
Optical cavities coupled to 2D materials: Wavevector and Polarization Studies

A thesis

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

by

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PUNE

CERTIFICATE

Certified that the work incorporated in the thesis entitled ("Optical cavities coupled to 2D materials– Wavevector and Polarization Studies") submitted by **Shailendra K Chaubey** was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other University or institution.



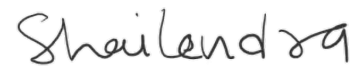
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Abstract

Controlling and manipulating light-matter interaction is one of the major goals of nanophotonics. Studying the interaction of light with materials has wide implications, including the development of sensors, photodetectors, phototransistors, LED, lasers, and other device. After the discovery of graphene two dimensional emerges as a major field of research as it possesses unique optical, mechanical, electrical, and chemical properties. TMDs are a special class of material as they are direct band semiconductors with high exciton binding energy. Their bandgap lies in visible to near-infrared wavelength range and they shows high oscillator strength and valley selective optical properties. Engineering optical emission from two-dimensional transition metal dichalcogenides (TMDs) materials is important for creating and understanding nanophotonic devices based on two-dimensional materials. To achieve control over the emission properties of TMDs, one has to achieve control over parameter of the emitted light like intensity, polarization, and wavevectors. One of the approaches to control and manipulate these parameters is to place these materials inside the cavity. Coupling TMDs materials to optical cavities results in enhanced quantum yield of excitonic emission, and can provide the control over other emission properties enabling advanced quantum optics and nanophotonics devices.

Herein, we discuss the effect of different metal film-based cavities on the wavevector and polarization of the emission from TMDs. We probed various metal-dielectric and metal-metal cavities using Fourier plane microscopy and spectroscopy. First, we have studied the wavevector and polarisation states TMDs sandwiched inside silver nanowire on mirror cavity and achieve the directional emission. Next, we have used the bent plasmonic nanowire on mirror cavity to further reduce the angular spread and reduce the back-reflected light. Finally, we discussed the effect of placing TMDs inside the microsphere on mirror. We have achieved beaming of TMDs photoluminescence using this cavity.

List of Publications

Included in thesis:

- **Shailendra K. Chaubey**, Gokul M A, Diptabrata Paul, Sunny Tiwari, Atikur Rahman, G V Pavan Kumar, Directional Emission from WS₂ Monolayer Coupled to Plasmonic Nanowire-on-Mirror Cavity, *Advanced Photonics Research*, 2100002, (2021)
- **Shailendra K. Chaubey**, Sunny Tiwari, Ashutosh Shukla, Gokul M. A., Atikur Rahman, G V Pavan Kumar, Directing Monolayer Tungsten Disulfide Photoluminescence using a Bent Plasmonic Nanowire on a Mirror Cavity, *European Physical Journal-Special Topics*, Under Review,(2022).
- **Shailendra K. Chaubey**, Sunny Tiwari, Gokul M. A., Diptabrata Paul, Atikur Rahman, G.V. Pavan Kumar, Beaming of WS₂ Photoluminescence from a film coupled microsphere antenna, *arXiv:2110.10387*. (2021).

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- Vrinda Narayanan P, Gokul M. A., Tamaghna Chowdhury, Chandan K Singh, **Shailendra K. Chaubey**, Takashi Taniguchi, Kenji Watanabe, Mukul Kabir, GV Pavan Kumar, Atikur Rahman, Giant Photoresponse Enhancement in Mixed-Dimensional Van der Waals Heterostructure through Dielectric Engineering, *Advanced Materials Interfaces*, 2102054, 2022
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- Sunny Tiwari, Adarsh B. Vasista, Diptabrata Paul, **Shailendra K. Chaubey**, and G. V. Pavan Kumar, Beaming Elastic and SERS Emission from Bent-Plasmonic Nanowire on a Mirror Cavity, *The Journal of Physical Chemistry Letters*, 12, 6589-6595 (2021).

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Dedicated to Dadu

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Chapter 1

Introduction

Controlling and engineering the light-matter interaction plays a crucial role in science and technology. Historically this problem has been tackled from various viewpoints, and several milestones have been achieved. Diffraction limit of the light was problem for a long time in imaging nanoscale entities. Tip-enhanced field proved essential in pushing this barrier and achieved the resolution far beyond diffraction limit. Another key area of research is to control and manipulate the absorption and emission of photons in atoms and molecules. Emission and absorption of light form the basis of many emerging and mature technology like modern spectroscopy, lasers, X-ray sources, light-emitting diodes, photo-diodes, and solar cells. Advancement in the field of micro and nano-fabrication enables the control and fine-tuning of emission properties. Studying light-matter interaction inside a cavity has grown as an important field of research in last two decades[1–6]. Fabrication of subwavelength size structures increases the applicability of light-matter interaction.

Emission cross-section depends on the local density of optical states (LDOS). Hence, changing the LDOS might inhibit or enhanced the spontaneous emission of molecule or atom. In 1946 It was shown for the first time by E M Purcell that placing an emitter inside micro-cavity can modify the rate of spontaneous emission[7, 8]. This effect was further demonstrated by Drexhage in 1966 in a fluorescence experiment in front of a mirror[9]. There are many strategies to modify the LDOS from coupling the emitter to metamaterials to placing the emitter inside cavity. Placing the emitter inside cavity modifies the LDOS by means of high electric field and cavity and resonances. LDOS inside a cavity critically depends on the architecture and the dimension of cavity. There are many cavity designs that have been studied to engineer light-matter interaction[10–13]. To count a few metal nanoparticles on a mirror for detecting the signal molecule Surface-enhanced Raman Scattering (SERS) signal and to enhance the photoluminescence and molecular fluorescence. Dielectric micro-cavity has been used for lasing and sensing application, label-free single-molecule detection[3, 5, 14–16] and many other application.

Next, We will briefly discuss spontaneous emission and Raman scattering. We will discuss the different types of micro and nano-cavity and how they can be used to control and modify the spontaneous emission and Raman scattering cross-section. After that, we will discuss the basic properties of two-dimensional materials and their applications. We will also discuss how these micro and nano-cavities can be utilized to modify the emission properties of these two-dimensional materials.

1.1 Spontaneous Emission

Upon excitation of an atom or molecule to a high energy state, it stays in an excited state for a short time and returns to the ground state after emitting a photon as shown in figure 1.1. This process is called spontaneous emission. Depending on excitation source, this spontaneous emission process can be called photoluminescence, chemiluminescence, or thermoluminescence. When excitation source is light or photon it is photoluminescence[17–19].

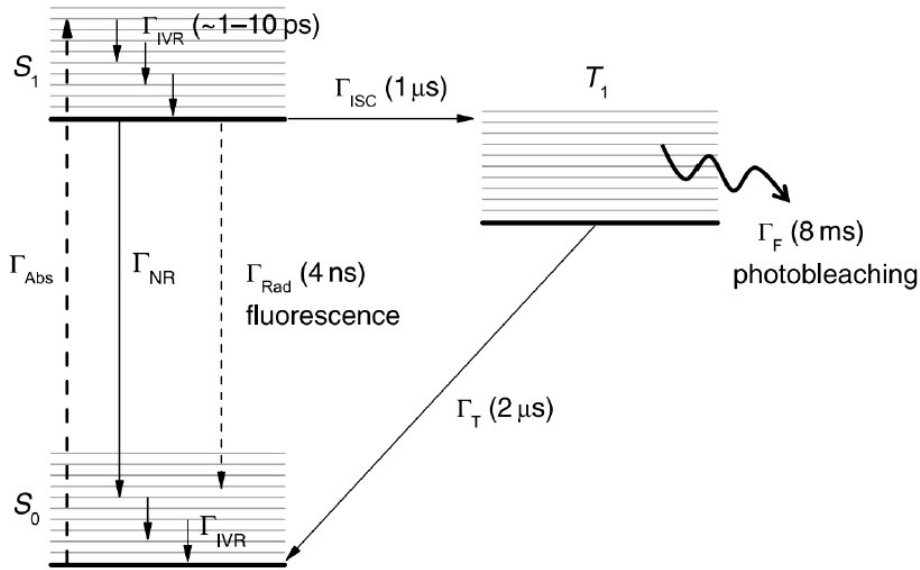


FIGURE 1.1: Schematic showing the photoluminescence process. S_0 and S_1 are two singlet states while T_1 is a triplet state. When molecules or atoms are excited using light, electron jumps to S_1 from S_0 . From S_1 electron jumps back to the ground state by emitting a photon or goes to a metastable triplet state T_1 and comes back to the ground state by a radiative transition. The Figure reproduced with permission from[19]

The absorption of a photon by an atom or molecule depends on its absorption cross-section P_{abs} . Usually, the excited electron relaxes to a singlet ground state S_0 and goes back to the ground state after emitting a photon. The absorption cross-section of

molecules is usually measured by illuminating a beam of polychromatic light through molecules and measuring the transmitted power P_{trans} and then calculating the extinguished power $P_{ext} = P_{inc} - P_{trans}$. Thus one can define the extinction cross-section P_{ext} as the sum of scattering and absorption cross-sections:

$$\sigma_{ext} = \sigma_{abs} + \sigma_{scat} \quad (1.1)$$

Scattering cross-section for the molecules and quantum emitter is negligible hence the extinction cross-section is mostly dominated by the absorption. In the case of the molecule and quantum emitters, the absorption cross-section gives information about the optical extinction.

The rate of the spontaneous emission can be defined by the probability of the transition from the excited state to the ground state by emitting a photon which is called radiative decay. Radiative decay rate Γ_{ij} is given by the Fermi golden rule[20].

$$\Gamma_{ij} \propto S_{ij} \rho(f_{ij}) \quad (1.2)$$

Where Γ_{ij} is the transition probability for an electron to going from excited state i to lower energy state j . S_{ij} is the transition matrix and $\rho(f_{ij})$ is the density of the optical state available to the emitter at the frequency f_{ij} . To control and modify the emission one can modify either of these two. Since LDOS depends on the local environment of the emitter, transition probability can be modified easily by placing the emitter inside a cavity. An atom or molecule in an excited state can also lose its energy by nonradiative decay. If Γ_r and Γ_{nr} are the radiative and nonradiative decay rate, total transition probability can be written as $\Gamma_{total} = \Gamma_r + \Gamma_{nr}$. The lifetime associated with the radiative transition can be written as the inverse of the Γ_{total} .

Sometimes atoms or molecules in the excited state reached to metastable triplet state and relax for a longer time as shown in figure 1.1. Radiative decay from the triplet state results in phosphorescence. Phosphorescence is dominant in some materials and its lifetime varies from a few milliseconds to seconds[21, 22].

1.1.1 Modifying Spontaneous Emission

In previous sections, we have discussed the phenomena of spontaneous emission. Spontaneous emission can be modified and controlled by different way such as impurity doping, gating, heating, twisting and placing them in the cavity[23, 24]. When atoms or molecules are placed in a very high electric field their absorption cross-section and decay rate change. At the same time, other properties of the emitted light are governed by the local environment of the emitter. The emitted light can be characterized by four

parameters and can be modified or controlled by controlling these parameters. We will briefly discuss these four parameters and how they can be controlled.

- **Energy:** Energy is one of the most important parameter associated with the emitted light. It can be measured by measuring the frequency or the wavelength associated by emitted photon. Spectroscopy is commonly used to measure the energy associated with the emitted photon however there are other methods based on photo-diode [25] and metasurfaces[26] has been used for the same. Energy associated with a emission process can be modified by modifying the local environment or coupling the emitters to plasmonic nanostructures[27].
- **Intensity:** Intensity of the light is defined as the square of amplitude of EM wave. For emitted light it is associated with is number of photon emitted and give information about the quantum yield of the material. When an emitter is placed in a high electric field the absorption and decay rate changes substantially[7, 19]. The total emission enhancement is a combination of enhanced photoluminescence yield and the enhancement in absorption cross-section. Intensity of the emission depends on the rate of the absorption or absorption cross-section. The enhancement in the emission as a function of change in the absorption can be written as

$$M_{abs} = 3 \left| \frac{E_{local}}{E_{inc}} \right| (e_{mol} \cdot e_{laser})^2 \quad (1.3)$$

where E_{local} and E_{inc} are local electric field experienced by the molecule and incident electric field respectively. e_{mol} represents the orientation of the molecular axis, e_{laser} represents polarization of the incident light. Absorption will be nonzero only when electric field orientation has a component along the orientation of molecule. Hence the enhancement in the absorption is directly dependent on the local electric field. The Quantum yield of an emitter can be modified by placing it near a metal.

- **Polarisation:** Polarisation of light is defined as the plane of oscillation of the electric field. A light beam can be azimuthally, linearly, circularly or elliptically polarised based on the amplitude and the direction of the electric field associated with the beam. Polarisation of the emitted light depends on the factors which include the band structure, local environment of the emitter, structure, and symmetry of the emitter molecules, energy of incidence light, and the polarisation of the incidence light. TMDs show valley polarisation when they are excited with

circularly polarised light with energy close to their bandgap[28]. Molecular fluorescence shows vectorial polarisation when they are coupled with the whispering gallery mode of the microsphere. Most of cavity-coupled molecular emissions show a very strong polarization signature[29].

- **Wavevector:** Wavevector is another very important parameter to characterize the emitted light. Wavevector gives information about the propagation direction of the emitted light. Studying the wavevector distribution is crucial for fundamental understanding of the quantum cavity electrodynamics as well as for designing the nanoantenna and other directional sources. Wavevector distribution of emitted light depends on the molecular orientation of the emitter as well as on the local environments. Figure 1.2 shows the wavevector distribution of molecular fluorescence and surface-enhanced Raman scattering (SERS) forming a plasmonic nanowire on a mirror antenna[30].

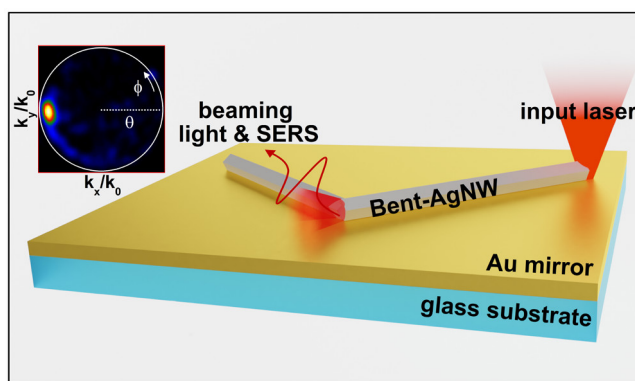


FIGURE 1.2: Schematic of a bent silver nanowire on mirror cavity. One end of the nanowire was excited using a laser beam. Light out-coupled from the bent part of the nanowire was filter using a pinhole and projected onto the detector for the Fourier plane imaging. Inset shows the Fourier plane image of the emission from the bent part of the nanowire. It is clear from the Fourier plane image that light outcouples in a directional manner (See the inset). The Figure reproduced with permission from[30]

1.2 Raman Scattering

In the previous section, We have discussed spontaneous emission and its cross-section. Now we discuss another important concept, Raman Scattering. It was discovered back in 1926 by Sir C V Raman and hence named Raman Scattering[31–33]. When light scatters from the molecules of any material predominant scattering is elastic scattering. While C V Raman observed that after scattering from some material, some energy is gained or loosed by the molecules which result in the change in the frequency of some

of the scattered photon. In the scattering spectra of these materials, there are discrete frequencies present in scattered light other than incidence frequency. Later it is found that these discrete inelastic frequencies are the fingerprint of the materials and are associated with the properties and structure of that materials, such as bond length and polarisability. This effect is known as the Raman effect serves as a basic building block for many applications.

Scattered light from any material can be divided into three-part on the basis of the frequency of scattered light :

- **Rayleigh scattering:** It is the most prominent of the three processes and is elastically scattered light from the material. As a result, the scattered and incident light has the same frequency. ($\nu_{\text{scatt}} = \nu_{\text{inc}}$). Central peak labeled by laser line in figure 1.3 is Rayleigh line or elastically scattered light of Raman spectra.
- **Stokes scattering:** This is the result of inelastic scattering from the material or molecule. When the frequency/energy of the scattered photon is less than that of the incidence photon it is called Stokes scattered photon. This is part of Raman scattering and the difference between these two frequency is called the Raman shift ($\nu_{\text{stokes}} < \nu_{\text{inc}}$). Peak situated on positive x-axis of the figure 1.3 represents the stokes part of Raman scattering spectrum.
- **Anti-stokes scattering:** Similar to Stokes scattering this is the result of inelastic scattering from the material or molecule. When the frequency of the scattered photon is greater than that of the incidence photon it is called Anti-stokes scattered photon. This is the part of Raman scattering and the difference between these two frequency is called the Raman shift ($\nu_{\text{anti-stokes}} > \nu_{\text{inc}}$). Peak situated on negative x-axis of the figure 1.3 represents the stokes part of Raman scattering spectrum.

Raman scattering is a weak process and it is very difficult to detect a Raman scattered photon from most of the atoms or molecules. Raman scattering cross-section depends on the Raman scattering cross-section and the power of the input light.

1.2.1 Enhanced Raman Scattering

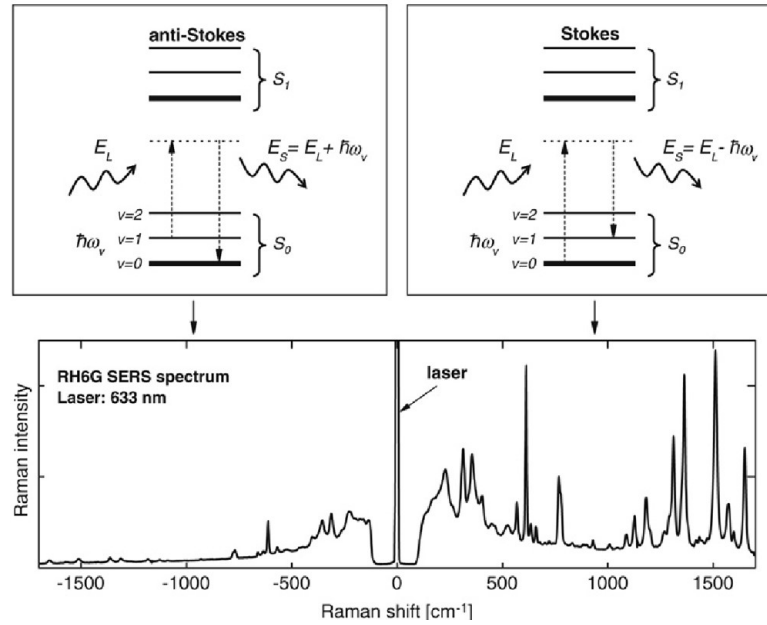


FIGURE 1.3: Surface Enhanced Raman Scattering (SERS)

Top left and right panel showing the schematic of the stokes and anti-stokes part of Raman scattering. S_0 and S_1 are two singlet states. There are multiple vibrational level within these states labeled by $\nu = 0, 1, 2, 3, \dots$ and E_L is a virtual state. Bottom left and right panel are Stokes and Anti-stokes part of the SERS from rhodamine 6G molecules.

As the cross-sections of Raman scattering are small, it's difficult to detect Raman scattered light from many materials and molecules. Similar to spontaneous emission scattering cross-section can be modified by modifying the local environment. Surface-enhanced Raman scattering (SERS) is the most common approach for increasing the Raman scattering cross-section. It was discovered by Fleischmann accidentally in 1974 while performing Raman spectroscopy on rough silver electrodes with pyridine[34]. When molecule are placed on the metallic surface or in confined in small cavity, Raman Scattering cross-section increases by a large factor because of excitation of localised surface plasmon at the metallic surface. Enhancement is largest when plasmon frequency is in resonance with the radiation. For the enhanced scattering oscillation of the surface plasmon must be perpendicular to the surface. To satisfy this criteria roughened metal film or the assembly of plasmonic nanoparticle are commonly used. Figure 1.3 shows the SERS spectra of Rhodamine 6G molecule taken using 633 nm laser. It is very powerful spectroscopic technique which can detect single molecule and have application in many field.

1.3 Two-Dimensional Materials and their properties

In the previous section we have discussed the molecular emission and how they can be modified. Now we will discuss a special class of emitter called 2D materials. They are called 2D material because of their atomic scale thickness. After the discovery of graphene and the Nobel prize of Andre Geim and Konstantin Novoselov, two-dimensional materials are in limelight and are being explored from every possible aspect. A lot of two-dimensional materials have been discovered and now it covers a large spectrum, and now it includes everything from insulators (e.g., hexagonal boron nitride(hBN)) to semiconductors (e.g.,TMDs) and other semi-metals (e.g., black phosphorus) and shown in figure 1.4. A wide range of optical, mechanical, chemical, and electric phenomena have been realized using these materials. [35–37].

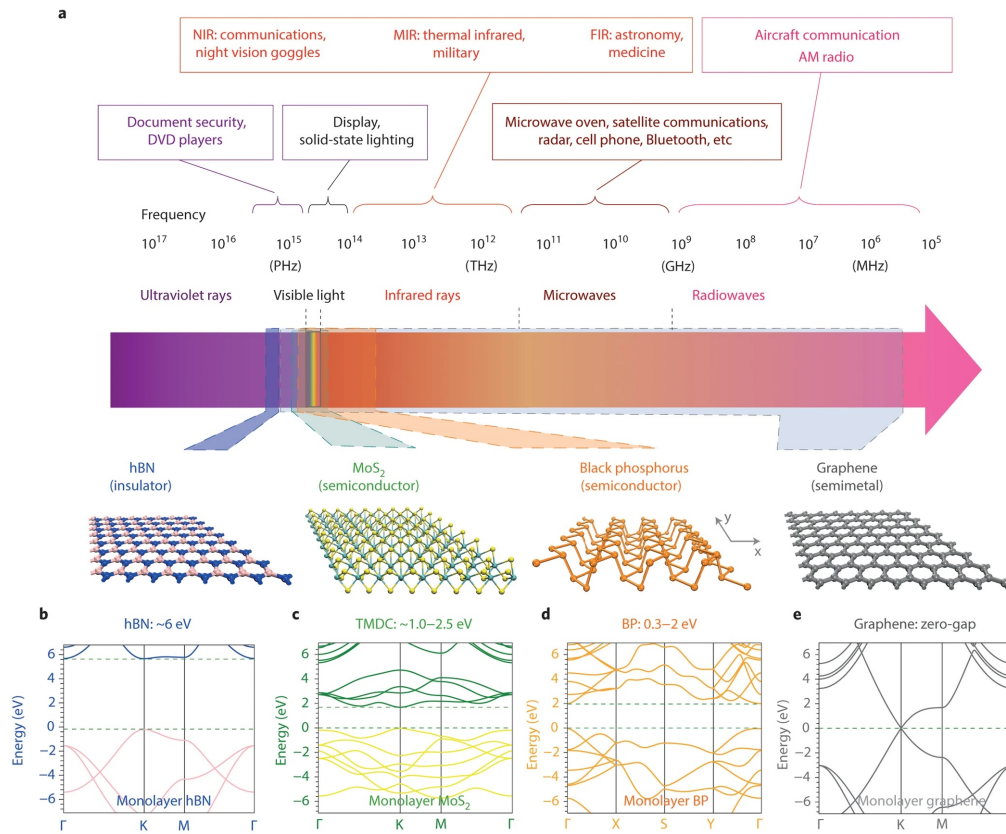


FIGURE 1.4: a. Different application of two dimensional materials over a large spectral range. MIR, NIR, and FIR are the short form of mid, near, and far-infrared, respectively. Atomic structure of various two dimensional materials has been shown in the middle panel with respective band gap for BN, MoS₂, black phosphorus, and graphene. b–e, Shows the band structures of single-layer hBN (b), MoS₂ (c), BP (d), and graphene (e). The Figure reproduced with permission from [35]

In 2010, the discovery of MoS_2 as a direct band semiconductor added another functionality to it toward high-end electronics and optoelectronics applications[38–42]. This field has been revolutionized since then and several other materials in this family have been discovered with slightly different properties. This whole family is called transition metal dichalcogenides (TMDs). Monolayer TMDs are formed by sandwiching the a hexagonal network of transition metal atoms (Mo, W) between two hexagonal network of chalcogen atoms (S, Se) as MoS_2 , WS_2 , MoSe_2 , WSe_2 . The empirical formula for these materials is MX_2 . (where M is Mo or W and X is S or Se). These materials contain very rich physics as well as are very important for the application purpose. They are unique in comparison to graphene and hexagonal boron nitride as their bandgaps are in the range of visible to near-infrared wavelength range. Strong Coulomb interaction and reduced dielectric screening results in sharp excitonic resonances. Inversion symmetry breaking in the monolayer TMDs leads to the direct bandgap transition at the degenerate K (K') point at the edge of the Brillouin zone, which shows valley-selective circular dichroism[43]. This property leads to valleytronics, which utilizes valley pseudo-spin manipulation to transmit information. Due to these unique optical and electronic properties, these material has been utilized for a large number of optoelectronic applications such as photodetectors, phototransistors, modulators, light-emitting diodes, quantum emitters, and lasers. Recently these materials coupled with metasurfaces have been used for quantum computation[28, 43–53].

For materials with such large implications, it is important to achieve control over their properties. Along these lines, coupling these materials to cavities for tailoring and controlling their emission properties has gained relevance. Inside cavity, modification of the local density of state alters the emission properties of the emitters placed inside cavity. Emission properties can be controlled by designing the different cavity architectures.

1.4 Cavity structures to modify the emission properties of TMDs

In previous sections, it was discussed that by changing the local environment, we can modify the properties of the emitter. Placing the emitter inside micro and nanocavity changes the LDOS which changes the rate of spontaneous emission. As we discussed above, other properties of the light can also be changed by placing the emitter inside cavity. Since the properties of the emitted light is very sensitive to the local environment, cavity design become crucial to control these properties. There are several cavity

designs depending on the application and we will broadly divide it into two parts Plasmonic cavity and Dielectric cavity. Figure 1.5 shows the different cavity designed for various application. Figure 1.5 (a) and (b) shows two fabry-perot based cavity utilised for the strong coupling with emitter. Another nano-triangle based cavity in figure 1.5 (c) is used to enhance the excitonic emission form WS_2 . In Figure 1.5 (d) a bent-nanowire on mirror cavity is used for directing the wavevector of the excitonic emission to small range of wavevectors.

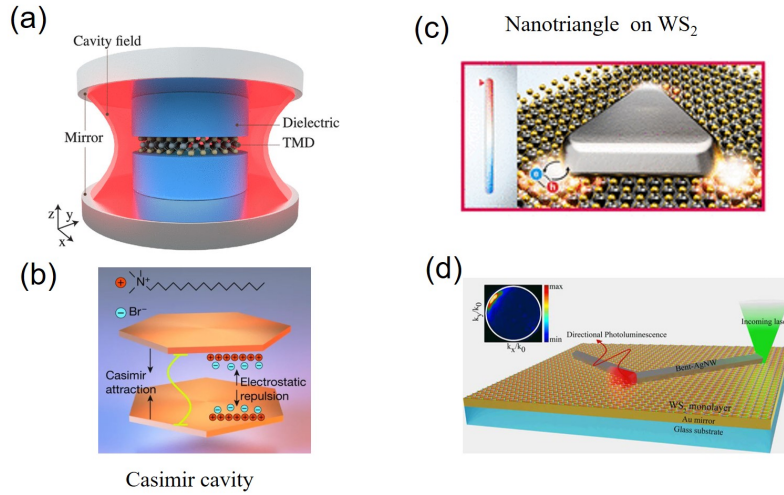


FIGURE 1.5: Schematic of different cavities utilized to modify the spontaneous emission. (a) Used for the mixing of bright and dark exciton spectral features and strong coupling. (b) Casimir cavity for the strong coupling in 2D materials. (c) Nanotriangle is used to tune the neutral and charged exciton in spectral features. (d) Bent NW on mirror cavity is used to direct the emission to the narrow range of wavevectors. The Figure reproduced with permission from[54–57]

1.4.1 Surface plasmon and plasmonic nano-cavity

Plasmonic cavities are nanometric structures that use surface plasmon excitations to concentrate electromagnetic fields into sub-diffraction volumes. Plasmons are the coherent and collective oscillation of the electron in the metals. Surface plasmons are plasmons that are confined on the surface of the metal. Surface plasmon interacts strongly with the light called surface plasmon polariton as shown in figure 1.6 (a). Resonances associated with the electron oscillation are called surface plasmon resonance. Different plasmonic nanocavity has been utilized for many applications Surface plasmon can be divided into many categories depending on the structure and dimension and structure of the material.

- **Localized surface plasmons :** When any quasi zero-dimensional nanostructure (nanoparticle) is illuminated by electromagnetic radiation, the surface electrons tend to oscillate following the illumination. This creates a strong local electric field near the metallic nanostructure. When the illumination frequency is equal to the natural frequency of the structure, there is a large electromagnetic response from the structure. This state is called localized surface plasmon resonance, as the electric field is localized near the surface of the structure[58] as shown in figure 1.6 (b) and (c).
- **Propagating surface plasmons :** Metallic thin films and nanowires have an additional degree of freedom for the surface excitation to propagate. To couple the incident light energy to propagating surface plasmons one has to satisfy the momentum matching criterion, as momentum of surface plasmons is larger than that in free space. For semi-infinite thin films, this can be matched by providing additional momentum through different means: coupling through the grating, exciting through a prism, etc. In the case of wires, symmetry breaking at the ends of the wire provides the additional momentum needed and hence one can excite propagating surface plasmons in the wire[59, 60].

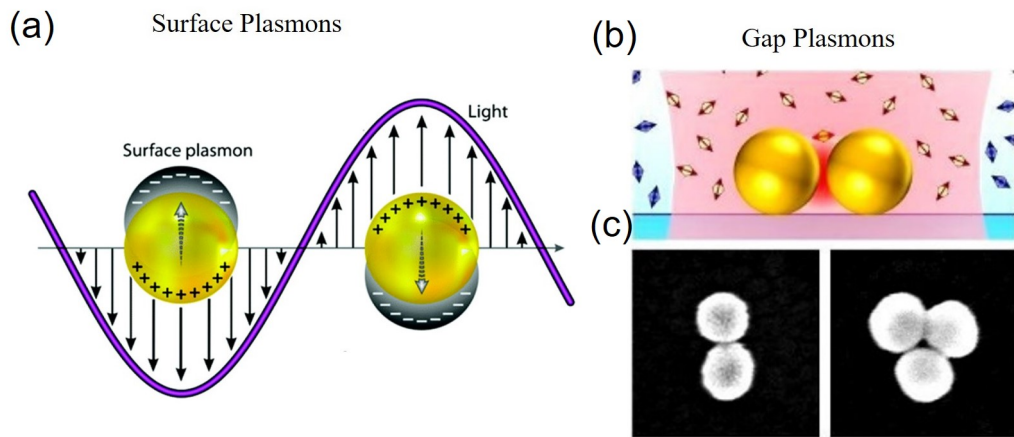


FIGURE 1.6: Schematic of the surface plasmon polariton, (a) showing the oscillation of electron cloud when illuminated with an electromagnetic wave, (b) schematic of the gap plasmon polariton in the small cavity formed by two gold nanoparticles and (c) FESEM image of the cavities formed by 100nm gold nanoparticles. The Figure reproduced with permission from[61, 62]

1.4.2 Dielectric micro-cavity

In the previous section we discussed the plasmonic nanocavity in details. Plasmonic nanocavity provide high electric field enhancement, on the other hand they suffer large

ohmics losses. Instead of using metal, using dielectric micro-cavity provide high-quality factor and sharp resonances. Quality factor, Q can be defined as $Q = 2\pi \cdot (\text{Time average energy stored at a resonant frequency}) / (\text{Energy dissipated in one period of this frequency})$. There are many ways to achieve optical confinement in a dielectric cavity. In photonic-crystal defect cavities or mirror based cavities, optical confinement is achieved through constructive interference of reflected or scattered light. In the micro-sphere and micro-ring, it is achieved by total internal reflection. Resonance frequency in such a resonator is called whispering gallery or fabry-perot mode. Microspheres and ring resonators have been widely used in dielectric micro-cavity because they provide high-quality factors and low losses[14, 63–68].

1.4.3 Whispering Gallery mode

Whispering gallery modes (WGMs) are sharp resonances (eigenfrequencies) associated with a wave (acoustic waves, electromagnetic waves) inside a resonator or a cavity with smooth edges as shown in figure 1.7 (a) in top right panel. The waves travel around cavity by total internal reflection experiencing interference and hence certain frequency components get enhanced due to the constructive interference. These resonances are very sensitive to the structure of the cavity, hence they are called morphology-dependent resonances. The concept of acoustic WGMs can be found in the classic architectures of the 17th century like the St. Paul's cathedral in London. In these architectural wonders, a whisper uttered at one end of the dome travels over the surface of the dome and can be heard at the other end. It was experimentally discovered with light in micron-sized particles, but the name WGM stuck on. This is represented in figure 1.7. Since the resonances in the WGMs depend on the structure of the resonator and the concept of interference, the Q factors in WGM-based resonators are very large. WGMs of a resonator are eigenmodes of the resonator and can be derived by solving wave equation with suitable boundary conditions. The complex amplitude of a wave (sound wave or a component of an electromagnetic wave) inside a cavity, u , satisfies the scalar wave equation given by,

$$\nabla^2 u - \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2} = f(r, t) \quad (1.4)$$

where v is the velocity of light in cavity with refractive index n , and $f(r, t)$ is any wave field source. The above equation can be solved by taking an ansatz $u(r, t) = \psi_e(r) e^{-i\omega_e t}$ with $\text{Re}(\omega_e) > 0$. Using the ansatz, equation 1.4 can be written as,

$$\nabla^2 \psi_e + \frac{\omega_e^2}{v^2} \psi_e = f(r, t) e^{i\omega_e t} \quad (1.5)$$

This is an eigen value equation with eigen value (ω_e) and eigen function $\psi_e(r)$. Resonance frequency (ω_e) can be obtained by solving the differential equation 1.5. For microsphere one of the solution to the equation 1.5 is the Bessel function of first kind using the boundary condition at the surface of the microsphere. Using the boundary condition.

WGMs can be excited by the near-field coupling of a light-carrying waveguide coupled to a microresonator[14] by placing an emitter in near-field[69]. When excited through broadband molecular emission like fluorescence, modes that are supported by the resonator will get enhanced due to the WGMs. This phenomenon has been used in various contexts including single-molecule sensing[69], lasing [70–72]etc.

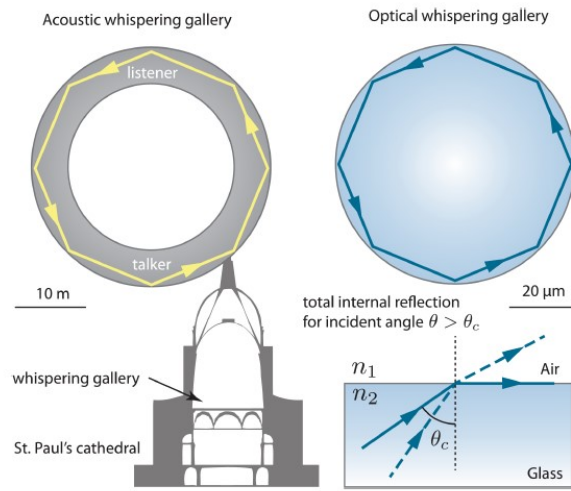


FIGURE 1.7: Schematic representation of whispering gallery mode right optical wave regime and left acoustic wave regime. Schematic shows the excitation of whispering gallery mode in the cathedral on acoustic wave regime. The Figures reproduced with permission from[73]

WGM modes of cavity has been utilised for many application in from lasing to sensing. It is widely used in medical sensing, label free single molecule detection and other application.

1.4.4 Photonic Nanojet effect

A photonic nanojet is a narrow and relatively high intensity light beam propagating in a medium when a microsphere or microcylinder of dimension greater than the wavelength is illuminated by a plane wave. It is a nonresonant phenomenon and can be observed when the dimension of the microsphere or the cylinder is approximately greater than 10λ . It also depends on the refractive index contrast of the microsphere or the cylinder. It was first observed by Chen et al. using the finite difference time domain solution of

the Maxwell equation for the dielectric microcylinder. They showed that illuminating the plane wave to a dielectric microcylinder can result in generating a narrow, high-intensity, sub-diffraction beam waist propagating in the background medium from the other side of the cylinder. It was further shown that it is very sensitive to the position of any other cylinder or particle in a way and the slightest perturbation in its path results in an order of magnitude higher backscattered light. Photonic nanojet for the microsphere was first reported by Li et al. in 2005[74]. figure 1.8 for the simulated photonics nanojet at 850nm wavelength for the microsphere with different diameter and refractive indices. Since the photonic nanojet is very sensitive to perturbation it has been widely utilized as a position sensor at the nanoscale. Subwavelength diffraction beam waist has been widely utilized for superresolution imaging, directional imaging and many other applications.[75–79].

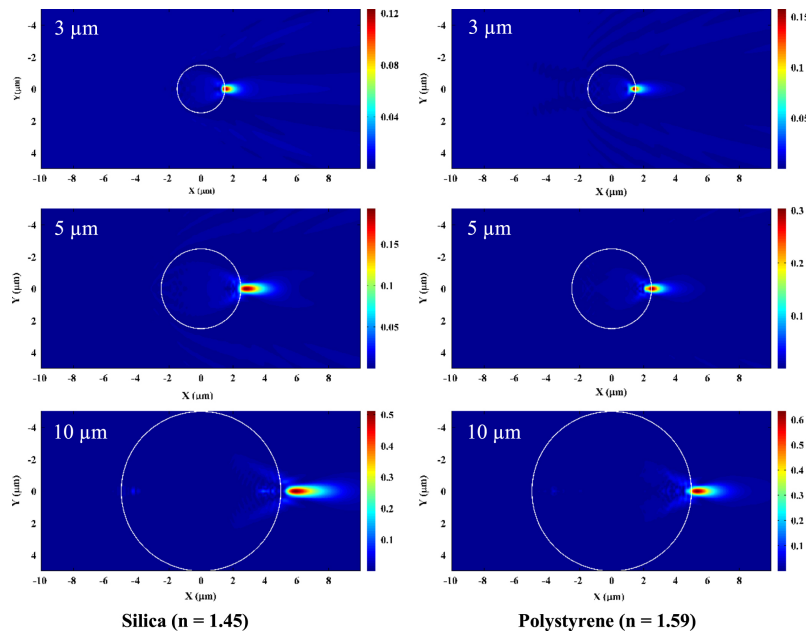


FIGURE 1.8: Effect of size and refractive index on the characteristics of photonic nanojet at wavelength 850 nm. The Figure reproduced with permission from[80]

1.5 Scope and Outline of the thesis

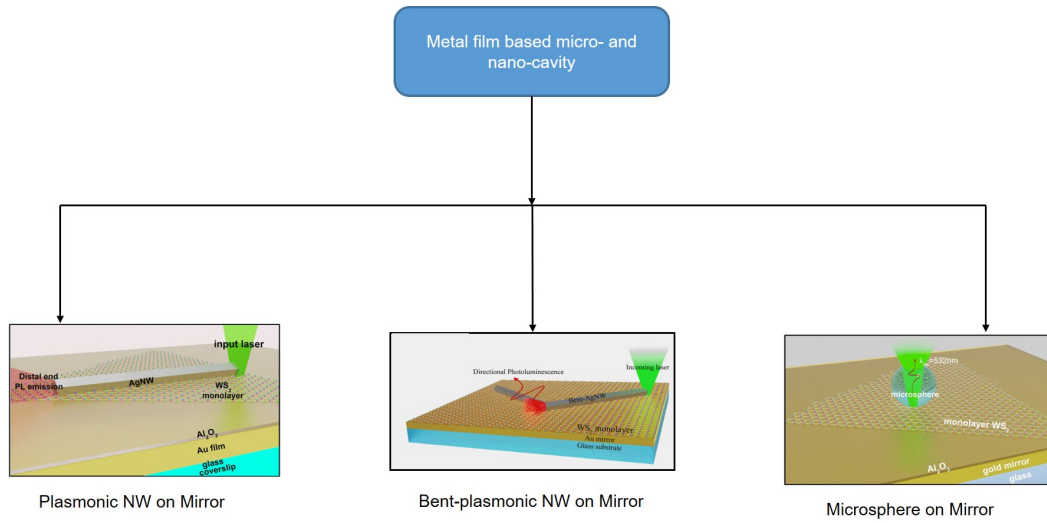


FIGURE 1.9: Schematic representation of the outline of the thesis. The Figure reproduced with permission from[57, 81]

In previous sections we have discussed the different strategies to modify and control the molecular emission. In this thesis, we Focus on modifying the emission properties of Transition metal dichalcogenides (TMDs) giving special attention to the directionality of the emission and studying wavevector distribution. As discussed before, molecular emission can be modified by modifying the LDOS in cavity. Herein we have utilized the plasmonic and dielectric nano-cavity to tune the wavevector distribution and control the directionality of the emission. Scope of this thesis covers controlling the emission properties of transition metal dichalcogenides especially the wavevector distribution and the polarisation of emission under the broad umbrella of light-matter interaction. Figure 1.9 describes the outline of my thesis. Three different structure has been utilized to direct the photoluminescence emission from the transition metal dichalcogenides.

Chapter 2 In this chapter our focus will be on the experimental and numerical methods used in the study. Measurements technique like Fourier plane microscopy and spectroscopy used to probe the photoluminescence wavevector distribution is discussed. Further, the nano and micro-fabrication technique is introduced and major fabrication techniques photolithography, electron beam lithography, thermal vapor deposition, and chemical vapor deposition are discussed. Further we have discussed the COMSOL-based numerical simulation methods used for the analysis and understanding cavity architecture by solving the Maxwell equation using the FEM methods.

Chapter 3 In this chapter we will discuss the effect of placing monolayer WS₂ inside cavity formed by plasmonic silver wire and gold mirror. This gap plasmon-based

cavity-enhanced photoluminescence emission from the WS_2 monolayer and directs the signal into a narrow range of wavevectors. Detailed analysis of polarization-dependent wavevector distribution and spectral feature is performed.

Chapter 4 In this chapter we will discuss how a bent silver nanowire on a mirror cavity can be used to direct the photoluminescence emission from the WS_2 monolayer to a very narrow range of wavevector. We will compare the angular distribution of a straight nanowire on a mirror cavity and discuss how a bent nanowire on a mirror cavity provides better directionality. We will corroborate the experimental results with FDTD numerical calculation.

Chapter 5 In this chapter we will focus on the dielectric microsphere on mirror cavity. We will discuss how the dielectric microsphere on mirror cavity can be utilized to achieve extreme directionality in case of direct excitation of TMDs. We will show the beaming of photoluminescence emission from the WS_2 monolayer using a polystyrene microsphere on a mirror antenna. We show the coupling of PL emission with WGMs of microsphere which can be utilized for sensing applications. **Chapter 6** In this chapter we will talk about the advantage and limitation of present study and challenges for the future. We will discuss the possibility of coupling lithographically fabricated nanostructures to TMDs and its possible implications. We will discuss the strategies to fabricate the device from the 2D materials.

Chapter 2

Experimental methods: Microscopy, Spectroscopy, and Nanofabrication

Light-matter interaction plays an important role in understanding electromagnetic-magnetic fields and matter and also play a key role in today's technology. It has been at the heart of the development of many technologies like modern spectroscopy, light-emitting diodes, photo-diodes, solar cells, high-energy particle detectors, and advanced microscopy methods. Usually, light-matter interaction is weak, however coupling light to material with small dimensions behaves differently. Light confined to the nanoscale dimensions shows completely different polarization, wavevectors, and dispersion relations. To control and probe these properties we need micro and nanoscale structures and an optical microscope that can observe these effects at the nanoscale. We also need the numerical tools to understand the light-matter interaction and to corroborate the experimental findings. In this chapter, we focus on these aspects and discuss the methods used to study the coupling of two-dimensional materials with optical cavities. I discuss the Fourier plane imaging and spectroscopy which can probe the wavevectors and dispersion relation for the interaction. I also discuss the different fabrication techniques used to fabricate the micro and nanostructures. Photo-lithography and electron-beam lithography are the most commonly used tools for the fabrication of micro and nanostructures. Further, I discuss the thin film deposition technique "Thermal vapor deposition" used to prepare the gold mirrors and other micro and nanostructures used in the experiments. Finally, I will discuss the Numerical simulation methods used to understand and corroborate the experimental findings.

2.1 Fourier plane Imaging

One of the important parameters to describe an electromagnetic wave is its propagation direction. Wavevector $\vec{k}$ represent the propagation direction of the emitted light in space. For example, a tungsten bulb emits in many directions and has a large range

of wavevectors, but the emission from a LASER is confined to a very small range of wavevectors and hence called a directional source. To probe the directionality of the emission at the nanoscale we need to image the $\vec{k}$ space also called momentum space and detect the wavevector associated with the emitted light. To probe the wavevector of the emission at the nanoscale we can use Fourier space (Also called momentum space) imaging. Fourier plane microscopy is based on Fourier transform property of a lens [82]. Essentially, if an emitter/scatterer is placed at the front focal plane of a lens, imaging the back focal plane (BFP) of the lens gives information about wave vectors of the emitted/scattered light. Fourier plane microscopy is a well-understood technique [82] and was known as conoscopy[83, 84] in the early days. I suggest review[85] for recent applications in Fourier plane imaging.

2.2 Concept of Fourier plane imaging and its implementation in the microscopy system

The Fourier plane imaging technique is geometrically explained in figure 2.1 [82]. Light emission from an emitter placed at the front focal plane of the lens can be expressed as a weighted sum of the plane waves emanating at different angles (θ_x, θ_y) . When a plane waves pass through a lens, it get focused on a point $(\theta_x f, \theta_y f)$ at the back focal plane (second focus of the lens), here f is the focal length of the lens. The figure shows three plane waves emanating at different angles (represented with three different colors) that get focused at three different points. Hence in this way, each direction in the real plane corresponds to a point in the Fourier plane. For a three-dimensional emitter Fourier plane project the emission directionality in the two-dimensional plane.

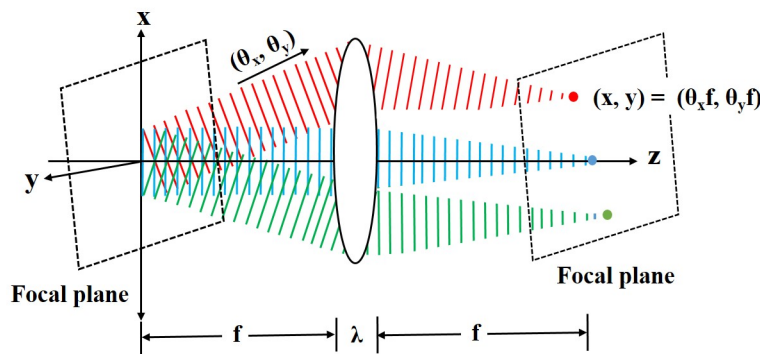


FIGURE 2.1: Schematic for the geometrical explanation of Fourier transform property of a lens. The figure has been reproduced from [82] with permission.

It is clear from figure 2.1 that one has to record the back focal plane (BFP) of the imaging lens to perform Fourier plane imaging. But BFP of a microscopic objective lens is formed close to its back aperture and is difficult to be captured on an imaging camera experimentally. An alternate method to capture BFP is using relay lenses as shown in figure 2.2 (a). Schematic shows placement of tube lens and Bertrand lens in $4f$ configuration. In the $4f$ configuration, the tube lens (TL), placed at f_{TL} (focal length of TL) distance from the BFP of the objective lens forms a real plane image of the sample at its BFP. Now Bertrand lens (BL), placed at f_{BL} (focal length of BL) distance from BFP of TL, Fourier transforms the real plane image and creates conjugate BFP at the camera, placed f_{BL} distance away from BL. Figure 2.2 (b) shows the schematic mapping of the emission from the real plane to the Fourier plane. Photoluminescence emission from WS_2 coupled to a microsphere on mirror metallo dielectric antenna. A real plane bright-field image of WS_2 coupled to microsphere on mirror antenna is shown in the bottom panel of figure 2.2 (b). The emission direction from the microsphere on mirror antenna is shown by the red blob on the surface of the hemisphere. Any point on the surface of the hemisphere can be represented in terms of the angle θ and ϕ . Fourier plane is the two-dimensional projection of θ and ϕ . Hence directionality of the emission can be majored directly by imaging the Fourier plane of the emission. Top panel of the figure 2.2 (b) shows the Fourier plane image of emission WS_2 coupled to microsphere on mirror antenna.

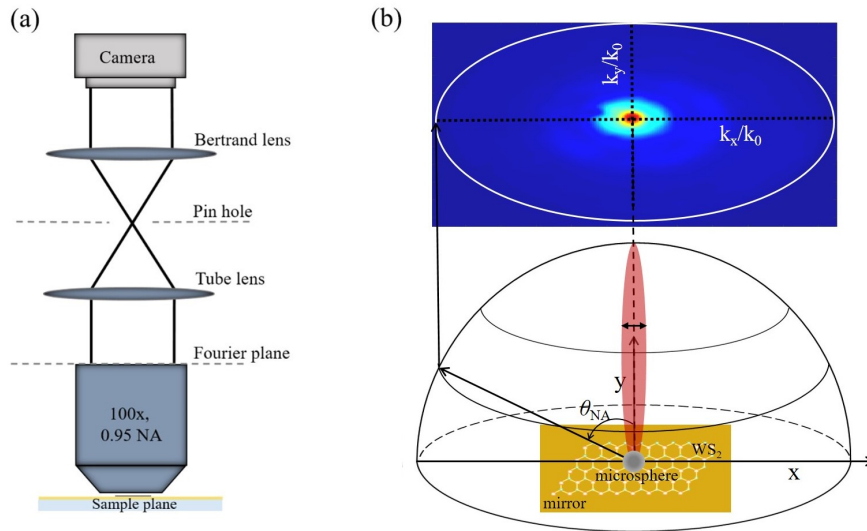


FIGURE 2.2: Schematic showing the implementation of the Fourier plane imaging technique in a microscopy system. (a) A ray diagram shows the relaying of the back focal plane (BFP) of the objective lens (OL) using tube lens (TL) and Bertrand lens (BL) onto the camera. (b) Show real plane to Fourier plane or back focal plane mapping for the emission from microsphere on a mirror cavity. θ and ϕ coordinates representing the directionality in the real plane have been mapped to experimentally measured Fourier plane image.

2.3 Energy momentum spectroscopy

The back focal plane of the emitted/scattered polychromatic light can be projected to the spectrometer slit to perform energy-momentum spectroscopy. The spectrometer slit selects a narrow range of wave vectors along an axis of the BFP image and the grating of the spectrometer disperses it. In this way, we have information about wavevector on one axis and wavelength information on another axis, giving an energy-momentum image. Figure 2.3 shows an energy-momentum image of molecular signals from a plasmonic NW-film cavity [86]. The energy-momentum diagram shows the difference in wavevector distribution of Raman and fluorescence signal from the cavity. Raman signal is uniform along all wave vectors, but the maximum fluorescence signal is directional and comes at large wavevectors. This differentiation of wavevectors of two signals, which overlap in the spectral range is not possible using only Fourier imaging.

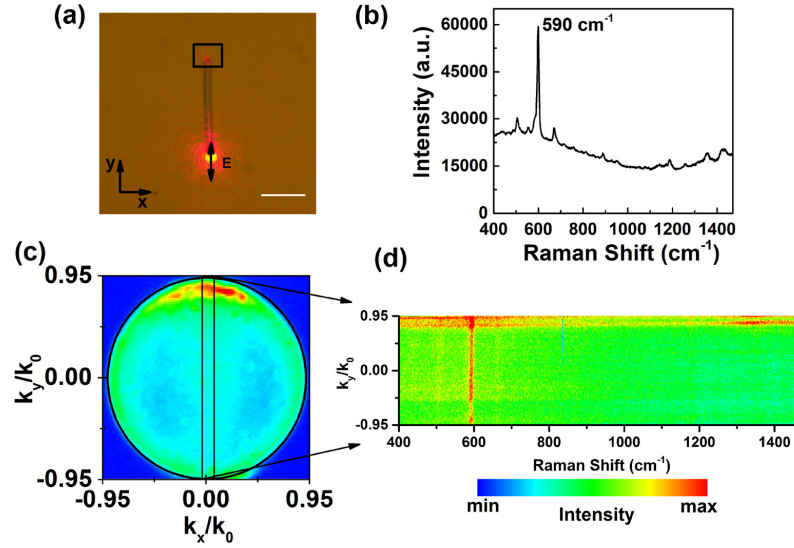


FIGURE 2.3: (a) Excitation of plasmonic NW-film cavity using 633 nm laser. (b) Spectrum showing overlapping of Raman and molecular fluorescence of Nile blue molecules from the cavity. (c) Selection of a strip along k_y/k_0 of BFP using slit of the spectrometer. (d) Energy momentum diagram of the molecular signals. The figure has been adapted with permission from [86–88].

2.4 Micro and Nanofabrication

Micro and nanofabrication are the most important basis for the development of electronics, optoelectronics, photonics, and other nanotechnology. The term nanofabrication means the creation of a structure of an artifact whose dimension is in nanometers. One of the key processes in the micro or nanofabrication is the transfer of the pattern and called lithography. There are several lithography techniques has been developed to fabricate the nanostructures and pattern like photo-lithography, E-beam lithography, X-ray lithography, and focussed ion beam lithography to count a few. photo-lithography and E-beam lithography are the most commonly used techniques to fabricate the micro and nanostructures and I discuss them in detail.

2.4.1 Photo-lithography

Photo-lithography, also known as laser writing or UV-lithography, is technique to fabricate the micrometer size pattern on a substrate. A geometric design is transferred from a photo-mask to photoresist on the substrate using light. Photoresist is a light sensitive polymer which become soluble in developer after getting exposed with light. Following that, a succession of chemical (developer and remover) treatments either etch the exposure pattern into the material or etches the unexposed part of the photoresist, depending

on whether it is a positive or negative photoresist. Removal or etching of the exposed part (in case of positive photoresist) allows the deposition of the new material into the etched part, fabricating the pattern of desired materials. Negative resist is used to fabricate a grooved pattern or negative pattern on a substrate or to etch out the specific part of the substrate itself. This is the most common lithography technique used for the fabrication of transistors or chips in the foundry industry. Briefly, the fabrication procedure we followed can be divided into multiple steps as follows:

- **Substrate Cleaning:** First the substrate was cleaned using ethanol and isopropanol followed by the plasma cleaning to remove any impurity on the substrate. After the cleaning substrate was baked at 110°C for 2 minutes to remove the moisture.
- **Photoresist Coating:** Photoresist was spin-coated on the substrate at a rate of 4000 rpm. To polymerize the photoresist substrate was baked at 100°C for 2 minutes after photoresist coating.
- **Patterning:** Pattern was transferred to the laser-writer and the mask was aligned on the substrate to transfer the pattern. The pattern was transferred to the photoresist using a laser beam of 405nm wavelength.
- **Pattern Development:** After the transfer of the pattern sample was placed in the developer solution to develop the transferred pattern. In this process exposed part of the photoresist will be removed in case of (positive resist) and vice versa.
- **Metal Coating:** After the development of the pattern onto the substrate, the sample was coated with chromium, and gold was deposited. Placing the sample in acetone will remove the resist with metal from the unexposed part of the substrate.

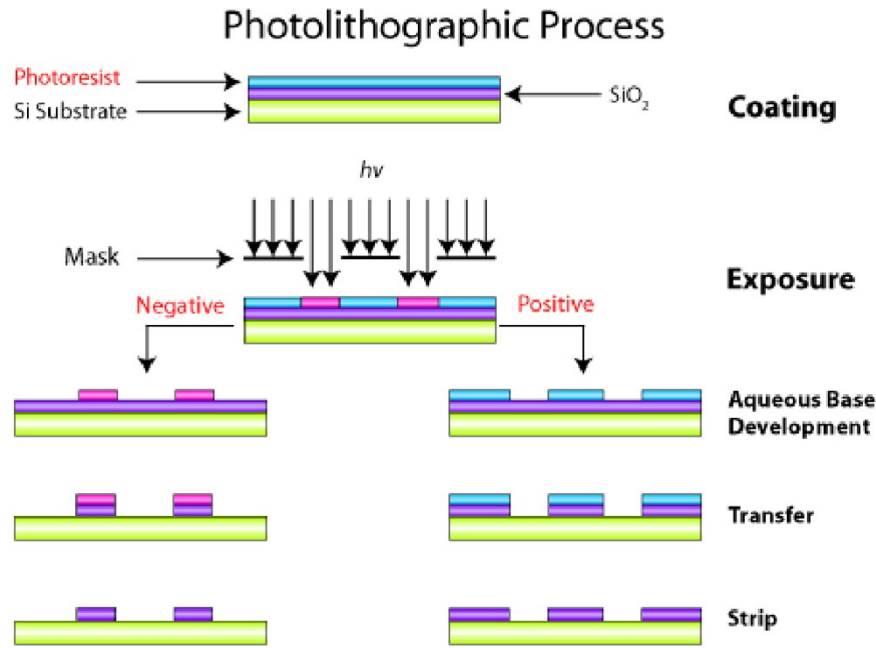


FIGURE 2.4: Schematic for the steps of photolithography process for the positive and negative resist respectively. The figure has been adapted with permission from [89].

Figure 2.4 shows the schematic of the fabrication method for both positive and negative resist approaches. The negative resist was used when a pattern was need to be grooved in the substrate followed by etching of the substrate, while in the case when a pattern need to be made using some other material positive photoresist is used and followed by the material deposition on the substrate.

We fabricated many patterns using photolithography for various purposes. Some of the them are shown in the figure 2.5. Figure 2.5 (a) shows the bright filed image of the marked slide, we use for to correlate and identify the probed nanostructure in high resolution scanning electron microscope image. Since using an optical microscope it is not possible to visualise the morphology of nanostructure. To find the exact morphology of probed nanostructure we do correlation microscopy between optical and electron microscopy. Figure 2.5 shows a holography fork prepared by photolithography to generate Laguerre Gaussian beam. Spatial light modulator is commonly used to generate the structured light however they can't sustain high power. To performed the experiment at higher power we design and fabricate the similar pattern on glass slide to generate the structured light with higher power. Figure 2.5(c) and (d) are the micro triangles prepared by photolithography method for the assembly of colloidal microsphere.

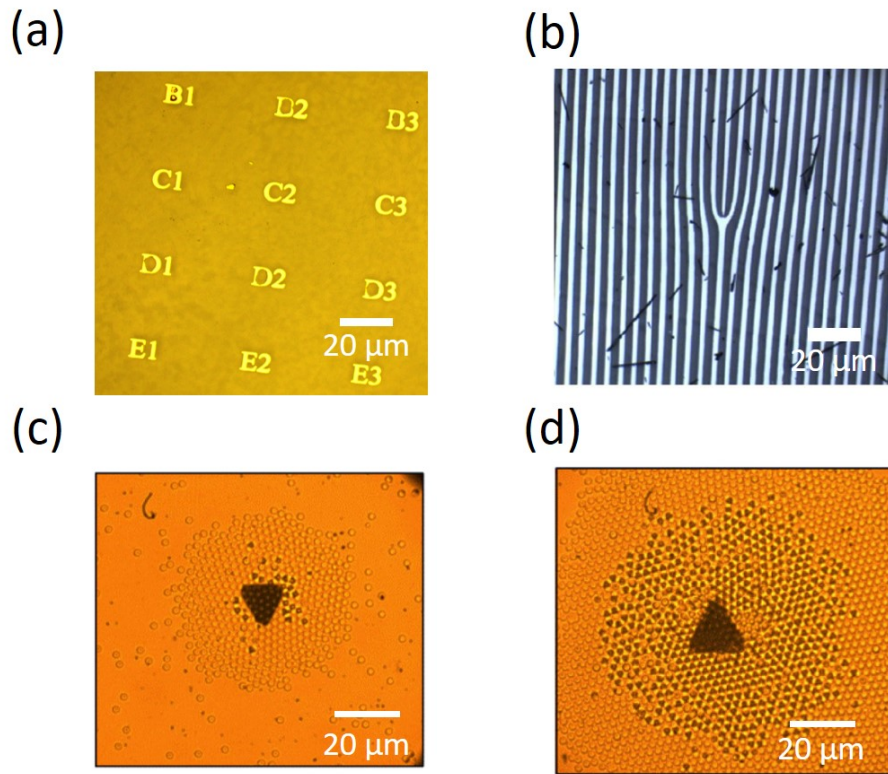


FIGURE 2.5: Multiple micro-structures prepared by photolithography. (a) Marked slide prepared by photolithography followed by metal deposition for the correlating the microscopy image with electron microscope image. (b) A fork hologram prepared by same method for the generation of structured light. (c) and (d) are the micro triangle prepared by same method for the assembly of colloidal microsphere. Figure has been adapted with permission from [90]

2.4.2 E-beam Lithography

E-beam lithography follows a similar process with a high-energy electron beam instead of using an ultraviolet light beam. Resist used in this are the different sets of polymers called E-beam resist. Polymethyl methacrylate (PMMA) and Hydrogen silsesquioxane (HSQ) the most commonly used positive and negative E-beam resists.

A schematic of the E-beam lithography is shown in Figure 2.5. To perform the E-beam lithography, pattern is first transferred to the E-beam mask. Steps of the E-beam lithography are very similar to the photo-lithography with a different set of chemicals used as resist and developer. Positive and negative resist is used for the metal deposition and substrate etching approach respectively. Optimization of and control mechanism for the electron beam lithography and photolithography is completely different as beam have completely different properties. In E-beam lithography we need to optimize the irradiation power in such a way that one can avoid the excess scattering and sufficient

to burn the resist. To avoid the charging of the substrate generally substrate was coated with a conductive liquid or metal layer.

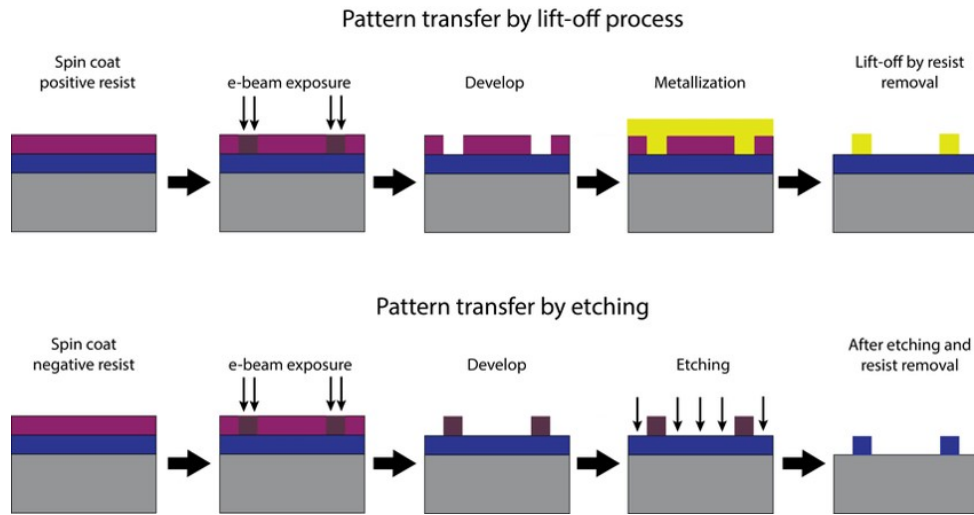


FIGURE 2.6: Schematic for the steps of E-beam lithography process for the positive and negative resist respectively. The figure has been adapted with permission from [91].

2.4.3 Thin-film deposition

It is the process of depositing very thin layer of materials ranging in thickness from a few nanometers to a few micrometers, or a few atoms onto a substrate. Thin film deposition is at the core of technology manufacturing industry such as solar panel, semiconductor, and optical device. Thin-film deposition can be broadly divided into two categories *Physical Vapor Deposition* and *Chemical Vapor Deposition*.

- **Physical Vapor Deposition :** This method refers to a wide range of technologies that use mechanical, electromechanical, or thermal processes to release material from a source and deposit it on a substrate. Thermal evaporation and sputtering are the two most prevalent Physical Vapor Deposition (PVD) processes.
- **Chemical Vapor Deposition :** When a precursor reacts on the surface of the substrate a thin layer of the material is formed on the substrate. This is the widely used technique in industry for the growth of semiconductors and high purity crystals. Because of the large area growth it is the most widely used technique for the growth of two-dimensional materials.

Thermal Vapor Deposition and *Sputtering* are the two most commonly used PVD methods to deposit the material.

Thermal Vapor Deposition : In thermal vapor deposition we heat a solid target until it melts and evaporates. Evaporation of the target results in producing vapor pressure. This happens inside a vacuum chamber because a low vacuum favors the vapor rise. This evaporated substance is now a vapor stream, which may flow without interacting or scattering against other atoms due to the vacuum and stick to the surface of the substrate. This method is commonly used for the coating of metals like gold, silver, copper, aluminium and chromium. Most of these material does not have a good binding with commonly used glass or silicon substrate. A thin layer of titanium or chromium is commonly used to make as adhesive layer. One of the main advantages of this method is that one can achieve a high coating rate and smooth surface morphology. Figure 2.7 shows the schematic of the thermal vapor deposition, where a filament boat is heated with Jule heating inside the vacuum. When material inside the boat evaporates it goes upward because of vapor pressure and sticks to the substrate making a thin film of the material. Rate thickness and other parameters can be controlled using the controller attached to the setup.

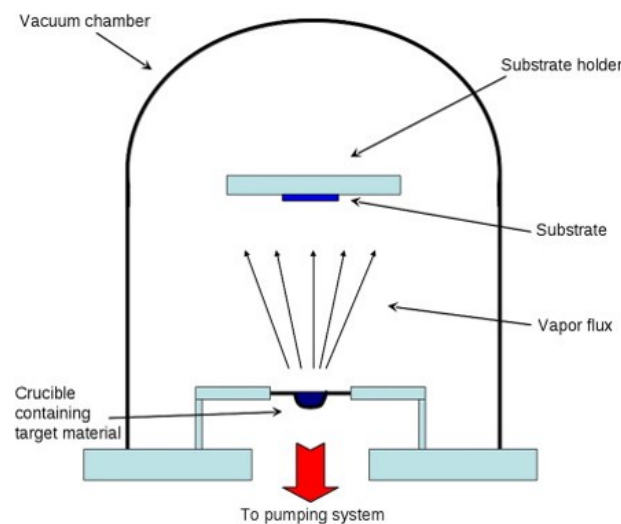


FIGURE 2.7: Schematic of the thermal vapor deposition system. The figure has been adapted with permission from [92]

Sputtering: In sputtering target emits high energy micro particle when bombarded by plasma of high energy gas. The substrate are placed in a vacuum chamber containing an inert gas. These micro particles emitted from the target materials deposited on the substrate forming a thin layer of the material. This method is used for coating of both metal as well as oxide. Surface morphology of the thin films prepared by this method are granular in nature.

2.5 Numerical Modeling

Numerical simulations are crucial to corroborate and understand the experimental findings and optimize the experimental parameters. We have used the finite element method (FEM) based numerical simulation to calculate the mode of Silver nanowire on mirror cavity and to calculate the near-field electric field distribution for the microsphere on mirror cavity.

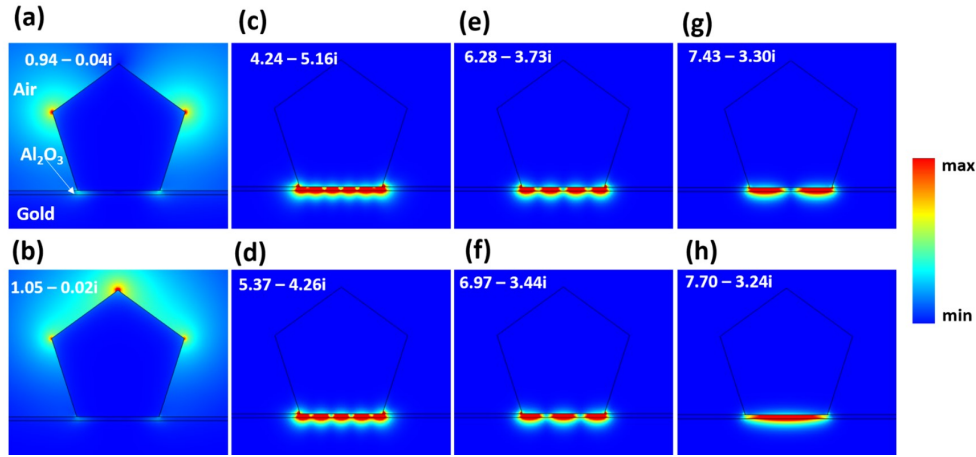


FIGURE 2.8: Modes of the MIM waveguide. Their corresponding mode index is given. (a) and (b) are higher-order modes. (c-h) Lossy gap plasmon mode.

2.5.1 Mode of the Silver wire on mirror cavity:

To calculate the mode of the AgNW on mirror cavity an infinitely long silver nanowire with penta-twin cross-section has been placed on gold mirror with 5 nm gap to account for the Al_2O_3 layer and pvp coating on the nanowire. The diagonal length of the pentagon is defined as the diameter D of the NW as 350 nm. The simulations are conducted with commercial finite element-based software Comsol Multiphysics 5 (Mode Analysis in RF module). The permittivity and refractive index of the data of silver and gold adopted in simulations are taken from Johnson-Christy at 630 nm. For AgNW on mirror cavity, we observed eight modes. The high order SPP mode (Fig. (a) and (b)) have larger propagation length as their imaginary part of the effective mode index is small. In contrast, the six bound modes (Fig. 2.8 (c)-(h)) exhibit high loss owing to the very high imaginary component of the mode index.

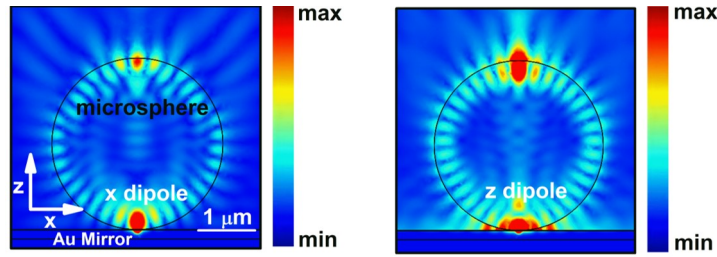


FIGURE 2.9: Calculated Near-field electric field for microsphere on mirror cavity for in plane (left) and out of plane dipole(right)

2.5.2 Near field electric field of Microsphere on mirror Cavity

To calculate the near field electric field of microsphere on mirror cavity a polystyrene microsphere of diameter is place on the 150 nm gold film placed over glass substrate. There is gap of 5 nm between gold mirror to account for Al_2O_3 and TMD. In plane and out of plane dipole are placed at the center of the gold mirror and microsphere. The simulations are conducted with commercial finite element-based software Comsol Multiphysics 5 using the physics-controlled meshing. Figure 2.9 show the near field electric field for the in plane (left panel) and out of plane dipole (right panel) orientation.

2.6 Conclusion

In summary, this chapter has provided a brief overview of the various experimental and computational approaches used in wavevector analysis from a subwavelength-sized system. Fourier microscopy and spectroscopy and their experimental implementation is discussed in detail. Fourier microscopy and spectroscopy can be used to explore periodic structures such as metamaterials, and not limited to individual nanostructures. Further we have discussed the various micro and nano-fabrication techniques like photolithography electron beam lithography and thin film deposition in detail. In the end we discussed the numerical techniques used to corroborate the experimental findings.

Chapter 3

Directing emission form Tungsten Disulfide Monolayer using plasmonic Nanowire-on-Mirror Cavity

This chapter is an adaptation of the research article "Adv. Photonics Res.2021,2, 2100002". This article discusses the wavevector distribution and polarisation state of photoluminescence emission when WS₂ monolayer is placed inside the silver nanowire on a mirror cavity.

3.1 Introduction

In the last few years, Two-dimensional transition metal dichalcogenides (TMDs) have attracted significant attention because of their novel optical and electronic properties[38–41] Direct bandgap in their monolayer makes them a suitable candidate for electronics applications[40–42]. Very high oscillator strength leads to a narrow peak with a pronounced optical transition[93, 94]. In addition, TMDs exhibit valley polarization effects, making them a suitable candidate for spin-orbit interaction studies[95, 96]. Coupling 2D materials such as tungsten disulfide (WS₂) monolayer to plasmonic nano-cavities can enhance and influence light-matter coupling. This chapter is based on our experimental studies of directional photoluminescence from WS₂ monolayer sandwiched in a unique kind of cavity: Ag nanowire on a gold mirror. Plasmonic nano-cavities are important architectures to study because of the very high electric field inside the cavity caused by the hybridization of gap plasmon[97]. Ultrasmall volume inside the cavity provides a large Purcell enhancement factor[13, 98]. To this end, nano-cavity formed by a nanoparticle on gold film has been utilized for strong-coupling at the single-molecule level[58], single-molecule Surface-Enhanced Raman Scattering (SERS)[19, 99], controlled reflectance properties[100], and enhanced spontaneous emission[98,

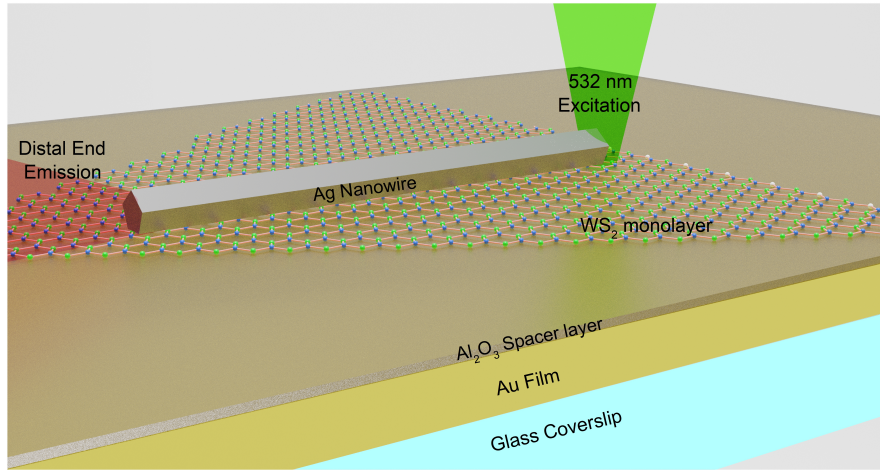


FIGURE 3.1: Schematic of the experimental setup. The WS_2 monolayer was placed over a gold film separated by a 3nm Al_2O_3 spacer layer. Single AgNW was placed over the monolayer WS_2 flake. One end of the NW was excited with a 532nm laser. WS_2 PL from the excitation point couples to the NW plasmons, which is further out-coupled from the distal end of the NW. The emission from the distal end was collected and projected to spectrometer and EMCCD for spectroscopy and Fourier-plane imaging, respectively.

[101]. Of relevance to this study is the Ag Nanowire on a gold mirror cavity. Nanocavity formed by a silver nanowire (AgNW) on the gold film, apart from the above advantages, can also work as an Opto-plasmonic waveguide of cavity's emission, as shown recently by our group[29]. Such nanocavities are also studied in the context of Purcell enhancement[101], remote excitation of the molecules[29], spontaneous emission enhancement[101], wave-vector distribution[29], and trion enhancement[102].

Coupling surface plasmon polaritons to TMDs can facilitate interesting optical properties. To this end, studying the optical transition characteristics of TMDs in the vicinity of a plasmonic nanostructure near resonance has gained relevance[103–106]. A variety of prospects like Photoluminescence (PL) and Raman enhancement[107, 108], enhanced spin-orbit interaction[102, 109], remote excitation of SERS[110], spectrum tailoring[27], strong coupling[111], and trion enhancement[102] have been achieved using such configuration. For these purposes many plasmonic structures like bowtie antenna[112], nano-disk array[113], nano-cube[27], nanoparticle[111], and nanowire[102, 110] have been either fabricated over TMDs[114] or TMDs is transferred onto the structures[115]. Specifically, in the context of 2D materials, TMDs have been coupled to a single AgNW for studying remote SERS[110], second harmonic generation[116–119], logic operation[120], Rabi splitting[121], and plasmon-exciton interconversion[102]. Silver film - Ag nanowire cavity has been recently utilized for the Trion enhancement

and enhancing the spin-orbit coupling[102]. Apart from these effects, a plasmonic Ag NW can act as a subwavelength waveguide as well as a nanoscale antenna which can be harnessed to route an excited signal and emit the signal at the distal end[122]. This utility of Ag nanowire both as a plasmonic cavity and as a waveguide for 2D materials has not been explored, which we do in this chapter.

Figure 3.1 shows the studied geometry. It contains a WS_2 monolayer sandwiched between a plasmonic silver nanowire and a gold mirror (AgNW- WS_2 -Au cavity). A thin, Al_2O_3 layer is deposited on gold mirror which acts as a buffer layer. In such waveguide-cavity systems, wavevector analysis becomes an important aspect of the study to quantify the emission process. Motivated by this, our study focuses on the wavevector distribution of the PL emission in the AgNW- WS_2 -Au cavity. Specifically, we excite one end of the cavity with a focused 532nm laser and study the PL spectrum from the other end of the cavity as a function of angle and polarization. To achieve this, we employ polarization-resolved Fourier-plane optical microscopy to study the emission direction of the AgNW- WS_2 -Au cavity and quantify the in-plane angular distribution. By studying the angular distribution and polarization-resolved spectra, we show that AgNW- WS_2 -Au cavity can modify the spectral feature of WS_2 monolayer by interconversion between exciton and trion.

3.2 Experimental Methods

3.2.1 WS_2 Synthesis

The WS_2 monolayers were grown using atmospheric pressure chemical vapor deposition (APCVD) on a 300 nm SiO_2 coated silicon wafer following the procedure mentioned in ref. [123] and [124]. The substrates were sonicated in acetone and IPA for 10 min each and blow-dried. They were further cleaned using O_2 plasma at 60 W for 5 min. The substrates were loaded onto an alumina boat containing 500 mg of WO_3 with the smooth side facing the powder. The boat containing the WO_3 was placed inside a quartz tube of 3.5 cm inner diameter in the heating zone of the furnace. Another boat containing 500 mg of Sulphur was placed upstream inside the tube, 15 cm away from the WO_3 boat. The Sulphur boat was placed outside the furnace and was heated separately using a heater coil. Initially, the tube was flushed with 500 standard cubic centimeters per minute (SCCM) of argon for 10 min, and then the flow was reduced to 30 SCCM and was maintained throughout the experiment. The furnace was ramped up to 850 $^\circ\text{C}$ at a rate of 5 $^\circ\text{C}/\text{min}$. As the furnace reached 850 $^\circ\text{C}$ the heater coil was heated to 240 $^\circ\text{C}$ to evaporate Sulphur. These temperatures were maintained for

10 min for growing WS₂ monolayer. After the growth, the system was allowed to cool naturally.

3.2.2 Optical Characterization

A chemically synthesized WS₂ monolayer was further characterized by PL and Raman spectroscopy. PL and Raman spectra of the same are shown in Figure 3.2.

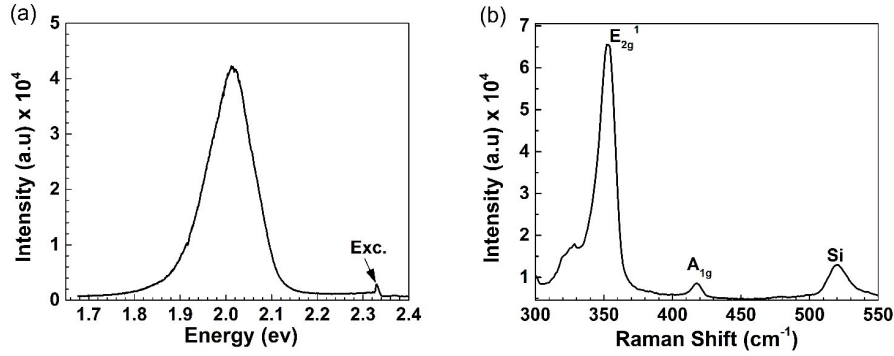


FIGURE 3.2: Raman and Photoluminescence spectrum of the Monolayer WS₂, (a) Photoluminescence spectrum including excitation wavelength to make sure that we are efficiently rejecting the Raleigh scattered light. The excitation wavelength shown with an arrow has a negligible intensity in comparison to photoluminescence intensity. (b) Raman spectrum of the monolayer WS₂ where peak E_{2g}^1 and A_{1g} are at 350 cm⁻¹ and 417 cm⁻¹. Since WS₂ was first grown on Si/SiO₂ we can see the silicon peak at 520 cm⁻¹.

3.2.3 AgNW-WS₂-Au cavity preparation

Ag nanowires with an average diameter of 300 nm have been synthesized by the polyol process as reported in.[125] FESEM image of the two typical nanowire is shown in figure 3.3. For the preparation of the gold mirror, 160 nm gold film has been deposited on the glass coverslip using thermal vapor deposition. Monolayer WS₂ flakes have been transferred onto the gold mirror. Polystyrene is used as a support film for this transfer as reported here[126]. 3nm Al₂O₃ spacer layer was placed using atomic layer deposition in between the gold mirror and WS₂ to prevent the charge screening with the aim to avoid PL quenching. To form a cavity, Ag nanowires were dropcasted on the gold mirror with WS₂ sandwiched in between them. NW at which we have performed the experiment is 300 nm thick and approximately 13 μm in length.

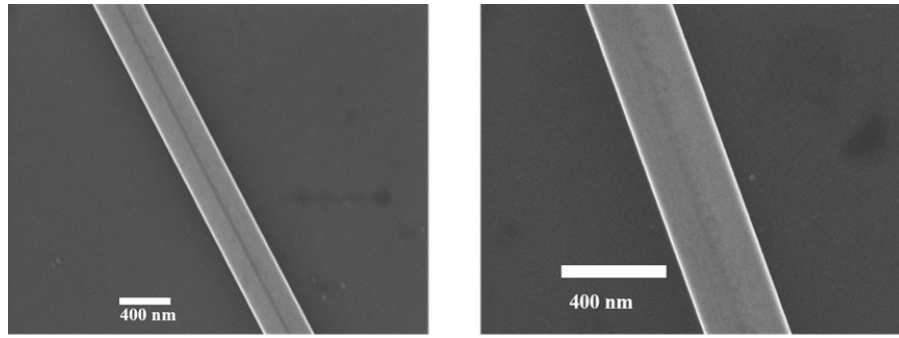


FIGURE 3.3: FESEM image of two typical Silver nanowires

3.2.4 Experimental Setup

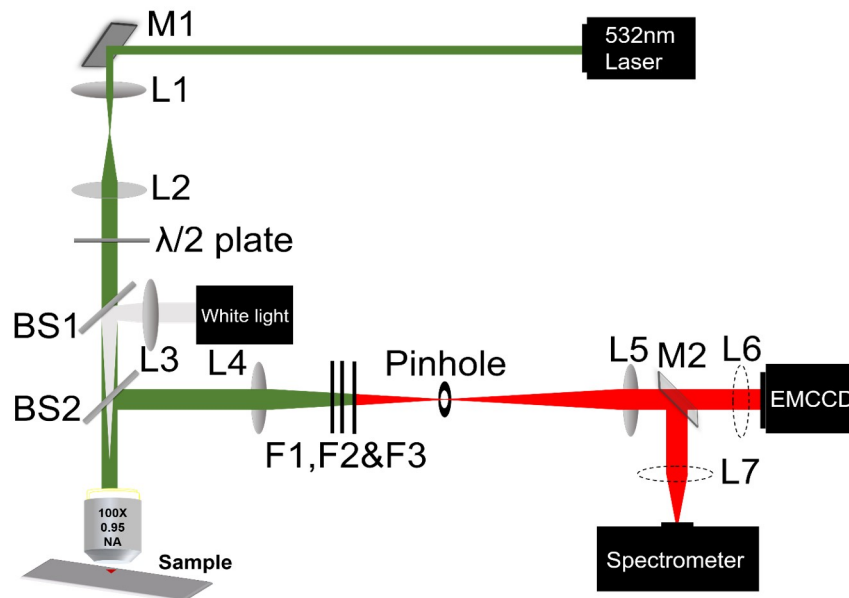


FIGURE 3.4: The sample was excited using a high numerical aperture 100x, 0.95 NA objective lens. The backscattered light was collected using the same lens. The 532 nm laser light was expanded using a set of two lenses L1 and L2. M1 is a mirror. The polarization of the incoming laser was controlled by a $\lambda/2$ waveplate in the path. BS1 and BS2 are beam splitters to simultaneously excite the sample with laser and its visualization using white light. Lens L3 is used to loosely focus white light on the sample plane. F1, F2, and F3 are set of two edge filters and one notch filter to reject the elastically scattered light for SERS spectroscopy and Fourier plane and energy-momentum imaging. Lenses L4 and L5 are used to project the emission to the Fourier plane onto the spectrometer or EMCCD. M2 is a flip mirror, used to project the light on the spectrometer for spectroscopy and energy-momentum imaging. Lenses L6 and L7 are flip lenses used to switch from real plane to Fourier plane.

One end of the AgNW-WS₂-Au cavity has been excited using a 532 nm laser with polarization along the cavity. 100x, 0.95 numerical aperture (NA) objective lens was used in the backscattered configuration for both excitation and collection. Signal from the distal end of the nanowire is collected by spatially filtering the region, and the real/Fourier plane is projected into the EMCCD/spectrometer. To transfer the Fourier plane from the back aperture of the objective lens to the EMCCD, 4f configuration is used[127]. High NA excitation ensures efficient excitation of surface plasmon in the nanowire as well as high electric field in the cavity. Combination of edge and notch filter has been used to efficiently reject the elastically scattered light. It can be seen from the PL spectra in figure 3.2 a that the contribution from the elastic scattering is negligible. A polarizer and half-wave plate are used in the input path to control the input polarization. An analyzer is used in the output path to analyze the output light for polarization resolved measurements. Detailed experimental setup is shown in figure 3.4 and our previous reports[128] for detailed experimental setup of Fourier plane optical microscopy.

3.3 Directing the emission using AgNW-WS₂-Au cavity

Figure 3.5 is the bright-field image of the Ag nanowire placed on a gold mirror AgNW-WS₂-Au cavity. Excitation of nanowire end, with a tightly focused 532 nm laser excites the propagating plasmons along the nanowire. In addition, the excitation of hybridized gap plasmons between the AgNW and metal film creates a high local electric field, which enhances the PL emission from WS₂ monolayer. Because of the near field interaction, the PL emission gets coupled to the nanowire SPPs travelling along the length of the nanowire. Because of the spatial discontinuity at the nanowire end, these SPPs are out-coupled as free-space photons. In figure 3.5 b, we observe strong PL emission from the AgNW-WS₂-Au cavity not only from the excitation and distal ends but also throughout the nanowire. This is because of the high electric field in the nanowire on a metal film cavity, which acts as a hot-line along the length of the cavity.

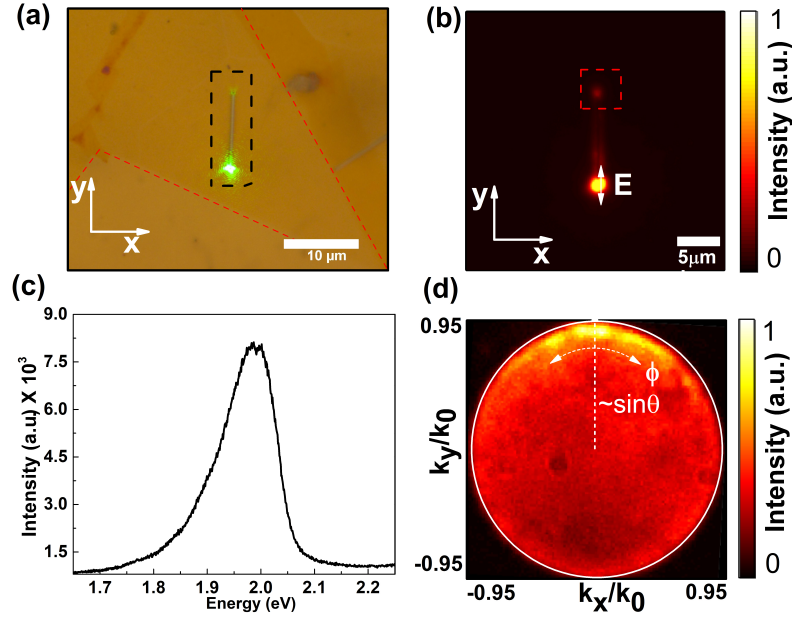


FIGURE 3.5: Directional emission from the distal end of Ag nanowire (a) Bright-field image of nanowire over WS₂, which is placed over a gold mirror with 3 nm spacer layer of Al₂O₃. WS₂ monolayer boundaries are shown with red dotted lines. One end of the nanowire was excited with 532 nm laser with polarization along the long axis of the nanowire. (b) PL image of the nanowire after rejecting the elastically scattered light using a combination of edge and notch filters. The dotted box shows the distal end collection of the nanowire. (c) WS₂ PL spectrum collected from the distal end of the nanowire as per the configuration in (b). (d) Fourier space intensity distribution of the PL out-coupled from the distal end of the nanowire showing directional emission in narrow range of wavevectors.

Figure 3.5 c shows the emission spectrum collected from the distal end of the AgNW-WS₂-Au cavity. To study the wavevector of emission from the cavity, we performed Fourier plane imaging, which maps the emission wavevectors in terms of θ and ϕ spreading. Radial coordinate in Fourier plane is $NA = n \sin \theta$, and ϕ is tangential coordinate varies from 0 to 2π . Fourier plane image Figure 3.5 d shows that the emission from the nanowire end is directed towards higher k_y/k_0 and covers only a small range of radial and azimuthal angles, indicating highly directional emission.

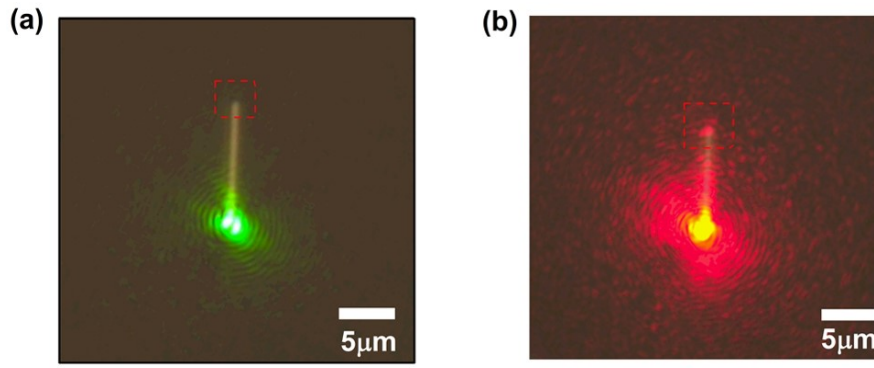


FIGURE 3.6: Bright-field image of Wire on WS₂ without a gold mirror in between. (a) No propagation is observed on the glass coverslip because of high absorption from WS₂ monolayer. (b) Propagation of nanowire plasmons along the length of the nanowire when the laser used is 633 nm. With 633nm laser, the absorption is very minimal and the plasmons out-couple at the distal end of the nanowire.

A relevant question to ask is how does the presence of a gold mirrors influence the performance of the cavity on and off the absorption band of WS₂ monolayer? To explore this, we performed experiments similar to figure 3.5, but placing the WS₂ on a glass coverslip and drop-casting the Ag nanowire over it and exciting it with 532nm and 633 nm lasers. In the case of 532 nm excitation, we do not observe any plasmon-assisted propagation from the distal end of the nanowire because of high absorption of the incoming laser by WS₂ and NW, whereas for 633 nm excitation, we do observe plasmon propagation as shown in figure 3.6. Although we observe plasmon propagation with 633 nm, the PL of WS₂ cannot be excited at this wavelength. To understand the role of the AgNW-Au cavity we have calculated the modes of the cavity. For the AgNW-Au cavity, we have observed eight modes. The higher-order SPP modes as shown in figure 2.8 a and b have a larger propagation length as their imaginary part of the effective mode index is small. In contrast, six bound modes as shown in figure 2.8 (c)- h) exhibit high loss owing to a very high imaginary component of the mode index. These higher-order modes for which near field is distributed near the top of the NW contribute to the propagation[129]. An inference we draw from this is that the presence of a gold mirror enhances the propagation length.

3.4 Polarization resolved angular emission from AgNW-WS₂-Au cavity

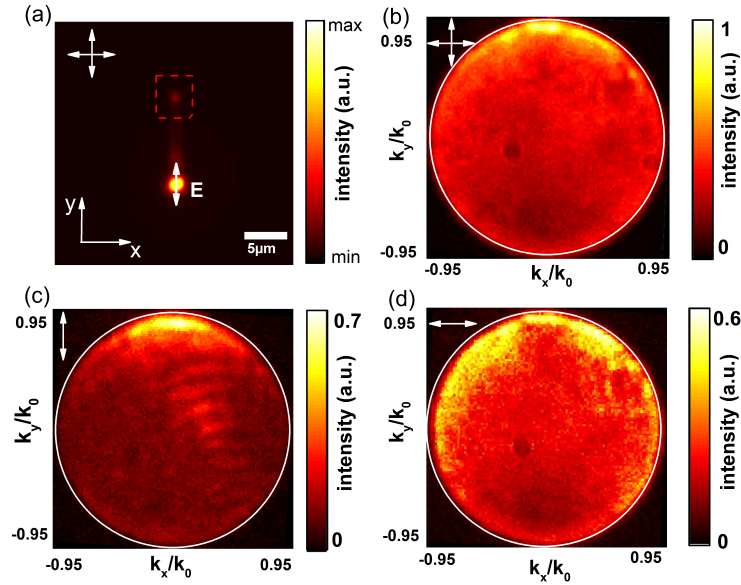


FIGURE 3.7: Emission-polarization-resolved Fourier plane imaging of distal end PL emission, which indicates the momentum-space distribution of the emitted light from a particular region in the geometry. (a) Real-plane PL intensity distribution of the nanowire captured using EMCCD integrated over, all polarizations (indicated by orthogonal arrows); (b) corresponding momentum space PL intensity distribution, collected from the distal end of the nanowire (shown by dotted box in (a)). Momentum space PL intensity distribution of the emission from the distal end of the nanowire when polarization is analyzed (c) along the long axis of the nanowire and (d) transverse to the long axis of the nanowire

The emission at the distal end of the nanowire is mediated through the SPPs of the nanowire, which generally show a rich polarization signature. In addition to this, emission from the WS₂ which is confined in the AgNW-WS₂-Au cavity is enhanced and out-couples through the nanowire end, after propagating through the cavity. To study the effect of nanowire and metal film cavity, we performed polarization resolved Fourier plane imaging on the PL emission from the distal end of the nanowire. Figure 3.8 a represents the PL image of the AgNW-WS₂-Au cavity after rejecting the elastically scattered light captured using EMCCD. Figure 3.8 b is the momentum space image of the PL emission from the distal end of the nanowire. Figure 3.8 c is the momentum space image analyzed for the polarization along the long axis of the nanowire and Figure 3.8 d represents the momentum space image analyzed for the polarization transverse to

nanowire. For the output polarization along the nanowire, we observe that light is directional and most of the emission is centered around $\phi = 0$. While in the case of the output polarization transverse to the axis of the nanowire, the ϕ spread is more. This means that photons which are polarized along the wire are more directional in comparison to the photon whose polarization is transverse to the nanowire. This is attributed to the polarization maintaining properties of surface plasmon polaritons in a nanowire[130].

3.5 Polarization-resolved photoluminescence AgNW-WS₂-Au cavity

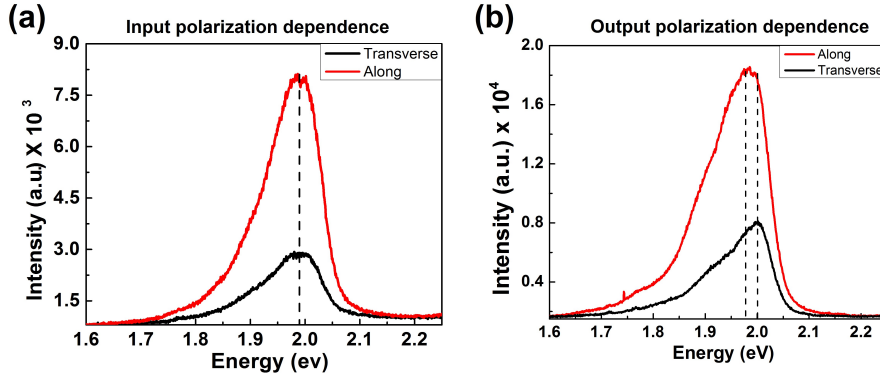


FIGURE 3.8: Dependence of PL spectral features from the distal end of AgNW-WS₂-Au cavity as a function of excitation and collection polarization. (a) PL spectrum as a function of excitation polarization along (red curve) and perpendicular (black curve) to the nanowire axis. (b) PL spectrum as a function of analyzed polarization along (red curve) and perpendicular (black curve) to the nanowire axis. Apart from the reduction in the intensity, the change in polarization also leads to a redshift in the peaks. PL spectrum collected from the distal end of the nanowire, red and black curve corresponds to the input polarization along the long axis of the nanowire, and transverse to the long axis of the nanowire.

In the previous section, we discussed how polarized excitation and collection can influence the directional emission from the AgNW-WS₂-Au cavity. This further motivated us to study the spectral characteristics as a function of excitation and collection polarization. First, we checked the excitation polarization dependence. The red and black curves in Figure 3.9 a are the PL spectrum from the distal end of the nanowire AgNW-WS₂-Au cavity when input excitation polarization is along and transverse to the long axis of the nanowire, respectively. It can be clearly seen that output PL intensity is

greater when excitation polarization is along the long axis of the nanowire. With this hindsight, we fixed the excitation polarization along the long axis of the wire, and collected the polarization-resolved PL emission from distal end. In figure 3.9 b, the red and black curve represents the PL emission along and perpendicular to the long axis of the nanowire. It can be clearly seen that intensity in the case of output polarization along the long axis of the nanowire is more in comparison to the transverse output polarization. It is also observed that the PL peak in the case of the output polarization along the long axis of the nanowire is red-shifted in comparison to the output polarization transverse to the long axis of the nanowire. This redshift is found to be approximately $\Delta E = 23$ meV.

Since the PL spectrum has the contribution of both the neutral exciton and the charged exciton (trion), such redshift can be attributed to the exciton to trion conversion[131]. Trions are essentially formed when exciton is bound by an excess of electron or hole, also called charged exciton. Photoionization and doping are the two main ways to convert exciton into trion[132, 133]. In this case, WS_2 is slightly n doped, so the trions in the system are negatively charged. Exciton to trion conversion is reported by coupling with SPP in the MIM cavity (metal insulator metal) cavity[102]. In the AgNW- WS_2 -Au cavity there are two kinds of plasmon involved. One is propagating along the wire and the second is localized in the cavity[134]. The intensity component along the NW is larger as compared to the transverse to the NW.

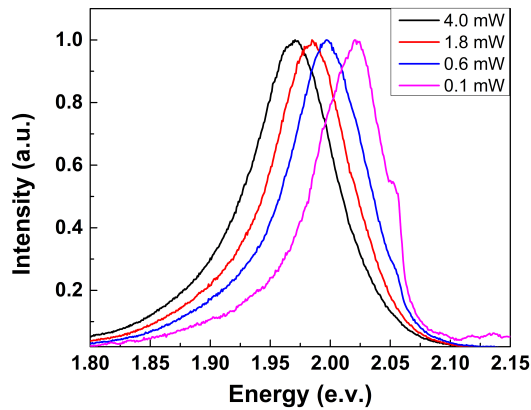


FIGURE 3.9: Power dependence photoluminescence spectrum of monolayer WS_2 showing the red-shift with increasing power

At higher irradiation power, it has been observed that exciton converts into trion; which leads to redshift in PL spectra as shown in figure 3.10 [133]. To further confirm this, we deconvoluted the PL spectra into two peaks by Voigt function double fit as shown in figure 3.11. The deconvoluted spectrum is consistent with the reported

exciton and Trion peak[132], and Trion binding energy is found to be around 50 meV, which is consistent with the reported value[102, 135]. However, the propagating SPP may experience reabsorption by WS₂, NW or gold film during the propagation which leads to the redshift for the component having polarization along the wire. Since the absorption coefficient is fairly constant above 550 nm for WS₂[136], so the contribution from the reabsorption of WS₂ is negligible and redshift is caused by the exciton to trion conversion in the cavity.

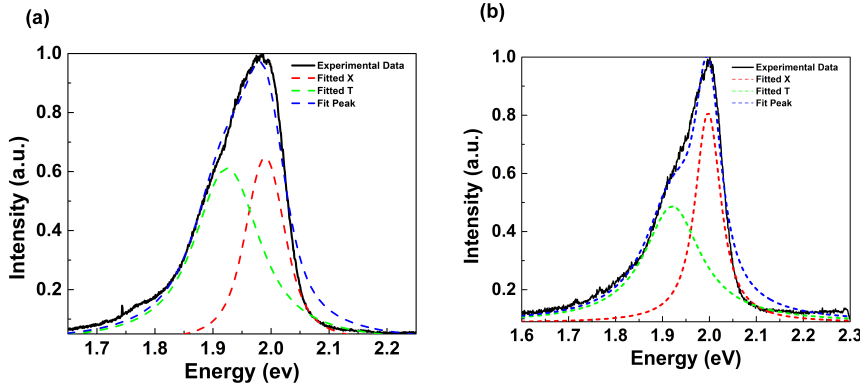


FIGURE 3.10: Output polarization analyzed spectrum (a) Analyzed along the long axis of the nano wire is de convoluted into exciton (Red dotted curve) and trion (green dotted curve). (b) Analyzed perpendicular to the long axis of the nanowire is deconvoluted into exciton (Red dotted curve) and trion (green dotted curve).

3.6 Conclusion

To summarize, we have experimentally studied the polarization-resolved directional PL emission from the AgNW-WS₂-Au cavity as a function of angular and spectral signatures. Through detailed experiments and analysis, we have shown the role of each component of the cavity, and how it influences the directional emission characteristics of the WS₂ monolayer. By performing polarization- and momentum-resolved PL spectroscopy from the distal end of the AgNW-WS₂-Au cavity, we reveal the possibility of studying exciton to trion conversion at room temperature. It is to be noted that nanowire based cavities inherently facilitate waveguiding characteristics, which means the excitation and collection in the geometry is spatially off-set. Such separation of excitation and collection of optical locations can be of relevance in 2D material-based nonlinear nanophotonic chips and open-cavity nano-lasers. We envisage that the confined electric

fields facilitated by the spatially-extended cavity can be further harnessed by engineering various parameters such as: the composition, shape, and size of the nanowire and the underlying gold mirror.

Chapter 4

Directing Tungsten Disulfide Monolayer PL using a Bent Nanowire on a Mirror Cavity

This chapter is an adapted version of the research article "European Physical Journal: Special Topics (2022) Accepted". The article discusses the directionality of emission when monolayer WS₂ is placed inside a plasmonic nanowire cavity and its comparison to a straight nanowire.

4.1 Introduction

Controlling and manipulating spontaneous emission is a principal indispensable task in nanophotonics[137–140]. The emergence of cavity electrodynamics has provided an excellent framework to study and manipulate spontaneous emission[7, 141, 142]. Molecular fluorescence coupled to micro and nano-cavities has been widely studied from the fundamental point of view as well as for application purposes[29, 143, 144]. Of late, studying spontaneous emission from emitters confined in the plasmonic cavity has gained relevance. Specifically, plasmonic cavities formed using mirror substrates have gained special attention because of the ease of preparation and very intense electric field inside the cavity formed between the structure and its image across the mirror substrate[29, 58, 111]. To this end, various cavities have been utilized for field enhancement by placing nanoparticles[58], nanocube[27]s, and nanowire[29, 101] on mirrors. Out of these, nanowires not only provide enhancement but also direct the light from molecules placed between the nanowires and mirror[29, 81]. Furthermore, bending the nanowire has been shown to enhance the directionality of the secondary emission from molecules placed on the nanowire or in the gap between the nanowire and mirror cavity.

4.2 Architecture of the System

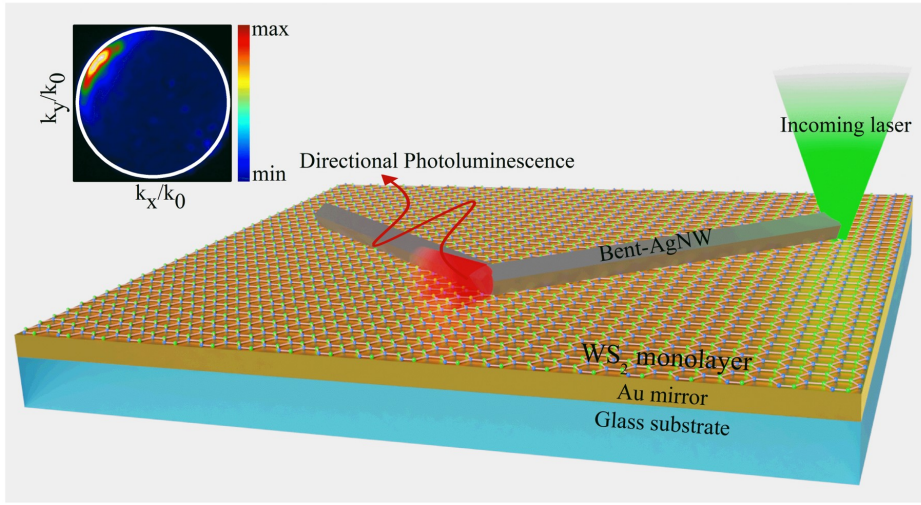


FIGURE 4.1: Schematic representation of the experimental configuration. A monolayer of WS_2 is grown and transferred onto the top of a gold mirror. A bent silver nanowire was dropcasted on a gold mirror thus forming a bent nanowire on a mirror (B-NWoM) cavity with the monolayer inside the cavity. One end of the nanowire was excited using a high numerical aperture objective lens and the emission from the kink region was spatially filtered for spectroscopy and Fourier plane imaging. The emission from the kink is directional in nature and covers a very narrow range of angles.

The gap between the particle-image particle can be controlled by placing either molecular monolayer or two-dimensional materials of finite thickness[29, 30, 58]. Recently two-dimensional transition metal dichalcogenides (TMDs) have emerged as new quantum emitters with high exciton binding energy, which lead to well-pronounced optical transitions[38–41, 94]. The direct bandgap of monolayers of TMDs makes them suitable for switching and optoelectronics devices[41, 94]. Well-defined molecular orientation and dipole moment of a monolayer of TMDs makes it a more suitable candidate to study quantum cavity electrodynamics[88, 145, 146]. TMDs show other unique optical properties such as strong spin-orbit interaction[147, 148], valley polarization[96, 149], second harmonic generation[150–152], and chiral Raman[153]. Plasmonic and dielectric cavities coupled to TMDs have been utilized for strong coupling[54, 111, 154, 155], photoluminescence enhancement[108, 113, 114], tailoring the emission[27], trion enhancement[102] and chiral routing of Raman[109] and photoluminescence[156]. Motivated by coupling TMDs to mirror-based plasmonic cavities, we study a bent plasmonic nanowire on a mirror cavity with a monolayer of WS_2 placed in the cavity. We show that the cavity can direct the WS_2 photoluminescence (PL) emission to a very narrow

range of wavevectors when the emission is collected from the kink region, upon excitation of the nanowire end. Using Fourier plane imaging[87, 127, 157, 158] we image the PL emission wavevectors and corroborate and understand the experimental findings using three-dimensional finite-difference time domain-based numerical calculations.

Figure 4.1 shows the schematic of the experiment configuration. A monolayer of WS_2 was sandwiched between a gold mirror and a bent-silver nanowire thus confining the monolayer in an extended cavity. One end of the nanowire was excited using a focused laser source of wavelength 532 nm with polarization along the length of the nanowire. Propagating surface plasmon polaritons (SPPs) outcouple from the kink part of the nanowire, exciting the cavity-enhanced monolayer photoluminescence (PL) of WS_2 . The fundamental SPPs along the nanowire and incoming laser source at the nanowire end also excite the cavity-assisted PL emission from the WS_2 . This PL emission also get couple to the nanowire SPPs because of near-field coupling and out-couple from the kink part of the nanowire. The emission from the kink of B-NWoM cavity was collected using spatial filtering and was routed to the spectrometer for spectroscopy or EMCCD for Fourier plane imaging.

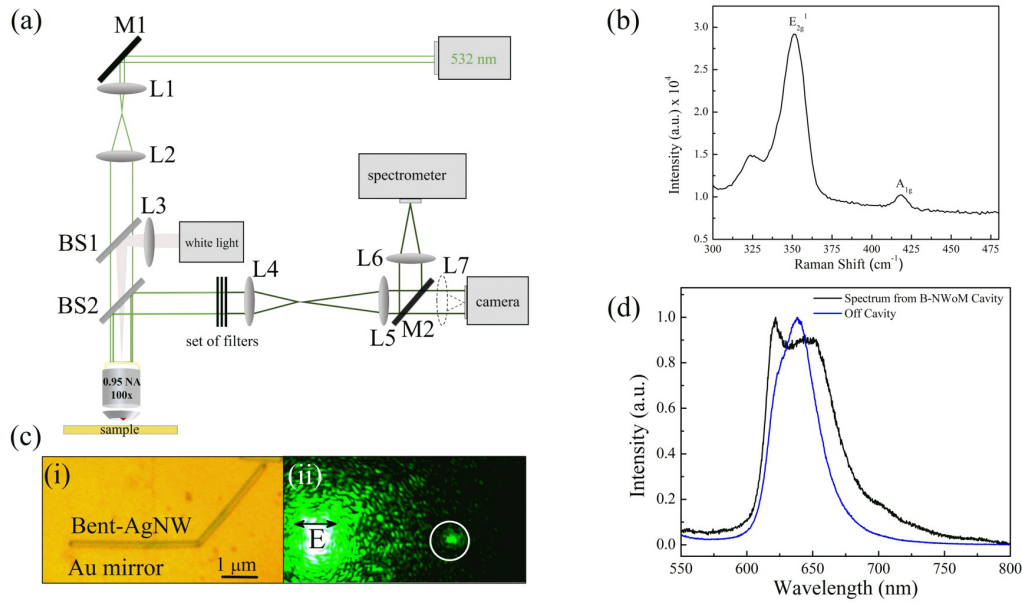


FIGURE 4.2: Optical imaging and PL spectroscopy. (a) Schematic of the experimental setup used to probe the Fourier plane imaging of WS_2 PL from the B-NWoM cavity. (b) Raman spectroscopy of the WS_2 layer confirming the monolayer. (c) Optical imaging of B-NWoM cavity. (i) Bright-field image of a 350 nm thick bent nanowire placed on a gold mirror of thickness 160 nm with a monolayer of WS_2 inside the gap. (ii) Elastic scattering image of the same bent nanowire when one end of the nanowire was excited with a 532 nm laser. (d) WS_2 PL spectrum collected from the kink part (shown as a white circle in figure 4.2c (ii)) of the bent nanowire upon excitation of one end of the bent nanowire (black curve), and spectrum collected only from the WS_2 monolayer placed on the gold mirror (blue curve). A detailed optical setup is shown in figure 4.2(a). The sample was excited using a high numerical aperture 100x, 0.95 NA objective lens. The backscattered light was collected using the same lens. The 532 nm laser light was expanded using a set of two lenses L1 and L2. M1 is a mirror to direct the laser into the microscope. The polarization of the incoming laser was controlled by a half wave-plate in the path. BS1 and BS2 are beam splitters to simultaneously excite the sample with laser and its visualization using white light. Lens L3 was used to loosely focus white light on the sample plane. A set of two edge filters and one notch filter were used to reject the elastically scattered light for PL spectroscopy and Fourier plane imaging. Lens L4 was used to recreate the real image for spatial filtering. Lens L5 was used to image the Fourier plane on the camera or CCD whereas lens L7 was used to flip lenses used to switch from real to Fourier plane. Mirror M2 and Lens L6 were used to route light towards the spectrometer and to focus the light onto the spectrometer, respectively.

4.3 Experimental Details

A detailed optical setup is shown in figure 4.2(a). The sample was excited using a high numerical aperture 100x, 0.95 NA objective lens. The backscattered light was collected using the same lens. The 532 nm laser light was expanded using a set of two lenses L1 and L2. M1 is a mirror to direct the laser into the microscope. The polarization of the incoming laser was controlled by a $\lambda/2$ waveplate in the path. BS1 and BS2 are beam splitters to simultaneously excite the sample with laser and its visualization using white light. Lens L3 was used to loosely focus white light on the sample plane. A set of two edge filters and one notch filter were used to reject the elastically scattered light for PL spectroscopy and Fourier plane imaging. Lens L4 was used to recreate the real image for spatial filtering. Lens L5 was used to image the Fourier plane on the camera or CCD whereas lens L7 was used to flip lenses used to switch from real to Fourier plane. Mirror M2 and Lens L6 were used to route light towards the spectrometer and to focus the light onto the spectrometer, respectively.

Figure 4.2(b) shows the optical characterization of the monolayer WS₂. Monolayer WS₂ was grown using atmospheric pressure chemical vapor deposition at 300 nm SiO₂ coated silicon wafer following the procedures given in the references[123, 124]. The gold mirror was prepared by depositing 160 nm gold on a glass coverslip using thermal vapor deposition. Monolayer WS₂ was then transferred to the gold mirror by wet transfer method using polystyrene support film[126, 159]. After the transfer, WS₂ layers were characterized by PL and Raman spectroscopy. Figure 4.2(b) shows the optical characterization of the monolayer WS₂. High PL intensity confirms the sample probed was a monolayer. In the Raman spectrum, the intensity of the E_{2g}^1 is much higher than A_{1g} and the peaks E_{2g}^1 and A_{1g} are positioned at 351 cm⁻¹ and 417 cm⁻¹, respectively, which matches with the reported Raman spectra for monolayer WS₂[159, 160].

Silver nanowires (AgNWs) with an average diameter of 350 nm were synthesized using the polyol process[125]. The nanowires were sonicated for 30 seconds to bend the nanowires[161]. Post bending the AgNWs were dropcasted on the WS₂ transferred gold mirror. This leads to the placement of the monolayer WS₂ in the cavity formed between the bent nanowire and mirror (B-NWoM cavity). The optical images of the monolayer WS₂ placed in the B-NWoM cavity is shown in figure 4.2(c). The bright-field image shows a bent silver nanowire of thickness 350 nm placed on a gold mirror. One end of the nanowire was excited using a focused laser source of wavelength 532 nm with polarization along the length of the nanowire to efficiently excite the propagating nanowire SPPs[122]. The light out couple from the kink portion of the nanowire was spatially filtered for spectroscopy and Fourier plane imaging. Spectral signature

collected from only the kink portion of the B-NWoM cavity shows a modulated spectrum as compared to the spectrum collected from the WS₂ monolayer placed only on the gold mirror (figure 4.2(d)). This modulation can be attributed to exciton to trion conversion caused by coupling of surface plasmon polaritons[81, 102].

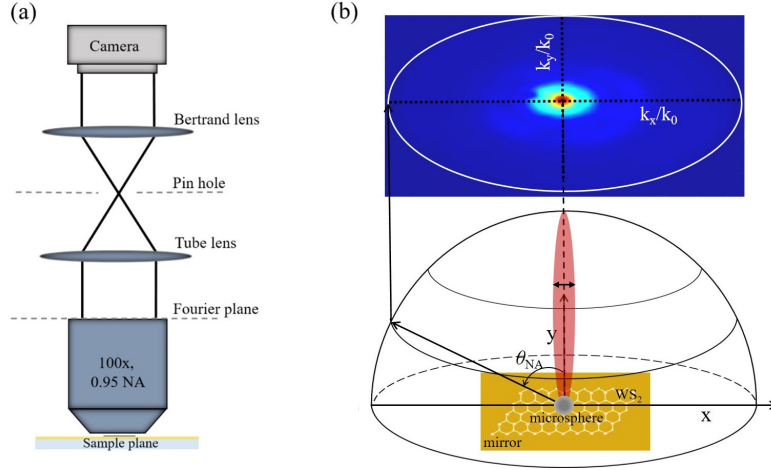


FIGURE 4.3: Schematics to visualize the Fourier plane imaging. (a) Experimental configuration to image the Fourier plane using an objective lens. 4f configuration was used to reimage the Fourier plane from the back aperture of the objective lens to the camera. (b) The emission direction from the sample plane is marked as a point on the hemisphere. θ and ϕ are the radials and azimuthal coordinates in the Fourier plane. Schematic showing the direction emission in the real plane (red curve) and Fourier plane is the two-dimensional projection of the emission. The black curve shows the maximum angle corresponding to the numerical aperture of the objective lens.

Figure 4.3(a) shows the schematic to visualize the directionality of the emission. The emission from the sample plane was collected using the objective lens, which forms the Fourier plane at its back aperture. To image the Fourier plane it was recreated onto the camera, using a combination of tube lens and Bertrand lens. A pinhole in the path was placed to selectively collect the emission from the kink part of the B-NWoM cavity using spatial filtering. Figure 4.3(b) shows the schematic to understand the projection of the emission direction from the sample plane to the Fourier plane. Every point on the hemisphere represents a direction and can be written in terms of radial and azimuthal angles θ and ϕ . The bent nanowire, placed in the x-y plane, emits the light in directions θ_{em} and ϕ_{em} as shown by red arrows. Fourier plane is the two-dimensional projection of the emission in radial (θ) and azimuthal angles (ϕ_{em}). The directionality of the emission can be quantified from the spread in θ_{em} and ϕ_{em} . The black curve shows the maximum angle (θ_{NA}) corresponding to the numerical aperture of the objective lens.

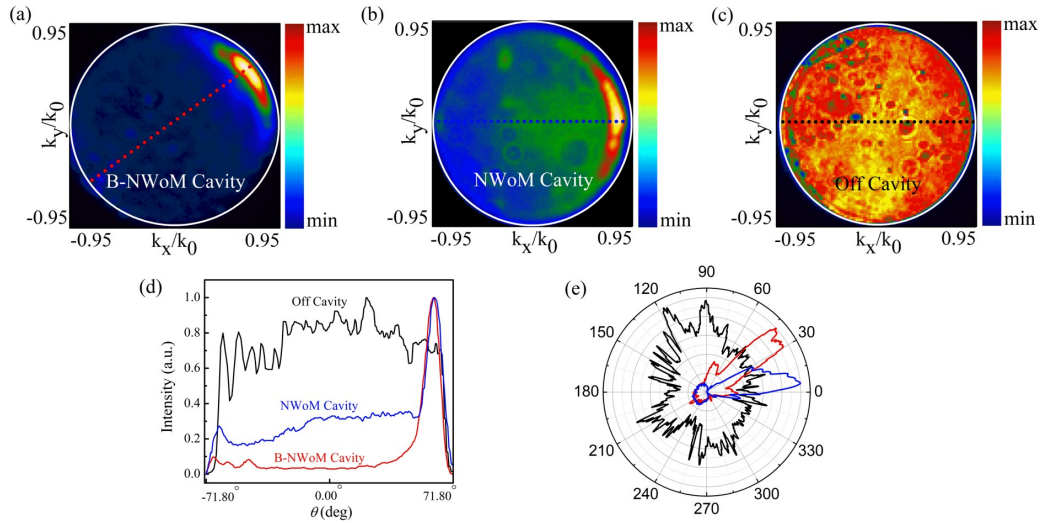


FIGURE 4.4: Fourier plane imaging of WS_2 PL emission. (a) Fourier plane image of PL emission from the kink portion of B-NWoM cavity upon excitation of one end of nanowire after rejecting elastic scattering light. (b) Fourier plane image of PL emission from the distal end of a nanowire placed on a mirror cavity (NWoM cavity) upon excitation of one end of nanowire after rejecting elastic scattering light. (c) Fourier plane imaging of WS_2 PL emission from a monolayer of WS_2 placed on a mirror. (d) Intensity cross-cuts along the red dotted line in (a), blue dotted line in (b), and black dotted line in (c). (e) Intensity profile of azimuthal angles (ϕ) for θ corresponding to maximum intensity in the Fourier plane images (a-c).

4.4 Directing the PL using B-NOM cavity

To study the angular distribution of the WS_2 PL emission spectrum from the kink portion of the B-NWoM cavity, we performed Fourier plane imaging on the WS_2 PL emission. Figure 4.4(a) shows the Fourier plane image of the PL emission collected from the kink portion of the B-NWoM cavity using the spatial filtering technique. The emission is confined to a narrow range of wavevectors and is directed towards the higher k_x/k_0 and k_y/k_0 . On the other hand, the Fourier plane imaging performed on the PL emission from the distal end of the nanowire without the bending shows that the emission is directed towards higher angles and the majority of the emission is along the nanowire length (figure 4.4 (b)). For comparison, the Fourier plane image of off-cavity emission from only the monolayer WS_2 on a gold mirror is shown in figure 4.4(c). The emission is isotropic in nature and covers a large range of angles. The intensity cross-cuts along the red, blue, and black dashed lines in figures 4(a-c) are shown in figure 4.4(d). The emission in the case of B-NWoM is very narrow in radial angles with a full width at half maxima of 11.0° . The intensity profile of azimuthal angles (ϕ) for θ corresponding

to maximum intensity in the Fourier plane images 4(a-c) are shown in figure 4.4(e). Along with the confinement in radial angles, the emission is also confined in terms of azimuthal angles in the case of the B-NWoM cavity with a full width at half maxima of 25.1° . The nanowire on mirror (NWoM) cavity also facilitates the directional emission but with a slightly broader radial and azimuthal angular spreading, 11.4° and 31.7° respectively. Because of the finite reflection from the nanowire end the emission is also directed towards the $-k_y/k_0$ direction which decreases the forward to the backward ratio of emission55 figure 4.4(d). On the other hand, the kink portion of the bent nanowire does not reflect the emission in the backward direction and out-couples the maximum of the mission in one direction only. This makes the B-NWoM cavity an excellent geometry for directing TMDs emission to a narrow range of angles.

4.5 Numerical Simulation

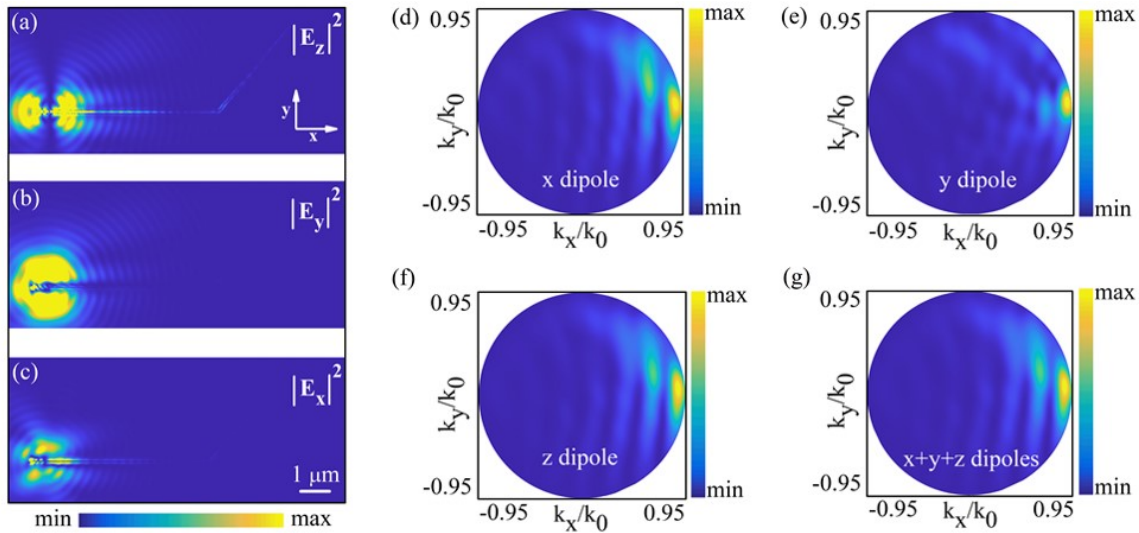


FIGURE 4.5: FDTD based numerical calculations to understand the directional PL emission from the B-NWoM cavity. (a-c) The component-wise magnitude of the near-field electric field in the B-NWoM cavity upon excitation of one end of the nanowire with a focused Gaussian laser source of 532 nm. Calculated Fourier plane images of the emission from the kink portion of B-NWoM cavity, upon excitation of nanowire end by a dipole oscillating along the x-axis (d), y-axis (e), z-axis (f), and an incoherent sum of emission from all three dipoles (g). The dipoles are oscillating at a wavelength of 620 nm, which is near the maxima of monolayer WS_2 PL.

To corroborate and understand the experimental results we performed finite difference time domain-based numerical calculations in Lumerical Software. The bent nanowire

was modeled by combining two cylindrical silver rods of length 6 μm . The radius of the cylinder was 125 nm and to make the kink portion, the radius was made to be 110 nm. The thickness of the gold mirror was set to be 100 nm. A 5 nm gap is set between mirror and nanowire to account for the molecular monolayer thickness and the PVP coating on the nanowire[162]. Figure 4.5(a-c) shows the component-wise near-field electric field in the cavity upon illumination of one end of the nanowire using a high numerical aperture objective lens. The polarization of the incoming laser was set along the x-axis, which is along the length of the nanowire for efficient excitation of the propagating nanowire SPPs. The E_z field is much more enhanced in the cavity as compared to the E_x and E_y fields. The large electric field present in the gap enhances the emission from the WS_2 monolayer. To see how the molecular orientation affects the far-field emission wavevectors, we excited the cavity by placing dipoles oscillating in different orientations at a wavelength of 620 nm at one of the ends of the bent-nanowire. A two-dimensional monitor was placed near the kink part of the B-NWoM cavity and the near-field was projected to the far-field using the in-built feature in Lumerical software. Figure 4.5(d-f) shows the Fourier plane images when the nanowire end was excited by dipoles oscillating along the z, y, and x-axis respectively. Figure 4.5(g) shows the Fourier plane image of the incoherent addition of the emission from the x, y, and z oriented dipoles. In all four cases, the emission is directional in nature and the result matches well with the experimentally obtained Fourier plane image. This suggests that both in-plane and out-of-plane exciton emission out-couple from the cavity in the same manner which makes it difficult to distinguish their individual contribution.

4.6 Conclusion

To conclude we show how a bent silver nanowire placed on a gold mirror can direct monolayer WS_2 PL which is otherwise isotropic in nature. The emission is confined to a narrow range of angles with a full width at half maxima in radial and azimuthal angles of 11.0° and 25.1° , respectively. We have compare the results with a straight nanowire and shown that the a bent nanowire can reduce both radial and azimuthal spread and also reduce the back reflected signal. Because of high out of electric field this architecture can be used to probe the dark exciton in TMDs and direct them to small range of wavevectors. Furthermore, using finite difference time domain-based numerical calculations we understood the effect of dipole orientation on the radiation pattern of PL emission. We believe that the results presented here will be extrapolated to direct enhanced Raman signal from TMDs and to design on-chip directional optical sources using various other class of TMDs.

Chapter 5

Beaming of Tungsten Disulfide Monolayer PL using metallo-dielectric antenna

The chapter explores the effect of coupling a microsphere on mirror based metallo-dielectric antenna to the excitonic emission of monolayer WS₂. We have experimentally shown that this antenna can direct all the photoluminescence to a very small range of wave-vectors and beaming of the WS₂ PL is observed in Fourier plane image.

5.1 Introduction

Two-dimensional transition metal dichalcogenides (TMDs) have attracted major attention in recent years because of their unique optical and electronic properties [38–40]. High exciton binding energy and direct bandgap make them suitable candidates for optoelectronic device applications[40–42]. TMDs show other unique properties such as valley polarization which make it suitable for valleytronics and spin-orbit interaction studies[96, 149]. Influencing and controlling the emission properties of the TMDs are key to improving the efficiency of optoelectronic devices. Recent advancements in the field of plasmonic and dielectric nanoantennas have enabled control over the fundamental emission properties such as wavevector distribution and Purcell enhancement[13, 98, 137, 163]. Furthermore, plasmonic nanostructure coupled to TMDs has been studied for strong coupling[111, 154, 155], photoluminescence (PL) enhancement[107, 108, 112, 113], surface-enhanced Raman scattering[110, 164], spectrum tailoring[27, 105], trion enhancement,[102] and directional emission[81]. Although plasmonic nanostructure provides great control over the emission properties, they suffer large Ohmic losses and have broad resonances[165]. On the other hand, dielectric structures such as microdisk, cylinder, and microsphere show low absorption and sharp resonances, which make them a suitable candidate for controlling the emission, properties without much loss. To this

end, studying the optical transition characteristics of TMDs coupled whispering gallery mode of the dielectric microsphere and disk has gained relevance. A variety of prospects like PL enhancement[166], lasing[166–168], directional emission[169], and out-of-plane dipole excitation[170] have been achieved using such geometries. Recently hybrid metallo-dielectric cavities have been used to enhance light-matter interaction[95, 171, 172], build hybrid metasurfaces[173], tailor the quality factor[174], and in designing directional sources[175–178]. Especially, dielectric particle on mirror is one such geometry which is widely used for hybridizing surface plasmon and whispering gallery modes (WGMs)[173], studying wavevector and polarization state of emission from fluorescent dye[128], and probing magnetic resonances[179]. Although, basic emission properties of TMDs such as Purcell enhancement and polarization of emission have been studied in great detail but the wavevector distribution is relatively less explored using geometries involving complicated fabrication and etching techniques[180].

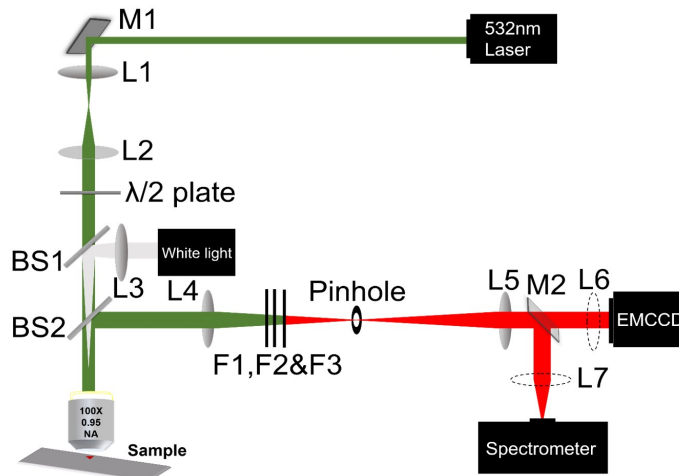


FIGURE 5.1: The sample was excited using a high numerical aperture 100x, 0.95 NA objective lens. The backscattered light was collected using the same lens. The 532 nm laser light was expanded using a set of two lenses L1 and L2. M1 is a mirror. The polarization of the incoming laser was controlled by a $\lambda/2$ waveplate in the path. BS1 and BS2 are beam splitters to simultaneously excite the sample with laser and its visualization using white light. Lens L3 is used to loosely focus white light on the sample plane. F1, F2, and F3 are set of two edge filters and one notch filter to reject the elastically scattered light for SERS spectroscopy and Fourier plane and energy-momentum imaging. Lenses L4 and L5 are used to project the emission to the Fourier plane onto the spectrometer or EMCCD. M2 is a flip mirror, used to project the light on the spectrometer for spectroscopy and energy-momentum imaging. Lenses L6 and L7 are flip lenses used to switch from real plane to Fourier plane.

In this context, tunability of directionality of the optical emission from nanostructures coupled to TMDs remains a challenging problem, and highly directional emission

from TMDs is yet to be achieved. Motivated by this, we study the optical emission properties of a monolayer WS_2 coupled to a metallo-dielectric antenna formed by placing a dielectric microsphere on the gold mirror. Specifically, we report the PL beaming from monolayer WS_2 coupled to this antenna. We study the wavevector distribution of monolayer WS_2 coupled to a metallo-dielectric antenna. Using Fourier plane imaging, we characterized the PL beaming and found the divergence angle to be as narrow as $\theta_{1/2} = 4.6^\circ$. Furthermore, we numerically study the near-field and far-field properties by using finite element method-based simulations.

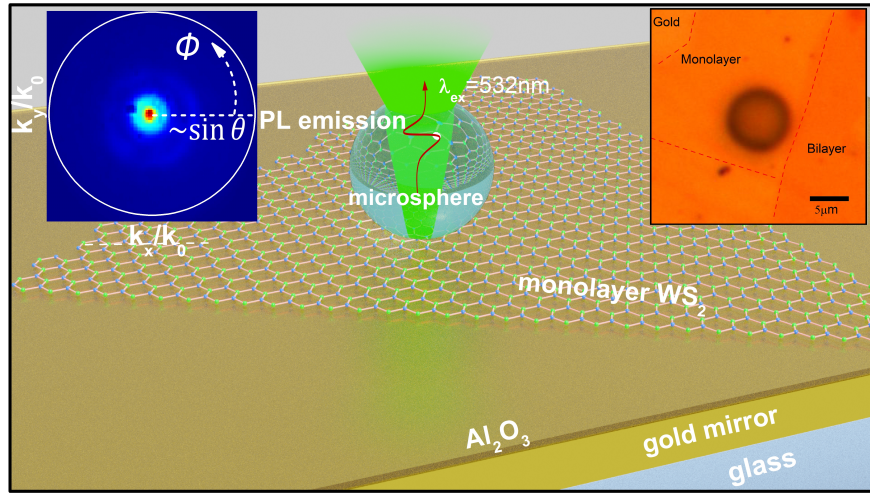


FIGURE 5.2: Schematic of the experimental configuration. A WS_2 monolayer was placed over a gold mirror separated by a 3 nm Al_2O_3 spacer layer. Polystyrene microspheres of a diameter $7\mu\text{m}$ were placed over it. A single microsphere was excited using a 532 nm laser. Insets show the bright field (right) and Fourier plane (left) images. Boundaries of the monolayer are shown with red dotted lines.

5.2 Experimental Methods

- **Sample preparation:** WS_2 monolayer were grown using chemical vapor deposition. Polystyrene microspheres were purchased from Sigma-Aldrich. Gold mirrors were prepared by thermal vapor deposition (TVD) by depositing 160 nm gold film on a glass coverslip. Monolayer WS_2 flakes were transferred onto the gold mirror using the wet chemical method. Briefly, polystyrene solution is spin-coated on the WS_2 sample followed by baking at 100°C . Sample was placed in water, and WS_2 was fished on the desired substrate with polystyrene support film when it started floating in the water. Polystyrene was removed using toluene, followed by cleaning the sample using acetone and IPA. Al_2O_3 spacer layer was

deposited using atomic layer deposition. After transferring the WS₂ monolayer on the Al₂O₃ coated gold mirror, microspheres were dropcasted on it, and the sample was dried in a vacuum desiccator.

- **Experimental setup:** The sample was excited using a 532 nm laser. 100 X, 0.95 numerical aperture objective lens was used in the backscattered configuration for both excitation and collection. The collected signal was projected into EMCCD and spectrometer for imaging and spectroscopy. Horiba iHR 320 spectrometer with 1800 grooves/mm and 300 grooves/mm grating was used for Raman and PL measurements, respectively. Schematic of detailed experimental setup is shown in figure 5.1.

5.3 Beaming of WS₂ PL using metallo-dielectric antenna

Figure 5.2 shows the schematic of the experimental configuration. Monolayer WS₂ has been grown using chemical vapor deposition (CVD)[123, 124] and characterized using Raman and PL spectroscopy as shown in figure 5.3. Raman and PL spectrum match well with the reported Raman and PL spectra[159, 160]. WS₂ flakes were transferred to Al₂O₃ coated gold mirror using a wet chemical method[126]. A 3 nm Al₂O₃ layer is used between WS₂ and the mirror to avoid the charge screening, which might lead to PL quenching. Microspheres were dropcasted on a monolayer WS₂ placed on a gold mirror. A single microsphere placed on the mirror was excited by a 532 nm laser using a 100x, 0.95 numerical aperture (NA) objective lens. The backscattered signal was collected using the same objective lens and projected onto EMCCD and spectrometer for imaging and spectroscopy. A microsphere placed on a gold mirror acts as a directional metallo-dielectric antenna to direct the WS₂ PL to a narrow range of wavevectors which was probed using Fourier plane imaging. To project the Fourier plane from the back aperture of the objective lens to the EMCCD, 4f lens configuration was used[87, 127]. A combination of edge and notch filters were used in the output path to efficiently reject the elastically scattered light, which can be observed in the PL spectrum shown in figure 5.3. Details of the experimental setup can be found in reference[128]. Figure 5.4(a) shows the PL spectrum collected from the WS₂ coupled to the metallo-dielectric antenna. The microsphere was excited using a 532 nm tightly focused laser beam. The microsphere focuses the incoming laser to a small region because of the photonic nanojet effect[181, 182], which excites the PL of the WS₂ monolayer. The PL emission from the monolayer acts as a near-field source that excites the WGMs of the

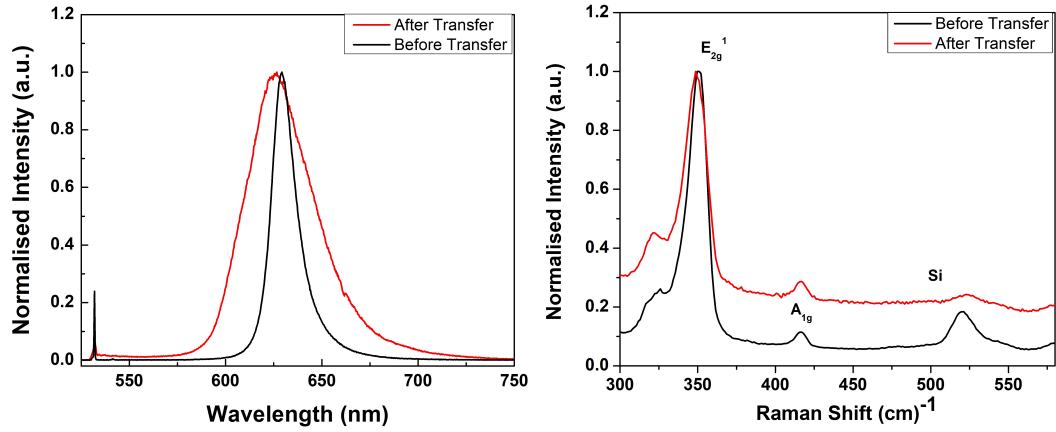


FIGURE 5.3: Optical characterization of WS₂ (a) Photoluminescence (PL) spectrum of WS₂ before and after the transfer to the gold mirror, the arrow represents the excitation wavelength, (b) Raman spectrum of the WS₂ before and after the transfer. High PL intensity confirms that WS₂ probed is a monolayer. After transferring the monolayer onto the gold mirror, emission becomes slightly broader while the Raman spectrum remains the same. In the Raman spectrum, Peak E_{2g}^1 and A_{1g} are positioned at 351 cm⁻¹ and 417 cm⁻¹, respectively, and the intensity of the E_{2g}^1 is an order of magnitude higher than A_{1g} , which matches well with reported Raman spectra [1, 2]. In the Raman spectrum of WS₂ after the transfer, there is a small peak near 520 cm⁻¹, which might be because of the small remains of Si after the transfer

microsphere. WGMs are the sharp resonances supported by the dielectric microstructures [168]. WGMs of the microsphere can be seen as sharp peaks riding over a broad PL spectrum.

To study the wavevector distribution of the PL emission from the metallo-dielectric antenna, Fourier plane microscopy and spectroscopy were performed. Fourier plane image maps the wavevectors of the light in terms of θ and ϕ coordinates. The radial coordinate in the Fourier plane image is the numerical aperture (NA) = $n \sin(\theta)$, and ϕ is the azimuthal coordinate that varies from 0 to 2π . Figure 5.4 (b) shows the Fourier plane image of the PL emission. It can be observed from figure 5.4 (b) that the θ spread is very small, and the majority of the emission is beaming at the center of the Fourier plane image.

The PL generated below the microsphere gets out-coupled from the upper side of the microsphere in a narrow range of angles because of the reverse of the photonic nanojet effect [181]. To quantify the spread of the emission wavevectors, we plot the intensity profile along the white dotted line in the Fourier plane image (Figure 5.4(b)). The measured intensity profile was fitted using the Lorentzian function, which shows that the divergence angle, $\theta_{1/2}$, half of the full width at half maxima (H-FWHM), of

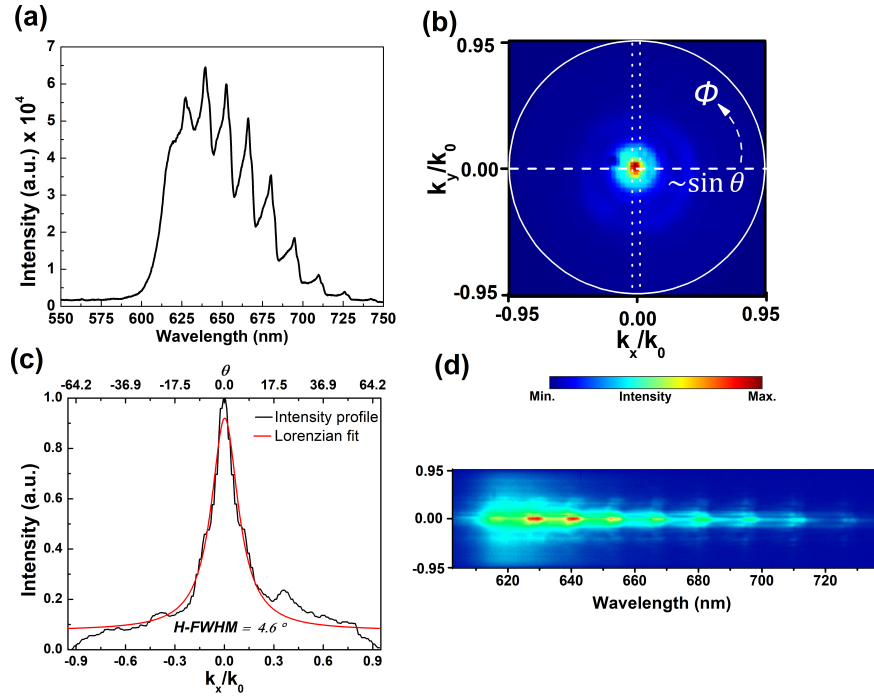


FIGURE 5.4: Beaming of WS_2 PL. (a) PL spectrum of WS_2 monolayer coupled to a metallo-dielectric antenna. (b) Fourier plane image of the PL emission from the WS_2 coupled to the antenna. (c) Intensity profile of the Fourier plane image along the white dashed horizontal line in the Fourier plane image. (d) Energy-momentum image of the PL emission along the white vertical rectangular region.

the emission is only 4.6° . For various microspheres (five microspheres) the divergence angle varies slightly with an average of $(5.2 \pm 0.6)^\circ$ (See figure 5.5).

To further confirm that both WGMs coupled and uncoupled emissions get directed to a narrow wavevector range from the metallo-dielectric antenna, we performed energy-momentum imaging (figure 5.4(d)). For this, the Fourier plane image (figure 5.4(c)) was projected onto the slit of the spectrometer to get the wavelength information. The energy-momentum image shows that both WGMs coupled and uncoupled emission is out-coupling from the microsphere towards the center of the Fourier plane image with a narrow range of angles. Additionally, this further rejects the possibility of elastically scattered light at the center of the Fourier plane image.

To highlight the significance of the gold mirror, similar experiments were performed on different configurations. Figure 5.6(a) shows the wavevector distribution of WS_2 PL on the Si/SiO_2 substrate. The PL emission from WS_2 monolayer is isotropic in nature and covers a broad range of wavevectors. Figure 5.6(b) shows the wavevector distribution when a microsphere is placed over Si/SiO_2 substrate. Placing the monolayer between the microsphere and Si/SiO_2 substrate results in confining the wavevectors.

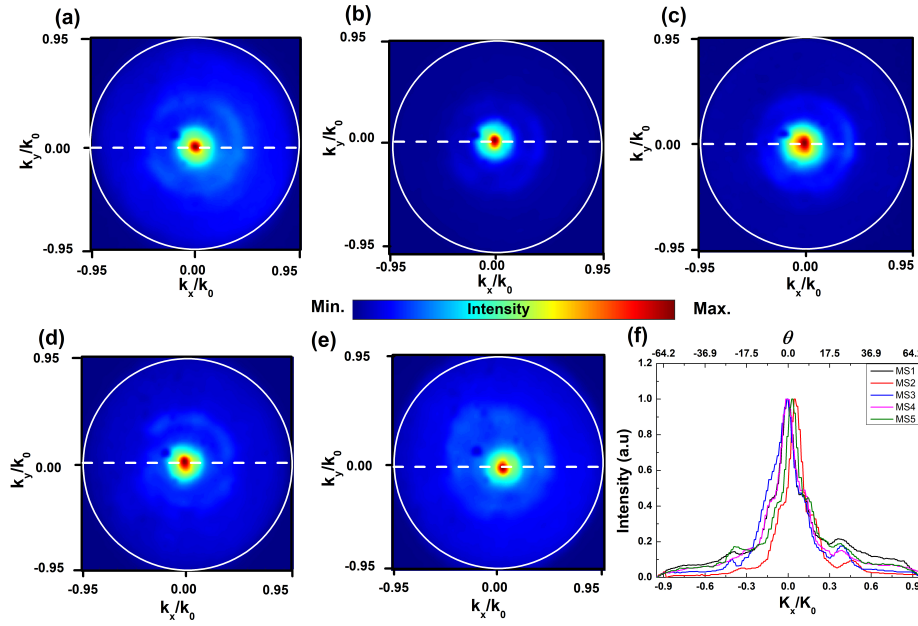


FIGURE 5.5: Multiple measurements showing the beaming of the emission, (a-e) Fourier plane image showing the PL beaming from five different microspheres. (f) Shows the intensity profile along the white dotted line. The divergence angle was calculated by fitting the Lorentzian function for each intensity profile. The average value of divergence angle is $(5.2 \pm 0.6)^\circ$.

Using a metallic mirror as a substrate further reduces the angular divergence and results in the beaming of emission from the monolayer sandwiched between the microsphere and the mirror (figure 5.6(c)). This can be understood by the localization of the electric field in the gap between the microsphere and the gold mirror. We corroborated and understood this result using finite element method (FEM) based numerical calculations, which is discussed later in the chapter. Intensity profiles along the white dotted lines in figure 5.6(a-c) are plotted in figure 5.6(d). Angular divergence ($\theta_{1/2}$) for the gold and the Si/SiO₂ substrate is 4.6° and 11.5° , respectively. For various microspheres (three microspheres), the divergence angle varies slightly with an average $(13.2 \pm 1.1)^\circ$ for Si/SiO₂ substrate as shown in figure 5.7. To study the effect of microsphere size on the angular divergence of the emission, we performed experiments on microspheres of sizes 3, 5, 7, and 10 μm . Figure 5.8 shows the angular divergence for the different sizes of the microsphere on mirror antenna. The angular divergence decreased when the microsphere size was chosen to be 7 μm as compared to the divergence obtained with a microsphere of size 3 or 5 μm . A further increase in the microsphere size (10 μm) leads to an increment in the divergence angle.

Since in photonic nanojet effect microsphere act as a micro-lens[182], emission wavevectors are sensitive to the position of the beam waist of the nanojet. The focus of

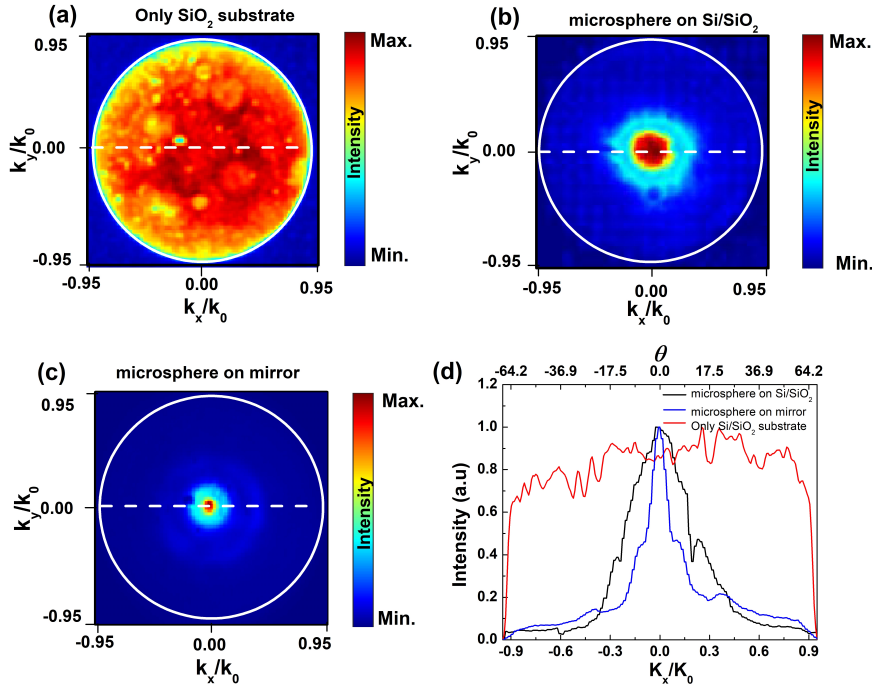


FIGURE 5.6: Significance of using the gold substrate. Fourier plane images (a) on Si/SiO₂ substrate, (b) with microsphere on Si/SiO₂ substrate, and (c) microsphere on mirror. (d) Intensity profile across the white dotted line in (a-c).

the microsphere can be treated as the waist of the nanojet. Focusing dependent experiment was performed to probe the wavevector as a function of beam waist position. Input light was focused in the different planes of the microsphere, and wavevector distribution of PL emission was studied. Figure 5.9 (a-d) are the different focusing schemes, and (e-h) are the corresponding Fourier plane images. The light green cone represents the focusing of the excitation laser beam using the objective lens, while the dark green cone shows the effective focusing of the laser beam. It is observed that the divergence was smallest when the input laser was focused slightly below the microsphere. The smallest angular divergence for the position of the waist just outside the microsphere confirms that the beaming of the emission is caused by the reverse of the photonics nanojet effect of the microsphere. To corroborate and understand the experimental findings, we performed finite element method-based numerical calculations in COMSOL Multiphysics. We performed near-field calculations and calculated Fourier plane images by using reciprocity arguments[183]. We calculated the near-field profile of a 3 μm diameter polystyrene microsphere placed on a 160 nm thick gold mirror. The gap between the microsphere and gold mirror was set as 5 nm for accounting for the Al₂O₃ and molecular layers. Figure 5.10(a) shows the experimentally measured Fourier plane image of the emission from a WS₂ monolayer coupled to a metallo-dielectric antenna

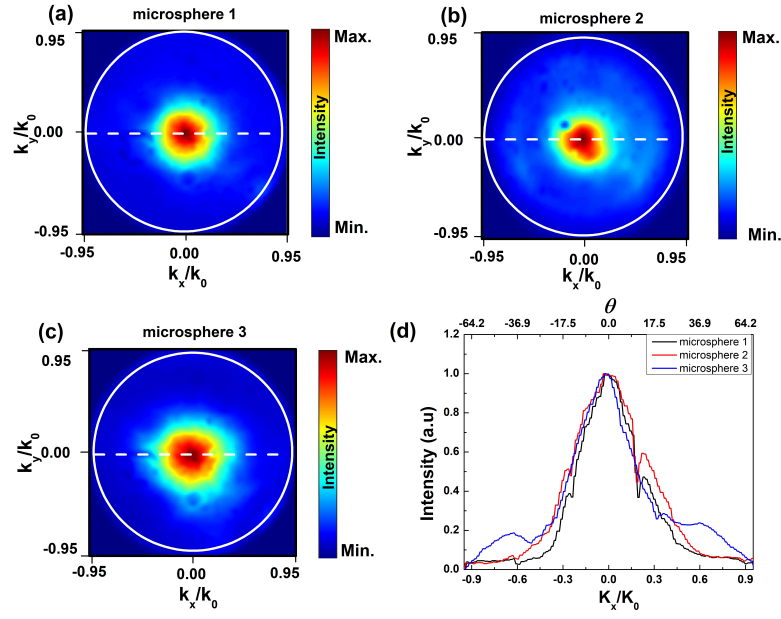


FIGURE 5.7: Multiple measurements for microsphere on Si/SiO₂, (a-c) Fourier plane images of three microspheres on Si/SiO₂ substrate, (d) their intensity profile across the white dotted line. The divergence angle was calculated by fitting the Lorentzian function for each intensity profile. The average value of divergence angle is $(13.2 \pm 1.1)^\circ$.

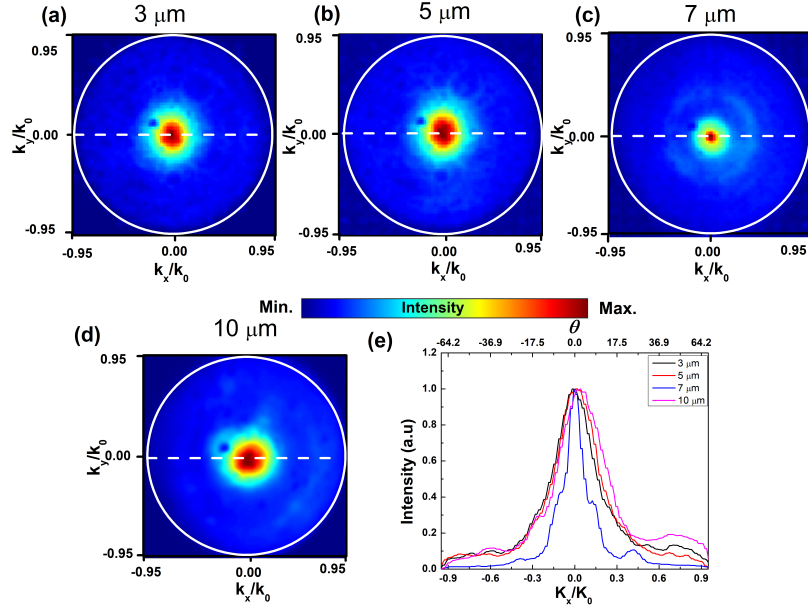


FIGURE 5.8: Microsphere size dependence, (a-d) Fourier plane image for the microsphere of the size 3, 5, 7, and 10 μm . (e) Intensity profile along the white dotted line in figure 5.8 (a-d). The divergence angle was calculated by fitting the Lorentzian function for each intensity profile. The divergence angle corresponding to these four Fourier plane images is 9.0° , 9.5° , 4.6° , and 9.9° , respectively.

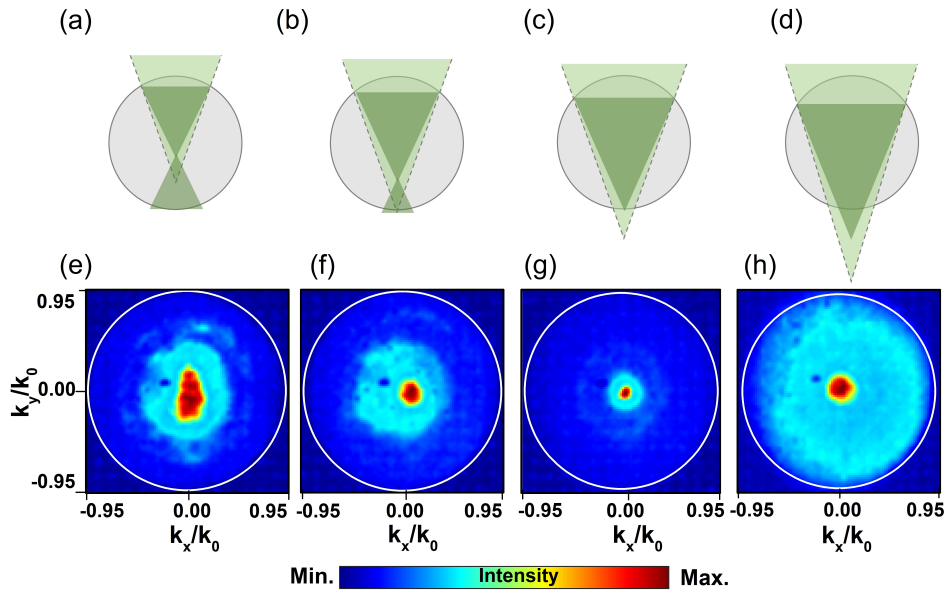


FIGURE 5.9: Effect of focusing of excitation laser in different planes on angular diversion of emission from the metallo-dielectric antenna. (a-d) Schematic of different focusing schemes and (e-h) are corresponding Fourier plane images. The light green cone represents the focused laser excitation using the objective lens, and the dark green cone shows the effective focusing of the incoming laser by the microsphere.

formed by a 3 μm polystyrene microsphere and gold mirror. We calculated the near-field electric field of a 3 μm polystyrene placed on a gold mirror and excited by placing in-plane and out-of-plane dipoles. We placed an oscillating dipole at 645 nm oriented along the in-plane (x-axis) (figure 5.10(d)) and out-of-plane (z-axis) (figure 5.10(e)). We chose the wavelength of oscillation to be 645 nm as the PL emission has a peak around this wavelength. The experimental Fourier plane image figure 5.10(a) matches well with the calculated Fourier plane image for the in-plane dipole figure 5.10(b).

Figure 5.11 shows the near field electric for a Gaussian beam focused using a microsphere of diameter 2 μm (a) on the glass substrate and (b) gold mirror. The electric field is more confined when the substrate is gold mirror as compared to a glass substrate. This is confirmed by performing numerical calculations by exciting microsphere placed on glass and gold substrates with a focused Gaussian beam.

To see how the localization of near-field electric field leads to the narrowing of wavevectors, three dipoles were placed at the center of the microsphere separated by 80 nm from each other in the first case and 240 nm in the second case as shown in figure 5.12 (a-b). The calculated near-field electric field was projected to the far-field by using reciprocity arguments(See figure 5.12 (c-d)). The spreading of the wavevectors is less in the former case as compared to the spreading obtained in the latter. This explains the narrowing down of the wavevectors in the case of a microsphere placed on a gold

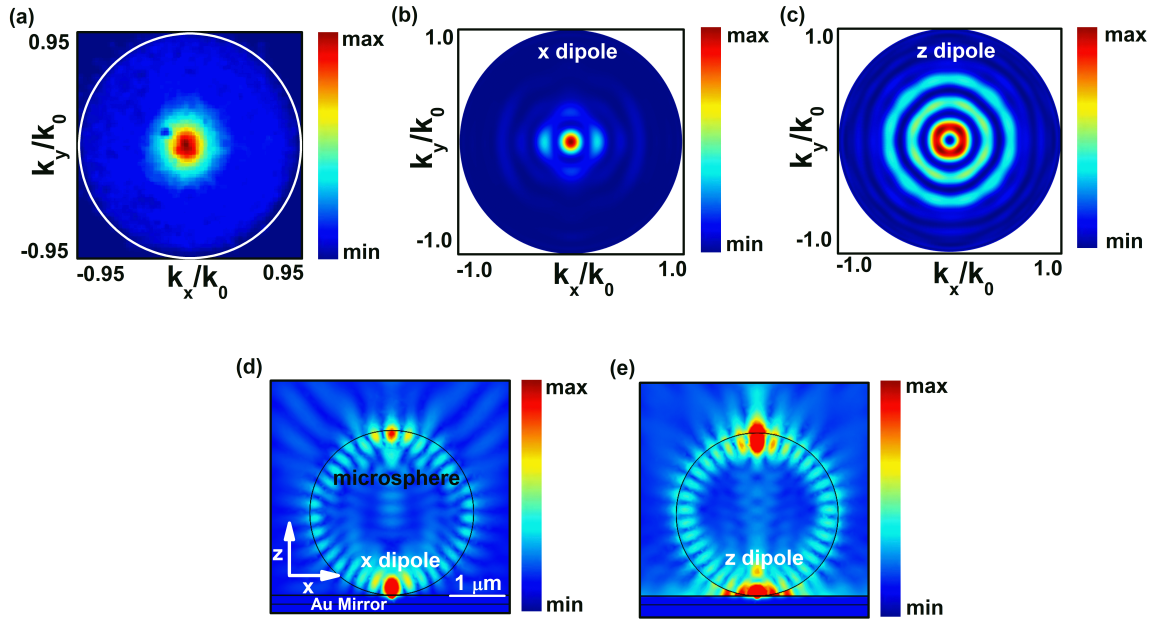


FIGURE 5.10: Calculated Fourier plane imaging of emission from dipoles placed between microsphere and mirror. (a) Experimentally measured Fourier plane image of emission from a TMD monolayer sandwiched between a 3 μm polystyrene microsphere and 160 nm gold mirror. Calculated Fourier plane image of emission from a dipole oscillating in-plane (x-axis) (b) and out-of-plane (z-axis) (c) Calculated near-field electric field of a 3 μm polystyrene microsphere placed on a gold mirror excited by placing an oscillating dipole at 645 nm wavelength with in-plane (x-axis) (d) and out-of-plane (z-axis) dipole in the gap between microsphere and mirror (e).

mirror.

For the in-plane dipole (x-axis), the calculated Fourier plane image matches very well with the experimentally obtained Fourier plane image. The majority of the light is coming out in a beaming manner and is confined to a very narrow range of wavevectors. The calculated Fourier plane image for the out-of-plane dipole shows that the emission is coming out in a doughnut-shaped pattern and is also directed towards the center of the Fourier plane image. The results show that the contribution of in-plane dipoles is more pronounced in the case of metallo-dielectric antennas.

5.4 Conclusion

To summarize, we have experimentally studied the wavevector distribution of PL and coupled it to a metallo-dielectric antenna. By performing the experiment in the different configurations, we have shown that the PL emission of WS_2 , sandwiched between

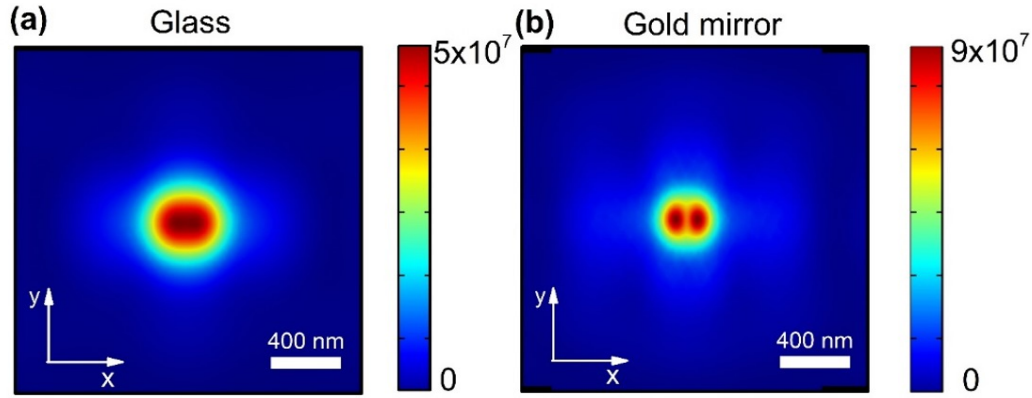


FIGURE 5.11: Near field electric field distribution in x-y plane for a microsphere of size $2\ \mu\text{m}$ when excited using a Gaussian beam of 532 nm wavelength. (a) When microsphere is placed on a glass substrate (b) when microsphere is placed over gold mirror. In the case of the gold mirror substrate, the electric field is more localized in comparison to the glass substrate. This is because of a hotspot formation around the contact point of the microsphere and the gold mirror. This result implies that for the gold mirror, the emission will be more localized

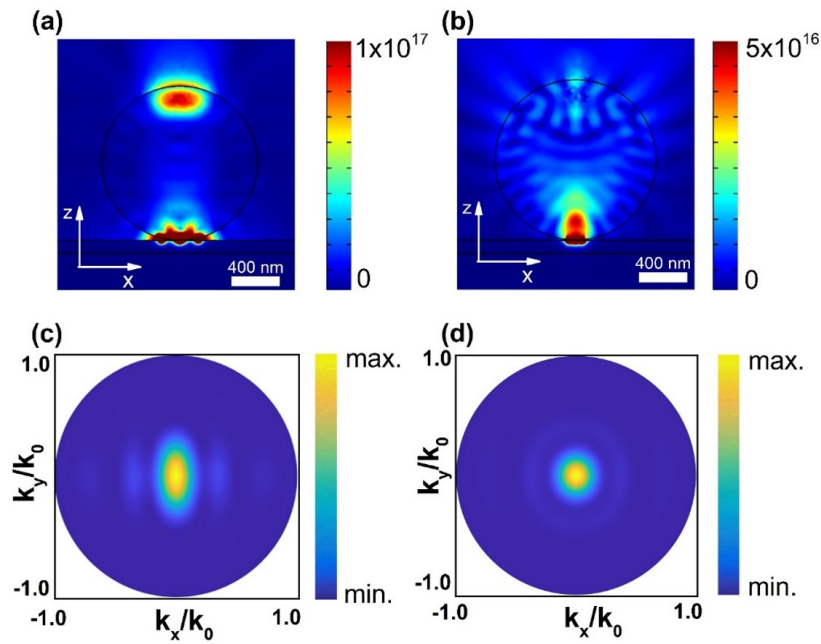


FIGURE 5.12: Near field and far-field electric field for a microsphere of diameter $2\ \mu\text{m}$: Near field electric field distribution when 3 dipoles were placed (a) 240 nm apart and (b) 80 nm apart, (c) and (d) are the corresponding Fourier plane images. Since the electric field was more localized in the case of the gold mirror substrate, dipoles were placed closer to mimic the gold mirror case. It can be seen from figure 5.12 (c and d) that the divergence in the case of the localized emitter is lesser.

microsphere and gold mirror out-couples in a beaming manner. The microsphere on the mirror geometry acts as an excellent metallo-dielectric antenna to direct the emission from TMDs in a very small range of wavevectors. In the Fourier plane image, the angular divergence $\theta_{1/2} = 4.6^\circ$ was achieved. The experimental findings were corroborated with three-dimensional finite element method-based numerical simulations. This hybrid directional antenna will find relevance in two-dimensional material-based nanophotonic chips and nano-lasers.

Chapter 6

Conclusion and Future Directions

In conclusion, this thesis focuses on understanding the light-matter interaction inside the optical cavity. Interaction of light confined inside the cavity with 2D materials is discussed. We have explored the directionality of emission when 2D materials were placed inside the different cavities. We have shown that the directionality and wavevector distribution of the 2D materials can be tuned and can be controlled by placing them inside different cavity structures. Highly directional emission in remote excitation, as well as indirect excitation, is achieved. Surface plasmon polariton of the silver nanowire is used to direct the light into a small range of wavevectors in remote excitation configuration. We have also shown that a microsphere can be used as a micro-lens to collect the emission from the 2D materials and project it to a very narrow range of wavevectors by the photonic nanojet effect.

Future direction:

Till now our focus was on designing the antenna which can direct the emission from the 2D materials to a narrow range of wavevectors. It will be important to understand the process underlying these phenomena in more detail. This will not only help in the fundamental understanding of the system but also helpful in generalizing this phenomenon for a wider range of applications.

As we discussed in chapter 3 and chapter 4, PL emission from the distal end is the convolution of three processes:

First: The large local electric field at the excitation spot leads to the coupling of WS 2 PL to the nanowire plasmons, which outcouples from the distal end.

Second: The fundamental plasmon polaritons at 532 nm outcoupling at the distal end as free space photons and excites the WS2 PL.

Third: The fundamental plasmon polaritons (532 nm) propagating along the nanowire over film excites the photoluminescence throughout the length of the nanowire which

further couples to the nanowire plasmons because of the near field coupling and outcouples from the distal end. The de-convolution of these three processes can give important insights into the propagation length, coupling, and out-coupling of the light from the nanowire ends. This requires a detailed study and we are planning experiments to understand this phenomenon in the future.

In chapter 5, We have discussed the photonic nanojet of the microsphere to direct the emission to a small range of wavevectors. However, another important aspect is the coupling of photoluminescence with the whispering gallery mode of the microsphere. TMDs coupled with the whispering gallery mode of the microsphere has been utilized for the lasing and probing out of plane dipole. These modes of the microsphere play a crucial role in understanding and designing WGMs-based devices. PL coupled to WGMs of a microsphere on a mirror is not have been studied in detail which might lead to the interesting phenomena like strong coupling. I would also like to understand the far-field pattern associated with the different TE and TM modes.

Till now we have utilized the bottom-up synthesized micro and nanostructures to direct and study the photoluminescence from TMDs. However, fabricated micro and nanostructures offer more room in terms of controlling and making devices based on these materials. Utilizing the top-down fabrication method to couple these materials with metasurfaces and controlling the other properties of TMDs is another direction to work on. Recently dark exciton in TMDs has been probed using the plasmonic nanocavity. The cavity design proposed here can be utilized to probe and direct the dark exciton emission from TMDs monolayers.

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