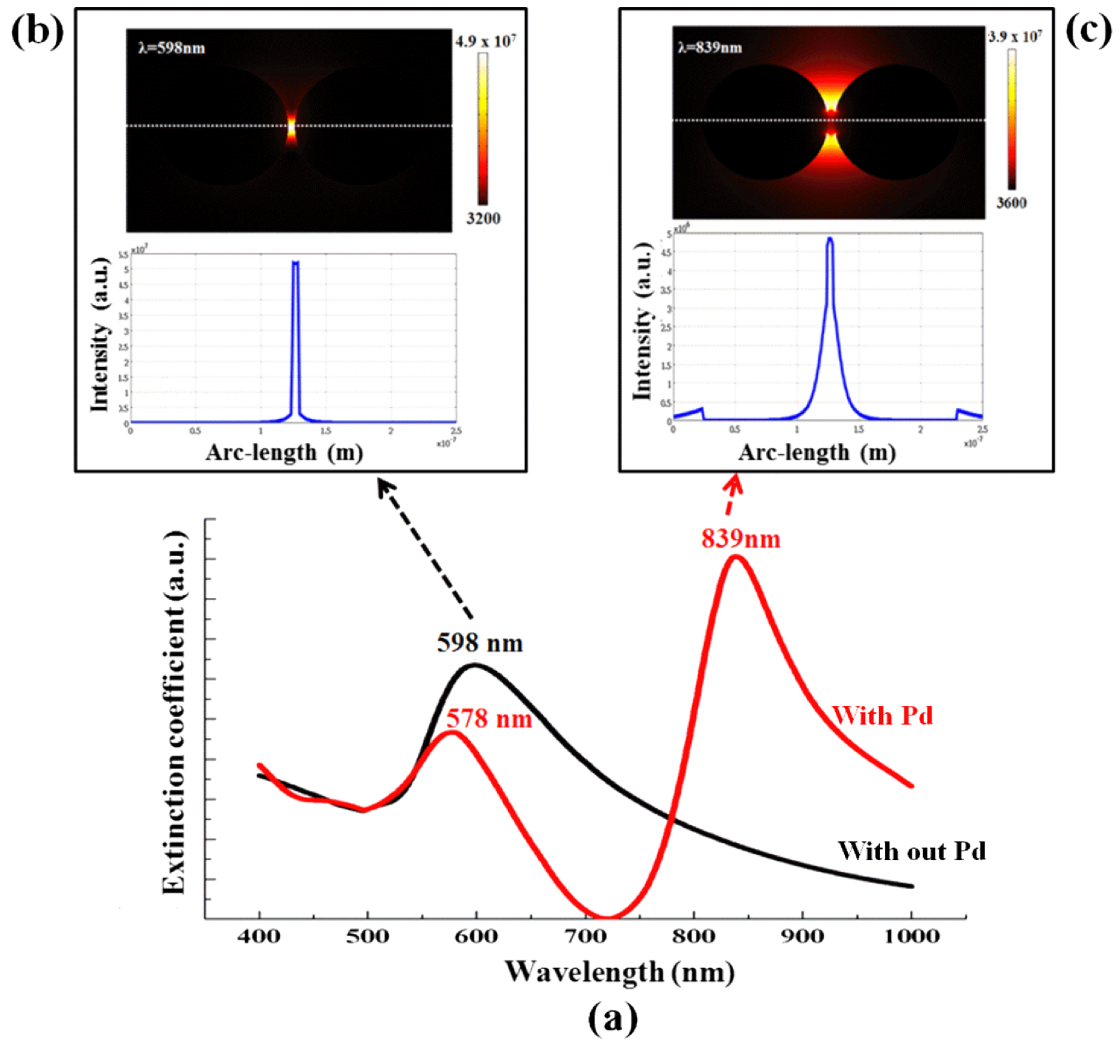


FIGURE 2.6: (a) Extinction spectra of Pd bridged Au nanodimer without and with Pd bridge. Near-field optical simulation map and field distribution of Au nanodimer (b) without Pd bridge, (c) with Pd bridge. The dotted line in near-field maps of (b) and (c) represents the plotted arc length.

transfer between the cylinders through the conductive Pd bridge. This charge transfer plasmon (CTP) mode corresponds to charge oscillation along the entire dimer[131–133]. At the same time, the BDP mode blueshifts to 578nm. Due to the presence of the conductive bridge the interacting charges in the gap are screened and the mode is now called screened bonding dimer plasmon (SBDP) mode which is quadrupolar in nature[132–134]. Such distinct hybrid modes have also been observed in Au nanodimers in conductive contact limit[135].

Apart from modification of the far-field extinction, we also observed modification in the near-field intensity of the system. Figure 2.6b and c show the electric field map around the dimer junction in absence and presence of the Pd bridge. We evaluated the magnitude and distribution of near field intensity at resonant wavelengths 598nm and 839nm for the two cases. We have also plotted the field distribution along the interparticle axis (the white dotted line). The resonant near-field intensity at the junction for conventional dimer was around 4.5×10^7 arbitrary units (a.u.) and the corresponding value for Pd bridged Au dimer was 3.0×10^6 a.u.. The reduction in the magnitude of intensity was also accompanied by larger spread across the gap junction. This can also be seen in the intensity vs arc-length graph in figure 2.6 b and c. The alteration of the magnitude and distribution of the near-field intensity across the junction can be explained as a consequence of redistribution of surface charges in conductively coupled plasmonic dimer system[134–137].

2.4.3 Tuning the plasmon resonance of Pd bridged Au nanocylinder dimer

It is well known that the plasmon resonance of a plasmonic nanostructure can have well defined correlation with its geometry. Such correlation allows the tuning of plasmon resonance of the system by slight variation in the plasmonic geometry. In this section, we will discuss how the LSPR of the Pd bridged Au nanocylinder dimer can be tuned simply by varying the width (w) and length (l) of the Pd bridge. First we examined the effect of w on LSPR position of the dipolar CTP mode (839nm) for constant $l = 5nm$. The variation of the peak position with the w is plotted in figure 2.7a. A nonlinear blueshift in the CTP mode can be observed with increase in w . It is to be noted that for variation in larger values of w (40 to 16nm), the shift in the peak position was incremental (800-900 nm), whereas for variation in smaller widths (16 to 4 nm), the peak shift was more significant (900 to 1125nm). Such nonlinear shift in the CTP mode is due to the redistribution of surface charges resulting in drastic change of electrical conductance for thinner conductive bridge[137, 138]. Similar effect has been experimentally observed in cases of Au threaded Au nanoparticle dimer[133].

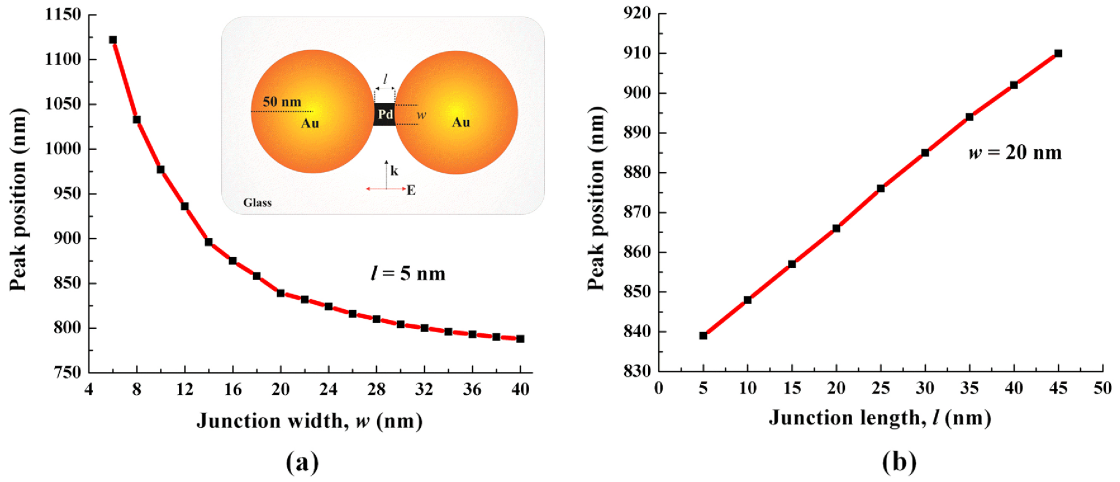


FIGURE 2.7: Tuning the dipolar plasmon mode of Pd bridged Au nanocylinder dimer by varying (a) width w and (b) length l of the Pd bridge. The values of $l=5$ nm and $w=20$ nm were kept constant in (a) and (b), respectively

Next, we analysed the effect of l on the same plasmon mode for a constant $w = 20$ nm (see figure 2.7b). This time a linear redshift was observed as the l was increased. This linear trend of plasmon mode with respect to increasing bridge length has been numerically studied by Romero et al., in the context of Au nanodumbbells and their surface charge density[137]. As the CTP mode corresponds to charge density oscillations along the entire geometry, this can be considered as standing-wave like modes. Therefore, such red shift in the resonance wavelength with increasing l can be explained as a result of increased wavelength of the standing-wave due to growing length of the dumbbell[137].

2.5 Pd bridged Au nanocylinder dimer for hydrogen sensing³

The speciality of Pd is it has high catalytic activity and the crystal lattice of Pd can adsorb large amounts of hydrogen to form palladium hydride in reversible manner. The free electrons from the adsorbed hydrogen modify the Fermi-level of Pd and change its electric permittivity. Therefore, the electrical properties of Pd are very sensitive to hydrogen exposure. This property makes Pd a suitable candidate for electrical and optical sensing of hydrogen[139–146]. Recent studies used plasmonic nanoantennas for hydrogen sensing which opened up the gate for miniaturization of the hydrogen

³Results published as full article in *Applied Optics*, Vol 51, pp1688-1693, 2012.

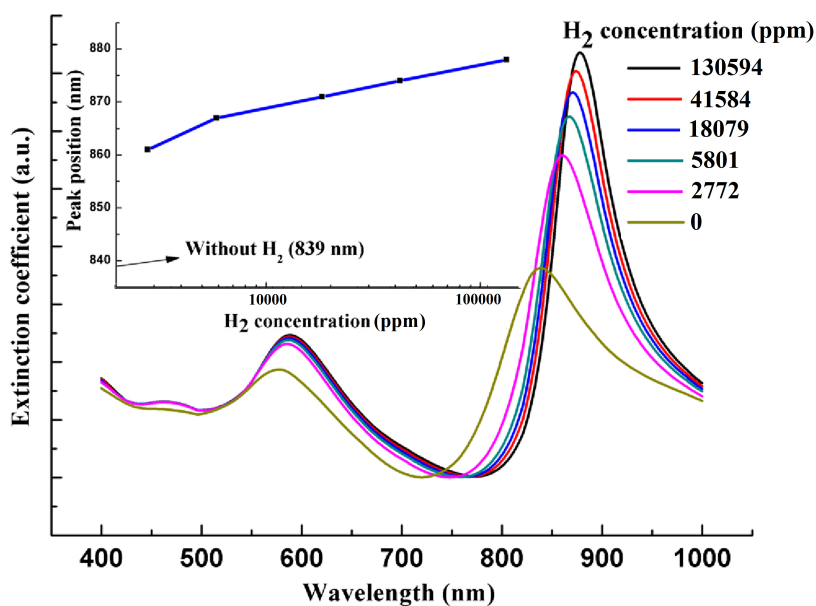


FIGURE 2.8: Far-field extinction spectra of Pd bridge Au nanocylinder dimer for various values of hydrogen concentration. The inset shows the variation of dipolar plasmon mode as a function of hydrogen concentration.

sensors without sacrificing on the sensitivity. Liu et al have shown that the plasmon resonance of an Au nanotriangle placed near to a Pd disc is very sensitive to the hydrogen concentration of the environment[79]. Atmospheric hydrogen concentration also has similar effects on Pd adjoined gold splittings[147]. In addition to these, many subwavelength palladium nanostructures have been explored for realizing nanooptical hydrogen sensing[148–153]. There is further need for optimization and adapt for more simple structures such as nano plasmonic dimers for sensing application. Compared to other structures, plasmonic dimers can be produced both by top-down[154] and bottom-up[155] approaches. With the objective of using Pd bridged Au nanocylinder dimer as a hydrogen sensing platform we investigated the effects of hydrogen concentration on the extinction spectra of the system[128]. The hydrogen concentration dependent dielectric constant of the Pd was taken from the experimental values provided by Vargas et al[129]. In their work, they experimentally measured the variation of dielectric function of hydrided Pd as a function of optical wavelengths for different hydrogen concentration. The measurements were done on Pd thin films; hence, size correction of the used Pd dielectric constant values would provide more accurate results. The geometrical parameters of the Pd bridge w and l were kept constant at 20 and 5nm respectively throughout the study. Figure 2.8 shows variation in the extinction spectra of system as

the hydrogen concentration was increased from 0 to 130594 ppm. A very small shift was observed in the BDP mode but a gradual red shift was observed in the CTP mode as the hydrogen concentration was increased. The plot in the inset shows the redshift in the LSPR of the system as function of hydrogen concentration. The dipolar CTP mode was shifted to 860 nm from 839nm for a hydrogen concentration of 2772 ppm. We also observed that for three order of magnitude (0 to 130594 ppm.) change in hydrogen partial pressure in the atmosphere the CTP mode had a red shift of 40nm. This revealed how sensitively hydrogen can be detected using the proposed plasmonic nano-geometry. These kinds of plasmonic sensors are advantageous as the spatial footprint of such miniaturized, reversible nanodetectors are so small (<500nm) that they can be used for on-chip hydrogen sensing. In addition to this, these sensors are devoid of the statistical averaging and inhomogeneous broadening effects that are inherent to detectors based on ensemble measurements.

2.6 Conclusions

To conclude the chapter, we have numerically studied the plasmonic properties of Pd bridged Au nanocylinder dimer. The filling of the gap between the nanocylinders with Pd changes the field localization characteristics at the junction. As a result, distinct LSPR modes are observed in the extinction spectra. One major advantage of such geometry is; they can be used as tunable plasmonic substrates. Here, the LSPR resonances can be tuned by varying the geometrical parameters (length and width) of the Pd bridge. Such tunability is important in context of using these nanoarchitectures to build wavelength dependant excitation and detection schemes in specialized detectors. Furthermore, we showed that this nanogeometry can work as a very sensitive detector for detecting hydrogen concentration in the surrounding. This observation paves the way for building similar LSPR based on-chip nanooptical gas sensors.

Chapter 3

Plasmonic nanowires: SPP based optical waveguiding

In the preceding chapter, we presented how localized surface plasmons in a plasmonic nanogeometry can be utilized to alter near-far-field responses of the system. From hereon, the thesis will be mainly focused on how propagating surface plasmon polaritons (SPP) in extended 1-dimensional (1D) structures such as plasmonic nanowire geometries can be used to manipulate optical fields. Plasmonic nanowires are one of the most common examples of SPP waveguides. These wires are known for their ability to propagate optical fields upto tens of microns distance while keeping them confined in sub-diffraction limit area in the transverse direction. Therefore, plasmonic nanowires are envisioned as the building blocks for future nanophotonic circuits. This will help us to replace the electronic circuits with highly miniaturized nanophotonic one which in turn may help us reducing the size of many electronic and photonic devices[156]. Although, plasmonic nanowires have been studied for different kinds of nanophotonic circuital applications for example routers, logic operations and waveguides; very few studies have explored their ability to work as optical antenna by selectively localizing electric fields to different positions or by spatially redirecting the optical radiations. Before we go on to present our experimental results, here in this chapter, we shall briefly discuss the mechanism behind SPP propagation in plasmonic nanowires and the methods to excite them. Furthermore we will also discuss the characteristics of SPP modes generated in our systems of interest i.e., serially coupled silver nanowire dimers and silver nanowire-nanoparticle systems.

3.1 Electromagnetic modes supported by a nanowire

Electromagnetic modes of a nanowire can be easily calculated by modelling the system as a cylinder, suspended in a homogeneous dielectric medium[157]. The solutions are well known and we discuss it in the following section.

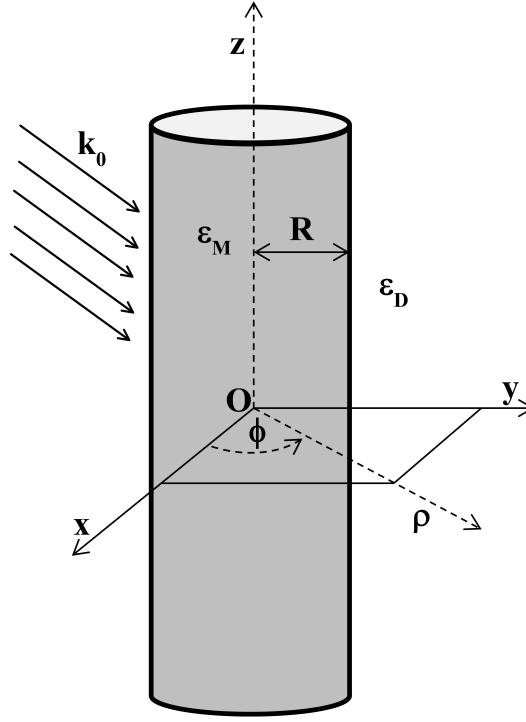


FIGURE 3.1: Illustration of the cylindrical co-ordinate system used for calculating electromagnetic modes in a metallic cylinder.

3.1.1 Electromagnetic modes in an infinitely long metallic cylinder

Let us consider an infinitely long cylinder of radius R which is illuminated by plane electromagnetic wave. The polarization of the electromagnetic wave can be represented as a combination of electric field oscillations in the plane containing the incident k vector and the axis of the cylinder or in the planes perpendicular to that. The used cylindrical co-ordinate system (ρ, ϕ, z) is illustrated in figure 3.1. Let us consider, the dielectric constant of the metal is ϵ_M and for the surrounding dielectric medium it is ϵ_D . We also consider the mediums to be non-magnetic and hence $\mu_D = \mu_m = 1$. The wave equation that the electromagnetic field satisfies in this case is given by[158, 159],

$$\nabla^2 \begin{Bmatrix} \mathbf{E}(\mathbf{r}) \\ \mathbf{H}(\mathbf{r}) \end{Bmatrix} + \frac{\omega^2}{c^2} \epsilon(\mathbf{r}) \begin{Bmatrix} \mathbf{E}(\mathbf{r}) \\ \mathbf{H}(\mathbf{r}) \end{Bmatrix} = 0 \quad (\text{Eq 3.1})$$

The Eq 3.1 can be solved by applying boundary conditions[158, 159]:

1. The tangential component of electric ($\mathbf{E}^{\parallel}$) and magnetic ($\mathbf{B}^{\parallel}$) fields must be continuous.

$$\mathbf{E}_M^{\parallel} = \mathbf{E}_D^{\parallel}; \mathbf{H}_M^{\parallel} = \mathbf{H}_D^{\parallel} \quad (\text{Eq 3.2})$$

2. The normal components of electric displacement ($\mathbf{D}^\perp = \epsilon \mathbf{E}^\perp$) and magnetic induction ($\mathbf{B}^\perp = \mu \mathbf{H}^\perp$) at the plane, tangent to the metal-dielectric interface must be conserved i.e.,

$$\mathbf{D}_M^\perp = \mathbf{D}_D^\perp; \mathbf{B}_M^\perp = \mathbf{B}_D^\perp \quad (\text{Eq 3.3})$$

The scalar solutions of the Eq 3.1, satisfying necessary boundary conditions (Eq 3.2 and Eq 3.3) take the form $\psi_M = J_m(k_{M\perp}\rho)e^{im\phi+ik_{\parallel}z}$ and $\psi_D = H_m(k_{D\perp}\rho)e^{im\phi+ik_{\parallel}z}$ inside and outside the metallic cylinder respectively. Here, J_m and H_m are Bessel and Hankel functions of first kind of order m (azimuthal quantum no.). $k_{i\perp} = \sqrt{k_i^2 - k_{\parallel}^2}$ and $k_i = \omega\sqrt{\epsilon_i}/c$ where $i = M; D$ represent the case inside and outside the cylinder. It should be noted that J_m is well behaved at $\rho = 0$, while $H_m(x) \sim e^{jx}$ for large x satisfy out-going wave conditions. It is easy to verify that two independent vector solutions of Eq 3.1 can be given by $\mathbf{v}_i = \frac{1}{k_i} \nabla \times (\hat{z}\psi_i)$ and $\mathbf{w}_i = \frac{1}{k_i} \nabla \times \mathbf{v}_i$. Now, the curl relations of the Maxwell's equations imply that $\mathbf{E}$ and $\mathbf{H}$ must take the form;

$$\mathbf{E}_i(\mathbf{r}) = a_i \mathbf{v}_i(\mathbf{r}) + b_i \mathbf{w}_i(\mathbf{r}) \quad (\text{Eq 3.4})$$

$$\mathbf{H}_i(\mathbf{r}) = -\frac{j}{\omega\mu_0} k_i [a_i \mathbf{w}_i(\mathbf{r}) + b_i \mathbf{v}_i(\mathbf{r})] \quad (\text{Eq 3.5})$$

where a_i and b_i are constant coefficients. When these two expressions are expanded in details, we obtain

$$\begin{aligned} \mathbf{E}_i = & \left\{ \left[\frac{jm}{k_i\rho} a_i F_{i,m}(k_{i\perp}\rho) + \frac{jk_{\parallel}k_{i\perp}}{k_i^2} b_i F'_{i,m}(k_{i\perp}\rho) \right] \hat{\rho} \right. \\ & \left. + \left[-\frac{k_{i\perp}}{k_i} a_i F'_{i,m}(k_{i\perp}\rho) - \frac{mk_{\parallel}}{k_i^2\rho} b_i F_{i,m}(k_{i\perp}\rho) \right] \hat{\phi} + \frac{k_{i\perp}^2}{k_i^2} a_i F_{i,m}(k_{i\perp}\rho) \hat{z} \right\} e^{j(m\phi+k_{\parallel}z)} \end{aligned} \quad (\text{Eq 3.6})$$

$$\begin{aligned} \mathbf{H}_i(\mathbf{r}) = & -\frac{j}{\omega\mu_0} k_i \left\{ \left[\frac{jk_{\parallel}k_{i\perp}}{k_i^2} a_i F'_{i,m}(k_{i\perp}\rho) + \frac{jm}{k_i\rho} b_i F_{i,m}(k_{i\perp}\rho) \right] \hat{\rho} \right. \\ & \left. - \left[\frac{mk_{\parallel}}{k_i^2\rho} a_i F_{i,m}(k_{i\perp}\rho) + \frac{k_{i\perp}}{k_i} b_i F'_{i,m}(k_{i\perp}\rho) \right] \hat{\phi} + \frac{k_{i\perp}^2}{k_i^2} a_i F_{i,m}(k_{i\perp}\rho) \hat{z} \right\} e^{j(m\phi+k_{\parallel}z)} \end{aligned} \quad (\text{Eq 3.7})$$

where $F_{M,m}(x) = H_m(x)$ and $F_{D,m}(x) = J_m(x)$.

Now upon applying boundary conditions, the relation between a_i and b_i can be fixed. As the tangential component of electric and magnetic fields E_ϕ , E_z , H_ϕ and H_z are needed to be continuous across the metal dielectric interface, we get a linear system

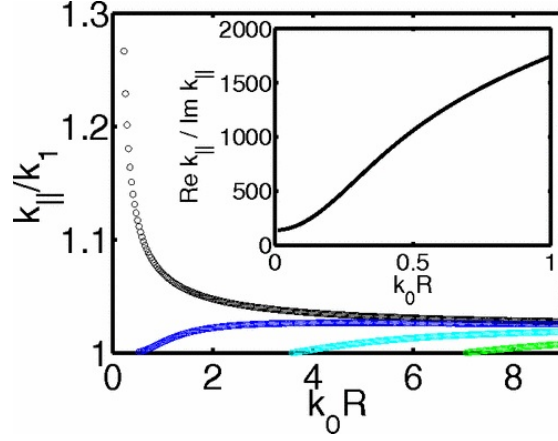


FIGURE 3.2: $k_{\parallel}$ as a function of radius R for allowed plasmon modes in a silver nanowire embedded in dielectric of $\epsilon_1 = 2$ for frequency corresponding to vacuum wavelength $1\mu m$. $m=0$ mode (black curve shows no cut-off radius whereas $|m| = 1, 2, 3$ modes show gradual increase in cut-off radius at nano wire limit. Inset shows the estimation of propagation losses as a function of radius.[157].

of four equations which can be written in the abbreviated form

$$M \begin{bmatrix} a_M \\ a_D \\ b_M \\ b_D \end{bmatrix} = 0 \quad (\text{Eq 3.8})$$

A non-trivial solution of the Eq 3.8 can be obtained by setting $\det M = 0$, which after some simplifications gives the mode equation[157–159],

$$\frac{m^2 k_{\parallel}^2}{R^2} \left(\frac{1}{k_{M\perp}^2} - \frac{1}{k_{D\perp}^2} \right) = \left[\frac{1}{k_{D\perp}} \frac{J'_m(k_{M\perp} R)}{J_m(k_{M\perp} R)} - \frac{1}{k_{D\perp}} \frac{H'_m(k_{D\perp} R)}{H_m(k_{D\perp} R)} \right] \times \left[\frac{k_M^2}{k_{M\perp}} \frac{J'_m(k_{M\perp} R)}{J_m(k_{M\perp} R)} - \frac{k_D^2}{k_{D\perp}} \frac{H'_m(k_{D\perp} R)}{H_m(k_{D\perp} R)} \right] \quad (\text{Eq 3.9})$$

This equation determines the allowed values of $k_{\parallel}$ as a function of m , R and ϵ_i .

Allowed modes in a nanowire and their behaviour

Now, if we focus on subwavelength conducting metal wire, it is well known that all the modes are not supported. The modes, $|m| \geq 1$ have a cut-off wire radius, below which they cannot be present. Here, we would like to present theoretical calculations produced by Chang *et al.*[157] in which they studied the allowed values of $k_{\parallel}$ as a

function of R for few lowest order modes ($|m| = 0, 1, 2, 3$) for silver nanowire using Eq 3.9. The excitation wavelength λ_0 and the dielectric constant of the medium ϵ_D was set to $1\mu m$ and 2 respectively. The results are shown in figure 3.2. It is to be noted that the longitudinal component of the wave vector exceeds the wavevector in uniform dielectric medium, $k_{\parallel} > k_D$ which immediately makes the perpendicular component $k_{i\perp} = \sqrt{k_i^2 - k_{\parallel}^2} = j\kappa_{i\perp}$ purely imaginary. This implies that the plasmon modes are non-radiative and confined near the metal-dielectric interface. The length scale of the confinement is determined by $\sim \frac{1}{\kappa_{i\perp}}$.

Now, it is interesting to note the behaviour of plasmon modes near the nanowire limits $|k_i|R \ll 1$. All higher order modes ($|m| > 1$) exhibit a cut-off as $R \rightarrow 0$. Only the fundamental mode ($m = 0$) exhibits a unique $k_{\parallel} \propto 1/R$ behaviour. This indicates that the wavelength of these surface plasmons can be strongly reduced with respect to the free space wavelength. Physically in this limit, the $m = 0$ mode can be visualized as the charge density waves along the wire. The $1/R$ scaling of $k_{\parallel}$ also makes $\kappa_{D\perp} \propto 1/R$ which implies the field outside the wire is also confined in a transverse direction on a scale $\propto R$ around the wire. In particular, these are the surface waves which are confined well below the diffraction limit.

Again ϵ_M having a small imaginary component means that the propagating plasmon modes suffer from absorption losses. The inset in figure 3.2 shows the plot of $Rek_{\parallel}/Imk_{\parallel}$ as function of R . This quantity is proportional to the decay length of plasmons in terms of plasmon wavelength $\lambda_{sp} = \frac{2\pi}{Rek_{\parallel}}$. Note that, as R decreases the ratio decreases but even at $R=0$ it has a non-zero value. Therefore, even at the limits $R \rightarrow 0$, plasmons can travel several times the wavelength λ_{sp} which is very useful for device applications.

m=0 mode is a transverse magnetic mode

The fundamental mode $m = 0$ can be analysed by putting $m = 0$ in Eq 3.9. In that case one of the two terms in right hand side of the equation must be equal to 0. Setting the first term to 0 corresponds to a transverse electric (TE) mode while the other case corresponds to a transverse magnetic (TM) mode. This can be verified by analysing Eq 3.6 and Eq 3.7. For a TM mode with no mode winding ($m = 0$), the component of $\mathbf{H}$ is along $\hat{z}$ by definition. This immediately sets the coefficient a_i to zero which again implies $E_{\phi} = 0$. Therefore the continuity of E_z and H_{ϕ} at the boundary requires that

$$\begin{pmatrix} \frac{k_{D\perp}^2}{k_D^2} H_0(k_{D\perp} R) & -\frac{k_{M\perp}^2}{k_M^2} J_0(k_{M\perp} R) \\ \frac{j}{\omega\mu_0} k_D H'_0(k_{D\perp} R) & -\frac{j}{\omega\mu_0} k_M J'_0(k_{M\perp} R) \end{pmatrix} \begin{pmatrix} b_D \\ b_M \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \quad (\text{Eq 3.10})$$

Setting the determinant of the first matrix in this equation to zero immediately yields

the second term in the R.H.S of the Eq 3.9 which is the mode equation for fundamental mode,

$$\frac{k_M^2}{k_{M\perp}} \frac{J'_0(k_{M\perp}R)}{J_0(k_{M\perp}R)} - \frac{k_D^2}{k_{D\perp}} \frac{H'_0(k_{D\perp}R)}{H_0(k_{D\perp}R)} = 0 \quad (\text{Eq 3.11})$$

The fields themselves can be obtained from Eq 3.6 and Eq 3.7

$$\begin{aligned} E_D &= b_D \left[\frac{jk_{\parallel}k_{M\perp}}{k_M^2} H'_0(k_{D\perp}\rho) \hat{\rho} + \frac{k_{D\perp}^2}{k_D^2} H_0(k_{D\perp}\rho) \hat{z} \right] e^{jk_{\parallel}z} \\ E_M &= b_M \left[\frac{jk_{\parallel}k_{D\perp}}{k_D^2} J'_0(k_{M\perp}\rho) \hat{\rho} + \frac{k_{M\perp}^2}{k_M^2} J_0(k_{M\perp}\rho) \hat{z} \right] e^{jk_{\parallel}z} \\ H_D &= \frac{j}{\omega\mu_0} k_{D\perp} b_D H'_0(k_{D\perp}\rho) e^{jk_{\parallel}z} \hat{\phi} \\ H_M &= \frac{j}{\omega\mu_0} k_{M\perp} b_M J'_0(k_{M\perp}\rho) e^{jk_{\parallel}z} \hat{\phi} \end{aligned} \quad (\text{Eq 3.12})$$

On the other hand, the TE mode equation does not have any solution. Therefore, the fundamental $m=0$ mode is a no-cut-off, axially symmetric transverse magnetic mode[160] resulting from electrons oscillating parallel to the axis of the wire.

Behaviour of $m=1$ mode

We have seen that the SP modes apart from $m=0$ mode have a cutoff in terms of the radius of the nanowire. Even then, the case $m=1$ mode should be studied carefully as the mode does not strictly have a cut-off size. Instead in the limits $R \rightarrow 0$ for $m=1$ mode $k_{\parallel} \rightarrow \sqrt{\epsilon_D}$ exponentially. This in turn makes the magnitude of $k_{D\perp}$ exponentially small which corresponds to an exponential growth in the spatial extent of mode volume[156, 157].

Now, let us define $\delta = k_{\parallel} - \sqrt{\epsilon_D}$. We are interested in finding an approximate solution of the Eq 3.9 in the limit of small δ . To do that, both sides of the equation are expanded separately. The left-hand-side takes the following form,

$$LHS = \frac{1}{4R^2\delta^2} + \frac{(3\epsilon_D + \epsilon_M)}{4R^2\sqrt{\epsilon_D}(\epsilon_D - \epsilon_M)\delta} + O(\delta^0) \quad (\text{Eq 3.13})$$

On the other hand, to expand the right-hand side, it is assumed that both the quantities $k_{D\perp}R$ and $k_{D\perp}$ will be small as $R \rightarrow 0$. The expansion after some simplifications takes the form,

$$RHS = \frac{1}{k_{D\perp}} \frac{H'_1(k_{D\perp}R)}{H_1(k_{D\perp}R)} \approx \frac{1}{4R^2\delta^2} \frac{\epsilon_D + 3\epsilon_M - 2R^2\epsilon_D(\epsilon_D - \epsilon_M)\log(\delta R^2\sqrt{\epsilon_D}/2)}{4R^2\sqrt{\epsilon_D}(\epsilon_D - \epsilon_M)\delta} \quad (\text{Eq 3.14})$$

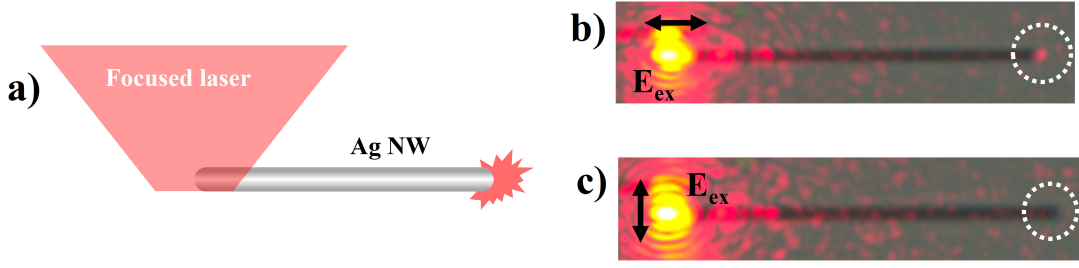


FIGURE 3.3: a) Schematic illustration of SPP excitation of SPP modes in a silver nanowire by focusing laser light at its termination. b) Light propagation through the nanowire when excitation laser was polarized along the nanowire. White dotted circle highlights the distal end from where propagating SPPs outcoupled as free photons. c) No propagating SPP modes were excited when the excitation laser was polarized perpendicular to the nanowire. The wire was of length $11\mu m$

Finally, by equating left and right-hand side to $O(\delta^{-1})$ we obtain the solution for δ .

$$\delta = \frac{2}{R^2\sqrt{\epsilon_D}} \exp \left[-\frac{2(\epsilon_D + \epsilon_M)}{R^2\epsilon_D(\epsilon_M - \epsilon_D)} \right] \quad (\text{Eq 3.15})$$

It follows that in the nanowire limit,

$$\begin{aligned} \kappa &= (k_{\parallel}^2 - \epsilon_D)^{1/2} \\ &\approx (2\delta\sqrt{\epsilon_D})^{1/2} \\ &\approx \frac{2}{R} \exp \left[-\frac{\epsilon_D + \epsilon_M}{R^2\epsilon_D(\epsilon_M - \epsilon_D)} \right] \end{aligned} \quad (\text{Eq 3.16})$$

These equations indicate that the $m = 1$ plasmon mode does not have a cut-off in the nanowire limit, but instead the longitudinal wavevector approaches $\sqrt{\epsilon_D}$ exponentially with corresponding increase in its transverse extent ($1/k_{D\perp}$) and mode volume. Therefore, these modes are very much localized and do not propagate at all. This justifies the mode cut-off. Hence, the SP modes $m = \pm 1$ correspond to charge oscillations in the plane horizontal and vertically perpendicular to the wire axis[156, 157].

3.2 Experimental techniques for exciting propagating SPPs in a silver nanowire

Local symmetry breaking at the terminal of a plasmonic nanowire is enough to provide the extra momentum required to the excitation light to excite SPPs in the nanowire[101,

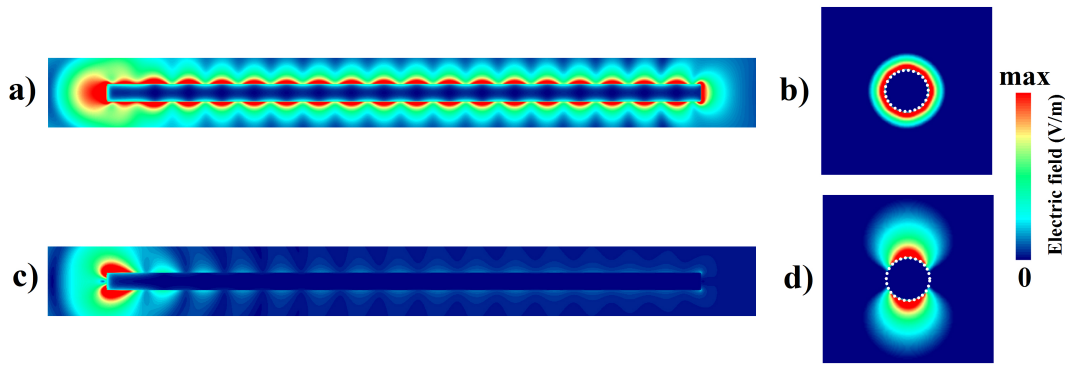


FIGURE 3.4: a) Calculated near-field map around the silver nanowire when the $m=0$ SPP mode was excited by incident laser, polarized along the length of the nanowire. b) Near-field map around the cross section of the nanowire for axially symmetric $m=0$ SPP mode. c) and d) corresponding near field maps when $m=1$ SPP mode was excited by incident laser, polarized perpendicular to the length of the nanowire.

[156, 161, 162]. Therefore, it is the most common way to excite SPP modes in a plasmonic nanowire. In general, a laser beam is tightly focused at the terminal of a nanowire using a high numerical aperture objective lens to excite propagating SPP modes [101, 161, 162]. Figure 3.3a shows a schematic of SPP excitation in metallic nanowires. The propagating modes are generated in the nanowire by selective phase matching of the incident laser with the SPP modes. Since propagating $m=0$ SPP modes correspond to the charge oscillation along the length of the nanowire, required phase matching can be obtained by an excitation laser being polarized along the length of the nanowire. Figure 3.3b and c show optical images of SPP excitation in silver nanowire. In these cases, a 633nm laser is focused at the terminal of the Ag nanowire. When the laser was polarized along the wire (figure 3.3), we see light coupling out from the distal end of the nanowire. This happens because this polarization excites the propagating $m=0$ SPP modes, which converge towards the end to couple out as free photons. When the laser is polarized perpendicular to the length of the nanowire $m=1$ SPP modes are excited which do not propagate. Hence, no light from the distal end was observed for this excitation polarization. For the intermediate input polarization states, the SPP modes generated in the nanowire are hybridization of $m=0$ and $m=1$ SPP modes [163]. Therefore, the propagation efficiency varies and hence the intensity of outcoupled light varies from being maximum when excitation laser is polarized along the nanowire length to minimum when excitation laser is polarized perpendicular to the length of the nanowire.

The numerical results for these excitation conditions have also been shown in figure

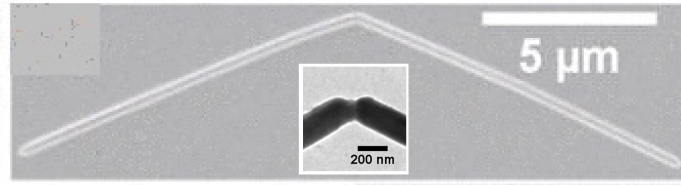


FIGURE 3.5: Scanning electron microscope image of a serially coupled Ag NW dimer and inset shows a TEM image of the junction of such systems.

3.4. The numerical calculations are done using 3-dimensional finite difference time domain (3D-FDTD) method. The near-field map around the Ag nanowire for the case of excitation laser being polarized along the length of the nanowire is shown in figure 3.4a. This shows the field distribution of the propagating $m=0$ SPP mode around the nanowire. The near-field map at the cross-section plane (figure 3.4b) shows that this is a axially symmetric transverse magnetic (TM_0) mode. The corresponding results for perpendicular polarization excitation is shown figure 3.4c and d. Which highlights the non-propagating nature of the $m=1$ SPP modes.

Apart from terminal excitation, there are also other ways to couple optical fields into SPP modes in a plasmonic nanowire; for example, evanescent coupling using optical fibres or scattering at a nanoparticle placed near the nanowire [164–166]. We extensively used terminal excitation to excite propagating SPP modes in nanowires.

3.3 Light propagation through a serially coupled Ag NW geometry

One of the nanowire geometry that we studied rigorously was serially coupled Ag nanowire (NW) dimers. Figure 3.5 shows a scanning electron microscope (SEM) image of the structure and inset of the figure 3.5 shows a tunnelling electron microscope (TEM) image of the junction of such system. The TEM image shows that the junction is fused in nature i.e., the two nanowires in the dimer are conductively coupled with each other. These nanowires were prepared chemically. The main mechanism behind chemical synthesis of Ag NW is; they are grown by nucleating many nanoparticles in a specific direction. These nanoparticles act as the seed. Now when we have a defect on these seeds, this nucleation can happen in a different direction. This might be the main reason behind such sharp curvature of the junction of Ag NW dimers [161, 167, 168]. The probability of creating defects can be increased slowing the rate of reaction.

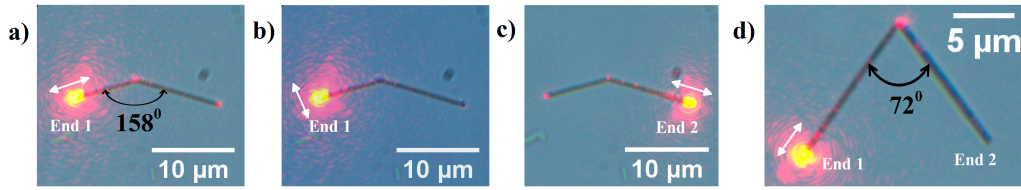


FIGURE 3.6: a) Light propagation through a serially coupled Ag NW dimer where coupling angle of the two wires is 158° when end 1 of the dimer was excited with incident laser being polarized along the length of the nanowire. Note that SPPs are coupling out as free photon from both the junction and the distal end. b) No propagating SPP modes were generated when incident polarization was perpendicular to the length of the nanowire. c) Junction can be excited by focusing laser at end 2 of the dimer as well. d) SPP modes in the other wire could not be generated when the coupling angle of the two wires was an acute 72° angle. No photons get out-coupled from the distal end.

Therefore, serially coupled Ag NW dimers are synthesised by following the conventional chemical synthesis protocol of Ag NWs but by slowing the rate of reaction. Our protocol for Ag NW dimer synthesis is described in chapter 4. Here, we will mainly discuss the light propagation characteristics through a coupled NW dimer. The speciality of such nanowire geometry is it supports propagating and localized SPs in the same platform[167, 168]. The junction acts as photon decoupling centre as well as a site for field localization[167, 168]. Figure 3.6 shows how propagating SPPs can be excited in these NW geometries. The most exciting characteristics is that the junction can be excited by illuminating either of free ends. Figure 3.6a shows the case when end 1 was illuminated with excitation laser being polarized along the respective wire and figure 3.6b shows the other case. In both cases, propagating SPPs are generated in the nanowire and propagate towards the junction to decouple as free photons. When the excitation laser was polarized perpendicularly, no propagating SPP modes were not excited and hence we didn't observe any light coming out from the junction 3.6c. Another interesting fact for such nanostructures is; the SPP modes in the excited wire can tunnel into the adjoined wire depending upon the coupling angle of the two wires in the dimer[168]. If the angle between two wires is an obtuse angle, SPP modes easily tunnel through the junction into the adjoined wire. This is the reason behind observing some light coupling out from the distal end for the wires with obtuse angle between two arms 3.6c. But if it is an acute angle, the tunneling is minimal and therefore no photon decoupling is observed from the distal end (figure 3.6d).

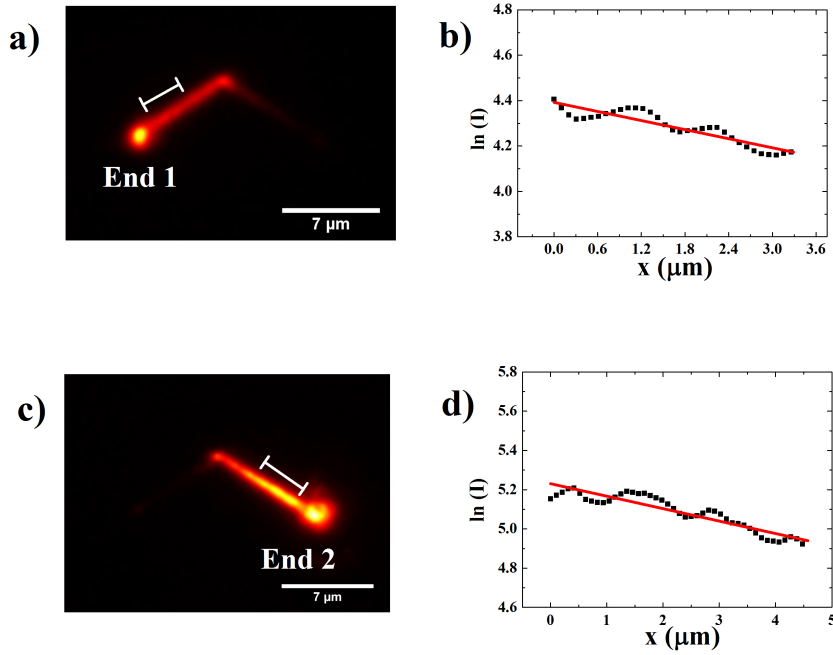


FIGURE 3.7: Plasmon propagation length calculation: a) Fluorescence image of a coupled wire when end 1 was excited. b) $\ln(I)$ vs distance (x) plot for the wire along the white line shown in the fluorescence image. c) Fluorescence image of the wire when end 2 was illuminated. d) Corresponding $\ln(I)$ vs x plot.

3.3.1 Propagation lengths of the SPP modes in a serially coupled NW dimer

To calculate propagation length of SP modes excited in the coupled wire dimer we performed the following experiment[169]. First we coated the dimers with a fluorescent dye, Nile blue-A and captured fluorescence optical images of the Ag NW dimer for single end excitations (see figure 3.7 a and c). The intensity of the fluorescence was measured at different points along the white line shown in the optical images. Generally propagating SP mode intensity decays with distance at a rate given by $I = I_0 \exp(-\frac{x}{L})$. Where x is the distance and L is the propagation length. We plotted measured intensities (I) as function of distances (x) in figure 3.7 b and d. The slope of the linear fit of the $\ln(I)$ vs x plot gives plasmon propagation length for the particular excited nanowire. In this case for excitation shown in figure 3.7 a, the wire had propagation length of $16\mu m$ and for excitation shown in figure 3.7 c, the wire had a propagation length of $14\mu m$. The wires we prepared had a propagation length ranging from $7\mu m$ to $17\mu m$ which is

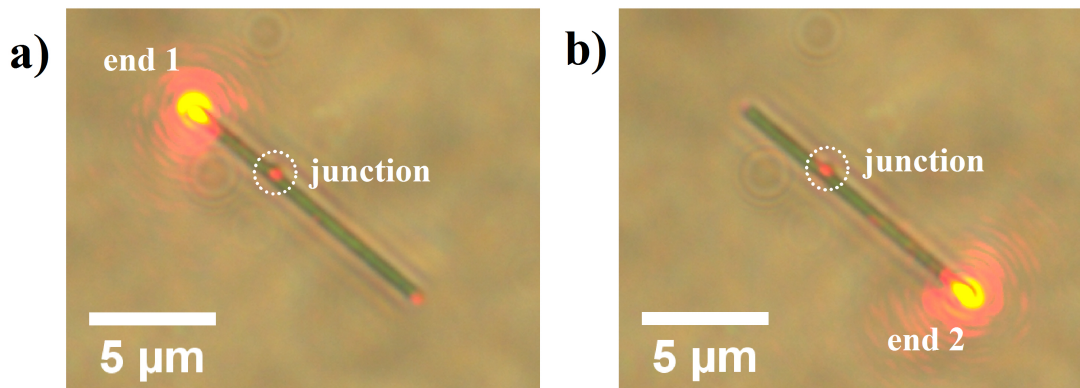


FIGURE 3.8: SPP propagation through Ag nanowire-nanoparticle system: Photon out-coupling from the NW-NP junction a) when end 1 was excited and b) when end 2 was excited with a focused laser being polarized along the length of the wire in both the cases.

similar to what is already reported in case of silver nanowires.

3.4 Light propagation through a nanoparticle coupled nanowire geometry

The other nanowire geometry, we extensively studied in context of their ability to localize fields is the Ag nanowire coupled with nanoparticles. These are also prepared chemically and the protocol is described in chapter 4. Figure 3.8a is an optical image of nanowire coupled with a nanoparticle. The nanoparticle being in contact with the nanowire acts as a photon decoupling region for SPP modes in the nanowires[164, 169]. Figure 3.8a shows the case when one of the ends (end 1) of such nanowire system was excited with a laser, polarized along the long axis of the nanowire. The input polarization state excites the propagating plasmons in the nanowire which decouple as free photons at the NW-NP junction. The local symmetry breaking due to the presence of the nanoparticle is the main reason behind the SPP modes, coupling out as free photons. Figure 3.8b shows the case when end 2 was excited. Again SPPs get converted into the free photons at the NW-NP junction.

In the following chapters, we will show how these plasmonic nanowire junctions which are acting as a photon decoupling centre can be used as a localized source or a directional emitter. These observations in turn will prove the ability of the nanojunctions to be harnessed as optical antennae.

Chapter 4

Remote Excitation Surface Enhanced Raman Microscopy Using Silver Nanowire Geometries

In the previous chapter, we mainly discussed about two types of nanowire geometries; serially coupled silver (Ag) nanowire (NW) dimers and Ag nanowire-nanoparticle systems. The SPP modes in these structures can be excited while illuminating either of the free ends of the system. The generated SPP modes radiate as free photons from the NW or nanoparticle junctions which allow the junction to work as a optical source which is spatially separated from the actual excitation point[77, 78, 167, 168]. Therefore, it opens up the possibility of utilizing such junctions for remote excitation of molecules, placed there. Now, as discussed in chapter 1, the amount of energy that can be delivered to the molecules placed at the junction will decide the ability of such geometries to work as a receiving antenna. To find that out, we needed to determine the degree of field localization at the junction. One of measuring the field localization under such remote excitation schemes is to perform remote excitation surface enhanced Raman scattering (SERS) at the NW and NP junctions. Apart from field localization measurements, remote excitation of molecules is important in context of biological measurements and drug optimization in cells where the sample can deteriorate upon direct exposure of light[170, 171]. In addition to this, the localized remote optical source created at the junctions of such systems can be of sub-diffraction limit dimension which can be helpful to improve the spatial resolution i.e, the lowest limit of excitation volume in Raman microscopes[170].

Motivated by all the above mentioned facts, we performed single and dual excitation remote SERS from the junction of coupled Ag NW dimers and Ag NW-NP junctions. By performing these experiments we explored how dual excitation induces higher field localization at the junction. Before presenting our actual experimental results on remote

excitation SERS measurements we will start by discussing the mechanism behind Raman microscopy and SERS. Then we will describe the experimental techniques we used to perform our experiments which will include the description of our dual excitation, spatial filter remote Raman microscope, specially designed for our study. Therefore, we start by discussing the principles of Raman scattering.

4.1 Principles of Raman scattering

When a photon is scattered by a molecule, usually it is scattered elastically and has same energy as the incident photon. But in some cases, the scattered photon can have energy different from the incident photon due to inelastic scattering from the molecule. The probability of this type of scattering is very low and is known as Raman scattering or the Raman effect[172]. This molecular scattering was discovered by C. V. Raman and K. S. Krishnan and had been theoretically predicted by Adolf Smarke.

Rayleigh, Stokes and anti-stokes scattering: To obtain Raman scattering the oscillating polarization state of the molecule has to couple to other polarization state of the molecule as well as the polarization state of the excitation photon. When either of these coupling is absent, the incident photon is scattered back with same energy and is known as Rayleigh scattered light. If the polarization in the molecule created due to incident photon couples to a molecular energy state, then the scattered photon will have energy different from the incident one. In perturbation theory, this intermediate polarization state of the molecule is referred as virtual state. Interestingly the difference in energy between the incident and scattered photon is same as the energy difference between two molecular energy states. When the molecule absorbs the incident photon, goes to a virtual state and comes back to an energy state, higher than the earlier energy state; the out-coming photon has lower energy and is known as Stokes scattered light. The shift in the frequency of scattered photon in this case is known as Stoke shift. This can be given by,

$$\nu_s = \nu_l - \nu_m \quad (\text{Eq 4.1})$$

where, ν_s = frequency of the stokes line,

ν_l = frequency of the laser line,

ν_m = frequency associated to the higher molecular energy level.

If this transition happens from the higher state to the lower state, the scattered photon has higher energy and the frequency shift is known as anti-Stokes shift. Probability of happening of this scattering is lower than the Stokes scattering as higher state will have lower population. Therefore, anti-Stokes line usually has lower intensity than the Stokes line but shift in frequency in both cases is same. Figure 4.1 is a schematic of

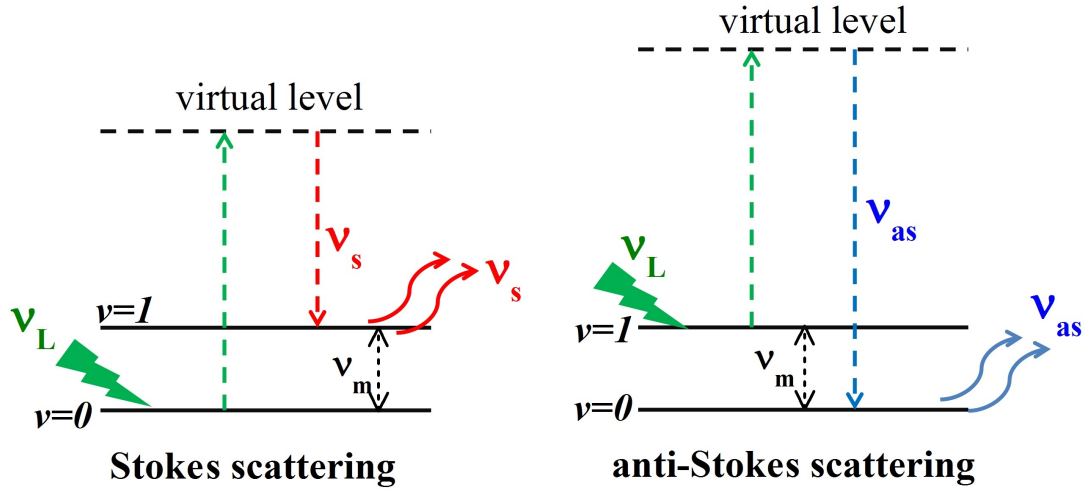


FIGURE 4.1: Schematic of emission mechanism in Raman scattering

molecular transition happening in case of Raman scattering. The frequency of the anti-Stokes line can be given by,

$$\nu_{as} = \nu_L + \nu_m \quad (\text{Eq 4.2})$$

The uniqueness of Raman scattering is that it does not need an excitation of specific wavelength as fluorescence. The Raman scattering is broadly used to identify molecular structure and molecular bond strengths. Apart from this, it also has applications in determining crystal structures of materials.

4.2 Principles of Raman microscopy

In case of Raman microscopes, usually a Laser is used as excitation source. The laser is focused on the sample using a microscope objective and the back-scattered light is collected by the same objective and then focused on a spectrometer equipped with a photo-detector. A Rayleigh rejection filter is used to reject the Rayleigh scattered light as it is very much intense than the Stokes and anti-Stokes lines. Usually, all these are added to a normal optical microscope to construct a Raman microscopy system[172, 173]. Figure 4.2 is a schematic of a conventional Raman Microscope. The spatial resolution of a Raman microscope i.e., the minimum excitation and collection volume is limited by the diffraction limit of the objective lens[173, 174], given by

$$d = \frac{\lambda}{2NA} \quad (\text{Eq 4.3})$$

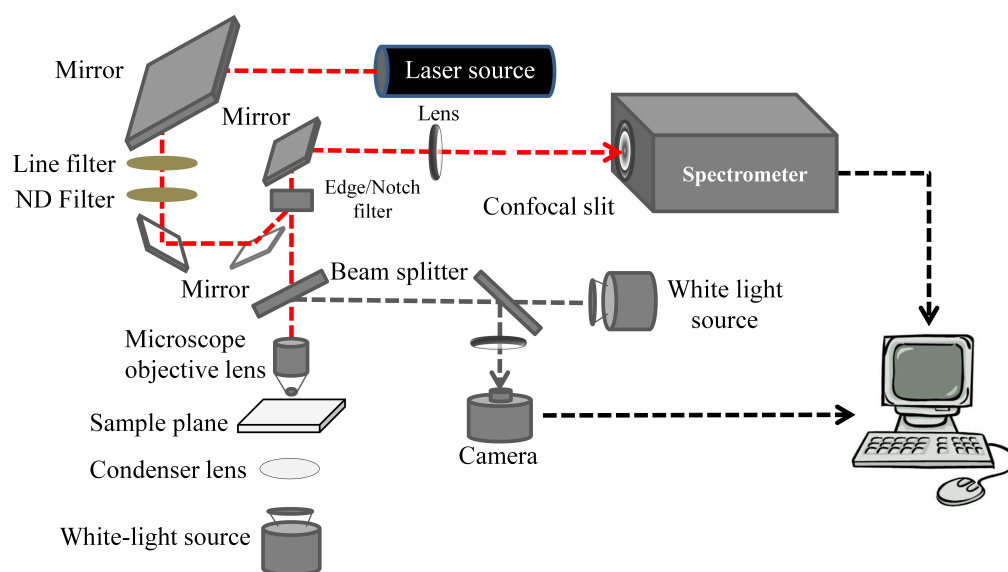


FIGURE 4.2: Schematic of a confocal Raman microscopy system

Where, λ is excitation wavelength and NA is the numerical aperture of the objective lens.

4.3 Surface enhanced Raman scattering

One of the spectacular applications of Plasmonics is surface enhanced Raman scattering. SERS is a surface based phenomenon which uses the highly localized electric field, generated near a metallic nanostructure to enhance the spontaneous Raman emission of a molecule[60, 62, 63]. The phenomenon was first observed in Pyridine absorbed on electrochemically roughened silver by Fleischmann et al in 1973[175]. As Raman scattering is a weak process, detection of small number of molecules is impossible using this process. In case of SERS this problem is solved by enhancing the typical Raman scattering cross-section by a factor of $10^9 - 10^{11}$ which makes even single molecule detection possible[69–72]. SERS is commonly performed at rough noble metal surfaces and nanoparticle aggregates. The reason behind this dramatic enhancement in the Raman signal was first described theoretically by Jeanmaire and Van Duyne in 1977[176]. Their theory is widely known as electromagnetic theory. According to this theory, the majority of this enhancement is resulted from highly enhanced fields near metal nanoparticles due to localized surface plasmons which are termed as hotspots[1, 2, 177, 178]. Apart from Raman scattering, the highly confined field at hotspots can enhance

other optical processes such as fluorescence as well. The molecule being directly in contact with the metal in case of SERS, the fluorescence gets quenched via non-radiative transitions[1, 2, 177, 179]. In this section, we will focus on the theoretical models to calculate the enhancement in Raman spectrum due to the metallic nanostructures.

As discussed earlier, Raman scattering is a spontaneous scattering process and hence the total power of the scattered scales linearly with the intensity of the incident light. Therefore, the power of Stokes scattered line can be expressed as,

$$P_s = N\sigma_{RS}I(\nu_L) \quad (\text{Eq 4.4})$$

Where N = no. of Stokes active scatterers, σ_{RS} = Raman scattering cross-section, $I(\nu_L)$ =intensity of the incident laser of frequency ν_L . Raman scattering is a weak emission process and its scattering cross-section σ_{RS} is lower than fluorescence cross-section σ_f . In general, $\sigma_{RS} \simeq 10^{-31}$ compared to $\sigma_f \simeq 10^{-29}$.

Now, in case of SERS, when the molecule is placed in the vicinity of a metallic nanostructure, we obtain the enhancement in the Raman signal. This enhancement in P_s can be due to two reasons:

- i. The change of environment around the molecule modifies the Raman cross-section in a way, $\sigma_{SERS} > \sigma_{RS}$. Such contribution to the enhancement is called chemical or electronic contribution and can be of the order 100 as suggested by theoretical models[175, 177, 180].
- ii. The most important contribution to the total enhancement of P_s comes from enhanced electromagnetic field near metallic nanostructures. The basis of which are a) the enhancement due to the resonant excitation of the LSP in plasmonic nanostructures[62, 176] and b) Crowding of electromagnetic field near sharp metallic interface, known as lightning rod effect. Out of these two, LSP resonance of a nanotstructure is dependent on the excitation wavelength while lightning rod effect is purely dependent on the geometry of the structure[1, 49, 180].

The enhancement factor due to field localization near metallic nanostructures can be expressed as,

$$L(\nu) = \frac{E_{loc}}{E_0} \quad (\text{Eq 4.5})$$

where E_{loc} is the local electric field amplitude at the SERS site and E_0 is the amplitude of the incident optical field. The total power of the Stokes beam of SERS can be given by,

$$P_s(\nu_s) = N\sigma_{SERS}L(\nu_L)^2L(\nu_s)^2I(\nu_L) \quad (\text{Eq 4.6})$$

since the difference in frequency between the incident beam and the Stokes line $\Delta\nu = \nu_L - \nu_s$ is much smaller than the line width of the LSP mode in general, we can always assume $L(\nu_L) = L(\nu_s)$. Therefore, the electromagnetic enhancement R in the SERS is proportional to the 4th power of the field enhancement factor.

$$R = \frac{|E_{loc}|^4}{|E_0|^4} \quad (\text{Eq 4.7})$$

Now, the enhancement $L(\nu)$ has the contribution both from LSP field and lightning rod effect and it can be expressed by,

$$L(\nu) = L_{SP}L_{LR} \quad (\text{Eq 4.8})$$

Here, L_{SP} is generally proportional to the polarizability α of the nanostructure for a given shape and on the other hand L_{LR} scales with the ratio of the permittivity of metal and surrounding dielectric medium. Therefore, SERS is directly proportional to the 4th order of field localization due to SPs in plasmonic nanostructures and can be utilized for measuring the degree of field localization at the site where SERS is performed.

4.4 Remote excitation SERS

Since its discovery, SERS has been very effective tool for molecular detection in many areas of biology and material science. It has been very important for in-vivo and in-vitro biomolecular molecular detection and drug optimization[66, 177, 181–186]. Normally, SERS is performed by directly focusing lasers on the detecting sample which is known as direct mode or local SERS. Hence, the SERS microscopy is performed in a system similar to the Raman microscope[170, 177]. In contrast, remote excitation SERS is performed by focusing the incident light at a position which is spatially separated from the point of detection. The excitation energy in this case is transferred to the detection point using a plasmonic waveguide which supports propagating SPPs to transport the optical fields to the desired location[170]. Generally, Remote SERS is performed at plasmonic nanowires with defects, nanoparticle junctions or at terminal ends of the nanowire where the propagating SPPs decouples as free space photons[77, 78, 187, 188]. Figure 4.3 is a schematic of a remote SERS geometry. Although, this technique of remote excitation suffers from the disadvantage of losing energy due to Ohmic damping of propagating SPPs in the metal, it provides some advantages over direct mode SERS such as,

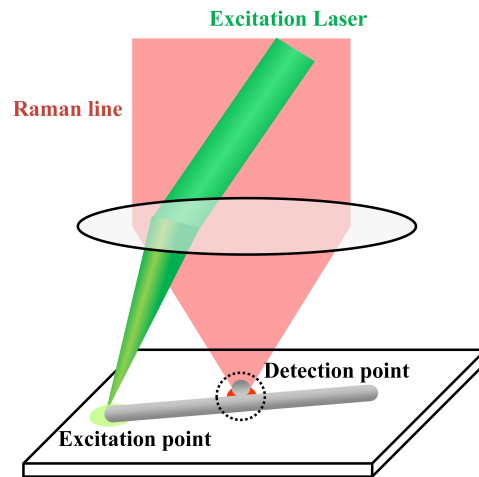


FIGURE 4.3: Schematic, showing how remote SERS is performed conventionally

- a) It can be used to remotely excite hotspot of nanometer dimensions. As the excitation field is localized at a sub-diffraction wavelength area[77, 78], it minimizes the background noise due to a large area excitation created by the focused laser beam in case of direct mode SERS[170].
- b) It avoids the heat from the focused laser illumination in case of direct mode SERS; thereby naturally reduces the possibility of damaging the sample[170].
- c) It is very useful to perform sensing of bio-molecules in-vivo in cells[188].

However, there are issues still remain unsolved i.e.,

- a) How to have better control over the optical fields in order to modulate the enhancement of SERS to obtain better signal to noise ratio Raman spectrum.
- b) Furthermore, new plasmonic nanogeometries are needed to be explored which can be easily amenable to far-field optics.

The presented work on remote excitation SERS in this chapter will also address all these issues regarding remote excitation Raman scattering. In the following section we describe the experimental techniques for performing remote excitation SERS.

4.5 Remote excitation microscopy set-up

Before describing our home-built remote excitation Raman microscopy set-up, first we will discuss about conventional remote SERS microscopes[170, 188]. Generally, remote SERS is performed on a conventional confocal Raman microscope shown in figure 4.2. Figure 4.3 is schematic representation of how remote excitation and spectra collection is performed using this microscope. Remote excitation is performed by tilting the excitation mirrors to move the laser focal point to one of the ends of the plasmonic nanowire while keeping the spectra collection point aligned with the confocal slit. The size of the slit is reduced to get rid of the contribution from the excitation point. Although this type of spectra collection technique has been used for performing remote SERS at nanowire-nanoparticle junctions and wire ends, it has some disadvantages and limitations like,

- a) As we know that efficiency of the SPP generation in plasmonic nanowires depend on the profile, polarization and phase of the excitation laser beam. When the laser is brought in a tilted angle the polarization states no longer remain same at the sample plane.
- b) The tilt in laser angle creates a larger excitation area by making the beam shape elliptical at the focal-point; thereby reducing efficiency of photon to plasmon conversion.
- c) The tilt in excitation angle also creates a phase mismatch at the wire ends which gives rise to excitation of more lossy higher order plasmon modes.
- d) Also the excitation technique provides only one excitation path.

*Dual excitation, spatial filter Raman microscope:*¹ To overcome these limitations of a conventional remote SERS system and according to our experimental requirements, we built a special remote excitation microscopy system which is capable of providing two excitation paths and spatially filtered collection[189]. The advantage of the system is the beam shape and polarization states remain unchanged at the focal point which increases the photon to SPP coupling efficiency. Therefore, more energy can be delivered to the point of spectra collection.

Figure 4.4a is a schematic of our home built remote SERS microscopy system. In this setup a 632.8nm wavelength He-Ne laser was used as excitation source. The laser was split into two using a polarization beam splitter and focused on two terminals of our Ag NW systems through a 100 X, 0.9 numerical aperture (N.A.) air immersion objective

¹Results published in **Applied Physics Letters; Vol 103, pp-151114, 2013**

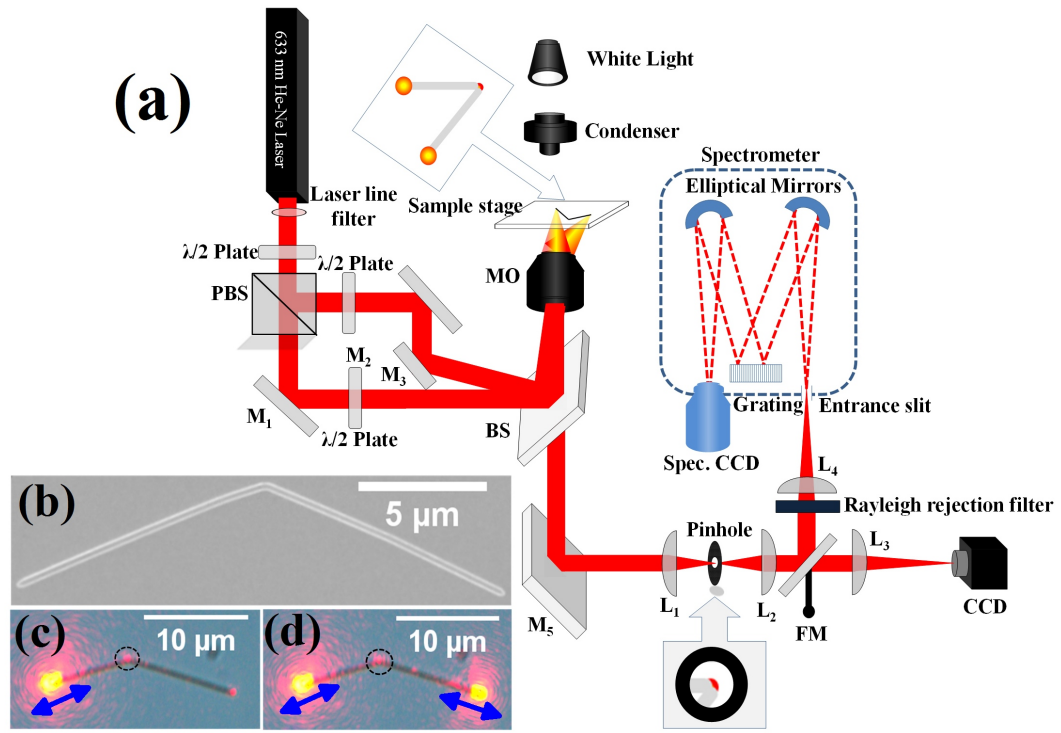


FIGURE 4.4: (a) Schematic diagram of the Raman microscope with dual-excitation and spatially-filtered collection optics; (b) Scanning-electron-microscopy image of a serially coupled Ag NW dimer. Each nanowire was approximately $10\mu\text{m}$ in length, 200nm in diameter and the angle between the two nanowires was 150° . Optical images of (c) single-path remote-excitation of the nanowire junction and (d) dual-path remote excitation of the same nanowire-junction. Polarization of the incident laser is indicated by blue arrows and black dotted-circles indicate spatially-filtered region from where the SERS signals were collected. M_1, M_2, M_3, M_4 and M_5 are mirrors, L_1, L_2, L_3 , and L_4 are lenses, PBS is polarizing beam splitter, BS is normal beam splitter and MO is microscope objective lens.

lens. The objective lens was housed on an inverted microscope (Olympus iX71). The laser was brought into the microscope objective using a plate beam-splitter (Chroma 50/50). Figure 4.4 b shows a scanning electron microscopy (SEM) image of a serially coupled nanowire dimer system (on which remote SERS experiments were performed). For single path excitation, the laser was focused on one of the free ends of the nanowire dimer as shown in the optical image in figure 4.4c. For dual path excitation, it was focused on both ends simultaneously (see figure 4.4d). The black arrows in the optical images signify the polarization of the incident beam which was along the wires in these cases. The Raman spectra collection was done by acquiring the back-reflected light from the sample by the same objective lens and routing it towards a telescope system consisted of two lenses (L_1 and L_2) of focal lengths 120mm and 150mm. This telescope system was used in order to create an intermediate real-space image plane which was used to spatially filter out the Raman scattered light from the desired position of the sample plane. In our cases it would be either nanowire dimer junctions or nanowire-nanoparticle junctions. A focal length of 120mm of lens L_1 implied a magnification of 100X at the intermediate image plane and we used a $100\mu\text{m}$ diameter pinhole for spatial filtering. A tube lens (L_3) was used after the telescope system to create image plane on a charge coupled device (CCD) camera for optical imaging. Upon spatial filtering we used a flip mirror to route the Raman scattered light towards a spectrometer (Jobin-Yvon, iHR 320). A 200mm focal length lens (L_4) was used to focus the light on the spectrometer entrance slit. The lens was placed on a three axis translation stage to accurately couple the light into the spectrometer. A Rayleigh rejection filter (Semrock 632.8nm high band pass filter) was used in the collection path to filter out the Rayleigh scattered light. The Raman spectra were recorded on Peltier cooled CCD (Synapse) housed in the spectrometer. Half wave plates were used for rotating the polarization of the incident laser beams. For optical imaging the flip mirror was flipped out of the optical path and once it was brought in, we were able to record the Raman spectra on the spectrometer.

4.6 Serially coupled silver nanowire junctions for single and dual excitation remote SERS²

This section is mainly dedicated to the presentation of our experiments on serially coupled silver nanowire dimer's ability to provide two excitation channels for performing single and dual channel remote SERS at the junction. The following experimental and

²Results published in *Applied Physics Letters*; Vol 103, pp-151114, 2013.

numerical simulations data will reveal how the dual excitation leads to further enhancement of the remote SERS signal from the junction. As we have seen in chapter 3, the polarization of incident laser plays important role in creating propagating SPP modes in plasmonic nanowire. Here, we will also discuss the possibility of modulating the SERS signal from the junction by varying input polarizations at the wire ends[189].

4.6.1 Sample preparation

Ag NW dimers were synthesized via polyol reduction of silver nitrate ($AgNO_3$)[167, 190]. First, 3ml 0.0854M solution of silver nitrate ($AgNO_3$) in ethylene glycol and 3ml 0.3416M solution of polyvinyl-pyrrolidone (PVP) in ethylene glycol were prepared separately. These two solutions were injected into the 5ml of ethylene glycol at a rate of 0.2ml/min at 160°C. The whole mixture was then stirred for one hour at 160°C. This solution contained nanowires along with nanoparticles. These nanoparticles were removed by centrifuging in deionized water and discarding supernatants. After sonication of the sample for 10 to 15min, we obtained a large fraction of nanowire dimers with various lengths.

The prepared wires were washed twice with acetone to remove excess ethylene glycol, six times with ethanol to remove PVP. Then the nanowires were dispersed in water. This nanowire suspension was mixed with 5 μm Nile Blue-A (NBA) in same volume ratio. The mixture was incubated for six hours and then spin-coated on a glass micro-slide. Prepared micro-slide contained a few isolated single nanowires and many dimer structures.

4.6.2 Single and dual excitation remote SERS

For remote SERS experiment, we have used the same Ag NW dimer shown in figure 4.4b. Two wires of the dimer were 10 μm and 11 μm long. These wires were coupled at an obtuse angle 150°. Figures 4.5a and b are single excitation remote SERS spectra acquired from the junction while insets show the optical image of experimental situation. The spectrum in figure 4.5a was obtained by exciting end1 of the wire with laser excitation being polarized along the wire which is indicated by the blue arrow. The black dotted circle shows the spatially filtered region from where the SERS signal was collected. Figure 4.5 b shows the spectrum when end 2 of the dimer was excited with incident polarization along the illuminated wire and SERS signal was collected from the junction. In both the cases, excitation laser power was 8mW. Figure 4.5c shows the dual-path remote excitation SERS spectrum from the junction. In this case, both the free ends of the same dimer were excited simultaneously. Incident light polarization

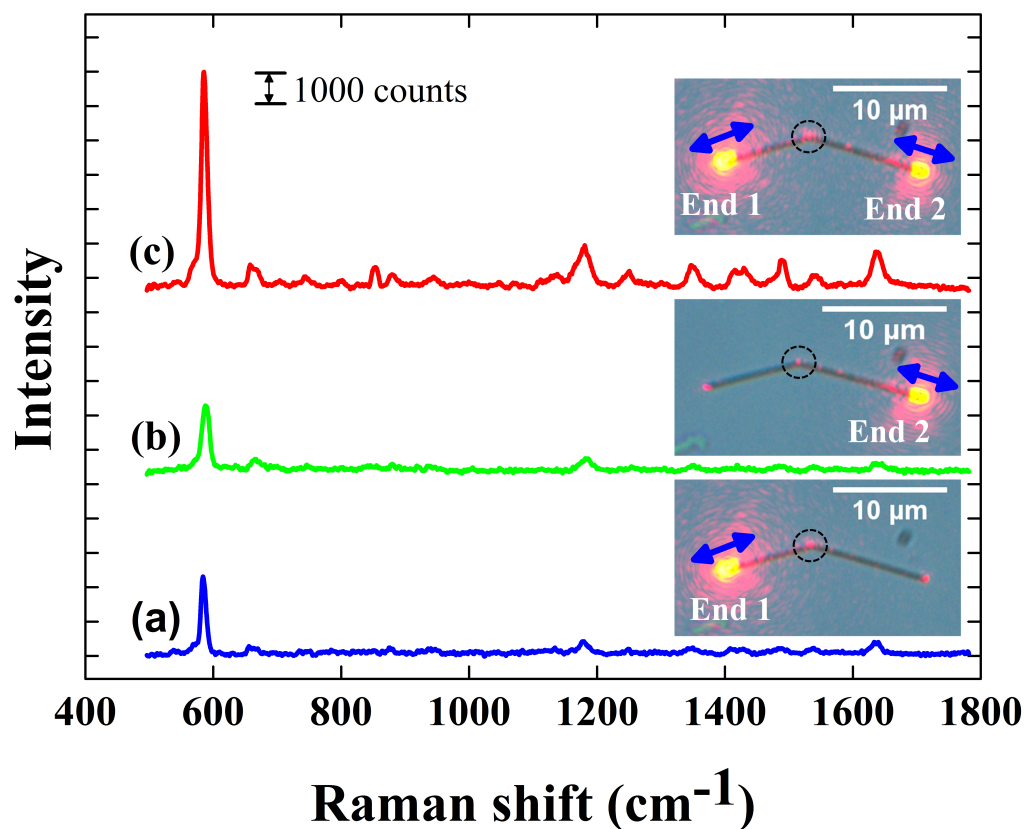


FIGURE 4.5: (a, b) Single- and (c) dual-path remote-excitation SERS spectra of Nile blue-A from the junction of coupled nanowires. In (a) and (b), the spectra were collected from the nanowire junction when end 1 and end 2 were individually illuminated with 8mW excitation power, and the spectra in (c) were collected from the nanowire junction when both ends were simultaneously illuminated with 4mW power, each. Insets show the corresponding optical images. Polarizations of incident lasers are indicated as blue arrows and black dotted circles indicate the collection areas of Raman signal. The spectrum (c) showed an enhanced SERS intensity compared to (a) and (b) despite the fact that identical laser powers were used for all the measurements. The spectra were stacked for clarity.

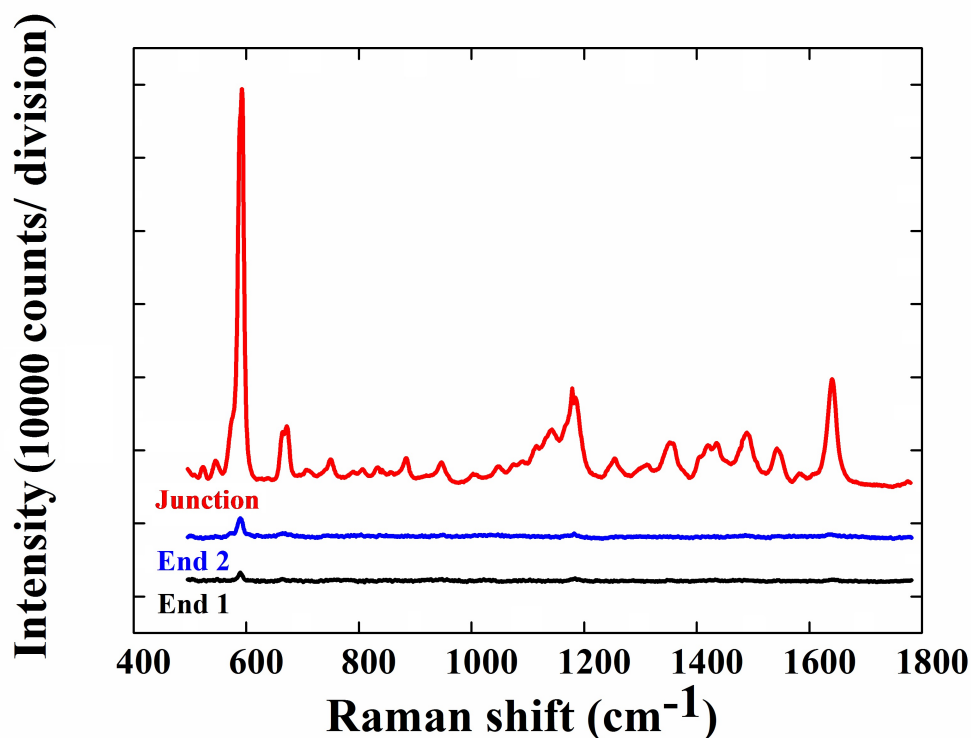


FIGURE 4.6: Directly acquired Raman spectra from the junction and two ends of the coupled AgNW system of fig 4.4). Red spectrum is when excitation laser was focused at the junction, black and blue spectra are when the laser was focused at end 1 and end 2, having polarizations along respective wires. Integration time was 5s in each case.

at both ends was along the respective wires as the previous cases but the illumination laser power was 4mW at each end. Acquisition time for all the spectra were 30s and we used a 100X 0.9 NA objective lens for the experiment. Note that the total laser excitation power for all the cases (single and dual path excitation) is fixed to 8mW but interestingly dual-path excitation (figure 4.5c) resulted in more enhanced SERS signal when compared to single-path excitation configuration (figures 4.5a and b). We also quantified the relative enhancement in the SERS spectra due to dual path excitation by calculating the integral intensity of 590cm^{-1} peak of NBA. All the values are charted in table 4.1. It was evident that despite of the total power being same, SERS signal intensity in case of dual-path excitation was approximately 70% more than single-path excitation.

To prove that the Raman signal collected in our study were indeed coming from the molecules at the junction; we collected direct SERS spectra from both the wire ends and the junction. These spectra are presented in figure 4.6. There were barely any detectable signals from the free ends compared to the intense signal coming from the Ag NW dimer

junction. To propagate these Raman scattered light from the ends towards the junction it will again have to go through major absorption losses in the metal. Therefore, it was unlikely that the Raman spectra, we collected in case of remote excitation SERS from the junction were the Raman scattered light which had propagated from the ends of the nanowire dimer.

TABLE 4.1: Comparison of remote SERS enhancement

Experimental Results(4.5)				Simulation Results(4.7)			
Incident Power (mW)				Power - P_0			
Observations	End 1	End 2	Relative enhancement	observations	End 1	End 2	E_{junc} (a.u)
Fig 4.5(a)	8	0	0.31	fig 4.7(a)	1	0	2.24
Fig 4.5(b)	0	8	0.30				
Fig 4.5(c)	4	4	1	Fig 4.7(b)	1/2	1/2	3.28

Numerical analysis

To understand the physical phenomenon, happening at the junction; we numerically simulated the experimental results using 3 dimensional finite difference time domain (3D FDTD)³ calculations. We used a commercially available “FDTD solutions, Lumericals inc” software for the numerical simulations. The serially coupled geometry was modelled as two $10\mu\text{m}$ long and 200nm diameter cylinders with spherical termini, placed face to face at an angle 150° . The wavelength dependent dielectric constants of silver were taken from experimental values provided by Johnson and Christy. For excitation we have used 633nm wavelength light. the FDTD source we used was a focused Gaussian source and excitation was done through a thin lens of NA 0.9 to match the experimental conditions. The simulation region was $0.5 \times 20 \times 3\mu\text{m}^3$ and a non-uniform mesh of minimum grid size 5nm was used. We used perfectly matched layer (PML) in our simulation to get rid off unwanted contribution from light reflected of simulation boundaries. PMLS are used in all the three directions. Injection axis of light source was X-axis and electric field was monitored in Y-Z filed. For dual-path excitation, the incident field amplitude at each end was kept $\frac{1}{\sqrt{2}}$ times the field amplitude, used in single path excitation. This ensures the excitation intensity at each end to be half of that in case of single-path excitation. The power of illumination was set to P_0 (see figure 4.7a) for single end excitation and for dual-path excitation, incident power was $P_0/2$ at each end so that total excitation power remains constant at P_0 (see figure 4.7b). For single-path excitation with incident polarization along the length of illuminated wire, the calculation shows a maximum value of local electric field at the junction to be around 2.24

³For details of FDTD simulations see **Appendix B**

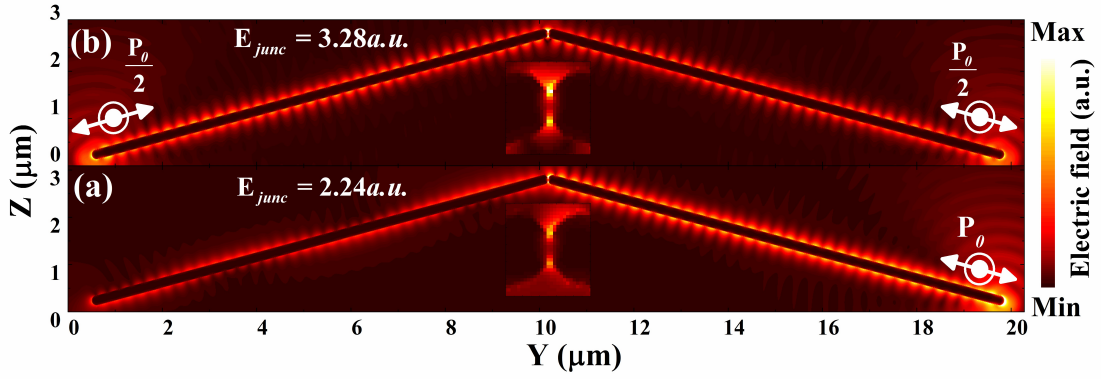


FIGURE 4.7: 3D-FDTD calculations of the electric-field distribution in serially coupled Ag NW dimers. (a) Electric field distribution when one of the ends of the Ag NW dimer was illuminated with focused monochromatic beam with polarization along the wire; (b) electric field distribution when each end of the Ag NW dimer was illuminated with half the power used in (a). Insets are the zoomed-in images of the junction. Note that the total power of illumination in (a) and (b) were identical (P_0), but the local electric field at the nanowire junction, E_{junc} , was 2.24 and 3.28, respectively. The white arrows indicate the polarization of excitation source.

(arbitrary units). However when the both ends were illuminated simultaneously having incident polarization along respective wire, the value of maximum electric field at the junction increased to 3.28 (arbitrary units). The results are charted in table 4.1. As discussed earlier in this chapter, for small stokes shift, the SERS enhancement due to local electric field can be quantified as $|\frac{E_{loc}}{E_0}|^4$ where E_{loc} is the local electric field at the junction and E_0 is total incident electric field which is set at the value 1 (arbitrary units). Therefore, these numerical calculations imply that the local electric field and hence the Raman enhancement at the junction increased significantly in case of dual-path excitation with respect to single-path excitation. This was also evident in our experimental results.

Why do we observe SERS enhancement in case of dual excitation? The enhancement obtained in dual excitation can be attributed to in-phase coupling of SPP modes in the individual wires at the junction which create a higher local field at the junction. The enhancement can be explained in terms of in-phase and out-of-phase coupling of SPP modes at conductively coupled Ag NW junctions which lead to bonding and anti-bonding interactions between the SPP modes [191, 192]. The bonding interaction can be the reason behind enhanced localization in case of dual excitation as for single excitations this interaction is absent. Further study of electron energy loss spectroscopy (EELS) [191, 193] of our serially coupled AgNW dimers can throw more

light on the interactions between plasmon modes and enhancement mechanism at the nanowire junctions.

4.6.3 Modulation in SERS signal

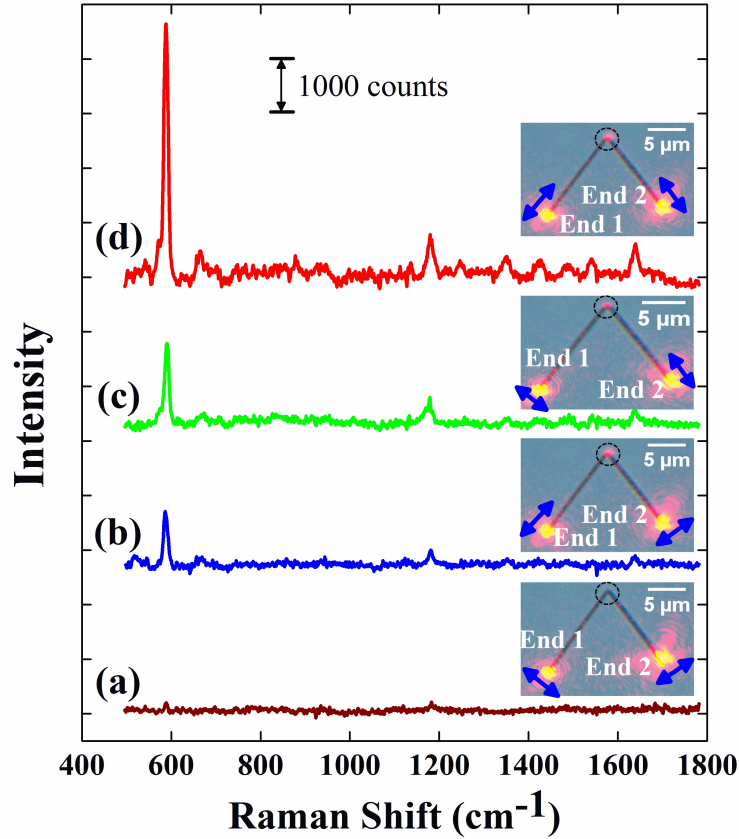


FIGURE 4.8: Polarization-assisted SERS intensity modulation at Ag NW dimer junction by dual-path remote excitation. SERS spectra obtained when: (a) both the ends of the NW dimer were excited by laser beams with polarization perpendicular to lengths of the nanowires; (b) end 1 was illuminated by polarization along the nanowire and end 2 illuminated with polarization perpendicular to the nanowire; (c) end 2 was illuminated by polarization along the nanowire and end 1 illuminated with polarization perpendicular to the nanowire; and (d) both the ends of the NW dimer were excited by laser beams with polarization parallel to the lengths of the nanowires. Insets show the corresponding optical images. The spectra were stacked for clarity.

In this section, we will discuss how the SERS signal can be modulated in case of dual path excitation by varying the incident polarization at the wire ends or by changing the angle between two wires in the dimer.

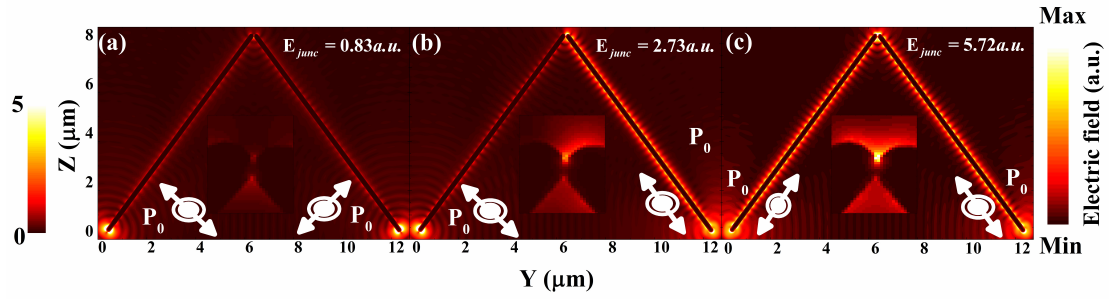


FIGURE 4.9: 3D-FDTD calculations of electric field for coupled AgNW (each wire are $10\mu m$ long and having 73° angle between them) (a) when both ends were illuminated with polarization perpendicular to the long axis of the wire (b) with polarization along the wire at one end and perpendicular to the wire at other end (c) when both ends are illuminated with along the respective wires. Insets are zoomed in view of the junction and colour bar at the left corresponds to inset electric field distribution.

Effect of varying polarization

The variation in input polarization at the wire ends can lead to change in the propagating SPP modes in the nanowire. When the input polarization is along the length of the illuminated wire, propagating $m=0$ SPP modes are excited which delivers maximum energy to the junction. On the other hand when the incident polarization is perpendicular to the long axis of the wire, $m=1$ SPP modes are excited which is lossy in nature and hence minimum energy can be delivered to the junction. We used this property to efficiently modulate the SERS signal obtained from the junction by using different combinations of input polarizations in case of dual-path remote excitation. For this experiment we have used an Ag NW dimer where each wire was $10\mu m$ long and the two wires were coupled at an angle 73° . Figure 4.8 shows four spectra for four different excitation configurations. Excitation power at each end throughout the experiment was kept at 8mW. Figure 4.8a shows the SERS spectrum obtained from the junction when the incident polarizations were perpendicular to both wires. This configuration lead to excitation of $m=1$ SPP mode in the wire and hence minimum energy could be delivered to the junction which result in no detectable SERS signal from the junction. For the spectrum presented in figure 4.8b, polarization at end 1 was rotated to match the orientation of the illuminated wire and hence a moderate amount of energy was delivered to the junction. Therefore, moderate SERS signal was obtained in this case. When a polarization combination opposite to that of figure 4.8b was used, again a moderate SERS signal was obtained from the junction. This spectrum is shown in figure 4.8c. When polarization at both ends were along the respective wires, maximum SERS signal could be acquired from the junction as shown in figure 4.8d. The relative enhancement in

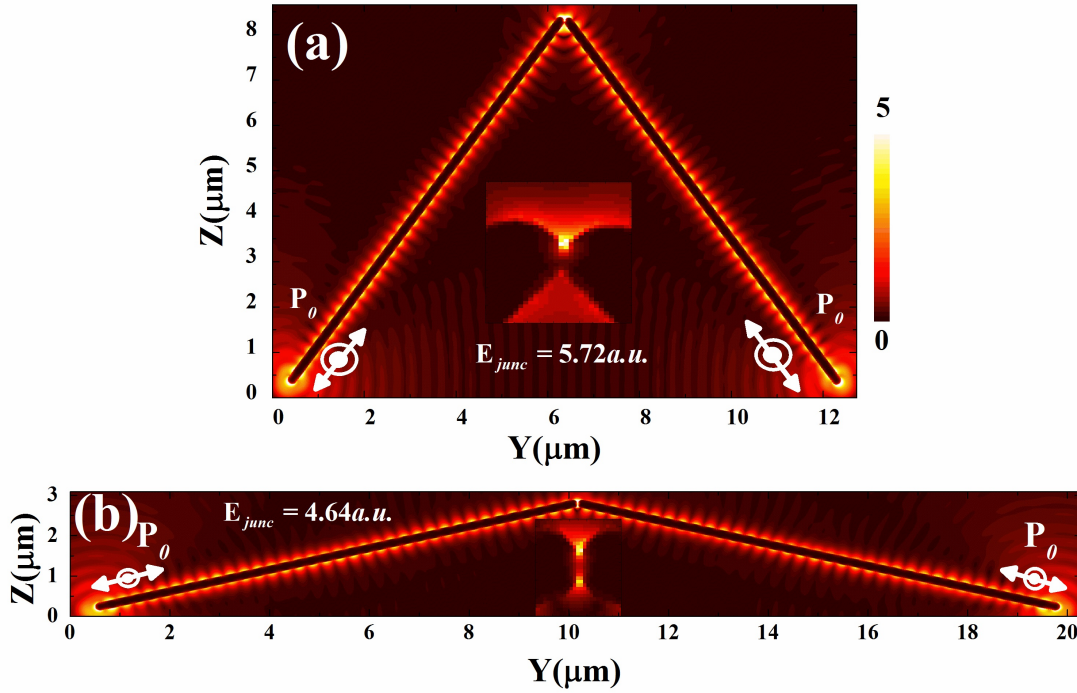


FIGURE 4.10: Simulated electric field map for dual path excitation of the junction of nanowire dimer. (a) when angle between two wires was 73^0 and (b) when angle between two wires was 150^0 . Insets are the zoomed in view of the electric field map at the junction and the colour bar is for inset electric field distribution.

case of 4.8d configuration was 94% with respect to the configuration in 4.8a and around 75% than the configurations in figure 4.8b and c. All the data are tabulated in table 4.2.

We have corroborated our experimental result with 3D-FDTD calculations. Here, the simulation geometry was matched to the experimental configuration. Figure 4.9 a shows the case where polarization at both ends were perpendicular to the respective wire axis. We found a local electric field value of 0.83 (arbitrary units) which was minimum

TABLE 4.2: Comparison of remote SERS enhancement

Experimental Results				Simulation Results			
	Incident Power (mW)				Power - P_0		
Observations	End 1	End 2	Relative enhancement	observations	End 1	End 2	E_{junc} (a.u)
Fig 4.8(a)	8⊥	8⊥	0.006	Fig 4.9(a)	1⊥	1⊥	0.83
Fig 4.8(b)	8	8⊥	0.23	Fig 4.9(b)	1	⊥	2.73
Fig 4.8(c)	8⊥	8	0.29		1	1	5.72
Fig 4.8(d)	8	8	1.00	Fig 4.7(c)	1	1	

among all the configurations. When polarization at one end was along the wire axis electric field at the junction increased to 2.73 (arbitrary units) as shown in figure 4.9b. For incident polarization being parallel to both wires (figure 4.9c), the junction local field further increased to the maximum value of 5.73 (arbitrary units). All these values are also tabulated in table 4.2 to show the one to one correspondence in the experimental and simulated data.

Effect of geometry

To show that the angle between the two wires also plays a major role in deciding the enhancement factor at the junction, we did the following 3D-FDTD calculations. Here, we have considered coupled Ag NW dimers with two different coupling angles; one being acute (73°) and the other being obtuse (150°). We found out that in case of angle 73° , the value of local field was 5.72 a.u. which was greater than 4.74 a.u., obtained when the coupling angle was 150° . The simulation results are shown in figure 4.10. Therefore, the angle between two wire in the dimer also plays a major role in deciding the enhancement factor in case of dual-path remote excitation SERS. The reason behind this can be following: in case of obtuse angle, more fraction of energy of the propagating SPP mode gets coupled to the other wire resulting in less amount of energy being dissipated at the junction. Therefore in dimers, coupled at an acute angle, more energy getting dissipated at the junction creates more enhancement in the SERS signal.

4.7 Remote excitation SERS from silver nanowire-nanoparticle junctions⁴

In this section, we will present that the silver nanowire-nanoparticle junctions can also be utilized in a similar fashion to obtain remote excitation SERS[194]. We have used the same microscope shown in figure 4.4 for this experiment. Figure 4.11 shows a SEM image of a silver nanowire-nanoparticle system where the wire was of $12\mu\text{m}$ length and 250nm diameter and the particle was of 160nm diameter. The fabrication method of this system is similar to that of the nanowire dimers. Here again, we used polyol synthesis method reported by Xia et al. During the synthesis of Ag nanowires, nanowire-nanoparticle coupled systems were also obtained. The $10\mu\text{l}$ aqueous suspension of nanowire-nanoparticles were mixed with $10\mu\text{l}$ of $5\mu\text{M}$ solution of NBA and incubated for 6h. After that, the mixture was spin coated on glass microslide.

⁴Results published in *Journal of Nanophotonics*; Vol 8 (1), pp-083899, 2014.

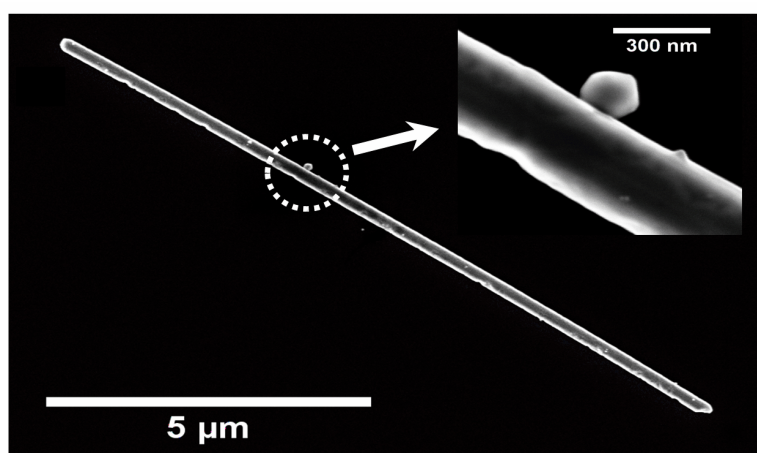


FIGURE 4.11: SEM image of the Ag nanowire-nanoparticle system, used for the study. Inset is a zoomed in view of the nanowire-nanoparticle junction.

4.7.1 Single path plasmon excitation vs counter-propagating plasmon excitation

The remote excitation SERS in this experiment was performed using a 632.8 nm He-Ne laser and a 100X, 0.9 NA objective lens. Figures 4.12 a,b and c show the optical image of single and dual end excitation of the system. In all the cases, incident polarization was along the wire axis and indicated by the white arrow in the images. The white dotted circle signifies the spatially filtered region of SERS signal collection. The total excitation power in all the cases was set to 0.2mW. Therefore, for dual excitation incident laser power at each end was 0.1mW. Spectra acquisition time in all cases was 10s. Figure 4.12d shows the remote excitation SERS spectra obtained from the experimental configurations shown in figures 4.12 a,b and c. The bottom black spectrum was obtained when the farther end of the NW-NP system was illuminated (figure 4.12a). This led to fairly intense SERS signal from the junction. When the NW-NP junction was excited by illuminating the nearer end, the spectrum (blue spectrum) was slightly intense than the previous case. The top red spectrum was obtained by illuminating both ends of the NW-NP system to excite counter-propagating plasmons. As evident from the figure 4.12d, spectral intensity for this configuration was much more compared to single channel excitations. The spectrum obtained from counter propagating plasmon excitation of the NW-NP junction was 4.5-7.0 times intense than that, obtained by single channel excitation. This enhancement factors were quantified for 590cm^{-1} NBA Raman peak.

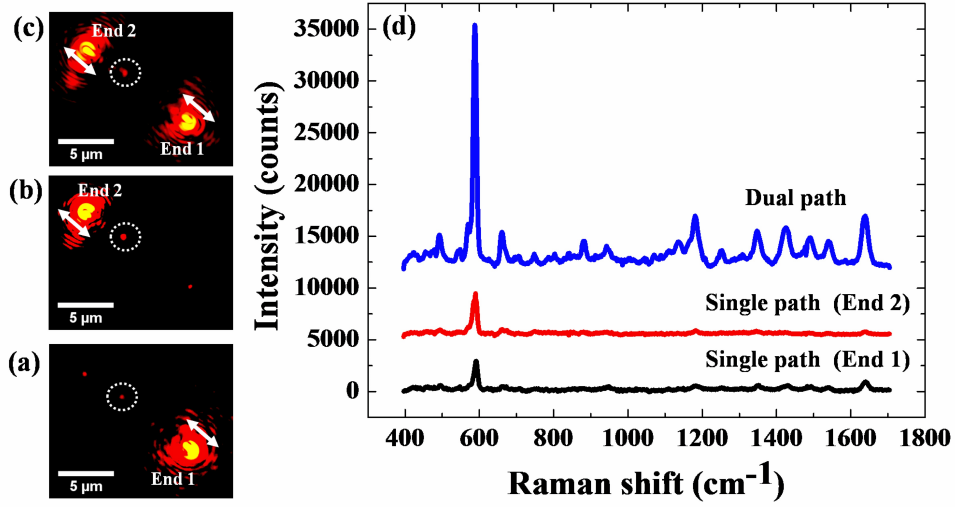


FIGURE 4.12: Single and dual path remote excitation SERS of nile blue-A from the silver nanowire-nanoparticle junction. Optical images of (a) single-path farther-end excitation (0.2mW power), (b) single path near-end excitation (0.2mW) and (c) dual-path, counter-propagating plasmon excitation (0.1mW + 0.1mW) of the nanowire-nanoparticle junction. (d) Remote excitation SERS spectra collected from the junction where black and red spectra are single path remote SERS when laser was respectively focused on end1 and end 2 of the nanowire with polarization along the wire. The blue intense spectrum was for counter-propagating plasmon excitation when the same laser was split into two and simultaneously focused on both ends of the wire.

Numerical analysis

To corroborate our experimental observations, we performed 3D-FDTD simulation on similar Ag NW-NP system. We mimicked the experimental configuration by placing a 160nm diameter spherical particle in the vicinity of a 12μm long and 200nm diameter cylinder. The distance of the nanoparticle from the two ends of the wire was kept same as the experimental sample. We used a 633nm wavelength focused Gaussian beam source for exciting the wire. Excitation was done through a 0.9NA thin lens and incident polarization was along the length of the wire. For single path excitation, ends were illuminated with excitation electric field amplitude 1V/m and for dual path excitation field amplitude at each end was $\frac{1}{\sqrt{2}}$ V/m. This excitation configuration allowed us to keep the total excitation powers same for all three cases. A non-uniform mesh of minimum grid size 3nm was used to simulate a 0.6X0.6X13μm³ simulation region. For single end excitation at the far end (figure 4.13a) we observed a maximum local electric

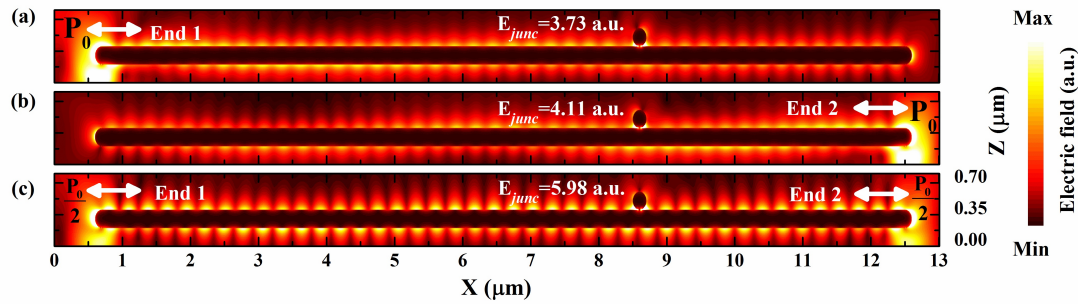


FIGURE 4.13: 3D FDTD calculation of electric field for silver nanowire-nanoparticle system where the wire was $12\mu m$ long and had a diameter of $200nm$ and the nanoparticle diameter was $200nm$. (a) Local electric field map when end 1 was illuminated with $633nm$ laser with electric field polarization along the wire. (b) Local electric field map when end 2 was illuminated with incident laser polarization along the wire. (c) Local electric field map when both ends were illuminated simultaneously with incident laser polarizations along the wire. Note that the total powers for all the three simulations were kept constant (P_0).

field $3.71V/m$ (figure 4.13b) and for excitation at near end we obtained a local electric field of $4.12V/m$. In case of counter-propagating plasmon excitation (figure 4.13c) of the junction, the local field increased to $5.98 V/m$. The results show similar trend as the experimental data where the counter propagating plasmons lead to greater enhancement followed by near and far end excitations.

The reason behind this result can be as following: When the ends were excited with incident polarization along the length of the wire propagating SPP modes were generated which coupled out at the junction to excite the SERS of the molecules. In case of the simultaneous excitation of both ends, counter propagating plasmons were generated which coupled with each other to create a higher enhancement of local electric field compared to single end excitation. This can be referred as constructive interference of counter-propagating SPP modes at the nanowire-nanoparticle junction.

4.7.2 Modulation of remote excitation SERS intensity by changing incident polarization in case of counter propagating plasmon excitation.

Similar to serially coupled Ag NW dimers, we checked the possibility of modulating the remote SERS signal intensity from the NW-NP junction by varying the incident laser polarization at each end in case of counter-propagating plasmon excitation. As discussed in chapter 3, two fundamental SPP $m=0$ and $m=1$ can be excited in silver

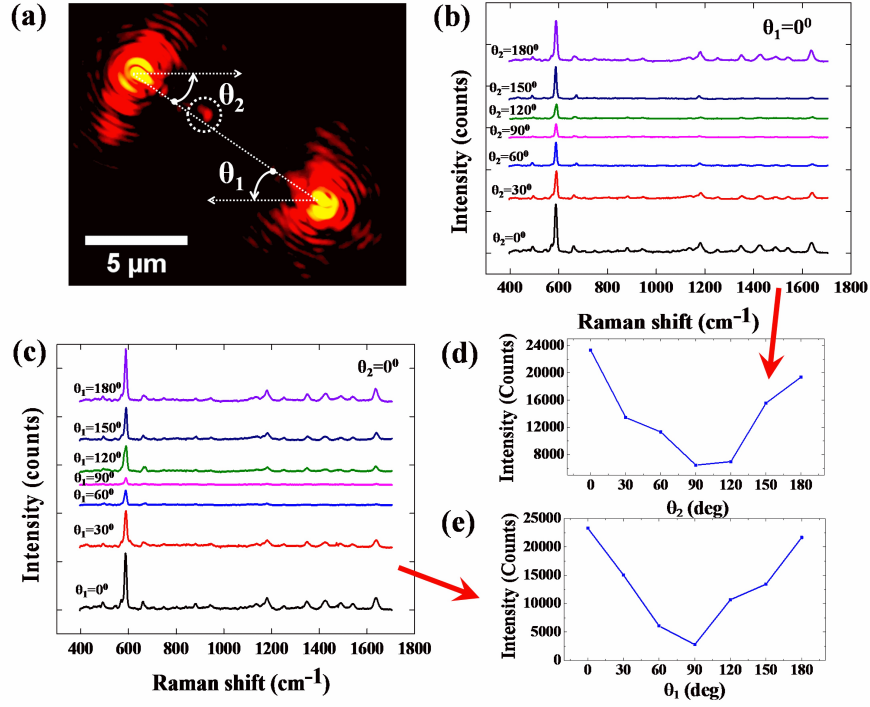


FIGURE 4.14: (a) Optical image of counter-propagating plasmon excitation ($0.1\text{mW} + 0.1\text{mW}$) of the nanowire- nanoparticle junction, where θ_1 and θ_2 represent directions of excitation-laser polarizations at end 1 and 2, respectively. (b) Modulation in SERS intensity for dual path remote excitation when θ_1 was fixed at 0° and θ_2 was varied from 0° to 180° . (c) SERS intensity modulation when θ_1 was varied from 0° to 180° and θ_2 was fixed at 0° . (d) Intensity variation of 590 cm^{-1} SERS peak of Nile-blue A from nanowire-nanoparticle junction as a function of θ_2 with θ_1 kept constant and (e) intensity variation of the same SERS peak as a function of θ_1 with θ_2 kept constant.

nanowires. The former can be excited by illuminating the wire with polarization parallel to the long axis of the wire and latter gets excited when the incident polarization is perpendicular to long axis. While the $m=0$ SPP modes are propagating in nature and have greater propagation lengths, the $m=1$ mode gets dissipated quickly and cannot generate propagating modes. For all other polarization between parallel and perpendicular, both the modes are generated and hence propagation is feasible but with reduced efficiency than the pure $m=0$ mode. We utilized this polarization anisotropy of plasmon propagation in a nanowire to modulate the remote SERS signal intensity from the NW-NP junction.

Figure 4.14a is an optical image of a counter-propagating plasmon excitation of a Ag

NW-NP junction. For this experiment laser power at both ends was kept at 0.1mW. Here the angle θ_1 and θ_2 represent the polarization of the incident beam at respective ends. First, we kept the polarization $\theta_1 = 0^0$ i.e. along the wire and varied θ_2 systematically from 0^0 to 180^0 and acquired the remote SERS signal from the junction. As shown in figure 4.14b, a systematic change in SERS intensity was observed. The intensity gradually decreased as we approached $\theta_2 = 90^0$. This was actually a situation similar to single end excitation as this polarization results in no propagating plasmons from the illuminated near end. Similar results were obtained when θ_2 was held at 0^0 and θ_1 was increased gradually. This is presented in figure 4.14c. The systematic variation in the SERS intensity of the 590cm^{-1} NBA Raman line in both cases have been plotted in figure 4.14d and e. This observation clearly shows how the SERS intensity and hence the local electric field enhancement can be modulated as a function of incident polarization in case of counter propagating plasmon excitation of the NW-NP junction.

4.8 Conclusions

In conclusion, in this chapter we have shown the field localization characteristics of coupled NW dimer junctions and the NW-NP junctions. By performing remote excitation SERS at those junctions, we could measure the degree of localization for single and dual path excitation. We found out that the degree of localization can be enhanced in case of dual path excitation of the junction. Also this localized field can be altered systematically by varying the input polarizations. Such optical field localization at a point being spatially separated from the actual excitation point opens up the possibility for using them as remote excitation optical source, not only for SERS but for other spectroscopy methods such as Fluorescence, photo luminescence, infra-red spectroscopy etc. Apart from this, the remote excitation geometry can be very useful to perform efficient in-vivo and in-vitro biological measurements since the samples can be made devoid of direct exposure of laser light. This will reduce the possibility of deformation of the samples due to direct exposure to huge amount of optical energy. One can extrapolate these remote excitation configurations to two colour sub-wavelength remote excitation SERS and several pump-probe spectroscopy schemes at nanoscale.

Chapter 5

Directing light using serially coupled silver nanowire dimers

In the previous chapter, we have presented how the propagating plasmons in a serially coupled nanowire dimer system can be localized at junction in a controlled manner. We have also used this localized field to remotely excite the molecules placed at the junction. Apart from localizing the optical fields near to its surface, plasmonic nanostructures are also able to redirect the far-field radiation and influence the emission direction of molecules, placed in close vicinity[1, 2, 24]. Therefore, in context of Ag nanowire geometries, a couple of questions remain unanswered such as,

- a) What would be the free space emission direction of the photons, coupling out from the junction of a serially coupled Ag NW dimer?
- b) How this localized field at the junction can be utilized to channel molecular emissions to specific directions?

These are very relevant questions in order to design nanoplasmonic circuits with light and complex light routing geometries at sub-wavelength scales. Spatial redirection of molecular emission is also very important to increase their detection efficiency.

Studies on isolated plasmonic nanowire system by Shegai *et al.*[91] and Li *et al.*[195] have shown that the photons coupled out from the distal ends of a silver nanowire when excited by a focused illumination at other end is unidirectional in nature. The emission direction is generally along the axis of the nanowire. The SPP modes in a silver nanowire have also been utilized to direct the emission from a single quantum dot[196]. Experimental results reported by Wang *et al.* showed that how the emission of quantum dots separated from silver nanowire by a very thin (few nm) dielectric layer can also be influenced. They were also able to tune the directivity of the quantum dots by varying the thickness of dielectric layers[197]. Recent studies also showed how to couple single emitters such as nitrogen vacancy centres with this kind of plasmonic geometries for quantum information processing[198]. Therefore, our serially coupled Ag NW can also

be explored in context of directional photon emission. The speciality of this nanoarchitecture is; here the junction acts as a photon loss channel while it can be excited at two different locations[167, 168].

In this chapter, we will present how single and dual excitation of the free ends can be used to direct and route far-field emission in specific directions. We will also show the influence of surrounding medium and the geometry itself on the directivity of the photons. Furthermore, we present the data where we explored the possibility of utilizing this kind of plasmonic nanowire dimer junctions to influence the emission from molecules placed in the vicinity of the junction. Before presenting our experimental results, we will briefly discuss the microscopy techniques that we have used for detection of directionality of light.

5.1 Back focal plane imaging microscopy

5.1.1 Basic Principles

Back focal plane (BFP) imaging microscopy works on the basic concept of the image formed at the back focal plane is a Fourier transformation of the actual image[199, 200]. This is derived from the phase -transforming property of a spherical lens[200, 201]. This phase transformation happens between an incoming plane wave with an arbitrary amplitude distribution $U_i(\xi, \eta)$ and the transmitted spherical wave having an amplitude distribution $U_t(\xi, \eta)$ where (ξ, η) are the coordinates in the plane of the lens. The relation is given by,

$$U_t(\xi, \eta) = t(\xi, \eta)U_i(\xi, \eta) \quad (\text{Eq 5.1})$$

where the transmittivity of the converging spherical lens $t(\xi, \eta)$ is given by

$$t(\xi, \eta) = e^{ikn\Delta_0} e^{-i\frac{k}{2f}(\xi^2 + \eta^2)} \quad (\text{Eq 5.2})$$

Here k is the wave number ($k = \frac{2\pi}{\lambda}$), Δ_0 is the maximum thickness of the lens and f is the focal length of the lens. The transmitted field amplitude at a distance f from the lens is given as a function of the incident field amplitude by,

$$U_f(x, y) = \frac{e^{i\frac{k}{2f}(x^2 + y^2)}}{i\lambda f} \iint_{-\infty}^{+\infty} U_i(\xi, \eta) e^{-i\frac{2\pi}{\lambda f}(\xi x + \eta y)} d\xi d\eta \quad (\text{Eq 5.3})$$

where x and y are the coordinates in the plane perpendicular to the optical axis of the lens at a distance f i.e, at the BFP. This expression has the form of a 2D Fourier transform for light incident on the lens from a sample. Therefore, light emitted from the

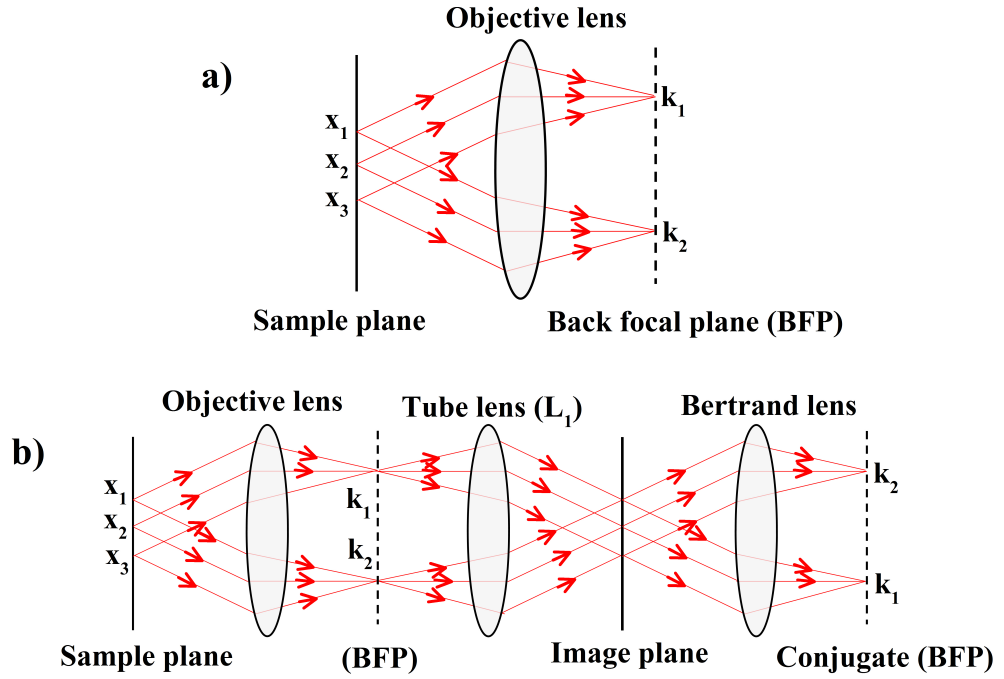


FIGURE 5.1: Schematic showing formation of image at BFP of an objective lens. b) Schematic showing basic concept behind BFP imaging microscopy.

sample plane is decomposed by the lens into individual plane waves. Every plane wave with same k vector is focused at unique point in the BFP of the lens. At the real image plane, the image is resolved spatially but at the back focal plane the imaged points are resolved by their emission direction. Figure 5.1 a shows a schematic of image formation at the BFP of a microscope objective. From the image it is clear that the rays which are emitted with same k vector meets at a particular point at the BFP. Therefore, each point at the BFP represents a different k vector direction.

In general, a BFP of objective lens is formed at a very short distance from the lens itself and hence placing an imaging detector at this plane is impossible. Due to this reason, a set of relay lenses are used to create a conjugate plane of the BFP on an imaging CCD, placed far away from the objective. Figure 5.1 b is a schematic representation of a BFP imaging procedure where a combination of tube lens and a Bertrand lens has been used to create a conjugate BFP outside the microscope objective. The Bertrand lens is the one which creates the conjugate BFP outside the objective lens[199–201].

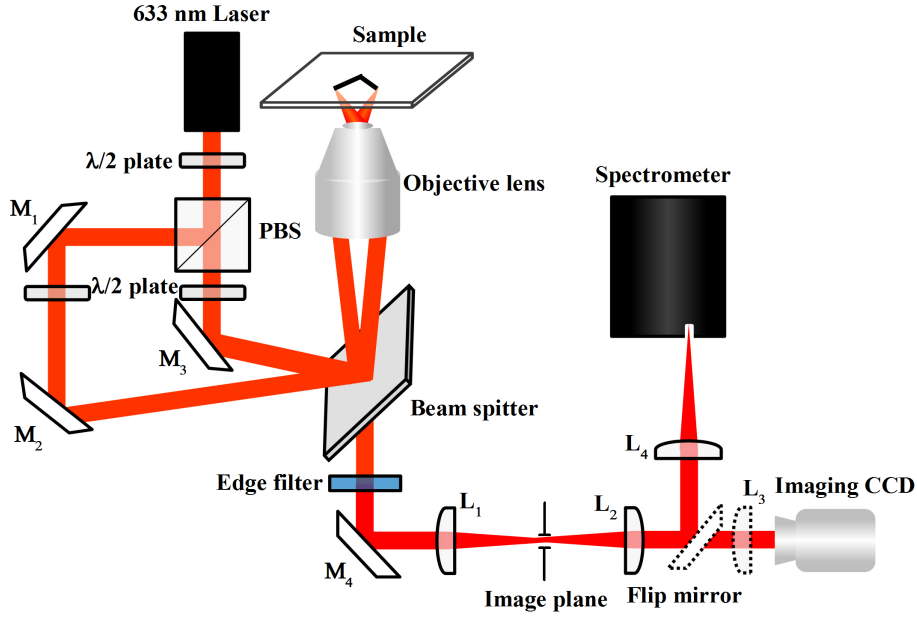


FIGURE 5.2: a) Schematic of the instrument designed for our study. M_1, M_2, M_3, M_4 are mirrors; L_1, L_2, L_3, L_4 are lenses and PBS is polarization beam-splitter.

5.1.2 Dual excitation spatial filter BFP imaging microscope

For our experiments, we modified a commercially available inverted microscope (Olympus iX71) into a BFP microscopy system where it was also capable of dual excitation and spatially filtered collection[202]. The schematic of the instrument is shown in figure 5.2. We used a high numerical objective lens (either a 100X, 1.3 NA oil immersion or a 60X 1.42 NA oil immersion) for our study on terminally coupled Ag NW dimers. For dual excitation of these Ag NW dimers, we split a 632.8 nm wavelength He-Ne laser into two beams using a polarizing beam splitter (PBS) and focused on the two free ends. Each focused laser spot was $1\mu m$ in diameter. The polarization of the excitation laser beams were controlled using two half wave plates. For single end excitation, one of the laser paths was blocked using a beam dump. The laser was brought into the microscope objective through a beam splitter. We collected the back-reflected light by the same objective for Fourier space imaging. A 4f correlator, consisted of two lenses (L_1 and L_2), each of focal length 150mm was used to create a conjugate BFP of the objective on the CCD camera. A 100-200 μm pinhole was used at the intermediate real

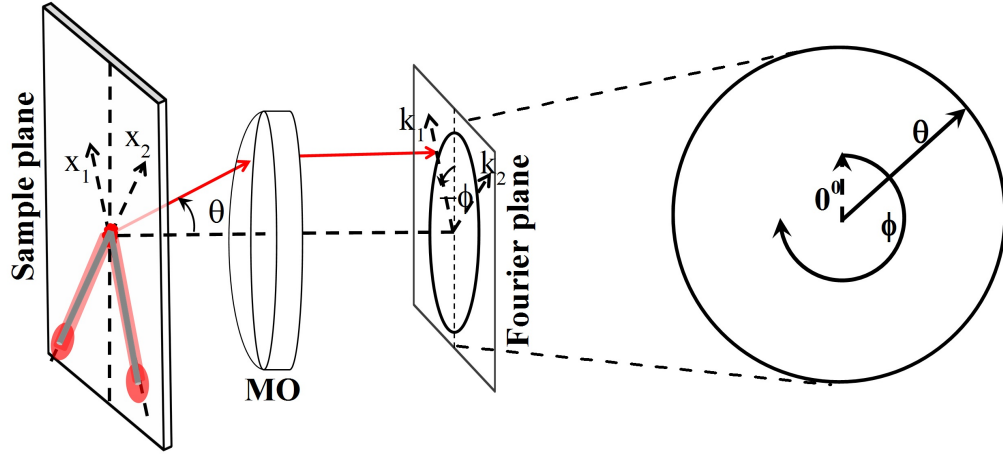


FIGURE 5.3: Illustration of image formation at the Fourier plane of a microscope objective lens and the co-ordinate system, used for the study.

image plane between L_1 and L_2 for spatial filtering. The spatial filtering method was specifically used to collect the light emitted from the junction of Ag NW dimer. A lens L_3 of focal length 100mm was used between the CCD and L_2 as a tube lens to facilitate a conjugate real image of the sample on the CCD chip. This lens was placed on a flip mount and placed at distance 100mm from the CCD chip. Once L_3 was flipped out of the optical path, we could directly monitor the BFP of the objective lens.

We also added the ability of spectroscopic analysis to this system by using a flip mirror and a lens L_4 of focal length 200mm to focus the light on a spectrometer (Jobin Yvon iHR 320) entrance slit. For spectra collection, the flip mirror was brought in the optical path to direct the light towards the spectrometer. For fluorescence studies, a Rayleigh rejection filter was introduced in the collection path, right after the beam splitter.

5.1.3 Co-ordinate system in the Fourier plane

Figure 5.3 is a schematic illustration for visualization of the co-ordinate system in the Fourier plane. As it seems from the schematic, the BFP of the objective directly monitors the angular distribution of far-field light intensity $I = I(\theta, \phi)$ as a function of spherical angles (θ, ϕ) . The radial direction in the BFP signifies the polar angle θ and scales as $n \sin \theta$ where $n=1.52$ is the refractive index of the underlying glass medium. Therefore, maximum angle (θ) of collection is constrained by the numerical aperture (NA) of the objective lens. For our study, we used either a 1.3 or a 1.4 NA objective lens which makes the maximum detectable θ to be 59.8° and 68° in the respective

cases. The tangential co-ordinate in the Fourier plane corresponds to the azimuthal angle ϕ ($0 < \phi < 2\pi$). In the schematic, x_1, x_2 represent the direction of orientation of the two wires in the object plane. k_1 and k_2 represent the same directions in the Fourier plane.

5.2 Leakage radiation microscopy

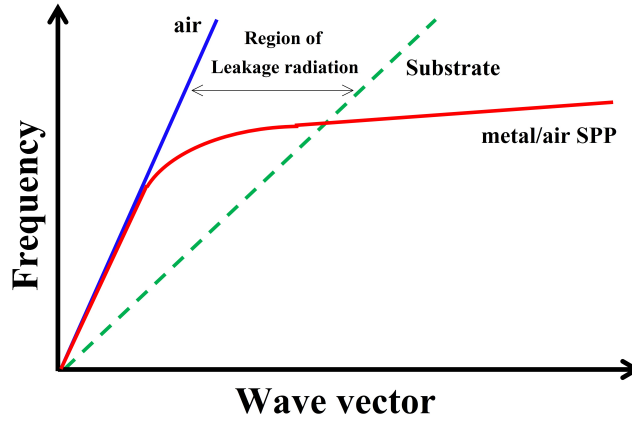


FIGURE 5.4: Dispersion curve of SPP at a air-metal interface. In the region between light line of air and the dielectric substrate, SPPs loose energy via leakage radiation into the substrate.

The phenomenon of SPP energy being dissipated in a radiative manner from a plasmonic nanostructure into the supporting substrate of high refractive index is called SPP leakage radiation[1, 2]. This occurs due to phase-matching of SPP with the free space photons. It can be explained from the SPP dispersion curve of metal films which is shown in figure 5.4. This shows that the SPPs, excited at the air interface of a metal film lies outside the light cone defined by $k = \frac{n_{air}\omega}{c}$ and hence do not suffer any radiation loss into the air region (in case of smooth metal surface). However, the light line for the dielectric (substrate) medium do intersect the dispersion curve. Therefore, radiation loss occur at all points of the dispersion curve that lie to the left of the light line of the substrate $\frac{n_s\omega}{c}$. Which is why, SPPs excited at the metal-air interface with propagation constant β , defined by

$$k_0 < \beta < k_0 n_s \quad (\text{Eq 5.4})$$

gets radiated into the underlying high refractive index medium substrate[1, 2].

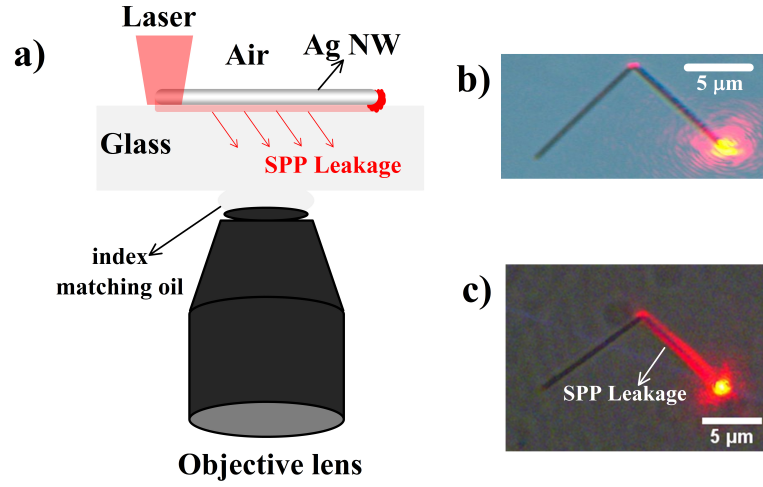


FIGURE 5.5: a) Scheme for collection of leakage radiation from Ag NW systems. b) Optical image of focused laser illumination of a Ag NW dimer from air side (no leakage detected). c) Optical image of the same nanowire collected through the glass substrate (SPP leakage detected).

For many years, leakage radiation had been considered only as a disadvantage as it provides a second loss channel to the SPP apart from absorption in the metallic medium[1]. In recent studies, researchers used this leakage to map the SPP propagation and near field of the nanostructures for SPP wave vectors having β less than the substrate light line[202–205]. The microscopy method at which this SPP leakages are imaged is called the leakage radiation microscopy. In case of Ag NW; when it is immobilized on a glass slide, the SPP modes at the metal-air interface leak into the glass medium. The leakage happening into the glass substrate can be collected using a microscope objective by using a refractive index matching medium between the objective lens and the glass slide. Schematic illustration of the method is shown in figure 5.5a. For our studies, the leakages collected through the glass substrate using oil immersion lenses which use a index matching oil of refractive index 1.52, same as the refractive index of the glass slides. Figure 5.5b shows light scattering by an Ag nanowire when it was excited by focused illumination at one end and imaged with a air immersion objective lens and imaging was done from the air side. In this case, we only see free photons which coupled out from the distal ends. This is because the SPP can not radiate into the air medium as their momentum is always higher than the light. When the same nanowire was imaged through the glass substrate using a oil immersion objective (see figure 5.5c) leakage of SPPs can be visible through-out the wire apart from the distal

end.

5.3 Engineering far-field scattering using serially coupled nanowire dimers¹

In this section, we will present the experimental results which will show how a serially coupled Ag NW dimer can be used for engineering far-field radiation in different manners. For the experiment, first we dispersed the nanowires on a glass micro-slide and used the BFP microscope shown in figure 5.2. The excitation of nanowire ends and imaging was done through the glass substrate. Figure 5.6a shows the SEM image of a nanowire dimer, used for our study. This nanowire dimer was consisted of two nanowires of $10\mu\text{m}$ length and 200nm diameter, coupled at an angle 72° . TEM images in figures 5.6b and c (not of same nanowire shown in figure 5.6a) show the junction of such nanowire dimers can be partially or completely fused in nature.

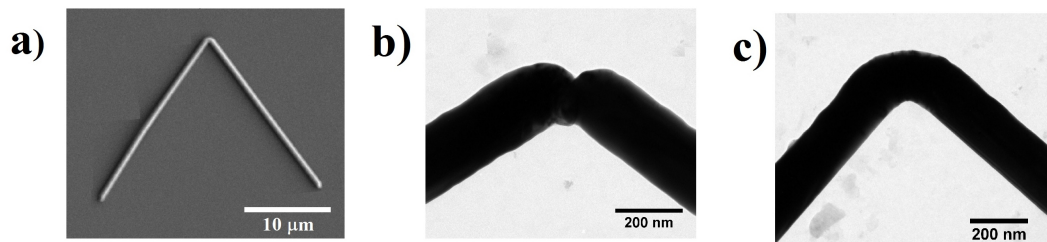


FIGURE 5.6: a) SEM image of the Ag NW dimer, used for the study. b) and c) are TEM images of Ag NW dimers which show fused nature of the junction.

5.3.1 Engineering far-field scattering using Ag NW dimer junction

First, we will discuss how same Ag NW dimer junctions can be utilized to obtain uni and dual directional far-field scattering depending upon the single and dual excitation of the free ends. For this experiment, we used the same nanowire shown in figure 5.6a. All the results of this experiment are illustrated in figure 5.7.

Unidirectional scattering

Optical image in figure 5.7a shows focused excitation of laser beam (632.8 nm) on end 1 of the Ag NW dimer. The excitation photons are converted into propagating SPPs and

¹Manuscript under review.

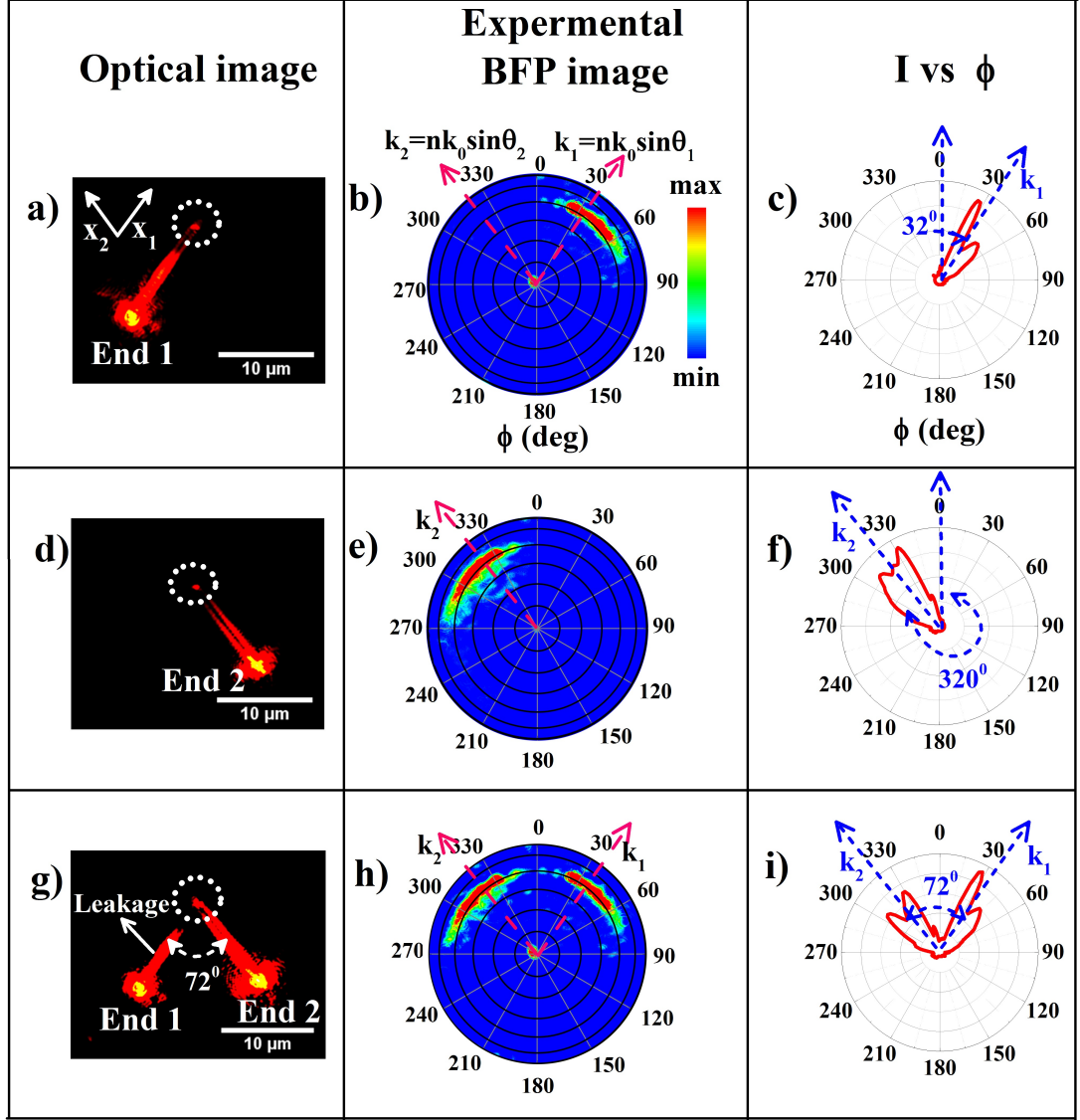


FIGURE 5.7: Uni- and dual-directional light scattering from junction of Ag NW dimer. a) Optical image of end 1 illumination of the Ag NW dimer. b) BFP image of the emission from the junction. c) Corresponding I vs ϕ graph. The second and third rows of the figure are the corresponding data for end 2 excitation and end 1 + end 2 excitations, respectively. White dotted circle in the optical images denote the area projected on to the Fourier plane. Black concentric circles in BFP image indicates θ at an increment of 100 and outer most black circle denotes maximum collection angle 59.80 for NA=1.3.

form the leaky modes which further decouples at the junction of Ag NW dimer. This emission from the junction was spatially filtered (indicated by the white dotted circle in the image) and recorded onto the BFP of the microscope objective lens. From the BFP image in figure 5.7b, it was evident that the junction exhibits unidirectional emission along k_1 ($\phi=32^\circ$). Black concentric circles in figure 5.7b indicate θ at an increment of 10° . The outer most circle signifies the maximum collection angle $\theta=59.8^\circ$ of the used objective of NA=1.3. The emission was maximum at around $\theta=42^\circ$, which is close to the critical angle (41.8°) at glass-air interface. The intensity (I) variation with ϕ is shown in figure 5.7c. It shows a spread of 25° in the ϕ emission. Here, it was interesting to note a local intensity minimum near $\phi = 32^\circ$. This dip in the radiation pattern may be due to partial tunnelling of SPPs at the junction, where part of the incident plasmons do not radiate but tunnel into the distal wire. The dip in the emission (figure 5.7c) can be considered as a signature of tunnelling of SPPs from one wire to other at a specific angle defined by the geometry of Ag NW dimer.

Next, we illuminated the other end of the Ag NW dimer and collected the emission from the same junction. Figure 5.7d is the optical image of end-2 excitation and figure 5.7e is the BFP image of the emission from the junction. Similar to the previous case, uni-directional emission was observed but along the direction k_2 ($\phi=320^\circ$). The emission again had a sharp peak at $\theta = 42^\circ$. I vs. ϕ graph for constant $\theta=42^\circ$ in figure 5.7f shows a spread of 35° in ϕ . The local minimum near $\phi=320^\circ$ i.e., along k_2 was also observed in this case.

Important inferences drawn from single-end excitation experiment were that: a) *The coupled Ag-NW junction supported unidirectional emission where transmission direction is defined by the geometry*, and b) *this emission direction could be flipped by changing the position of excitation source from one end of the dimer to other*.

Dual directional scattering

When both ends of the Ag NW dimer were illuminated simultaneously, leakages of SPPs along both wires were evident as shown in the optical image in figure 5.7g. The BFP image in figure 5.7h shows the junction is working as a dual directional emitter. Here, two emissions were observed along two directions k_1 ($\phi=32^\circ$) and k_2 ($\phi=320^\circ$) reciprocal to both the wire axes. Emission peaks occur at $\theta = 42^\circ$. Angular distribution of the intensity is shown in I vs. ϕ plot in figure 5.7i for constant $\theta = 42^\circ$. It is to be noted that the angular separation between directions of maximum emission (72°) mimicked the angle between the two nanowires of the dimer (72°). This experiment proves *dual directional scattering can be obtained from the same junction of an Ag NW dimer by illuminating both the free ends of the dimer simultaneously*.

Numerical analysis

The experimental observations were further validated by 3D FDTD calculation of far-field scattering² from the junction of identical geometry. We used a commercially available FDTD solver, “FDTD solutions, Lumericals inc”. Due to computational constraints wire lengths were shortened to $5\mu\text{m}$ each. Serially coupled AgNW geometry was designed by placing two cylinders face to face at different angles on a glass substrate. The modeled geometry consisted of two $5\mu\text{m}$ long wires of 250nm diameter. The angle between two wires was kept 72° to match the experimental configuration. The schematic of the design is shown in figure 5.8a. We used linearly polarized Gaussian beams for single and dual excitation of ends. Dielectric constant of glass was taken 1.52 and dielectric constant of Ag was taken from experimental values provided by Johnson and Christy[129]. We used an excitation of wavelength 632.8nm . The simulation region was $0.6 \times 10 \times 8 \mu\text{m}^3$ and a non-uniform mesh of minimum grid size 5nm was used. 25,000 time steps were used to ensure stability of the calculated solution. Figure 5.8b shows the calculated near-field distribution around the wire at a plane that cuts the wire vertically along its axis when one of the end was illuminated. This plane consists of air (top)-AgNW-glass (bottom). SPPs at air interface clearly exhibits longer plasmon wavelength than the SPPs at glass interface at the bottom. The cylindrical symmetry of the SP modes in case of homogeneous environment is lost now. This cylindrical symmetry is generally described by azimuthal quantum number $m=0$. Therefore, excitation of the wire end with incident polarization along the wire axis now produces a resultant of SP modes for individual uniform environment. The SP modes in the nanowire are now hybridization of glass-like plasmons and air-like plasmons. Although both types of plasmons are generated, the intensity of the field along the air medium (top) diminishes rapidly compared to the glass medium (bottom). Therefore, air-like leaky plasmons are the main source of leakage radiation in the glass substrate. Figure 5.8c is electric field map at the X-Y plane at AgNW-glass interface when end 1 was illuminated. It is evident that plasmons were mainly generated in the illuminated wire and very weak plasmon modes are visible in the other wire. For calculation of far-field radiation pattern, we used the built-in far-field projection calculator of the FDTD solver. For calculating far-field radiation pattern from the junction, we have only projected the area enclosed by the white dotted square (approximately 500nm of the both wires towards the junction). This way the aperture for spatial filtering of the junction in the experiment was simulated. The far-field radiation pattern in figure 5.8d shows similar unidirectional emission from the junction along the direction k_1 ($\phi = 36^\circ$), reciprocal to the axis of the excited wire. Simulated I vs. ϕ plot in figure 5.8e shows the

²For details see **Appendix B**

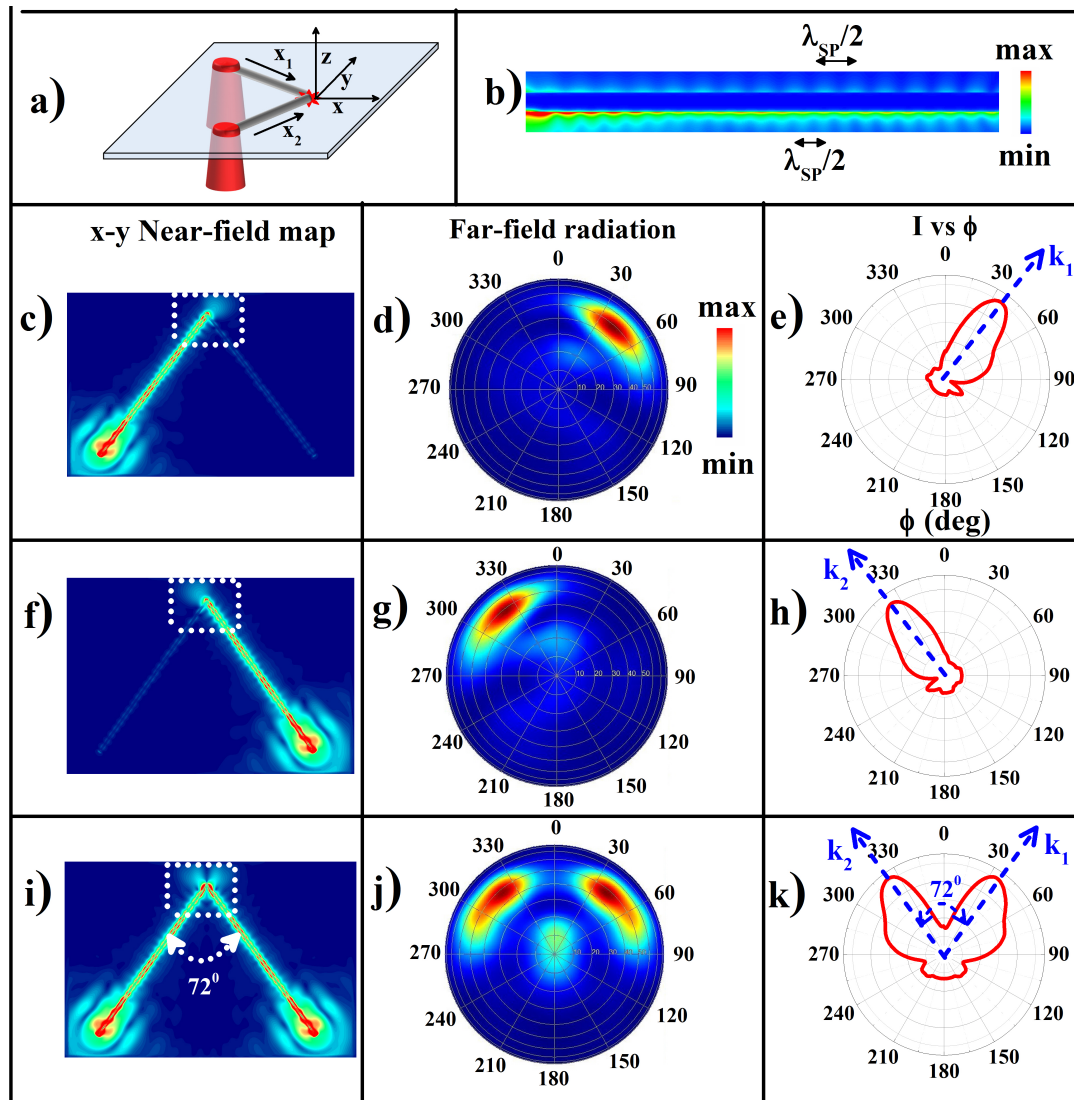


FIGURE 5.8: Numerical simulations for Uni- and bi-directional light scattering from junction of Ag NW dimer. a) Schematic of the simulation geometry. b) Electric field map at a plane consists of air(top)-wire-glass(bottom) interfaces along x_1 direction when the corresponding wire was illuminated. c) Near-field electric field map at x - y plane at wire glass interface for end 1 illumination. d) Simulated far-field radiation pattern. e) Corresponding I vs ϕ graph. f), g), h) and i), j), k) are the corresponding data for end 2 excitation and end 1 + end 2 excitations, respectively. White dotted rectangle in the near-field map denote the area projected for far-field calculations.

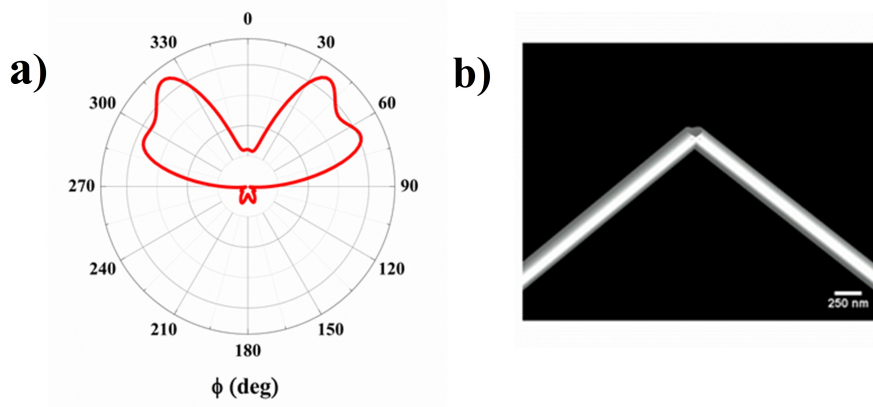


FIGURE 5.9: a) I vs ϕ graph for the junction emission in case of dual excitation when the mesh grid size was reduced to 3nm. b) A zoomed in view of the Ag NW dimer junction designed for the numerical calculations.

intensity variation with ϕ and corroborates the experimental data in figure 5.7c, except that the local minima around k_1 observed in experimental data is not clearly visible. This may be due to the grid size of the mesh. A slight dip in the simulated scattering diagram at $\phi = 55^\circ$ suggests the position of the dip may be also dependent on the morphology of the Ag NW dimer junction.

Similarly, when end 2 was illuminated excited SPP modes are visible along the excited wire (figure 5.8f). Calculated far-field radiation pattern and I vs ϕ in figure 5.8g and h support the experimental observations in figures 5.7e and f. For dual excitation shown in figure 5.8i, strong SPP modes are visible along both wires. Simulated far-field radiation pattern and I vs ϕ graph in figure 5.8j and k were also in agreement with experimental observations.

The effect of the mesh grid size on occurrence of the local minimum in the scattering diagram was checked in case of dual excitation by reducing the mesh grid size to 3nm. In this case, we observed two prominent dips around $\phi = 50^\circ$ and 310° (see figure 5.9a). This numerical result further proved that the position of local minima can also depend on the morphology of the geometry. The junction morphology of the simulated geometry is shown in figure 5.9b. Hence, the agreement between numerical simulation results and the experimental observations further prove the junction of serially coupled Ag NW dimer support single and dual directional emission.

Efficient waveguiding through the nanowires result in directional emission from the junction.

To understand the dual directional light scattering from the junction, we studied the characteristics of leaky guided modes in the geometry. Leakage of SPP into the glass substrate is governed by phase matching condition:

$$Re(k_{sp}||) = k_p \cos \alpha \quad (\text{Eq 5.5})$$

where $Re(k_{sp}||)$ is the real part of the SPP wavevector in the nanowire; k_p is the wavevector of photons, scattered in the glass substrate and α is the angle between the direction of photon radiation and the nanowire axis. The α is related to spherical angle θ by $\alpha = 90^\circ - \theta$.

Figure 5.10a is a BFP image captured from the whole Ag NW dimer structure with end 1 illumination (figure 5.7a). The illumination point was blocked while projecting the image to the BFP of the objective lens. This allowed us to directly measure the effective indices $n_{eff} = k_{sp}/k_0$ of the propagating SP modes, where $k_0 = 2\pi/\lambda_0$ is free space wavenumber[206]. For single channel illumination of end 1 of the Ag NW dimer, leaky SPP modes are observed along the illuminated wire and no detectable leakage was observed for the adjoined nanowire (figure 5.7a). The figure 5.10a shows a bright line across the plane implying a constant effective index at $+k_1/k_0 = 1.05$ and its orientation is perpendicular to the axis k_1/k_0 . This suggests a strong confinement of SP modes in a direction perpendicular to x_1 (axis of the excited nanowire) which is a well-known characteristics of one dimensional waveguide[207]. We did not observe any detectable signal along $-k_1/k_0$ which indicated very weak or no reflection of SPP modes from the NW junction. Also, note that we do not observe any detectable signal along k_2/k_0 direction which indicated very weak SPP tunnelling into the adjoined wire. All these observations further imply that the most part of the SPP energy is being decoupled as free photons at the junction. This decoupled light is efficiently scattered along the direction of the axis of the excited nanowire to conserve the energy and momentum of propagating SPPs.

The experimental observation in figure 5.10a was further corroborated with 3D-FDTD simulation. The simulated far-field radiation pattern is shown in figure 5.10b. The incident light was barred by not projecting the first $1\mu\text{m}$ of both wires. The simulated radiation pattern confirms the presence of a strong guided mode with effective index $n_{eff} = 1.11$. We also observe weak modes with higher effective indices $n_{eff} > 1.3$ which is higher than the experimental detection window.

Illumination of end 2 (figure 5.7d) of the nanowire and projection of leaky SPPs in

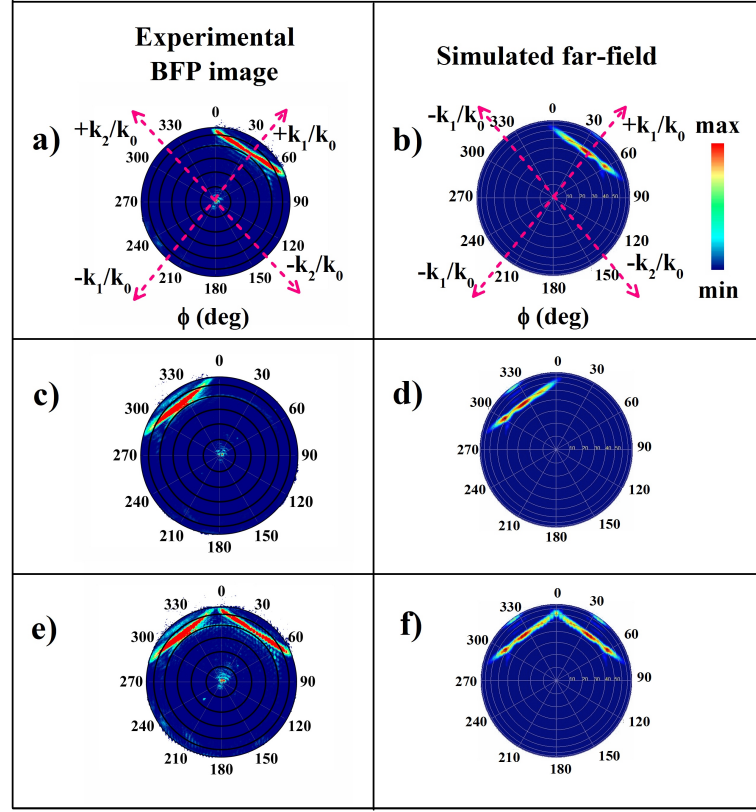


FIGURE 5.10: Guided modes in the Ag NW dimer geometry. a) Experimental data of the Fourier plane image of the guided mode when end 1 was illuminated. b) The corresponding simulated far-field image for end 1 excitation. c) Experimental Fourier plane image for end 2 illumination and; d) corresponding simulation data for end 2 illumination. e) Experimental Fourier plane image when both end 1 and 2 were illuminated and; f) corresponding simulated data for dual illumination.

the BFP of the objective lens showed the guided modes along $+k_2/k_0$ with $n_{eff}=1.05$ (see figure 5.10c). This observation explains the flipping of the unidirectional emission from k_1 to k_2 direction when the excitation point was changed from end 1 to end 2. Simulated far- field radiation in figure 5.10d supported the experimental observation in figure 5.10c.

When both the ends were illuminated simultaneously, as shown in optical image of figure 5.7g, we observed two leaky modes in the nanowires. Subsequent BFP image in figure 5.10e showed two guided SPP modes with constant effective indices along $+k_1/k_0$ and $+k_2/k_0$. Both these modes converge towards the junction, and therefore the emitted light was dual directional in nature. The two guided modes have also been verified in numerical simulations, and shown in figure 5.10f.

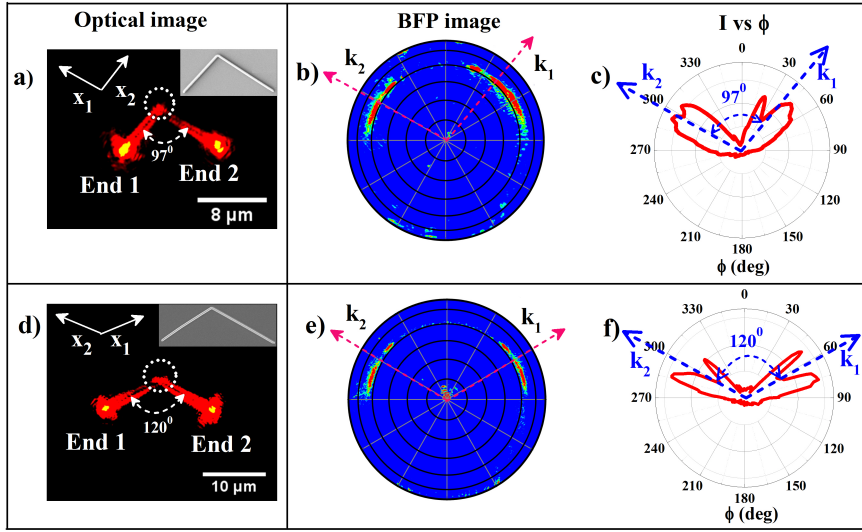


FIGURE 5.11: Directivity dependence on the angle between nanowires in the dimer configuration. a) Optical image of Ag NW dimer with a 97° angle between the wires. Inset shows the SEM image of the same NW dimer. b) BFP image of the dual directivity emission recorded from the junction region (dotted white circle) of Ag NW dimer; and c) corresponding I vs ϕ polar plot indicating the angular separation between the directional emission (97°), which is equal the angle between the nanowires. d) Optical image; e) BFP image and f) corresponding I vs ϕ plot for another Ag NW dimer with an angular separation of 120° .

5.3.2 Controlling angular separation between two radiation direction

With respect to directivity measurements discussed until now, a relevant question to probe is *How can the angular separation in ϕ between two emission direction be varied?* To find out the answer of this question, we performed the following experiment. The optical image in figure 5.11a shows an Ag NW dimer where the angle between wires was 97° . BFP images of the junction scattering in figure 5.11b shows that two emissions occur around $\phi = 37^\circ$ (reciprocal k_1 direction) and $\phi = 60^\circ$ (reciprocal k_2 direction). Plot of ϕ variation of intensity for fixed $\theta = 42^\circ$ in figure 5.11c is shown. The angle between k_1 and k_2 is same as the angle between two wires. Next, we tested a different Ag NW dimer where the two wires was coupled at an angle 120° . The optical image, BFP image and corresponding I vs ϕ graphs are shown in figure 5.11d,e and f respectively. Again, the angular separation between two radiation channels was same (120°) as the coupling angle of the two wires.

The experimental observations of figure 5.11 were further verified and confirmed with numerical simulation. For simulation we used a dimer where the angle between

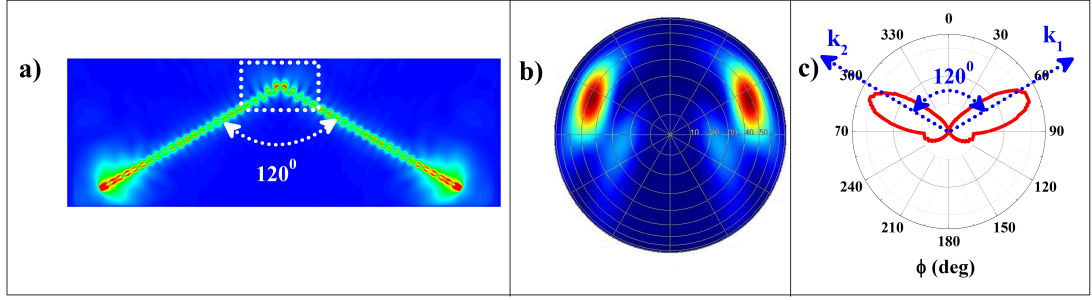


FIGURE 5.12: a) Near field electric field map at wire-glass interface (X-Y plane shown in fig 5.8a) dual excitation of a dimer where coupling angle of two wires was 120° . b) Calculated farfield radiation pattern from the junction. c) I vs ϕ graph for same emission from the junction. Angular separation between two radiation channels was same as the coupling angle of the two wires in the dimer.

two arms was 120° . Figure 5.12a shows the near-field map around the dimer and 5.12b shows the far-field radiation pattern from the junction. The far-field intensity pattern was calculated by projecting the near-field from the area enclosed by the white dotted rectangle. The calculated I vs ϕ plot is shown in figure 5.12c. The angular separation between two emission channels was 120° which is similar to experimental results shown in figure 5.11. Therefore, all the data indicate that by changing the angle between two wires in the dimer geometry, the angular separation between the two channels of emission can be varied. Such correlation between structure and function of an optical antenna can also be beneficial for lab-on-chip angular light routing in photonic circuits[197].

Here, we should also mention that the angle between two wires also decide the angle between two radiation channels in case of single end excitation. To prove that, we used the wire having 120° angle between two arms. As can be seen from the figure 5.13, excitation of end 1 of the wire led to a unidirectional radiation of photons from the junction at an angle around $\phi = 60^\circ$ (figure 5.13b). When end 2 was illuminated the emission direction was flipped to $\phi = 300^\circ$ (figure 5.13d).

5.3.3 Tuning θ directivity

In all the cases discussed above, the dual-directional emission peaked at around $\theta = 42^\circ$ which was close to the critical angle $\theta_c = 41.2^\circ$ for glass-air interface. Such observation on a single Ag NW has also been reported in the past[91]. This further implies that if the medium of refractive index around the Ag NW dimer was changed, then the value of θ where maximum emission occurs should correspondingly vary. To ascertain this,

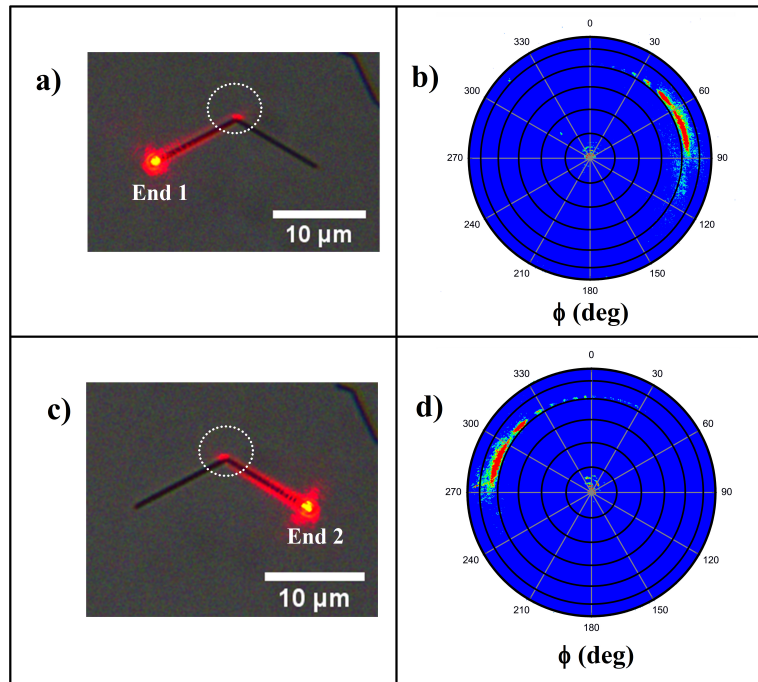


FIGURE 5.13: a) Modulation of emission direction from the junction for single end excitation. a) Optical image of single excitation of end 1. Sample is same as the sample used for experiments in fig 4b in main article. b) Fourier plane image of scattering from the junction for optical excitation of end 1. c) Optical image of single excitation of end 2. d) Corresponding Fourier plane image of scattering from the junction.

first we immobilized an Ag NW dimer at glass-air interface (figure 5.14a) and recorded the BFP image (figure 5.14b) and the corresponding I vs θ plots for the dual directional emission (figure 5.14c and d). Next, we changed the immersion medium of Ag NW dimer to water (figure 5.14e), and again recorded the BFP image (figure 5.14f) and the I vs θ plots for the dual directional emission (figure 5.14g and h). Then, we compared the change in θ position of the emission peaks. The I vs θ graph in figure 5.14c and d show two emission peaks occur at $\theta_{1p} = 42.3^\circ$ and $\theta_{2p} = 43^\circ$. The full-width-at-half-maxima (FWHM) for these two emissions were 4° and 7° , respectively. When the same Ag NW dimer was immersed in water (figure 5.14e), the leaky-plasmons were not visible. The emission from the junction was visible and further analysed using Fourier microscopy. The BFP image in figure 5.14f showed that the values of θ at which the emission peaked had varied upon changing the refractive index of the medium. From the I vs θ plots in figure 5.14g and h it was observed that θ_{1p} value was modified to 60.8° and θ_{2p} to 60.2° . These are close to critical angle at glass-water interface (61.2°). Correspondingly, the FWHM for the dual directional emission changed to 8° and 6° ,

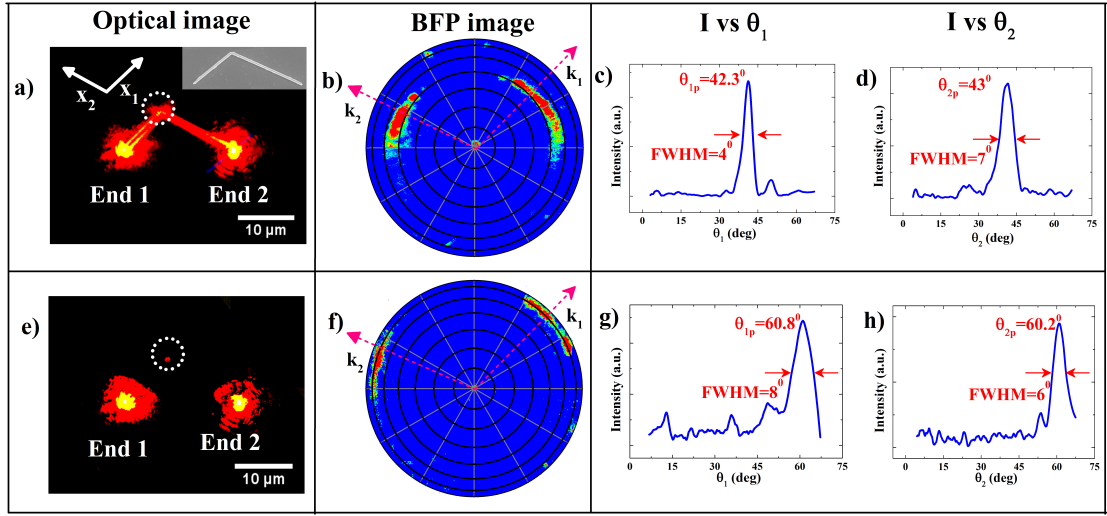


FIGURE 5.14: Change in refractive index contrast between the substrate and the medium around the wire modulates the angle θ (θ_p) at which peak emission occurs. a) Optical image of an Ag NW dimer at glass-air interface with the inset showing the SEM image; b) BFP image of the light emanating from the junction of NW dimer; I vs θ plot for the emissions cutting across c) k_1 and d) k_2 vectors. e) Optical image of the same NW at glass-water interface; f) BFP image and I vs θ plot for emissions cutting across g) k_1 and h) k_2 vectors. Note that the value of θ_{max} and full-width-at-half-maxima changed when the refractive index of medium was changed from air to water, indicating sensitivity to local dielectric changes.

respectively. For this experiment we used a high N.A.=1.4 60X objective lens.

For further understanding of this behaviour, we have numerically calculated the propagating modes that are getting excited in the Ag NW in both cases. For that, we calculated the guided modes present in a single nanowire of diameter 200nm. The results of this numerical simulation are presented in figure 5.15. When the wire was placed in air medium, strongest SPP mode had an effective index $n_{eff} = 1.05$. This is similar to our experimentally observed n_{eff} value (figure 5.10). Therefore this SPP mode leads to a emission from the junction happening at a θ value defined by, $\theta_p = \sin^{-1} \left(\frac{n_{eff}}{NA} \right) = 42^\circ$. On the other hand, when the wire was placed in water medium ($n=1.33$), strongest SPP mode had an effective index $n_{eff} = 1.32$ (figure 5.15). This should lead to a peak θ of emission $\theta_p = 60.2^\circ$ which is approximately same with the experimentally observed θ_p values (figure 5.14).

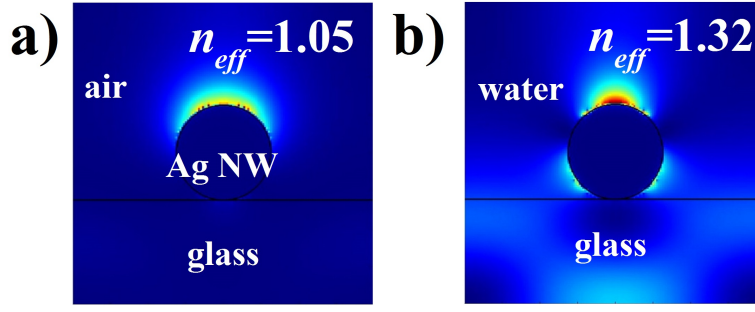


FIGURE 5.15: a) Near-field for SPP mode with $n_{eff} = 1.05$ map around the cross-section of a single nanowire placed at glass-air interface. b) Near-field for SPP mode with $n_{eff} = 1.32$ map around the cross-section of a single nanowire placed at glass-air interface.

5.3.4 Far-field light routing using Ag NW dimer for single excitation

The Ag NW dimer geometry facilitates excitation of SPP modes on the adjoined wire while one of the free end is illuminated. SPPs generated in the illuminated wire travels towards the junction and some of the energy couples out as free photon at the junction while remaining part tunnels into the other wire and propagates towards the distal end. This SPPs again convert into free photons there. For a dimer coupled at an obtuse angle, this tunnelling is more significant which results in stronger emission from the distal end. So, the next question we ask is *how does the directivity of the photon, emitted from distal end differ from the photons that emit from the junction?* To find out the answer, we used a dimer consisted of two 200 nm diameter and 7 μm long wires coupled at an angle 139° . The optical image of end 1 excitation is shown figure 5.16a. When the emission from the junction was monitored in the Fourier plane (figure 5.16b), we observed a unidirectional emission along the reciprocal direction k_1 of the axis of illuminated wire at $\phi = 64^\circ$. I vs ϕ graph in figure 5.16c shows that spread in ϕ was 45° . Next, we projected the emission from the distal end to the Fourier plane (see figure 5.16d) of the microscope objective to obtain the far-field radiation pattern from the distal end. Here we saw the emission direction was along the 2nd wire axis at $\phi = 105^\circ$, (reciprocal direction $-k_2$). I vs ϕ graph in figure 5.16e shows the variation of far-field intensity with ϕ . The angular separation between the light emitted from the junction and distal end was 41° . Interestingly, the angle between these two emission directions is defined by the angle (139°) between the two arms of the Ag NW dimer ($180^\circ - 139^\circ = 41^\circ$). This data explicitly shows how the geometry and emission angles are intimately connected in Ag NW dimer, and may have further implication in designing light routing architectures

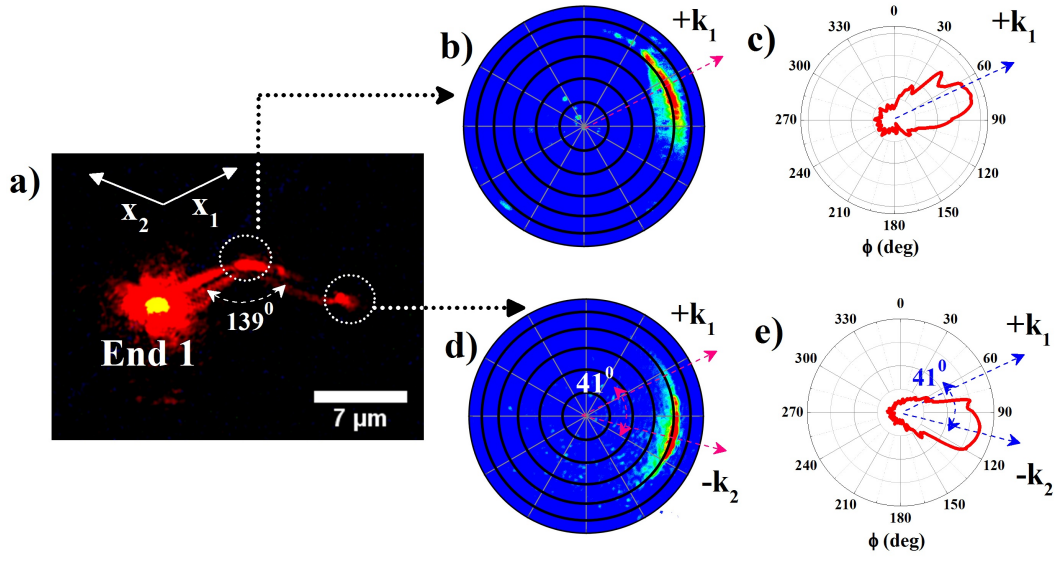


FIGURE 5.16: Far-field light routing using coupled wire geometry for single excitation when end 1 is illuminated. (a) Optical image of single end excitation of a coupled AgNW dimer. (b) Fourier plane image of Emission from the junction. (c) I vs ϕ graph at $\theta = 42^\circ$ for radiation from the junction. (d) Fourier plane image of light emitted from the distal end. Now the directionality happens to be along distal wire axis. (e) I vs ϕ graph at $\theta = 42^\circ$ for radiation from distal end.

for nanophotonic circuits. Also, the structure can be described as a sub-wavelength plasmonic beam-splitter where the direction of routed light and the splitting factor are defined by the coupling angle of the two wires in the dimer.

5.4 Coupled Ag NW dimer junction as single and dual channel antenna³

One of the main aspects of an optical antenna is its capability to direct radiation from a sub-wavelength source, such as molecules, to well defined directions. To show that the junction of a serially coupled Ag NW dimer can act as a unidirectional and dual directional antenna, we performed the following experiment. First, we deposited Ag NW dimer on a glass substrate and coated it with 30nm thick layer of poly vinyl alcohol (PVA) doped with a fluorescent molecule, Nile blue-A. The schematic of the prepared sample for the fluorescence study is shown figure 5.17a. Next, we carefully excited the individual ends of the Ag NW dimer followed by dual excitation by focusing a 633nm

³Manuscript under review.

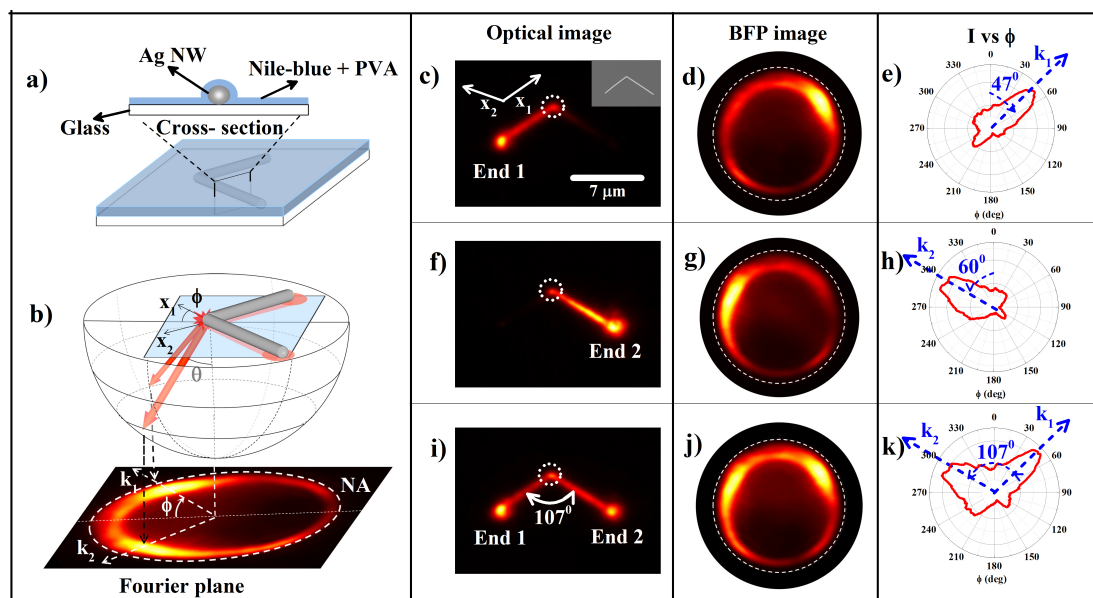


FIGURE 5.17: Directing fluorescence from molecules in close proximity to Ag NW dimer junction. a) Schematic of sample where a Nile blue-doped PVA film was casted over an Ag NW dimer. b) Illustration of image formation in back focal plane of a microscope objective and coordinate system used for directivity measurements. c) Fluorescence Optical image of end 1 illumination of the Ag NW dimer. Inset shows a SEM image of the wire d) BFP image of the emission from the junction. e) Corresponding I vs ϕ graph. The corresponding data for f), g), h) end 2 excitation and i), j), k) for end 1 + end 2 excitations, respectively. White dotted circle in the optical images denote the area projected on to the Fourier plane.

laser at free ends. The inset SEM image of the Ag NW dimer in figure 5.17c shows that the wires are coupled at an angle 107° . The fluorescence images of individual excitation (figure 5.17c and e) and dual excitation (figure 5.17g) were captured by employing long pass Rayleigh rejection (633nm) filter in the collection path right after the beam splitter (figure 5.2). From these images, it was evident that molecules placed near the surface of Ag nanowires were excited by the fields associated with propagating SPPs in the nanowire. Next we collected the emission from the junction and optically Fourier transform it to determine the directionality of the fluorescence emission from there for single (figure 5.17d and f) and dual excitation (figure 5.17h). These BFP images indicate single and dual directivity of the emission from molecules in close proximity of the junction. In case of dual channel emission, the angle between two emission directions mimicks the angle between the nanowires which is 107° for the particular case. Such function of directing fluorescence light essentially implies that the Ag NW dimer junction is acting as single and dual channel transmitting antenna when they were driven by

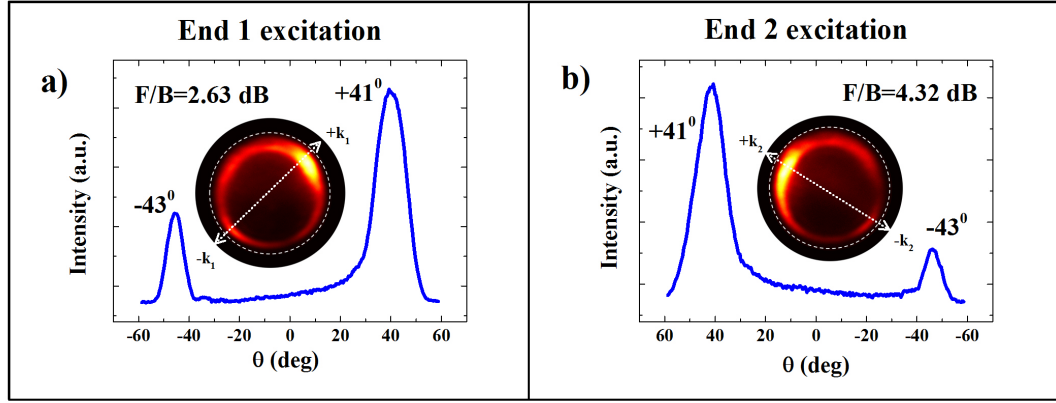


FIGURE 5.18: Degree of unidirectional emission. a) I vs θ plot in case end1 excitation. b) I vs θ for end 2 excitation. Intensity variation was taken along the white dotted line in inset BFP image for respective cases. This line represents the orientation of the excited wire.

a excitation source placed at the free ends. In case of single excitations, fluorescence emission happens along the axis of the excited nanowire. To quantify the degree of unidirectionality, we measured the forward to backward ratio of the fluorescence emissions. The intensity profiles as a function θ along the excited wire axes (k_1 and k_2) are shown in figure 5.18a and b. The forward to backward ratio in dB is calculated by using the equation, $f/b = 10\log(I_f/I_b)$. For end 1 excitation it was observed to be 2.63dB and for end 2 excitation it was observed to be 4.32dB. We also projected the fluorescence emission along the entire wire to the BFP of the objective lens for single and dual excitations. Here, we observed guided mode like signatures along the direction of SPP propagation (figure 5.19a,b and c). These observations hint towards the coupling of molecular emission to the SPP modes present in the wire. Note that in the BFP images an isotropic background is present apart from the bright lines. This indicates that the Plasmon coupling of the molecules only happen if the molecule is in close proximity of the nanowires.

Apart from directing light, another important aspect of an optical antenna is to influence the local photonic density of states thereby enhancing the light-matter interaction. Such property has direct implication on efficiency of an optical antenna[33]. In the present context, we were interested in exploring advantages of a dual excitation of the Ag NW antenna compared to single channel excitation. To address this issue, we performed single- and dual-channel remote excitation fluorescence spectroscopy with a 633nm laser source of total power of $50\mu\text{W}$. For single channel illumination, a $50\mu\text{W}$ excitation was focused at individual ends, whereas for dual excitation, a $25\mu\text{W}$ excitation was used at each end of the Ag NW dimer. Note that, the total power was

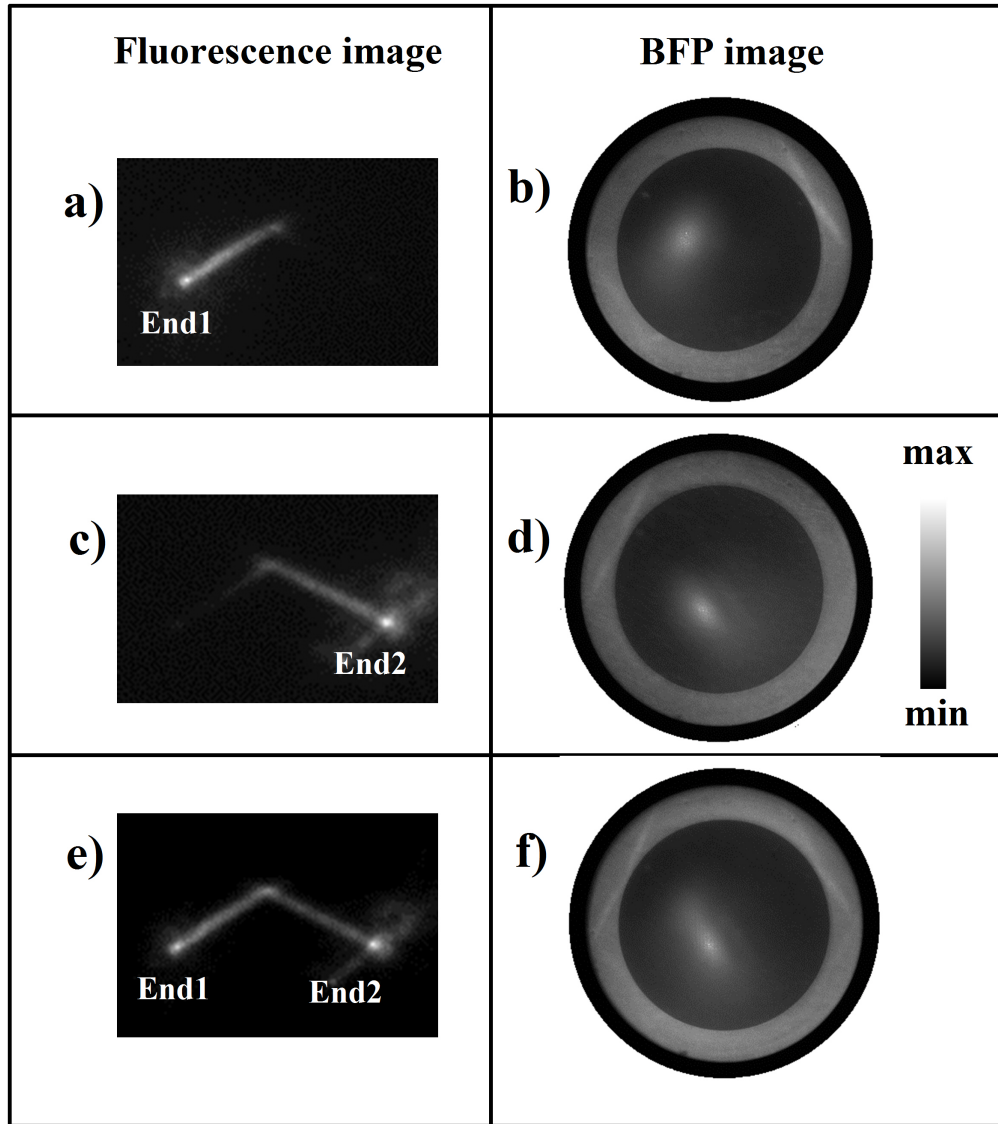


FIGURE 5.19: a) Fluorescence optical image of end 1 excitation. b) BFP image of end 1 excitation for the whole nanowire dimer barring excitation points and the junction. c), d) and e), f) are Fluorescence optical image and BFP of the same wire for end 2 excitation and end 1 + end 2 excitation.

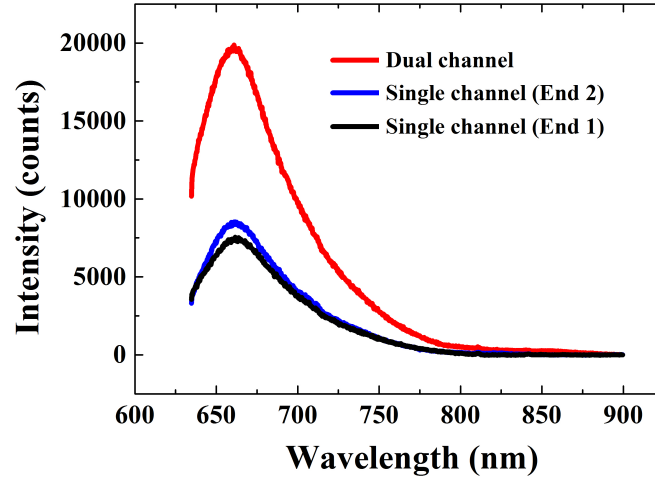


FIGURE 5.20: Remote excitation fluorescence spectra of Nile Blue A from the Ag NW dimer junction for single and dual channel excitation. Note that the total power for all the excitations was constant at $50\mu W$.

the same for single and dual channel excitation. Next, we captured the fluorescence spectra for the three configurations of illumination, and compared the 658nm emission intensity for each configuration (see Table 1). The collected spectra are shown in supporting figure 5.20. From table 1, we inferred that for the same illumination powers, dual excitation resulted in greater relative enhancement (value of 1) compared to single channel excitation (value of 0.37 and 0.39). We have already presented such enhancement in secondary emission from molecules due to dual channel excitation in context of remote-excitation surface enhanced Raman scattering in chapter 4 and attributed to the constructive interference of the plasmonic field at the NW junction as one of the reasons behind such enhancements[189]. In the present context, this implies that photon loss

TABLE 5.1: Comparison of relative fluorescence enhancement at Ag NW junction for single and dual channel excitations.

Mode of excitation	End 1 power (μW)	End 2 Power (μW)	Relative enhancement
Single channel	50	0	0.37
	0	50	0.39
Dual channel	25	25	1

at Ag NW junction not only facilitates dual-channel optical emission, but also provides enhanced optical fields to enhanced light-molecule interaction.

5.5 Conclusion

Junction of end to end coupled Ag NW dimer is largely considered as a site for enormous radiative losses in a plasmonic waveguides. We have shown how such photon loss channels can be utilized as an optical antenna. By utilizing spatially filtered Fourier-space optical microscopy, we have provided experimental evidence that shows this radiation can be directed in single and dual directions depending upon excitation methodologies. The junctions were shown to direct emission of elastic scattering, and inelastic fluorescence from molecules in close proximity to the NW junction. These observations were corroborated by 3D- FDTD simulations. We have established the fact that angle between the nanowire dimer can be used as a parameter to control the angle between the two emission channels in a dual channel optical antenna. The Ag NW dimer excitation not only provided dual emission channels, but also facilitated greater field enhancement compared to single channel emission, thus highlighting the prospect of improving the efficiency of an optical antenna. Furthermore, we showed that the emission directivities in the dual-channel antenna was sensitive to local refractive index changes, and can be harnessed in nano-optical sensing.

Chapter 6

Future Directions and Conclusions

The work presented in this thesis is mainly focused on exploration of the ability of various plasmonic nanojunctions to work as optical antenna; either by localizing light to subwavelength volume or by spatially directing light to specific directions. In chapter 2, we presented the field localization characteristics at the junction of Pd bridged Au nanocylinder dimer and used this localization for sensitive detection of hydrogen. These properties of the nanostructure were basically determined by the LSPs in the system. The LSP resonances are narrowband response compared to the broadband response of SPPs in extended plasmonic nanosystems. Therefore, working regime of SPP based nanostructures can cover broad range of frequencies. With this hindsight, we explored silver nanowire geometries which support SPPs to explore their ability to localize or direct optical fields. The nanowire geometries we explored; were serially coupled Ag NW dimer and coupled Ag NW-NP systems. In chapter 4 we characterized the light localization properties at coupled Ag NW dimer junctions and Ag NW-NP junctions. In chapter 5, we presented the evidence of directional out-coupling of light at coupled Ag NW dimer junctions. All these observations proved that the structure can work as a receiving antenna by creating localized field at the junction, as well as a transmitting antenna by spatially redirecting the far-field emission from the junction.

As for future direction in context of antenna like application, our main goal is to find out the directionality of light at different operational wavelength for a given nanostructure. This will allow us to determine the operational bandwidth of the optical antenna under use. One way for determining it is to perform spectroscopy at the BFP of the objective lens. Along the similar lines of BFP imaging techniques, here the BFP is projected on a spectrometer entrance slit. Hence, the image gets dispersed according to the wavelength and lets us measure the directivity of each part of the emitted light from the sample plane. This measurement technique is known as energy-momentum spectroscopy[208–211]. In the following section, we discuss how to setup a microscopy system, capable of performing energy-momentum spectroscopy and we will also present some preliminary results.

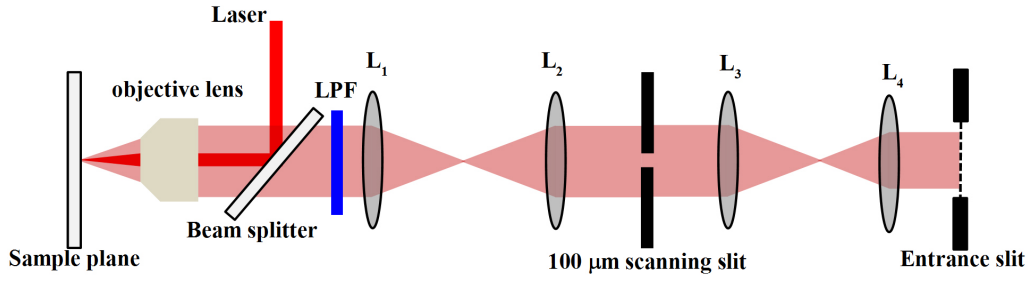


FIGURE 6.1: Experimental set-up for energy momentum spectroscopy (EMS). L_1 , L_2 , L_3 and L_4 are lenses and LPF is long pass filter.

6.1 Energy momentum spectroscopy

6.1.1 Experimental set-up

Our home built energy-momentum spectroscopy system is constructed around a commercial inverted microscope (Olympus, i71X). a schematic of the set-up is shown in figure 6.1. A laser of 633nm wavelength is reflected from a beam splitter and focused to the sample plane by an oil immersion ($n=1.52$) objective lens (Olympus, 100X, 1.3. NA). The Raman scattered light from the sample is collected back by the same objective lens. A Long pass Rayleigh rejection filter (LPF, $\lambda = 633nm$) is used in the optical path to block the Rayleigh scattered light. A set of relay lenses (L_1 and L_2) are used to create a first conjugate BFP of the objective lens. At this conjugate plane, constructed image has a magnification factor 1.5. A slit ($100\mu m$ wide) mounted on a translation stage, capable to move in transverse direction to the optical path, is placed. Another set of relay lenses (L_3 and L_4) create a second BFP image plane on the spectrometer (iHR 320, Jobin-Yvon) entrance slit with a further demagnification factor of 2. This makes the whole BFP image to be of $4.32mm$ diameter. The spectrometer entrance slit is kept wide open through out the experiment. This allows the BFP image size to match with the size of the CCD chip of the spectrometer CCD camera. The alignment of these lenses are done by moving each of them along the optical axis to check symmetric expansion and shrinking of the images about their positions. The purpose of the scanning slit is to carefully select a column from the BFP image. Each pixel in the column of the BFP image is dispersed by the spectrometer. Therefore, each row in the spectrometer CCD represents the spectrum of each pixel in the column of the BFP image. The step of translation of the scanning slit is $100\mu m$ and typically 58 measurements are taken to reconstruct the whole emission pattern in the BFP. As we have already discussed in chapter 5, the radius of the the emission pattern in the BFP image corresponds to the NA of the objective lens. Therefore, each pixel in the horizontal direction represents a

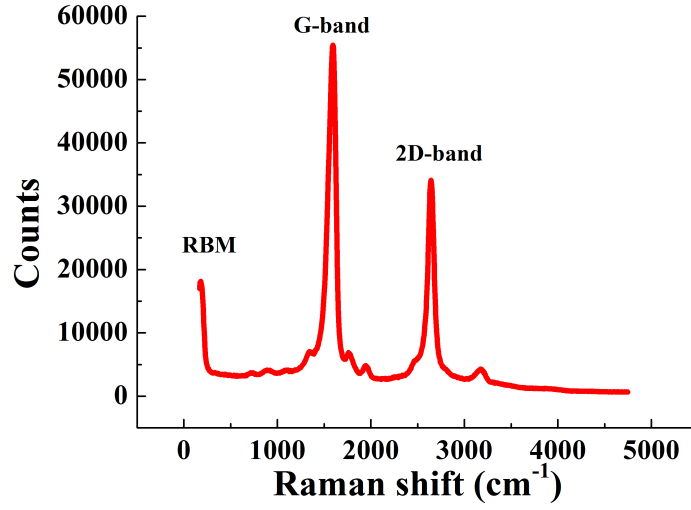


FIGURE 6.2: Raman spectrum of Carbon nanotubes

momentum resolution of $(2.6/58)$ NA=0.045 NA. In the vertical direction, the momentum resolution is defined by the number of vertical pixels of the CCD camera. We did 2×4 data binning of raw pixels to increase signal to noise ratio and hence, 4.32 mm diameter BFP image is spread over 45 pixel in the vertical directions. Therefore, the momentum resolution in the vertical direction is $2.6/45$ NA = 0.058 NA.

6.1.2 Data collection and interpretation

In this section, we present our preliminary results obtained using the spectrometer and will discuss how to interpret the obtained data. Here we will present the energy momentum spectroscopy data of carbon nanotubes (CNT) casted on a glass substrate. CNT has three characteristic vibrational Raman signals: (i) radial breathing mode (RBM) (165cm^{-1}), (ii) G-band (1594cm^{-1}) and (iii) 2D-band (2644cm^{-1}) (figure 6.2). Energy momentum spectroscopy allows us to separately measure the emission pattern of each Raman lines. This is done by separating the Raman signal from the background. the method is schematically illustrated in figure 6.3. As shown in the figure 6.1, we place a scanning slit at the first BFP image plane to carefully select each part of the BFP image. A second BFP image plane is created on the spectrometer entrance slit which is kept wide open as there is no provision for moving it horizontally. This allowed us to disperse the selected part of the image on the spectrometer CCD (figure 6.3b). Figure 6.3b shows a typical image recorded on the spectrometer CCD which is a 2D spectral map where x axis signifies the wavelength and y axis is the vertical position. The sharp lines in the spectral map represent the Raman lines. A broad background is also visible

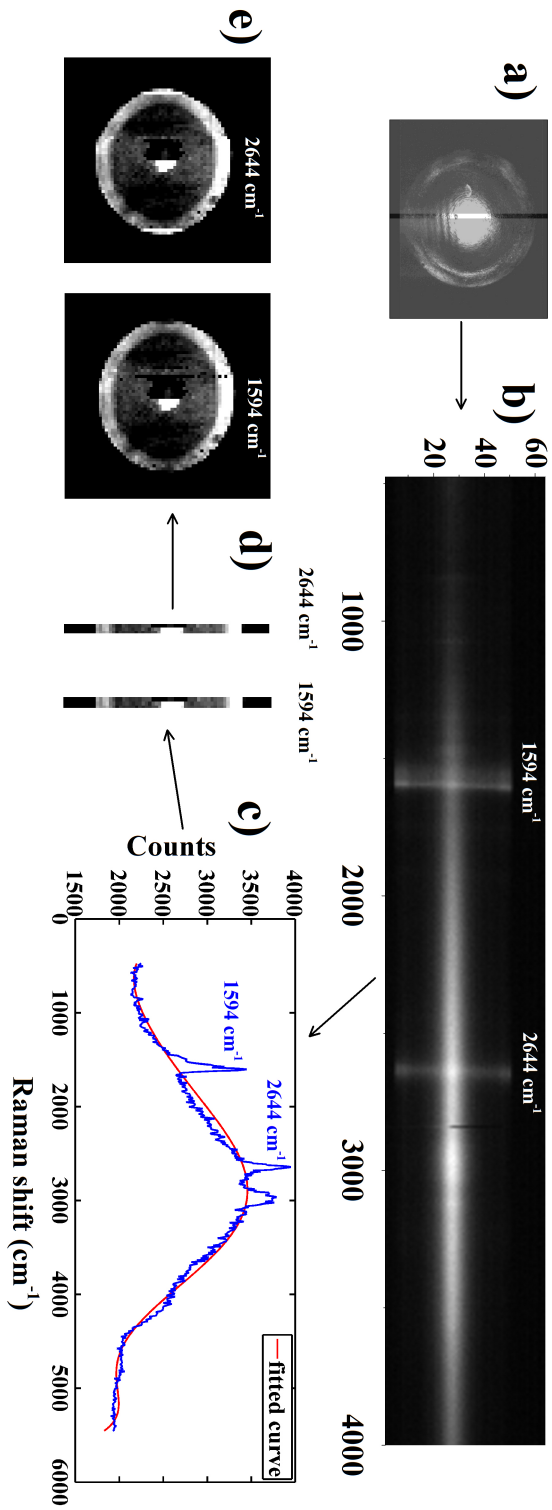


FIGURE 6.3: Schematic of Data collection in Energy momentum spectroscopy. a)BFP image of the objective lens where the blurred portions are filtered out by the scanning slit at the first BFP plane and the allowed portion of the image is projected on the spectrometer slit. b)2D spectral map of the image on the spectrometer CCD. c)Plot of the counts of one row of pixels. d)Intensity maps of 1594 cm^{-1} and 2644 cm^{-1} Raman lines at the spectrometer slit. e) Reconstructed emission patterns of 1594 cm^{-1} and 2644 cm^{-1} Raman lines.

here. Now, one row of pixels of the image in figure 6.3b is plotted in figure 6.3c. This is the Raman spectrum with Raman peaks seated on a background signal. We get rid of the background by creating a polynomial fit for the base counts of the Raman peaks and subtracting it from the actual signal. This way, counts of all the Raman line (RBM, G and 2D) can be found. This background correction is done for all the pixels in the vertical column which allow us to extract background corrected Raman image for the peak of interest (figure 6.3d). This whole procedure is repeated for each column of the BFP image by scanning the slit horizontally. This way, we obtain the emission patterns for each Raman lines. Here, we show emission patterns of G-band and 2D-band (figure 6.3e). As the molecules are placed on a dielectric medium, we see an isotropic emission for each Raman signal.

6.1.3 Future plans

With energy momentum spectroscopy, our first aim is to characterize the spectral properties of the directional emissions from serially coupled Ag NW dimer junctions. It will be interesting to find out if the directionality of Raman lines are different from the fluorescence emissions. In addition to that, use of energy momentum spectroscopy will allow us to determine the band width of a particular optical antenna. Which will let us know in what wavelength regime the antenna exhibits directional emission. These types of measurements are important for building various directionally enhanced spectroscopy techniques, specialized photo-detectors and directional optical sources.

6.2 Summary of the thesis

Plasmonics is an emerging field of science and technology. It deals with surface plasmons which is the coherent coupling of photons with collective oscillations of electrons at metal-dielectric interfaces in metallic nanostructures. This kind of light-matter interactions allow metallic nanostructures to confine, propagate and localize optical fields at sub-wavelength scales or to direct optical radiation from sub-wavelength sources to specific directions. All the above mentioned light manipulation abilities make plasmonic nanostructures work as optical antennae. In this thesis, we investigated various plasmonic nanojunctions i.e., i) Pd bridged Au nanocylinder dimer junction, ii) serially coupled Ag nanowire dimer junctions and iii) Ag nanowire-nanoparticle junctions for their ability to either localize optical fields or direct far-field radiation to realize optical antenna like operations. Localized fields near plasmonic nanostructures enhances energy transfer from light to a nanoscale emitter placed near-by and plasmonic influence on the directionality of the emission of emitters placed near the nanostructure

enhances energy transmission from the emitter. All these are important for building sub-wavelength optical communication devices where the working speed of the device can be much faster than the electronic counter-parts.

According to the type of the energy confinement, the field of plasmonics can be roughly divided into two branches: Localized surface plasmons and propagating surface plasmon polaritons. The former is resulted from the small volume confinement of the free electron oscillations in the small particles. This leads to alteration in the energy localization near the nanostructure depending upon the excitation optical wavelength which changes the light scattered by the particle. On the other hand SPPs are responsible behind subwavelength propagation of light and related energy transportation. In this thesis, we discussed how both kinds of excitations can be harnessed to obtain antenna like behaviour.

Under the category of LSP, we numerically investigated the structure: Pd bridged Au nanocylinder dimer junctions. Here, we demonstrated how the conductive Pd bridging alters the localization of optical fields at the junction compared to a dimer where the conductive bridging is absent. This leads to the occurrence of new LSP resonances in the extinction spectrum of the nanosystem. We demonstrated that the position of the LSP resonances can be tuned as a function of the geometrical parameters (length and width) of the Pd bridge. The special ability of Pd is to adsorb hydrogen at its surface. The free electrons of adsorbed hydrogen induce changes in the Fermi level of the Pd, thereby changing the electric permittivity. As the concentration of H_2 in the atmosphere changes, the amount of H_2 absorbed varies and hence the electric permittivity of Pd also varies as a function of H_2 concentration in the atmosphere. We demonstrated that this change in permittivity again influences the LSP resonances and therefore this plasmonic nanogeometry can be utilized as a nano-optical hydrogen sensor. The spatial footprint of such optical sensors is very small ($< 500nm$) so this work opens up the opportunity to explore such geometries to build lab-on-chip hydrogen sensing platforms. Such sensitivity to hydrogen at nanoscale can be harnessed to design nano-optical hydrogen detectors that can overcome the statistical averaging effects of ensemble based detection techniques[79]. The proposed ideas can be extrapolated to a variety of plasmonic geometries dimer, trimer and oligomers, where the Fano-type resonance can be exploited for ultra-sensitive hydrogen detection. Apart from filling the gap with palladium, it will be interesting to explore other gas adsorbing materials such as different metal organic frameworks for realizing other gas sensing devices.

Under the category of SPP, we demonstrated experiments on serially coupled Ag nanowire dimer junction and Ag nanowire-nanoparticle junctions. We showed that the sub-wavelength light propagation through such structures results in remote localization

of optical fields at the junctions when their free ends are excited by focused laser beam. This localization can be obtained by single and dual channel excitation. We measured the localized field by performing remote excitation SERS at those junction. It turned out that the dual excitation leads to better field enhancement compared to single excitation. We propose that this enhancement might be attributed to in-phase hybridization of SPP modes in individual wires at the junction. The light propagation through the nanowires can be controlled by varying the input light polarization and therefore the amount of energy delivered can also be controlled. We utilized this property to modulate the field localization and hence the SERS signal from the junction in case of dual excitation. These remote excitation geometries can also be used for other spectroscopic techniques such as fluorescence, photoluminescence and infra red spectroscopy etc. These are very important as the obtained signal is devoid of unwanted background due to the excitation laser. Our work on dual excitation presents how the signal-to-noise ratio of the otherwise remote SERS signal can be further enhanced. Apart from these, Remote excitation spectroscopy has important implications in in-vivo and in-vitro bio-measurements as direct laser exposure can deform the bio-sample and our geometry facilitates enhanced sensitivity for such measurements.

We also studied the directionality of the out-coupled photons from the junction of serially coupled Ag NW dimer junctions. Our observations regarding this establish the fact that these nanoarchitectures work as dual directional antenna not only by localizing field at the junction but also by directing far-field radiations to different directions specified by the position of the driving excitation source. Our experiments proved that these junctions can work both as single channel emitter as well as dual channel emitters. We also explored the possibility of manipulating the emission directions. We found out the angular separation between the two emission channels are actually defined by the coupling angle of the nanowires in the dimer. The θ peak of the emission can be tuned by changing the surrounding of the nanostructure and can be utilized for nano-optical refractive index sensing. These results show the ability of this nanostructure to route far-field emission to specific directions which is relevant for realizing communication between different elements of a plasmonic nanocircuits. Such works are also very important in context of enabling optical logical operations in a plasmonic nanochip. Apart from this, we also showed how the fluorescence of a nearby molecule can be in a similar way by the SPPs in the nanowires. Therefore, such structures not only enhance the molecular signals by enhancing the field localization they can also be used to direct the secondary signals to specific directions towards the detectors, thereby increasing their detection efficiency. Therefore, such nanogeometries can become test bed for developing similar directionally enhanced molecular detection units.

An interesting direction for future work would be to optically probe single emitters precisely placed at the junction of the NW dimer junction or NW-NP junctions. Such configurations have lately found enormous interest in nanoscale quantum information processing as single photon sources and our NW junctions and NW-NP junctions can be excellent candidates for such applications[212–216]. As we have emphasized, these nanowire geometries can be accessed via two spatially separated channels and hence can be utilized for remotely excited pump-probe experiments for ultrafast nanoplasmonics[217, 218] in real and Fourier space. The advantage of these dual excitation geometries might be the pump and the probe beams can be separated with each other by their directionality. Further more, other radiative lossy channels such as geometrical protrusions along a metallic nanowire or metallic thin film[217–219] can also be examined for similar kind of applications. The results produced for counter propagating plasmon based remote SERS from Ag NW-NP junctions shows their capabilities to utilize both propagating and localized surface plasmons which can lead to interesting optical microscopy methods such as remote-excitation four-wave mixing. Concepts such as one-dimensional Van Hove polaritons[220] and localized excitation of intersubband plasmon polaritons[221] in nanowires can also be probed with the discussed systems. Another interesting prospect is to replace the plasmonic nanoparticle in our experiment with a quantum dot, such that the counter-propagating plasmon can excite and modulate the spontaneous emission intensity of the single emitter. This can also open up new opportunities to probe quantum aspects of the plasmons. The counter-propagating scheme that we have discussed here can also be useful to excite exciton polaritons in organic nanowire systems[222], which can lead to new discoveries in organic nanophotonics.

In conclusion, we believe that the work presented in this thesis can be used as tools for developing various nano-optical and spectroscopic applications having significance in all avenues of science and technology ranging from physics, chemistry, material sciences to biology.

Appendix A

Finite element calculation of extinction spectra of nanoparticles

We calculated the extinction spectra and nearfield maps of the nanoparticles and their assemblies, discussed in chapter 2 using 2D/3D finite element method (FEM) calculation. The FEM is a numerical technique for finding approximate solutions to boundary value problems for partial differential equations. The technique is built on a simple approach where the whole problem domain is divided into simpler parts, called finite elements and appropriate boundary conditions are used to find the solution for each part. The ultimate solution is obtained by minimizing an associated error function. The way of problem solving is therefore based on variational method[114–116].

We performed our numerical simulations using a commercial software, RF module of COMSOL Multiphysics. The RF module in general is used to solve electrodynamic problems. It solves the Maxwell's equations over all the finite elements by imposing the boundary conditions at their boundaries. The size of the finite elements is defined by the mesh size. Here, we discuss how to model the numerical simulation for calculation of the near-fields and the extinction spectrum of a gold nanocylinder using COMSOL. First, we drew a cylinder of radius 40nm and length 40nm. Then we defined a simulation region by drawing a sphere around the cylinder. The boundaries of the sphere needs to be at least at distance of half the excitation wavelength away from the cylinder. In our case, simulation region was of $1\mu m$. diameter. We also defined a spherical perfectly matched layer (PML) at the outermost sphere of the computational region (figure A.1a). This PML layer was made to be 200nm thick. Introduction of PML made incident radiation to be absorbed at boundary without producing any reflection. Therefore, use of PML allowed us to numerical simulate field distributions in open boundary conditions. The PML formulation can be deduced from Maxwell's equations by introducing a complex-valued coordinate transformation under the additional requirement that the wave impedance should remain unaffected. The transformation for general coordinate t

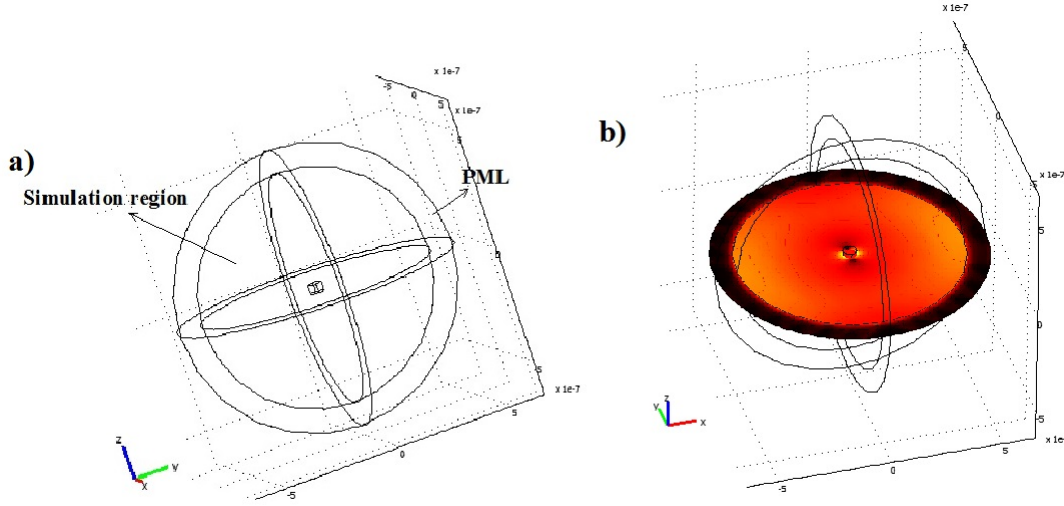


FIGURE A.1: a)Representation of the modelled geometry. b)Electric field map in the whole simulation region at x-y plane when illumination was along z axis with incident polarization along x axis.

is given by,

$$t' = t \frac{\lambda}{dt} (1 - i) \quad (\text{A.1})$$

where dt is the width of the infinite element region. Since our simulation region was spherical, we used a spherical PML which makes the layer absorbing in radial direction from a specific center point. Next, we defined the material of the nanocylinder to be gold by directly putting in experimentally measured dielectric constant values of gold provided by Johnson and Christy[129]. The material of inner and the outer sphere are assumed to be air. Scattering boundary conditions are used at the outer most sphere boundary. The calculations were done for a plane wave being polarized along the x axis and having a propagation vector along z axis. Since scattering boundary conditions inherently impose absorption of the reflected light from the boundary, simulation can be performed without having any PML. We used parametric solver to find solutions for a range of wavelengths i.e., 400-1000 nm. The calculated near field distribution for excitation wavelength of 520 nm is shown in figure A.1b. The scattering coefficient is calculated by integrating the far-field over the entire inner sphere boundary. Whereas, the absorption coefficient is calculated by measuring the Joule heating at the gold nanocylinder. As extinction is combination of both scattering and absorption by the particle, we calculated the extinction coefficient by summing up scattering and absorption coefficients. The resonances in the extinction spectrum are the localized surface plasmon resonances.

Modelling for all the other geometries and excitation conditions, discussed in chapter 2 can be done in a similar way.

Appendix B

Finite Difference Time Domain Simulations for Silver Nanowires

For the computational modelling of the light propagation through nanowires, we have used 3D finite difference time domain method (FDTD). This is a numerical analysis technique for modelling electrodynamics problems. Unlike FEM, it is a time domain technique and hence a wide frequency range can be covered in a single simulation run. FDTD method is built upon grid based differential numerical modelling methods where a set of well defined finite difference equations are solved to find out the solution of the problem. In FDTD modelling, the time dependent Maxwell's equations are discretized using central-difference approximations to the space and time derivatives over the whole simulation region. The solution is obtained by solving the resultant finite difference equations in a leapfrog manner i.e, for one instant electric field ($\mathbf{E}$) components are calculated over the space and for next instant the magnetic field ($\mathbf{H}$) components are calculated and the whole process is repeated until the steady-state electromagnetic field behaviour is obtained[117–119].

The time stepping for calculating $\mathbf{E}$ and $\mathbf{H}$ can be described as follows. $\mathbf{E}$ and $\mathbf{H}$ are discrete in time and can be expressed by,

$$\vec{E}(t) \rightarrow \vec{E}_{n\Delta t} \quad (\text{B.1})$$

$$\vec{H}(t) \rightarrow \vec{H}_{(n+1/2)\Delta t} \quad (\text{B.2})$$

where Δt is the time step and n signifies the time instant. FDTD follows the basic time stepping rule defined as,

$$\vec{E}_{n+1} = \vec{E}_n + \frac{\Delta t}{\epsilon} \times \vec{H}_{n+1/2} \quad (\text{B.3})$$

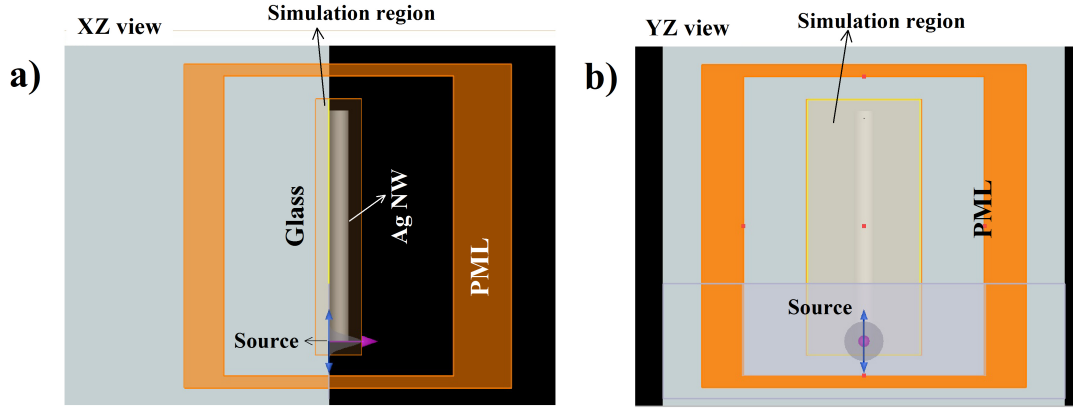


FIGURE B.1: a)XZ view of the modelled geometry. b)YZ view of the modelled geometry

$$\vec{H}_{n+3/2} = \vec{H}_{n+1/2} - \frac{\Delta t}{\mu} \times \vec{E}_{n+1} \quad (\text{B.4})$$

For space discretization, whole simulation region is divided into very small simpler parts, similar to FEM method. These small cells are called Yee cell. Electric and magnetic fields are calculated for each cell by solving the finite difference equations.

For our purpose, we used a commercial software, "FDTD solutions" from Lumericals inc. Here, we will discuss the modelling technique briefly. This is a 3D Maxwell solver specially designed for analyzing the interaction of ultraviolet (UV), visible and infra-red (IR) radiation with complicated structures, having wavelength scale features. Here, we will describe how to model light propagation through Ag nanowires immobilized on glass in Lumerical's FDTD solver. The simulation geometry can be designed using the solver's advanced graphic interface. The designed geometry is shown in figure B.1a and b. Then we define the perfectly matched layer (PML) which is an absorbing medium for minimizing reflections from the simulation region boundary. The PML layer must be put at a distance of half a wavelength away from the structure to avoid unwanted errors. We defined the materials by their dielectric constant values. For glass slide we used dielectric constant value 2.25 and for silver nanowire we used experimentally measured dielectric constant values provided by Johnson and Christy[129]. One of the terminals of the nanowire was illuminated by a laser source ($\lambda=633$ nm). The focusing was done by using a thin lens of numerical aperture 1.3. Now, as discussed earlier, in FDTD method, Maxwell's equations are solved on discrete mesh. This can cause field discontinuity in case of metal dielectric interfaces. Because, by

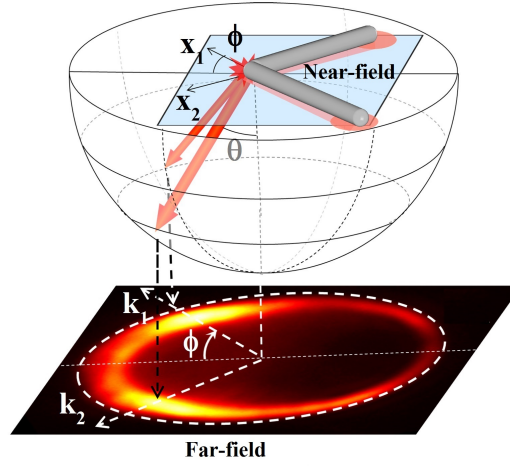


FIGURE B.2: Schematic of the far-field calculation methodology

normal meshing, position of the interface can not be resolved better than dx . Therefore, to overcome this, we used conformal meshing technology of the FDTD solver. This is a graded mesh which creates mesh of reduced size near the interface. The most notable advantage of conformal mesh technology is it uses an integral solution to Maxwell's equations near interfaces; thereby reduces unwanted staircasing effects in the solution produced due to normal meshing. This meshing in the solver is defined by many types of variants. For our purpose, at the metallic medium we used conformal variant (1) and at the dielectric medium we used conformal variant (0). The mesh size we used was of 3nm and therefore was much less than the required mesh size of $\lambda/10$. We used a high mesh accuracy of $\lambda/10$ to ensure accuracy in the simulated results. The simulation was run long enough to ensure stability.

The far field calculations were done using the near-field to far-field projection calculator of the solver. It calculates electromagnetic fields anywhere in the far-field. The near-field data is obtained by solving the problem using FDTD method and the far-field data is produced by following some post processing steps after that. The most simple way to describe this calculation is to view them as a decomposition of the near-field data using a set of plane waves propagating at different angles as the basis of the decomposition. After the simulation was done we ended up with near-field response to a continuous wave laser of wavelength 633 nm. When these near field data were projected to the far-field using the projection calculator, it propagates the field upto a hemisphere at a distance of 1m. The final result produced is the intensity profile on the surface of the hemisphere as viewed from the top (FigureB.2). This way we calculated the far-field responses presented in chapter 5

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