Manipulation of Light-Matter Interaction in Two-Dimensional Systems via Localized Surface Plasmons

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Manipulation of Light-Matter Interaction in Two-Dimensional Systems via Localized Surface Plasmons

Abstract
Localized surface plasmons (LSPs), which are collective charge oscillation confined by metallic nanoparticles, gained much interest in the field of optoelectronics due to its ability to confine light down to nanoscale without a diffraction limit. As light-matter interaction in nanoscale is becoming more important due to the demand in scaling down the optoelectronic devices, my thesis describes the work on manipulation of such light-matter interaction enabled by LSPs. First, periodically patterned two-dimensional arrays of bowties were investigated to study the localized surface plasmon (LSP) resonances via reflection measurements and numerical simulations. Due to the grating created by arrays of bowties, a new, lattice-coupled LSP (lattice-LSP) mode emerged. Comparing the calculated E-field enhancement of the bowtie arrays to the reflection spectra showed that the lattice-LSP mode positions are closely related to the dips in the reflectance spectra. After the study of bowtie arrays, we showed photoluminescence (PL) from bulk, planar silicon coupled with metal bowtie nanocavities, which is an indirect bandgap semiconductor with very low emission efficiency. This was due to the E-field concentrated inside the tips of the metal bowtie achieved by LSPR, leading to increased radiative decay rate. The approach of bowtie-coupled emitter was also applied to monolayer MoS2, a transition metal dichalcogenide semiconductor which transforms to a direct bandgap semiconductor in monolayer. Silver bowtie array coupled with monolayer of MoS2 showed a high enhancement in emission (Raman and PL) due to surface-enhanced fluorescence (SEF) from weak-coupling of MoS2 excitons and bowtie’s LSPR. By tailoring the design of bowtie arrays, we controlled the location of surface plasmon resonances which, coupled with MoS2 excitons, led to spectral modification of PL spectra. Furthermore, at low temperature, we achieved stronger coupling between the two systems in some designs of the bowtie array and observed Fano resonances in reflection measurements. The approach was extended to photocurrent studies in MoS2. Utilizing the helicity of monolayer MoS2 is suggested as future work to investigate the circular photocurrent in MoS2 induced by selective linear polarizations. Lastly, by fabricating nanoribbon arrays of fluorographene, evolution of localized surface plasmon mode of graphene in near-infrared wavelength range was studied via Fourier transform infrared spectroscopy (FTIR). The initial result showed possibility of tunable graphene IR plasmon resonance depending on the array design due to the localized surface plasmon mode created by the grating of alternating fluoro-graphene and graphene nanoribbons, confining E-field to excite the plasmon modes in IR range.

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MANIPULATION OF LIGHT-MATTER INTERACTION IN TWO-DIMENSIONAL SYSTEMS VIA LOCALIZED SURFACE PLASMONS

Joohee Park

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MANIPULATION OF LIGHT-MATTER INTERACTION IN TWO-DIMENSIONAL SYSTEMS VIA LOCALIZED SURFACE PLASMONS

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To my God, and my family.
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bilayer graphene (white dashed line), which all act as scattering sites. Scale bars, 100 nm. Reprinted with permission from ref. 9. © 2012, Macmillan Publishers.

**Figure 6.6** | Gate-induced modulation of transmission in graphene nanoribbon arrays normalized to transmission spectra at the charge neutral point (CNP). **a**, Nanoribbon-width dependence of optical transmission with $E_F = -0.37$ eV. Nanoribbon width is varied from 15 to 80 nm. **b**, Fermi level dependence of optical transmission in 50 nm-wide graphene nanoribbon array. $E_F$ is varied from $-0.22$ to $-0.52$ eV. The dotted vertical lines indicates the zone-center energy of the in-plane optical phonons of graphene. Reprinted with permission from ref. 13. © 2013, American Chemical Society.

**Figure 6.7** | **a**, Optical image of fluorographene square patterns on transferred graphene. Inset shows a magnified image of patterned fluorographene-graphene nanoribbon arrays. **b**, Raman spectra of CVD graphene showing the characteristic D, G, and 2D peaks, as expected, and of fluorographene which lost its graphene characteristics.

**Figure 6.8** | **a**, Transmission spectra for 600 nm-width arrays of graphene and fluorographene, doped with F-SAM. The spectra were measured three consecutive times. **b**, Transmission spectra for 400 nm-width arrays of graphene and fluorographene, doped with F-SAM. The spectra were measured four consecutive times.
Chapter 1. Introduction

Localized surface plasmons (LSP), coherent oscillations of electrons confined at the metallic interface of small nanoparticles, gained much interest in the field of optoelectronics due to its ability to concentrate light down to nanoscale without a diffraction limit. Since the recent advances in fabrication of nanoscale structures, LSP-enabled light-matter interaction has been widely studied. Thus, manipulation of light-matter interactions in nanoscale systems is critical for obtaining new optoelectronic functionalities and flexible devices. In this thesis, my work on two-dimensional manipulation of light-matter interaction in three materials systems, silicon, and MoS$_2$, and graphene, will be presented. In this chapter, concepts for the major constituents of my thesis will be discussed in order to set the base of understanding for the chapters to follow. Background on plasmons and how the plasmons confined by metal nanostructures, localized surface plasmon (LSP), enable interesting light-matter interaction when coupled to an emitter will be presented, as well as some of the important previous work. In the following chapters, study of plasmonic bowtie array structures will be presented, followed by the investigation of LSP-enabled manipulation of light-matter interaction in silicon and monolayer MoS$_2$ through the bowtie structures. Next, study of photocurrent in MoS$_2$ as well as study of IR plasmons in graphene-fluorographene nanoribbon arrays will be presented with future directions. Material-specific backgrounds will be included at the beginning of each corresponding chapter to help readers gain understanding of plasmonic properties in each material relating to the results and discussion to follow.
1.1 Plasmons and surface plasmons

The optical properties of materials are dictated by the complex dielectric function of the material, $\varepsilon(w,k)$, a function of frequency and wavevector. Assuming the wavelength of light incident on a material is much larger than the atomic unit cell spacing, the dielectric function may be considered only of a function of energy, which generally still holds true for metals up to UV frequencies. By assuming the time-varying $E$-field driving the free electron gas of a metal, the free-electron model, or Drude model, describes the dielectric function of metals as following:

$$
\varepsilon(w) = \varepsilon_{\infty} - \frac{w_p^2}{w^2 + iw\gamma}.
$$

Here $\varepsilon_{\infty} = \text{static permittivity}$, $w_p = \text{electron plasma frequency}$, $\gamma = \text{damping coefficient}$. Generally, the highly mobile electrons in the bulk metal can undergo collective oscillations which behave as plasmons.

When plasmons are driven at the interface of the metal and a dielectric such as air and glass (Fig. 1.1a), they have a dispersion such as shown in Fig. 1.1c, calculated from solving the Maxwell’s equation at the boundary between metal and dielectric surface for the propagating wave confined at the interface. This is known as surface plasmons (SPs). This oscillation is resonantly driven at specific optical frequencies to produce a strong charge displacement and associated field concentration. The field component perpendicular to the surface is evanescent, decaying exponentially with distance away from the surface, thus helping power to be contained within the vicinity of the metal (Fig. 1.1b).
1.2 Light-matter interaction via localized surface plasmons

Conventionally, dielectric lenses and resonators have been widely used to manipulate and confine light in a very small volume for numerous applications including low threshold lasers, sensors, and nonlinear optics. There has always been a demand in scaling down the optical resonators even further in order to confine light more and enhance light-matter interaction to achieve photonic devices for compact integrated optical circuits. However, due to the fundamental laws of diffraction, the focus of light in these dielectric optical resonators are limited only down to $(\lambda/2)^3$, where $\lambda$ is the wavelength of light inside the dielectric medium. Thus, optical resonators that can sustain surface plasmons and localize the electromagnetic (EM) energy in subwavelength scale are critical in achieving extreme concentration and manipulation of light for applications in optical biosensing, light harvesting, and optical nanoantennas. In most cases, this is achieved by metallic cavity, a waveguide material such as nanowires and
photonic crystals, in which light is confined due to refractive index mismatch between the material and the surrounding\(^4\). When a metallic cavity interacts with light, the surface plasmons localize at the metal surface, called localized surface plasmons (LSPs). The energy of LSP resonance (LSPR) depends on the design (size, geometry, and material) of the nanostructures as well as on the surrounding dielectric environment\(^7\).

1.2.1 Localized surface plasmon resonance (LSPR) for metallic nanoparticles

When light is irradiated on a metallic nanoparticle, the oscillating electric field induces SPs. This collective oscillations are known as localized surface plasmon resonances (LSPRs)\(^{21}\). The electron cloud is displaced relative to the nuclei leading to a restoring force due to Coulomb attraction between electrons and nuclei (Fig. 1.3). This leads to drastic change in the incident radiation pattern and interesting effects such as formation of high intensity hot spots on the nanoparticle surface and directional scattering of light\(^{12}\).

![Figure 1.2](image.png)

**Figure 1.2** | Plasmon oscillation of a sphere with the displacement of the conduction electron charge cloud with respect to the nuclei. *Reprinted with permission from ref. 8. © 2003, American Chemical Society.*
The density of electrons, effective electron mass, and the shape and size of the charge distribution determine the oscillation frequency. This collective oscillation of the electrons in the spherical metallic nanoparticle is called the dipole plasmon resonance of the particle. To relate the dipole plasmon frequency of a metal nanoparticle to the dielectric constant, interaction of light with a spherical particle of radius $a$ that is much smaller than the wavelength of light is considered. In this scheme, the electric field of the light can be assumed as constant, called quasistatic approximation. Using the wavelength-dependent dielectric constant of the metal particle, $\varepsilon_i$, and of the surrounding medium, $\varepsilon_o$, the polarizability, $\alpha$, is given by the following:

$$\alpha = g_d a^3; \quad g_d = \frac{\varepsilon_i - \varepsilon_o}{\varepsilon_i + 2\varepsilon_o}$$

(1)

As a radiating dipole, the particle contributes to extinction and Rayleigh scattering by the sphere (Mie theory states extinction = scattering + absorption). The extinction and scattering efficiencies, $Q_{\text{ext}}$ and $Q_{\text{sca}}$, are given by the following with $x = 2\pi a(\varepsilon_o)^{1/2}/\lambda$.

$$Q_{\text{ext}} = 4x Im(g_d)$$

(2)

$$Q_{\text{sca}} = \frac{8}{3} x^4 |g_d|^2$$

(3)

The efficiency is the ratio of the cross-section to the geometrical cross-section ($\pi a^2$). The scattering and absorption cross-sections, $C_{\text{sca}}$ and $C_{\text{abs}}$, are given by the following.

$$C_{\text{sca}} = \frac{8\pi}{3} k^4 a^6 |g_d|^2$$

(4)

$$C_{\text{abs}} = 4\pi ka^3 Im|g_d|$$

(5)
It can be seen from the expression of $g_d$ that the resonant enhancement occurs when $|\varepsilon_i + 2\varepsilon_o|$ is minimum, that is, $Re[\varepsilon_i(w)] = -2\varepsilon_o$ (Frohlich condition). At this condition, both scattering and absorption are highly enhanced. Moreover, for small particles ($a << \lambda$), absorption dominates over scattering whereas scattering dominates for larger particles. In the latter case, which most relates to fabricated metallic nanostructures, strongly enhanced $E$-field forms due to scattering resonance.

1.2.2 Emitter near metal nanostructures

We have seen in the previous chapter that strong $E$-field can be concentrated by metal nanoparticles at resonant conditions. Such LSPRs can also couple to the $E$-field emitted by materials in the vicinity of the metal nanostructures, leading to increase in the localized density of states (LDOS) and thereby strong modification of the radiative and nonradiative decay properties of the emitter\textsuperscript{16,17}. The two systems will interact with each other and the optical properties of the emitter can be manipulated\textsuperscript{11}.

Let us consider an emitter placed in a cavity. Depending on the parameters of the cavity such as dimensions, shape, and composition, certain electromagnetic modes will be supported. Thus, the cavity will allow only those final states as photons' decay channels. For example, the DOS will be maximum at the LSPR wavelength for an emitter placed close to a metal nanoparticle\textsuperscript{12}. An important concept to understand regarding how decay rate of an emitter is modified by the presence of a cavity is Purcell effect\textsuperscript{13,17}, which describes an enhancement of spontaneous emission rate of atoms resonant in a cavity. Purcell factor is a parameter describing the Purcell effect, important in judging the
effectiveness of light-matter interaction by quantifying the dissipation of energy inside the cavity. The Purcell factor is given by the following:

\[ F_P = \frac{\gamma_{\text{cav}}}{\gamma_{\text{free}}} = \frac{3}{4\pi^2} Q \left( \frac{\lambda^3}{n^3 V} \right) \] (6)

where \( \frac{\lambda}{n} \) is the wavelength of light inside the cavity with refractive index, \( n \), \( Q \) is the quality factor, and \( V \) is the mode volume of the cavity. It is the ratio of the decay rate of the emitter in the cavity, \( \gamma_{\text{cav}} \), to that in free space, \( \gamma_{\text{free}} \). Thus, when \( F_P > 1 \) the emission, or spontaneous decay rate, is increased whereas otherwise the cavity limits the emission. Quality factor describes the spectral mode energy density and is given by \( w/\Delta w \), where \( w \) is the center frequency (resonant) and \( \Delta w \) is the full-width half-maximum (FWHM) of the Lorentzian peak profile. Physically, it describes the energy loss relative to the stored energy in the cavity per oscillation cycle, or how damped the system is. Mode volume, \( V \), describes the spatial confinement of light in the cavity. It is calculated by the ratio of the total energy of the SP mode divided by the energy density at the position of highest field\(^1,15\). Plasmonic structures, or cavities, without high quality factors can still induce a strong enhancement of the decay rate in the emitters given their mode volume is highly reduced. This is achieved as the plasmonic structures confine \( E \)-field into subwavelength volumes, modifying the mode volume as given by \( \frac{\lambda^3}{n^3 V} \).

Similarly, the fluorescence of the emitter is modified by its optical environment\(^18,19\), which leads to changes in the frequency-dependent spontaneous emission rate\(^12,13\). When in resonance with LSP, the emission and absorption rate is
enhanced, also called Surface Enhanced Fluorescence (SEF)\textsuperscript{19,20}. In SEF, the emitter’s absorption enhances due to in-coupling and excitation rate increase. The emitter’s radiative decay rate is also enhanced due to strong local field from the metal nanostructures. For example, for a dye molecule, the fluorescence enhancement, $F_{\text{SEF}}$, of the detected signal is given by the following.

$$F_{\text{SEF}} = \left( \frac{\eta}{\eta_o} \right) \left( \frac{\Gamma_{\text{exc}}}{\Gamma_{\text{exc}}} \right) \approx \left( \frac{\eta}{\eta_o} \right) \left| \frac{u \cdot E_{\text{loc}}}{|u \cdot E_o|^2} \right|^2$$

(6)

Here, $E_o$ is incident $E$-field, $E_{\text{loc}}$ is local $E$-field at the molecule position, $\eta$ and $\eta_o$ is the quantum efficiency of the molecule\textsuperscript{14} near and far from the nanostructure, respectively, and $u$ is the transition dipole moment. The quantum efficiency is defined as follows.

$$\eta = \frac{\Gamma_r}{\Gamma} = \frac{\Gamma_r}{\Gamma_r + \Gamma_{\text{nr}}}$$

(7)

It is the ratio between the radiative decay rate, $\Gamma_r$, and the total decay rate of the molecule, $\Gamma$, which is the sum of the radiative and nonradiative decay rates, $\Gamma_{\text{nr}}$. The nonradiative decay rate reflects the absorption and intrinsic losses of the metal nanostructures. In a hot spot where $E_{\text{loc}}$ is much larger than $E_o$, eq. 6 suggests strongly enhanced fluorescence. However, the highest fluorescence enhancement is obtained when both ($\eta/\eta_o$) and $E_{\text{loc}}$ are amplified.
References


Chapter 2. Study and optimization of metal bowtie and bowtie array as plasmonic nanocavity


2.1 Motivation: Why study a bowtie?

We have seen in the previous chapter that metallic nanocavity which can sustain localized surface plasmon resonance (LSPR) can focus light into extremely small volume without diffraction limit. Along with the ease of integration into devices, 2-D thin-metal nanocavity was chosen to study the plasmonic effect in emitters. Among the nanocavity designs, a bowtie structure consisting of two coupled thin-film metal triangles was chosen as plasmonic metallic nanocavity for the study of light-matter interaction in the materials to be discussed later. In a bowtie nano-resonator, the paired metal triangles build up charges at the apexes (Fig. 2.1b), analogous to a capacitor due to the lightening rod effect, leading to very strong near-field confinement compared to a single triangle (Fig. 2.1c). It has also been shown to sustain strong LSP modes in comparison to other geometries such as single rod or coupled rods$^{1-3,13}$. Therefore, it will be beneficial if we can incorporate the bowtie structures, with right geometry and design, into a material system in order to activate the LSPRs and thus study how the light behaves in such coupled system.
Recently, experimental studies and calculation of single metal bowtie have been reported, suggesting that greatly enhanced absorption and an increased radiative emission rate lead to enhancement of the intrinsic quantum efficiency of the bowtie\(^2,8,12,13\). Figure 2.2 shows the numerical simulations of a single gold bowtie nanoantenna. Extinction efficiency spectra calculated for different bowtie gap separations show that, in polarization along the bowtie axis, the LSPR of a bowtie redshifts as the gap separation decreases. This is contrary to the case where polarization is perpendicular to the bowtie axis (higher energy plasmon resonance), where the redshift is absent. These lower and higher energy plasmon resonances are characteristics of a bowtie as a single-particle and as a dimer, respectively.
Figure 2.2 | a-b, $E$-field distribution at the LSPR frequency for incident light polarized along (a) and perpendicular (b) to the bowtie axis ($g = 30$ nm). c, Extinction spectra of the bowtie nanoantenna for polarization parallel (solid curves) and perpendicular (dotted curve) to the bowtie axis for different gaps. Reprinted with permission from ref. 8. © 2014, Springer Science+Business Media New York

2.2 Background: More than a single bowtie

When the bowties are periodically patterned into a 2-D array, the plasmonic near-fields of individual bowties interact with neighboring bowties leading to collective LSP resonances from this 2-D plasmonic crystal. Coherent coupling between the bowtie’s LSPs and the lattice diffraction modes produces new resonances with linewidths much
narrower than that of a single bowtie. This is explained by Wood anomaly arising from the diffraction condition of the pattern.

**Figure 2.3** | **a-b**, Calculated extinction efficiencies from Au bowtie arrays under parallel polarization, with varying horizontal pitch distance (a) and the vertical pitch distance (b). **c**, Electric field distribution at the LSPR frequency for the chosen bowtie array (both pitch periods of 525 nm, gap of 30 nm). *Reprinted with permission from ref. 8. © 2014, Springer Science+Business Media New York*

Although numerical simulation of LSPR in metal bowtie array excited in a single polarization has been reported, more systematic studies can be performed including experimental investigation. In this chapter, thorough understanding of LSPR in bowtie arrays will be demonstrated through experiments and the results will be corroborated by numerical calculations. By changing the design on bowtie arrays as well as polarization of light exciting the bowties, the spectral positions and linewidths of lattice-LSP modes will be modified over a broad optical range. This will enable selective, controllable modification of emission characteristics of an optical emitter and serve as a powerful method to tailor the light-matter interaction in the coupled system of bowtie array and the emitter.
2.3 Methods

2.3.1 Device fabrication

For nanosphere lithography, polystyrene (PS) beads with 350 nm diameter were dispersed on silicon substrate. 5 nm SiO2 interlayer was deposited by atomic layer deposition (ALD) followed by deposition of 30 nm-thick silver by e-beam evaporator (Lesker PVD 75). The PS beads were lifted off by dissolving in CH2Cl2 with sonication for 1 min. For etching of PS beads, oxygen plasma was used.

For electron-beam lithography, a single layer of PMMA A2 950 e-beam resist was spincoated and the bowties were patterned on silicon or SiO2/Si substrate, followed by the deposition of thin film (30-60 nm) Ag or Au by e-beam evaporator.

2.3.2 Experimental setup

Reflectance was measured by exciting the sample with a white light source in our home-built optical microscopy setup with a 60X (0.7 NA) objective. The samples were loaded in an optical microscopy cryostat (Janis ST-500) and cooled to 77 K with liquid nitrogen.

2.3.3 Numerical calculation

Three-dimensional finite-difference time-domain (FDTD) simulations were performed via Lumerical software package.
2.4 Results and discussion

2.4.1 Optimization of bowtie fabrication

Initially, bowties were patterned by nanosphere lithography, which utilizes the voids formed between the close-packed polymer beads to make triangular patterns\(^9\). Polystyrene nanospheres were dispersed on silicon substrate followed by 30 nm-thick Ag and 5 nm SiO\(_2\) interlayer deposition by e-beam evaporation and atomic layer deposition (ALD), respectively (Methods and Fig. 2.4). The separation between tips of the triangles was 200 nm (Fig. 2.3e).

![Figure 2.4](image)

**Figure 2.4** | a, Schematic of metal-dielectric bowties on silicon substrate. b, Diagram of nanosphere lithography. Reprinted with permission from ref. 9. © 1995, American Vacuum Society c, SEM image of PS nanosphere dispersed on silicon substrate. d-e, SEM images of silver-SiO\(_2\) bowties made by nanosphere lithography.
In order to achieve concentration of $E$-field inside the bowtie gap from the lightning rod effect, the gaps between the bowties needed to be much closer, around a few tens of nanometers. Thus, to achieve smaller gap separation between the triangles, oxygen plasma was utilized to melt the surface of the PS nanospheres and fill in the voids. Resulting bowtie structures following the SiO$_2$ interlayer and metal deposition shows much closer gap of 100 nm (Fig. 2.5a,b).

![Figure 2.5](image)

**Figure 2.5** | **a-b**, SEM images of bowtie structures after O$_2$ plasma etching of the PS nanospheres and deposition of metal (30 nm Au) and interlayer oxide (5 nm SiO$_2$).

Nanosphere lithography has a few limitations; metals thicker than the diameter of the nanospheres cannot be deposited due to difficulty in lift-off. This limits the study of thickness-dependent surface plasmon (SP) mode. Usage of larger diameter nanospheres, however, increases the gap separation. Also, the triangles will always have rounded tips that result from melting of the PS beads. In order to realize high concentration of $E$-field inside the bowtie gap, the tips need to be sharper. Moreover, there may be residue from the polymer beads even after a careful lift-off. To overcome these limitations, more
controllable method, electron beam lithography (EBL), was chosen to fabricate metal bowties.

For optimization of bowtie patterns via EBL, various parameters and conditions relating to the lithography process were tested. After trial and error, the beam current was fixed at 500 uC/cm² and the exposure time was varied in a range to optimize the shape of the bowties. Figure 2.6 shows the SEM images of underexposed, overexposed, and optimized bowtie shape.

![Figure 2.6](image)

**Figure 2.6** | Schematic of bowtie array with gap separation, g, and side length, s. SEM example image of an underexposed (a), overexposed (b), and optimized (c) silver bowtie.

### 2.4.2 Plasmon resonances in bowtie array

50 nm-thick silver bowtie arrays with varying geometrical factors were patterned on SiO₂/Si substrate via electron-beam lithography (Methods and Fig. 2.7a). Silver was used due to its strong plasmonic resonances as well as relatively low dissipation in the visible frequency range. In order to study the plasmon resonances of the bowtie array,
numerical calculations were carried out by finite-difference time-domain (FDTD) method (Methods). The calculated extinction cross-sections of a single bowtie (g = 20 nm, s = 100 nm) on a 300 nm SiO$_2$/Si substrate for both TE ($E$-field parallel to the bowtie axis) and TM ($E$-field perpendicular to the bowtie axis) polarizations are shown in Fig. 2.7b. The TE polarized LSP mode was obtained at 2.16 eV while the TM polarized LSP mode was located at a higher energy (2.5 eV) due to a stronger restoring force of the charge oscillation. Both LSP modes are very broad with ~0.4 eV linewidth, spanning most of the visible region of the electromagnetic spectrum. However, when the bowties are periodically patterned into a 2-D array, a new type of lattice-coupled LSP (lattice-LSP) resonances is produced with narrow resonance linewidths$^{4,6,7,10}$. As expected from the discussion in Background section, this is due to the coherent coupling between the bowtie’s LSPs and the grating modes created by periodic array. For example, the calculated quality factor ($Q$) of a lattice-LSP resonance at 1.9 eV (Fig. 2.7c, green curve) is 21, in comparison to a $Q$ of 6 for a single-bowtie LSP resonance (TE, Fig. 2.7b). Furthermore, mode tunability of lattice-LSP resonances improves significantly compared to single bowtie LSPs, as represented in the calculated $E$-field enhancement profiles in Fig. 2.7c. Spatial $E$-field profiles (insets in Fig. 2.7b,c) show that the plasmonic fields are mostly concentrated between the gaps or tips of the bowties with small optical mode volumes.
Polarization-dependent reflectance measurements were performed on a bowtie array in order to resolve the lattice-LSP modes. The differential reflectance ($\Delta R/R = (R_{\text{sample}} - R_{\text{background}})/R_{\text{background}}$) spectra measured in TE and TM polarizations show two broad dips for each polarization (Fig. 2.8a, solid curves). These are also in good agreement with the calculated differential reflectance (Fig. 2.8a, open circles). Comparison of the calculated $E$-field enhancement profiles and the corresponding $\Delta R/R$ profiles reveals that the lattice-LSP modes, which correspond to the peaks of the $E$-field enhancement spectra, are near the dips of $\Delta R/R$ (Fig. 2.8a,b). Thus, the lattice-LSP modes of bowtie arrays can be related to dips in the reflectance spectra. More comprehensive understanding of how the dips in $\Delta R/R$ relate to $E$-field enhancement is provided in Fig. 2.9. Also, similar to the calculated extinction spectra of a single bowtie (Fig. 2.7b), the
modes for TM polarization are located at higher energies compared to TE due to a stronger restoring force of the charge oscillation in the direction of the bowtie axis.

![Diagram](image_url)

**Figure 2.8 | Polarization-dependent reflection spectra of the bowtie resonator array.**

- **a**, Normalized differential reflectivity (ΔR/R) spectra of experimental and calculated lattice-LSP modes in TE and TM polarizations for bowtie array on SiO₂/Si substrate. Geometrical factors: s = 100 nm, g = 20 nm, p = (500 nm, 300 nm).
- **b**, Average E-field enhancements for bowtie array on SiO₂/Si calculated for the total area of the unit cell. Reprinted with permission from ref. 10. © 2015, American Chemical Society.

Figure 2.9 shows the relationship between E-field enhancement and reflectance. The calculated E-field enhancement in bowtie arrays corresponds to the location of lattice-LSP modes (red curves). Since lattice-LSP modes are a coupled system between individual bowtie LSPs and lattice modes, the reflection spectra are affected by both the superradiant LSP dipole modes and subradiant lattice (grating) modes due to radiation
progress in the plane of the bowtie array for normal excitation. In addition, a 300 nm thick SiO$_2$/Si substrate produces a broad reflection signal as a background (Fig. 2.9a, green curve). Therefore, the reflection spectra of the bowtie arrays are mainly composed of all these factors: the broad reflectance of 300 nm thick SiO$_2$/Si substrate, the backscattered signal from superradiant LSP dipole mode, and surface-propagating signals from the lattice modes. These signals interfere and result in the complex reflectance and $\Delta R/R$ spectra (Fig. 2.9, blue and black curves). The peaks of $E$-field enhancement spectra are located near the dips of the reflectance spectra. The lattice-LSP mode positions are thus near the dips in the reflection spectra, which is consistent in all four samples with different pitch values.
Figure 2.9 | Calculated average $E$-field enhancement, reflectance (ratio of reflected light to incident light intensity), and $\Delta R/R$ spectra for the bowtie arrays on SiO$_2$/Si substrate with different pitch values (a-d). $\Delta R/R$ shows enhanced features due to subtraction of the background. Bowtie geometrical factors: $g = 10$ nm, $h = 50$ nm, $s = 100$ nm. Reprinted with permission from ref. 10. © 2015, American Chemical Society.
In order to investigate how the lattice-LSP modes change as the distance between bowties are varied, pitch-variation study was performed. Five bowtie arrays with different pitches (Fig. 2.10b, A-E) were fabricated on a SiO$_2$/Si substrate under same lithography conditions. The reflectance spectra show that for both polarizations, the dip, or mode as the two are closely related (Fig. 2.8, 2.9), is close to a single dip at the largest pitch (blue curves, sample E). When bowties are separated far away from each other, they can be thought of as a single, uncoupled bowtie. Thus, this is consistent with the result in Fig. 2.7b which shows a single broad mode for each polarization. Also, note that the modes are generally located at higher energies for TM polarization, consistent with Fig. 2.8. As the pitch decreases and bowties are brought closer to each other, the positions of the two dips change, with increasing separation between the dips (Fig. 2.10c,d).
Figure 2.10 | Pitch variation study of bowtie arrays. a, Incident light polarization (TE and TM) with respect to the bowtie axis direction. Table shows the pitch \((p_x, p_y)\) values for the 5 bowtie arrays (A-F). b, SEM images of the 5 bowtie arrays with pitch values shown in (a). c-d, Experimental reflectance \((\Delta R/R)\) for the 5 bowtie arrays measured in TE and TM polarization. Bowtie geometrical factors: \(g = 20\) nm, \(s = 100\) nm.

The \(E\)-field enhancement spectra for 10 bowtie arrays with varying pitch in TE polarization were calculated. The calculated extinction cross-section of a single bowtie \((g = 20\) nm, \(s = 100\) nm) on a 300 nm SiO\(_2\)/Si substrate for TE polarization shows a broad LSP mode centered at 2.16 eV (dotted gray curve), which is compared to the calculated
lattice-LSP modes (solid curves). The $E$-field enhancements are calculated from the center of the bowtie’s gaps. It is shown that the linewidth of lattice-LSP modes are sharper than that of single bowtie LSP resonance.

**Figure 2.11** | Calculated $E$-field enhancements of Ag bowtie arrays with varying pitch ($p$) values (solid curves), compared with the calculated extinction cross-section of a single bowtie (dotted curve) for TE polarization excitation. Bowtie geometry: gap separation ($g$) = 20 nm, thickness of the metal deposition ($h$) = 50 nm, side length of a triangle ($s$) = 100 nm. *Reprinted with permission from ref. 10. © 2015, American Chemical Society.*

In order to study how the lattice-LSP mode depends on the gap separation, 4 bowtie arrays with varying gap were fabricated on the same substrate under the same lithography condition. Figure 2.12a shows the diagram of bowtie arrays patterned in both horizontal and vertical direction to avoid any difference in the initial excitation intensity due to the linear polarizer. Each of the 4 bowtie arrays was patterned in such way. For TE polarization (Fig. 2.12c), as gap separation increases from 20 nm to 80 nm, the lattice-LSP modes blueshift. This can be explained by the separation of field enhancement locations, or tips, in a bowtie. When a bowtie is excited with incident light polarized along the bowtie axis, charge separation and attractive force is induced,
lowering the plasmon energy. However, when the gap increases in a bowtie, dipolar coupling (a near-field effect $\sim 1/r^3$) decreases and the aforementioned effect starts to vanish until the two triangles effectively decouple. Thus, increasing the gap leads to overall blueshift of the lattice-LSP modes. Indeed, the spectra for 60 nm and 80 nm gap show smaller redshift compared to the redshift shown between 40 nm and 60 nm, indicating that the decrease in the dipolar coupling in the latter is being saturated.

Figure 2.12 | Bowtie gap variation study. a, Schematic of bowtie array patterns in horizontal and vertical direction. b, SEM images of the 4 bowtie arrays with varying gap separation (g = 20-80 nm). c-d, Reflection measurements for the 4 bowtie arrays measured in TE (c) and TM (d) polarization. Bowtie geometrical factors: s = 100 nm, p = (500 nm, 300 nm).
2.5 Conclusion

In this chapter, localized surface plasmon resonances (LSPRs) of a periodically patterned 2-D arrays of metal bowtie nanoantennas were investigated by reflectance measurements and numerical simulations. Due to the coherent coupling between a single bowtie’s LSPs and the grating modes created by periodic array, new resonances, lattice-induced LSP resonances, emerged as a result with narrower linewidths. Strong plasmonic local field is expected due to the lattice-LSP modes. These lattice-LSP modes showed spectral tunability which spans the entire optical wavelength regime, achieved by altering geometrical design parameters such as pitch, gap separation, and triangle side length. Tailoring the resonances of plasmonic structures as demonstrated in this work will be important, when combined with an emitter material, in realizing novel optical devices including detectors, sensors, and photovoltaics.
References


Chapter 3. Photoluminescence from bulk, planar silicon coupled with silver bowtie nanocavities


3.1 Motivation

Due to limitations in device speed and performance of silicon-based electronics, silicon optoelectronics has been extensively studied to achieve ultrafast optical-data processing\(^1\)\(^-\)\(^3\). However, the biggest challenge has been to develop an efficient silicon-based light source since indirect band-gap of silicon gives rise to extremely low emission efficiency. Although light emission in quantum-confined silicon at sub-10 nm lengthscales has been demonstrated\(^4\)\(^-\)\(^7\), there are difficulties in integrating quantum structures with conventional electronics\(^8\),\(^9\). It is desirable to develop new concepts to obtain emission from silicon at lengthscales compatible with current electronic devices (20-100 nm), and therefore cannot use quantum-confine ment effects. In bulk silicon, emission from hot-carriers (non-thermalized carrier recombination) has been observed by injecting carriers at large applied bias using a scanning tunneling microscope\(^10\), but the measured quantum efficiency is extremely low because of much faster hot-carrier relaxation time (intra-band; <1 ps) in comparison to the long radiative lifetime\(^11\),\(^13\). Since the reported radiative lifetime for hot luminescence in bulk silicon is ~10 ns at the \(\Gamma\) point\(^14\), the efficiency for hot luminescence across the direct band-gap is expected to be
very poor, \( \sim 10^{-4} \) at the \( \Gamma \) point. Furthermore, as hot-carriers relax, the radiative lifetime would increase due to the involvement of phonons in emission processes, resulting in lower quantum efficiencies.

However, visible light emission from hot-carriers in “bulk” silicon can be efficient if the radiative lifetime becomes comparable with the hot-carrier relaxation time. In addition, enhanced emission from hot-carriers in silicon can enable studies of photophysics of indirect bandgap materials, which is otherwise challenging due to low emission quantum yields. Although silicon photonic crystal nanocavities have recently demonstrated enhancements up to 100, the emission was mostly generated from thermalized carriers in the near-infrared wavelength range\textsuperscript{15,16}. Thus, it will be meaningful if we demonstrate light emission at room temperature from “bulk-sized” (no quantum confinement; >30 nm) silicon integrated with a plasmonic nanocavity via Purcell enhancement effect\textsuperscript{17,18}.
3.2 Background

In this chapter, as it is closely related to my work in the photoluminescence (PL) emission from planar nanocavity-coupled bulk silicon, I will discuss our previous work on the light emission with a high quantum yield (>1%) at room temperature from “bulk-sized” silicon integrated with a plasmonic nanocavity via Purcell enhancement effect\textsuperscript{17,18,20}. We have shown that highly concentrated electromagnetic fields inside plasmon nanocavities induce phonon-assisted light emission from hot-carriers before their thermalization to the lowest energy state (near X-point) in the conduction band (Fig. 3.1a). To generate light emission from hot-carriers, we fabricated the plasmonic nanocavity on single silicon nanowires (>30 nm diameter) by depositing a 5 nm SiO\textsubscript{2} interlayer followed by a 100 nm-thick silver \(\Omega\)-shaped cavity to support surface plasmon polariton modes (Figs. 3.1b to 3.1d). Room temperature micro-photoluminescence measurements were carried out on individual nanowire devices with an Ar\textsuperscript{+} laser excitation source (2.708 eV). Bright visible light emission was observed from single-plasmonic silicon nanowires (Fig. 3.1e). Since hot-carrier emission competes with intra-band relaxation, a broad hot luminescence band is expected ranging between the laser excitation and the indirect band-gap energies in silicon. Figure 1f shows broad band hot luminescence spectra with high counts obtained from a single silicon nanowire coupled with the \(\Omega\)-shaped cavity (Si diameter, \(d = 65\) nm), while no observable photon counts were detected from 5 nm SiO\textsubscript{2} coated silicon nanowires (\(d = 60\) nm) without the silver nanocavity where the length of silicon nanowires was typically 10 \(\mu\)m. These
observations suggest that the hot-carriers emit photons through a phonon-assisted recombination process during intra-band relaxation.

Figure 3.1 | Hot luminescence from silicon coupled to a plasmon nanocavity. a, Schematic of the electronic band diagram of bulk crystalline silicon illustrating phonon-assisted hot luminescence processes before the thermalization of the carriers to the minimum of the conduction band near the X-point. b, Schematic of an Ω-shaped plasmonic nanocavity coupled silicon nanowire device. c, Scanning electron microscope (SEM) image of the fabricated device. d and e, Optical images of a single-plasmonic silicon nanowire device obtained through the glass substrate under white light (d), and a focused laser excitation (e). f, Room-temperature photoluminescence spectra from single silicon nanowire device coupled with Ω-shaped (magenta) cavity (100 nm Ag film) having the silicon nanowire diameter, d, of 65 nm. Spectrum of a 5 nm SiO₂ coated single silicon nanowire without a plasmonic cavity (blue; d = 60 nm) is also shown, with no observable photon counts without the plasmonic cavity. Reprinted with permission from ref. 20. © 2013, Macmillan Publishers Limited.
To study the corresponding electromagnetic field distribution and the nanocavity Purcell enhancement, numerical simulations were performed for the $\Omega$-shaped devices. The simulated frequency-dependent electromagnetic field intensity inside the cavity ($d = 70$ nm) correctly reproduces the resonance peaks observed in the hot luminescence spectrum (Fig. 3.2a). However, the observed photoluminescence spectrum shows more structure, which is related to the complex phonon-related carrier relaxation channels (discussed later). Simulations further reveal a curved Fabry-Pérot like plasmonic cavity mode along the Ag/SiO$_2$ interface perpendicular to the wire’s long axis, as shown in Figs. 3.2b-d calculated at 2.505, 2.342 eV, and 2.179 eV. The unique structure of $\Omega$-shaped cavity leads to complex mode profiles due to the coupling of the cavity modes with the “rim” type modes (producing lightning rod effect) leading to mode asymmetries$^{19}$. For this highly confined plasmonic cavity modes, the quality factor was estimated to be $\sim$30 along with an ultrasmall mode volume of $\lambda^3/10^4$ ($\lambda$, free space wavelength), giving rise to a large radiative rate enhancement with Purcell factor $>10^3$ at 2.505 eV.
Figure 3.2 | Resonantly enhanced hot luminescence in plasmonic silicon. a, Room-temperature photoluminescence spectrum from a single silicon nanowire coupled with Ω-shaped plasmon nanocavity ($d = 70 \text{ nm}$). The calculated frequency-dependent electromagnetic field intensity inside the cavity reproduces the resonances correctly. b to d, Calculated electric field profile at cavity resonance energies of 2.51 eV (b), 2.34 eV (c), and 2.18 eV labeled as A, B, and C on the spectrum, showing the formation of a curved Fabry-Pérot like plasmonic cavity modes. The white outlines refer to the Si-SiO$_2$-Ag interfaces of the Ω-shaped cavity structure. Reprinted with permission from ref. 20. © 2013, Macmillan Publishers Limited.
3.3 Methods

3.3.1 Device fabrication

Si substrate was etched by O$_2$ plasma to remove the native oxide. A 5 nm SiO$_2$ interlayer was deposited by atomic layer deposition (ALD) (Cambridge Nanotech) by alternating O$_3$, 3-Aminopropyltriethoxysilane (APTES), and H$_2$O pulses at 150 °C. A single layer of PMMA e-beam resist (A2 950) was spincoated and the bowties were patterned on the substrate by electron-beam lithography, followed by the deposition of 30 nm-thick Ag by an e-beam evaporator (Lesker PVD 75).

3.3.2 Experimental setup

Ag bowtie nanocavities patterned on silicon substrate were optically excited through 1 mm-thick glass substrate using a home-built microscope equipped with a 60×, 0.7 NA objective (Nikon), having a spatial detection resolution of 500 nm. A continuous wave argon-ion laser (Coherent) tuned at a wavelength of 457.9 nm was focused to pump the bowtie structures with the beam spot size of 2 µm on the sample with an excitation power of \(~250\) kW/cm$^2$. Photoluminescence spectra were collected using a spectrometer (Acton-SP 500i) and a cooled charge coupled device (CCD) (Pixis 2K, Princeton Instruments) with a spectral resolution of 0.5 nm.

3.3.3 Numerical calculation

Three-dimensional finite-difference time-domain (FDTD) simulations were performed via Lumerical software package.
3.4 Results and discussion

PL was measured from bulk silicon substrate with hexagonal array of triangles made of gold and oxide interlayer patterned by nanosphere lithography. The sample was excited by 458 nm wavelength laser at room temperature with same power (Methods), in both Au bowtie area and Au thin film area, as the sample contained both types of areas. Whereas Au/oxide film on Si substrate shows very low counts, the Au bowtie/oxide on Si shows measurable PL, indicating the plasmonically enhanced emission from Si. Also, Au bowties fabricated without the oxide interlayer does not show PL, verifying that the measured emission is coming from modes that are formed in the oxide layer between Au and Si substrate. Mode is confined mostly in the oxide interlayer, acting as an energy reservoir and preventing rapid quenching of excitons through dissipative metals.
Figure 3.3 | a-b, SEM images of 30 nm gold bowtie structures fabricated by nanosphere lithography and oxygen plasma etching. c, Room temperature PL spectra of gold bowtie on bulk silicon compared with 30 nm thick gold film.

In order to test the generality of visible hot luminescence in plasmonically-coupled silicon, we performed experiments on planar silicon patterned with Ag bowtie structures (Fig. 3.4a and Methods). Silver was used due to its strong plasmonic resonances as well as relatively low dissipation in the visible frequency range. These devices displayed a similar spectrum as that of a plasmonic Si nanowires with hot luminescence bands at 2.51 and 2.34 eV (Fig. 3.4a). Simulations reveal strongly enhanced fields are formed between the tips of both triangles of the bowties (Fig. 3.4b),
which penetrate ~80 nm into the underlying Si substrate (Fig. 3.4c). However, the quality factors of the bowtie resonance modes are relatively low along with imperfect matching to the high-density phonon modes, resulting in low emission intensity.

**Figure 3.4 | Hot luminescence from planar silicon coupled with bowtie plasmon nanocavity.** a, Room-temperature photoluminescence spectrum showing the visible hot luminescence collected from 4 bowtie plasmon nanocavities on planar silicon substrate. Calculated spectrum of energy-dependent field intensity is also shown. Inset; SEM image of the device showing planar single crystalline silicon coupled with Ag bowtie plasmon nanocavities. Scale bar, 200 nm. b-c, Calculated electric field profiles in the bowtie device. cross-sectional view (b) and top view (c) at a resonance energy of 2.32 eV. The bowtie structure is outlined in white. Reprinted with permission from ref. 20. © 2013, Macmillan Publishers Limited.
3.5 Conclusion

In this chapter, utilizing the metallic bowtie arrays as a plasmonic cavities to obtain increased radiative decay rate of a planar, bulk silicon was demonstrated. High concentration of $E$-field in the bowtie array led to increase in radiative decay rate, which led to the measurable photoluminescence in the bulk silicon. It is done by the interplay of three (quasi) particle systems, carriers, phonons and cavity plasmons, which provide an interesting test bed to study such complex processes. The ability to obtain visible light emission from silicon devices which are compatible with lengthscales in current electronics (>20 nm) is important for possible integration with active Si-based photonics. Our method offers a way to obtain light emission from any indirect bandgap semiconductor and will be useful for the fabrication of monolithic devices utilizing optics for ultrafast data processing.
References

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Chapter 4. Fano resonance and spectrally modified photoluminescence enhancement in monolayer MoS$_2$ coupled with bowtie plasmonic nanoantenna array


4.1 Material background

MoS$_2$ is a transition-metal dichalcogenide semiconductor (TMDS) in space group P6$_3$/mmc, made of one Molybdenum layer between two Sulfur layers in a hexagonal form (Fig. 4.1a)$^{1,2,27,56}$. Each layer is weakly bound to the other layers by van der Waals force, whereas atoms in a layer are strongly bound with each other by ionic-covalent bonds. Also, strong spin-orbit coupling resulting from the d-orbitals of transition-metals induces a valence band splitting at K corresponding to the direct energy band gap of bulk MoS$_2$ (Fig. 4.1b)$^{27,56}$. However, as thickness of MoS$_2$ decreases, optical and electronic properties change drastically due to the decreased interlayer interaction. Especially in monolayer, the absence of interlayer interaction results in indirect-to-direct band-gap transition in MoS$_2$, leading it to become a direct band-gap semiconductor (Fig. 4.1b)$^{27}$. In monolayer MoS$_2$, the direct bandgap is at K point around 1.9 eV with each upper and lower valence band corresponding to A and B exciton, respectively.
Note that a bulk MoS$_2$ has an inversion center at the midpoint of a unit cell (Fig. 4.1a). In a monolayer, however, the inversion symmetry is absent. Without the inversion symmetry, the spin degeneracy is lifted and spins split, or are paired, into each valence band leading to an even bigger band splitting of $\sim 150$ meV (ref. 2,27,56). The consequence of the lack of inversion symmetry in monolayer MoS$_2$ will be further discussed in chapter 5.

![Figure 4.1](image)

**Figure 4.1** | **a**, Atomic structure of TMDS. **b**, Calculated electronic band structures of bulk, bilayer, and monolayer MoS$_2$. *Reprinted with permission from ref. 46. © 2011, American Physical Society.*

Since bulk MoS$_2$ is an indirect gap material, bandgap photoluminescence (PL) is a phonon-assisted process with very low quantum yield. However, much stronger PL is
expected from monolayer under such direct band gap transition. PL studies show strong PL from monolayer and very weak PL from the few layers of MoS\(_2\) (Fig. 4.2).

**Figure 4.2 | a-b**, Optical (a) and photoluminescence (b) images of suspended monolayer and few layer MoS\(_2\) on Si with etched holes. **c**, PL spectra of monolayer and bilayer MoS\(_2\). **d**, Normalized PL of 1-6 layer MoS\(_2\). *Reprinted with permission from ref. 1. © 2010, The American Physical Society*

In Raman spectrum, MoS\(_2\) shows two characteristic peaks around 380 cm\(^{-1}\) and 408 cm\(^{-1}\), which are in-plane mode (E\(_{2g}^1\)) and out-of-plane mode (A\(_{1g}\)), respectively, following the relative displacement between Mo and S atoms shown in Fig. 4.3b. The separation between the two modes increases as the number of layers increases, with E\(_{2g}^1\) mode redshifting and A\(_{1g}\) mode blueshifting in frequency. Within a classical model for
coupled harmonic oscillators, as additional layers are added from a single layer to bulk, vibration of these modes should become harder due to increase in the restoring force between the atoms coming from the stronger interlayer interactions\textsuperscript{3}. Although the blueshift in the frequency of the $A_{1g}$ mode as thickness increases is consistent with this, the $E_{2g}^{1}$ mode exhibits opposite behavior which may reflect the influence of stacking-induced structural changes. Alternatively, the anomalous behavior of $E_{2g}^{1}$ may be attributed to long-range Coulombic interlayer interactions\textsuperscript{3}.

Figure 4.3 | a, Raman spectra of thin and bulk MoS\textsubscript{2} films. b, Two Raman active modes ($E_{2g}^{1}$ and $A_{1g}$) in the unit cell of MoS\textsubscript{2} shown along [1000] direction. Reprinted with permission from ref. 3. © 2010, American Chemical Society.
4.2 Motivation

Thin-layer systems can be manipulated by integration with other low-dimensional systems\(^4\)\(^-\)\(^8\). However, their applications in photonic devices can be limited due to large nonradiative decay rates and small energy difference between different valleys with direct and indirect energy gaps, leading to extremely low photoluminescence (PL) quantum efficiency. Although increase in PL quantum efficiency of MoS\(_2\) has been achieved via chemical functionalization\(^1\)\(^5\) and integration with photonic crystal cavities\(^1\)\(^6\), the reported enhancements have been low and also requiring large device footprints. Therefore, in addition to achieving large enhancements in PL, it would also be desirable if the light-matter coupling in these systems can be tuned from weak to strong coupling limit, to enable a whole new suite of optoelectronic applications with precisely tailored responses.

In this chapter, significant tailoring of light-matter interactions achieved by a unique 2-D exciton-plasmon system composed of a monolayer MoS\(_2\) integrated with a silver nano-bowtie array will be discussed. Periodic patterning of bowties into an array leads to LSP resonance linewidths much narrower than that of a single bowtie because of Rayleigh-Wood anomaly arising from the diffraction condition of the pattern\(^2\)\(^0\),\(^2\)\(^2\)\(-\)\(^2\)\(^4\). By changing the geometrical parameters of the bowtie array, the spectral positions and linewidths of lattice-coupled LSP (lattice-LSP) modes can be modified over a broad optical range. Coupling of MoS\(_2\) with the lattice-LSP mode leads to largely enhanced, tunable PL and Raman scattering in MoS\(_2\) at room temperature. At low temperatures, as much stronger exciton-plasmon coupling is achieved due to the lower dephasing rate of
excitons, Fano resonances emerge in the reflection spectra. These results demonstrate tunable optical modulation of the 2-D active medium induced by the plasmonic nanoresonators, leading to improvements in emission intensity and new optical properties based on interference between different excitation pathways of the exciton-plasmon system.
4.3 Methods

4.3.1 Device fabrication

Monolayers of MoS$_2$ were grown on SiO$_2$/Si substrate (300 nm thermally grown SiO$_2$) via chemical vapor deposition as reported earlier$^{25,26}$. Bowtie structures were patterned on the PMMA-coated, as-grown MoS$_2$ substrate by Elionix ELS-7500EX e-beam writer. The bowtie patterns were developed by 1:3 MIBK:IPA solution and deposited with 50 nm silver by Lesker PVD75 e-beam evaporator. The sample was then lifted off in acetone.

4.3.2 Experimental setup

Photoluminescence and Raman measurements were performed on the NTEGRA Spectra Probe system equipped with a 0.7 NA objective (~400 nm spatial resolution). A continuous wave 532 nm wavelength laser focused to a spot size of 1 $\mu$m with an excitation power of 0.16 mW was used for all optical measurements. For reflectance measurements, the sample was excited by a white light source in our home-built optical microscopy setup with a 60X (0.7 NA) objective. The samples were loaded in an optical microscopy cryostat (Janis ST-500) and cooled to 77 K with liquid nitrogen.

4.3.3 Numerical calculation

Three-dimensional finite-difference time-domain (FDTD) simulations were performed to understand the optical properties of the Ag bowtie plasmonic nanoantenna structures on the SiO$_2$/Si substrate with and without MoS$_2$. 
4.4 Results and discussion

Initially, mono- to a few layer MoS$_2$ sample was prepared by exfoliation from a bulk MoS$_2$ onto SiO$_2$ substrate. Raman and photoluminescence (PL) measurements were performed at room temperature using the 532 nm line of an Argon ion laser focused to a spot size of 1 µm (see Methods). The Raman spectrum of the bare MoS$_2$ sample displays two modes around 400 cm$^{-1}$ corresponding to the in-plane ($E_{12g}^1$) and out-of-plane ($A_{1g}$) modes, as shown in Fig. 4.4, that are fingerprints of a monolayer of MoS$_2$ (Ch. 4.1 and ref. 3). Also, the progression of the two modes as thickness increases, e.g. separation between the two modes increases as the number of layers in MoS$_2$ increases, is also consistent with previous studies. As thickness decreases, $A_{1g}$ mode decreases and $E_{12g}^1$ mode increases in frequency. The origins of these have been identified as the influence of interlayer interaction on the restoring force of atoms and the increase of dielectric screening of long-range Coulomb interactions$^{48}$. 
Figure 4.4 | MoS$_2$ on SiO$_2$/Si substrate prepared by mechanical exfoliation. a-c, Optical microscope image (a), Raman spectra (b), and shifted Raman spectra for easy comparison (c) for monolayer, bilayer, and bulk MoS$_2$.

With the exfoliated sample, the photoluminescence was measured from the monolayer to bulk MoS$_2$. Figure 4.5 shows higher intensity A-exciton peak at $\sim$1.85 eV and a shoulder-like B-exciton peak at $\sim$2.0 eV for monolayer. These two peaks that arise from the direct band gap and strong spin-orbit coupling in monolayer MoS$_2$ (ref. 1,11). Using 532 nm laser, the PL spectra of exfoliated monolayer to bulk MoS$_2$ sample were measured as shown in Fig. 4.5b. Monolayer shows the highest PL emission despite the reduced material, indicating highest quantum efficiency (Fig. 4.2).
Figure 4.5 | a, Normalized PL emission from monolayer MoS$_2$ under excitation by 458 nm and 532 nm laser. b, PL emission spectra from monolayer, bilayer, and bulk MoS$_2$.

MoS$_2$ flakes were grown on SiO$_2$/Si substrates by chemical vapor deposition (CVD)$^{25,26}$. Experiments following the sample characterization were carried out with CVD-grown MoS$_2$ since such large area, high-quality monolayer MoS$_2$ allows for reliable and systematic studies using metallic bowtie nanocavities. 50 nm-thick silver bowtie arrays with varying geometrical factors were patterned directly on the MoS$_2$ flakes via electron-beam lithography (see Methods and Fig. 4.6a,b). Silver was used due to its strong plasmonic resonances as well as relatively low dissipation in the visible frequency range. The Raman spectrum of the bare MoS$_2$ sample displays modes at 384 cm$^{-1}$ and 403 cm$^{-1}$ corresponding to the in-plane ($E'_{2g}$) and out-of-plane ($A_{1g}$) modes respectively (Fig. 4.6c, black curve). Similarly, PL spectrum from bare MoS$_2$ (Fig. 1d, black curve) displays peaks corresponding to A- and B-excitons at $\sim$1.85 eV and 2.0 eV, respectively. Although the PL spectrum from the monolayer of MoS$_2$ shows excitonic
features at room temperature, the emission is not strong because of the low intrinsic emission efficiency in these systems, consistent with previous studies\textsuperscript{16,28}.

However, both the Raman scattering and PL from the monolayer MoS\(_2\) integrated with silver bowtie array (refer to the figure captions for the bowtie geometrical factors) display enhancements of more than an order of magnitude compared to bare MoS\(_2\) (Fig. 4.6c,d, red curves). Typically, the mechanisms behind enhanced Raman scattering and PL emission are surface-enhanced Raman scattering (SERS) and surface-enhanced fluorescence (SEF) respectively, as observed in molecular systems placed in the vicinity of plasmonic nanostructures\textsuperscript{29,30}. The enhancement due to SERS is given by:

\[ R_{\text{SERS}} = \frac{|E_{\text{loc}}|^4}{|E_o|^4}, \]

where \(E_o\) is incident \(E\)-field and \(E_{\text{loc}}\) is the \(E\)-field enhanced by LSPR. The enhanced emission at room temperature is due to the local field increase at the position of the emitter arising from the lattice-LSP resonances of the bowtie array, suggesting weak coupling between the MoS\(_2\) excitons and lattice-LSP\textsuperscript{21}. 

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To understand the correlation between the lattice-LSP modes and MoS$_2$ PL and Raman scattering intensity, detailed spectroscopic characterization including polarization-dependent reflectance, PL and Raman spectra were performed on individual
constituents and coupled MoS$_2$-bowtie array system. To resolve the lattice-LSP modes, reflection spectra from the bowtie array patterned on 300 nm SiO$_2$/Si substrate were measured in TE and TM polarizations. Figure 4.7a shows good agreement between the experimental and calculated differential reflectance ($\Delta R/R = (R_{\text{sample}} - R_{\text{background}})/R_{\text{background}}$) from the bowtie array on SiO$_2$/Si substrates, which features broad modes for both polarizations (Chapter 4.7). The emission from bowtie-MoS$_2$ exhibits distinct polarization dependence (Fig. 4.7c) and is closely related to the corresponding $E$-field enhancement (Fig. 4.7b). For example, in TE polarization (red curves, Fig. 4.7b,c), the maximum $E$-field enhancement at the A-exciton energy corresponds to enhanced A-exciton emission, while in TM polarization (blue curves, Fig. 4.7b,c), strong Raman scattering intensity is consistent with the maximum $E$-field enhancement near these Raman modes. These are also confirmed in the polarization-dependent 2-D intensity scans measured at the Raman and A-exciton energies (Fig. 4.7d,e), consistent with the simulated enhancements (Fig. 4.7b).
Figure 4.7 | Polarization-dependent reflection spectra of the bowtie resonator array and emission spectra of MoS$_2$ coupled with bowtie resonator array. a, Normalized differential reflectivity ($\Delta R/R$) spectra of experimental and calculated lattice-LSP modes in TE and TM polarizations for bowtie array on SiO$_2$/Si substrate. Geometrical factors: $s$ = 100 nm, $p$ = (500 nm, 300 nm). b, Average $E$-field enhancements for bowtie array on SiO$_2$/Si calculated for the total area of the unit cell. c, Experimental emission (PL and Raman) spectra for bowtie-MoS$_2$ system. Inset: zoomed-in spectra near the Raman active region. d, Optical microscope image of bowtie arrays patterned in two orthogonal orientations on a MoS$_2$ flake. e, 2-D intensity scans measured at the Raman mode and A-exciton energies. Scanning area indicated in d. Data in e shows different polarization response for Raman (horizontally patterned bowties) and A-exciton emission (vertically patterned bowties). Reprinted with permission from ref. 10. © 2011, American Physical Society.

The effect of spectral tuning of lattice-LSP modes on modification of MoS$_2$ emission was systematically studied by varying the geometrical factors of the bowtie
array (four representative patterns are shown in Fig. 4.8a, labeled (i)-(iv)). In order to obtain the lattice-LSP mode positions and correlate them to the emission profiles, $\Delta R/R$ spectra were measured for the four patterns on SiO$_2$/Si substrates (Fig. 4.8b). The frequency-dependent emission enhancements of the monolayer MoS$_2$ integrated with these four bowtie patterns (Fig. 4.8c,d) show that the increase of the emission in the bowtie-MoS$_2$ varies up to $\sim$40X depending on the spectral positions of lattice-LSP modes. When the lattice-LSP mode of the bowtie array is in resonance with A- or B-excitons, as in pattern (iii) or (ii) respectively, the PL of the bowtie-MoS$_2$ system increases at the corresponding spectral positions (Fig. 4.8c,d). On the other hand, detuning of lattice-LSP mode and the A- or B-exciton resonance leads to only minor PL enhancement, as observed for pattern (i). In the enhancement spectra (Fig. 4.8d) obtained for these patterns, a new maximum is observed at 1.83 eV, which occurs at the previously reported trion state$^{28,31}$. Although the origin of the enhancement of the trion state in our bowtie-MoS$_2$ system is unclear, it is possible that the excitons in MoS$_2$ interact with the metal leading to charge transfer, promoting the formation of trions.
Figure 4.8 | Spectral modification of MoS$_2$ photoluminescence coupled with bowtie resonator arrays with different lattice-LSP dipole resonances at room temperature. 

a, SEM images of four bowtie-array samples with different bowtie sizes and pitch values: (i) $s = 100$ nm, $p = (400$ nm, $500$ nm) (ii) $s = 100$ nm, $p = (400$ nm, $300$ nm) (iii) $s = 100$ nm, $p = (300$ nm, $200$ nm) (iv) $s = 170$ nm, $p = (500$ nm, $800$ nm). b, $\Delta R/R$ spectra associated with the lattice-LSP modes of the four different bowtie patterns on SiO$_2$/Si substrates. c, PL spectra of bare MoS$_2$ (black) and four different patterns. d, Wavelength-dependent PL enhancements (ratios of PL obtained for bowtie-MoS$_2$ sample to PL of bare MoS$_2$) for the four patterns on monolayer MoS$_2$. Inset shows the enhancement of A-exciton emission for all four patterns. e, Normalized PL spectra of bare MoS$_2$ (black) and the four different bowtie patterns on MoS$_2$. Reprinted with permission from ref. 10. © 2011, American Physical Society.
The normalized PL spectra from the four patterns (Fig. 4.8e) clearly show the changes in spectral shapes, which depend on the lattice-LSP mode positions. This feature, known as spectrally modified SEF, is typically observed in molecular systems coupled with plasmonic structures\cite{32-35}. For spectrally modified SEF, the total fluorescence enhancement is given by, \( g_{total} = g_{ex} \cdot g_{em} \), where \( g_{ex} \) and \( g_{em} \) are the excitation and emission rate enhancements, respectively. The increase in the excitation rate is due to the increased coupling between the incident light and the emitter, arising from the enhanced local field. In this case, the excitation rate enhancement depends only on the frequency of incident light (\( \omega_i \)), and should not affect the spectral shape. Figure 4.9 shows the calculated absorption spectra for bare MoS\(_2\) before and after its integration with a bowtie array. For bare MoS\(_2\), clear A- and B-exciton peaks are observed in the calculated absorption spectrum (blue curve). For the bowtie-MoS\(_2\) system, the overall absorption in MoS\(_2\) increases (red curve). Absorption increases in the coupled system by a factor of 1.8 at the laser excitation energy (2.33 eV/532 nm) as indicated by the dotted circles. Therefore, the calculated excitation rate increase, \( g_{ex} \), is expected to be 1.8 for this sample geometry. However, the observed PL enhancement is much higher. This in addition to the observed spectral modification in the bowtie-MoS\(_2\) system cannot be explained only by the enhancement of the excitation rate, which is not very high because the laser excitation energy (2.33 eV) is considerably far away from the lattice-LSP modes. In addition, sample (i) shows a high-energy tail above the B-exciton emission in the normalized PL spectrum (Fig. 4.8e, blue curve), corresponding to the lattice-LSP mode located at higher
energy (Fig. 4.8b, blue curve), attributed to the emission from non-thermalized excitons, similar to the hot-exciton emission observed in plasmonically-coupled CdS nanowires\textsuperscript{36}.

The emission enhancement ($g_{em}$) can be explained by the change in the quantum yield of the emitter in the presence of plasmonic resonators. The emission quantum yield ($k_r/(k_r+k_{nr})$), where $k_r$ and $k_{nr}$ are the radiative and the non-radiative decay rates, respectively, changes as both $k_r$ and $k_{nr}$ change when the emitter is coupled with plasmonic resonators. The radiative decay rate is affected mainly by the local plasmonic fields whereas the non-radiative decay rate depends on plasmonic losses and exciton quenching. Generally, in an electronic multi-level system, $k_r$ and $k_{nr}$ are frequency

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**Figure 4.9** | Calculated absorption spectra for bare MoS\textsubscript{2} monolayer and bowtie-MoS\textsubscript{2} system at room temperature. The calculated results are shown for sample (iii) in Fig. 3c of the main paper. Bowtie geometrical factors: $g = 20$ nm, $h = 50$ nm, $s = 100$ nm, and $p = (300$ nm, 200 nm). *Reprinted with permission from ref. 10. © 2011, American Physical Society.*
dependent and depend on the competition between the intra- and inter-band relaxation rates. Therefore, our frequency-dependent PL enhancement ($g_{\text{total}}(\omega)$) can only be explained by the quantum yield increase ($g_{\text{em}}(\omega)$), which is frequency-dependent. For our bowtie-MoS$_2$ (sample (iii)), the integrated fluorescence enhancement (over the entire spectrum) is ~25, which is an average enhancement over the measured area. Therefore, the actual enhancement inside the bowtie gap is expected to be much higher due to much higher fields inside the small mode volume of a bowtie. The average excitation rate enhancement in our system is only 1.8, which indicates that most of the fluorescence enhancement originates from the emission enhancement. This significant emission enhancement indicates effective coupling between 2-D excitons and lattice-LSP resonances and is in agreement with recent theoretical studies supporting the large increase in the radiative decay rate of an emitter in the bowtie gap$^{37,38}$. Recently, minor increase in PL from MoS$_2$ covering gold nanoantennas has been reported but the mechanism for PL enhancement is quite different from ours. Their PL enhancement is induced by mostly light absorption increase (in-coupling enhancement) mediated by plasmons and the heating of the sample due to large absorption of gold in the visible range$^{36}$. Further improvements in the emission yield can be achieved by inserting a thin dielectric layer between MoS$_2$ and metal structures to optimize the competition between exciton-quenching and plasmonic field enhancement at this interface.

Figure 4.10 shows the correlation of different lattice-LSP modes to the emission profiles, consistent with figure 4.8. Since the lattice-LSP modes are located at around the dips of the $\Delta R/R$ spectra, the PL enhancement in the bowtie-MoS$_2$ system is correlated to
\( \Delta R/R \) spectra of the bowtie arrays. By varying the array pitch and/or the side length of bowties as well as the polarization of incident light, the lattice-LSP resonance can be modified, as shown in different \( \Delta R/R \) spectra. Correlating the \( \Delta R/R \) spectra of the bowtie array to the corresponding PL spectra of the bowtie-MoS\(_2\) samples shows, as expected, that PL intensity increases the most when the dip position in \( \Delta R/R \) is closest to the A- or B-exciton energy.

![Figure 4.10](image-url) Lattice-LSP mode dependent spectrally modified PL enhancements of MoS\(_2\) coupled to Ag bowtie arrays. Top panel shows the \( \Delta R/R \) spectra of bowtie arrays with different geometrical factors and polarization, as noted above each spectrum. Bottom panel shows PL spectra of bowtie-MoS\(_2\) samples from the corresponding bowtie array. Reprinted with permission from ref. 10. © 2011, American Physical Society.

In order to study how the bowtie-MoS\(_2\) coupled system responds at low temperatures when the exciton-dephasing rate is reduced, the far-field \( \Delta R/R \) spectra for bare MoS\(_2\), bowtie array, and bowtie-MoS\(_2\) system were measured at 77 K (Fig. 4.11a).
Clear absorption dips associated with the A- and B-excitons in bare MoS$_2$ appear at 1.92 eV and 2.1 eV (black curve). $\Delta R/R$ of the bowtie array shows two broad dips (blue curve), with the lattice-LSP modes spectrally overlapping with the MoS$_2$ excitons. In the combined bowtie-MoS$_2$ system, however, an interesting phenomenon is observed; an asymmetric feature resembling Fano lineshape appears in the reflection spectra at the MoS$_2$ exciton energies (red curve). The Fano lineshape is a result of the spectral interference between a narrow discrete resonance and a broad continuum of states$^{40,41}$. In our case, the MoS$_2$ excitons with a sharp resonance at 77 K couple with the broad continuum of plasmons. Since the linewidth of the A-exciton is much narrower than that of the B-exciton, more distinct Fano lineshape was observed at the A-exciton spectral region.

FDTD calculation simulating the $\Delta R/R$ response of the experimental system (Fig. 4.11b) reproduces the reflection spectra of bare MoS$_2$ (black curve) and the bowtie array (blue curve) as well as the Fano lineshape of the integrated bowtie-MoS$_2$ system (red curve). To further investigate the physical mechanism of the observed Fano features, the absorption spectra (Fig. 4.11c) were calculated for bare MoS$_2$, bowtie array, MoS$_2$ in the combined bowtie-MoS$_2$ system, and the bowtie-array in the combined bowtie-MoS$_2$ system. Bare MoS$_2$ shows a sharp excitonic absorption (black curve) while the bowtie array shows broad plasmon absorption (blue curve), as expected. For the coupled bowtie-MoS$_2$ system, absorption in MoS$_2$ (green curve) shows absorption enhancement in comparison to the absorption of bare MoS$_2$ due to the strong plasmonic field. However, absorption in the bowties (red curve) in the coupled system features complex interference...
at the MoS$_2$ exciton energies compared to a typically broad lattice-LSP absorption. This demonstrates that the absorption in the bowtie array of the combined system exhibits Fano interference due to the strong interaction between MoS$_2$ and the bowtie array.

The physical mechanism (Fig. 4.11b, inset) behind the measured Fano resonance in the bowtie-MoS$_2$ system is the interference that occurs predominantly in the excitation process$^{42-44}$; in the exciton-plasmon coupled system, the exciton lifetime is much longer than that of plasmons and therefore the excitation rate of excitons increases without any significant changes in the spectral shape or position due to the enhanced local plasmonic field (Fig. 4.11c, green curve). On the other hand, absorption in the bowtie array can be significantly affected by the interference from the excitons with long lifetime via the exciton-plasmon dipole-dipole coupling. Thus, in the bowtie-MoS$_2$ system, two major optical paths exist for the excitation of plasmonic modes$^{43-45}$, i.e., direct excitation of the plasmons and their indirect excitation via the dipole-dipole coupling of MoS$_2$ excitons and plasmons. The dipole-dipole interaction increases due to the local field enhancement arising from the surface plasmons and leads to exciton-plasmon coupling beyond the perturbative regime into an intermediate state between weak and strong coupling regime. The constructive and destructive interference between the two optical pathways leads to Fano resonance measured in our reflection spectra, consistent with the large PL enhancement addressed earlier (Fig. 4.8).
Figure 4.11 | Fano resonance in the reflection spectrum of bowtie-MoS$_2$ at 77 K. Bowtie geometry: TE mode, s = 100 nm, p = (300 nm, 200 nm). a and b. Experimental and calculated $\Delta R/R$ spectra for bare MoS$_2$, bowtie array, and bowtie-MoS$_2$ system. Clear Fano resonances are observed at the A- and B-exciton spectral region. Inset in b shows the schematic for the mechanism of observed Fano resonance in the exciton-plasmon system. c. Calculated absorption spectra for the bare MoS$_2$ (black), bowtie array (blue), MoS$_2$ in the combined bowtie-MoS$_2$ system (green), and the bowtie in the combined bowtie-MoS$_2$ system (red). The dotted circle highlights the region of MoS$_2$ excitons where Fano resonances are observed in the refection spectra in a. Reprinted with permission from ref. 10. © 2011, American Physical Society.
Fano shapes vary in our experimental $\Delta R/R$ measurements depending on the linewidth of lattice-LSP mode and detuning between MoS$_2$ excitons and tunable lattice-LSP modes (Fig. 4.12). Three representative samples are compared to examine their Fano spectral features by controlling their geometric factors and hence their plasmonic resonances. For a very small detuning and sharper linewidth of bowtie resonances (Fig. 4.12a), much sharper Fano feature with more distinct asymmetry was observed in comparison to the samples with increasing detuning$^{9,42,47}$ (Fig. 4.12b,c). Moreover, no Fano response was observed in Fig. 5c due to almost no overlap between the exciton and lattice-LSP resonances. These observations strongly support the claim that our Fano features originate from the strong coupling between MoS$_2$ excitons and lattice-LSP modes.

Fano resonances appear in many systems ranging from autoionization of atoms to plasmonic nanostructures and metamaterials$^{9,12-14,17,40,41}$. However, most observations are in passive systems with no involvement of electronic resonances$^{12-14,17}$. Fano resonance is also observed in gated bilayer graphene but it is induced by the coupling between discrete phonon and continuous exciton$^{18}$. Recently, Fano resonance and Rabi oscillations have been demonstrated in J-aggregate dye molecules coupled with metal nanostructures due to the enhanced interaction between the excitons and LSPs$^{19,39,45,47}$. The bowtie-MoS$_2$ system with very small mode volume, displays Fano resonances due to the significantly enhanced optical coupling between the 2-D MoS$_2$ excitons and bowtie LSP resonances, which can be modulated via the spectral tuning of lattice-LSP resonances.
Figure 4.12 | Controlling Fano spectra of the bowtie-MoS\(_2\) system by tuning the lattice-LSP modes to overlap with MoS\(_2\) excitons at 77 K. a-c, Experimental \(\Delta R/R\) spectra of bare MoS\(_2\), bowtie, and bowtie-MoS\(_2\) system for three different samples with the following excitation polarization and geometrical factors. TE polarization, \(s = 100\) nm, \(p = (400\) nm, \(300\) nm) (a), TM, \(s = 140\) nm, \(p = (500\) nm, \(400\) nm) (b), TE, \(s = 100\) nm, \(p = (800\) nm, \(700\) nm) (c). Clear Fano resonances are observed when the bowtie lattice-LSP modes overlap with MoS\(_2\) excitons. Reprinted with permission from ref. 10. © 2011, American Physical Society.
4.5 Conclusion

Significant modification of the emission properties of monolayer MoS$_2$ was demonstrated upon its integration with silver bowtie nanoantenna arrays. The strong plasmonic local field from lattice-induced LSP resonances in the bowtie arrays gives rise to enhanced Raman scattering and PL in MoS$_2$ at room temperature. Depending on detuning of MoS$_2$ exciton and lattice-LSP mode, spectrally modified PL enhancement was exhibited. At low temperature, due to the strong dipole-dipole interaction between MoS$_2$ excitons and lattice-LSP modes with sharper resonances, quantum interference arises in the excitation process and is manifested as Fano-like asymmetric reflection spectra. Since the Fano resonance lineshape and spectral position is very sensitive to local perturbations, it can be utilized to assemble optical switches and sensors$^9$. Tailoring light-matter interactions between atomically thin semiconductor crystals and plasmonic nanostructures as demonstrated in this work will be critical to realize new physical phenomena and fabricate novel optical devices with applications ranging from improved light sources, detectors, and sensors to photovoltaics.
References


Chapter 5. Photocurrent in monolayer MoS₂

5.1 Motivation

Following the study of optical properties via plasmons in monolayer MoS₂, it will be meaningful to extend the understanding of MoS₂ to study other properties such as electrical transport and optoelectronic properties. Of particular interest is the realization of thin-layer MoS₂ into optoelectronic devices, which can detect and interact with light, such as photodetectors, optical switches, and solar cells⁴. As the electronic band structures of semiconductors affect the ability to absorb and emit light, single-layer MoS₂ with a direct semiconducting bandgap will have possibility for applications in optoelectronics. Combined with its processibility into atomically thin layers, monolayer MoS₂ provides great platform for transparent, flexible optoelectronic devices⁵.

5.2 Background

Aside from change in the band structure (Background, Ch.4), another important consequence of decreasing the thickness of MoS₂ down to a monolayer arises from the lack of inversion symmetry (Fig. 4.1), which renders it viable of valley-based optoelectronic applications. As stated in the previous chapter, each spin, up or down, is paired into each split valence band. Furthermore, when this broken spin degeneracy is combined with time-reversal symmetry (E↑(k)=E↑(-k)), the valley and spin of the valence band is also coupled (Fig.5.1)⁶. At K and K’ valleys, opposite spin is paired into each valence band. Consequently, circular light incident on the material can excite interband transitions at only one of the two valleys depending on left- or right-circular
polarization of the light. In other words, the helicity of incident light is a selection rule for which valley, K or K’, to engage in interband transition.

Figure 5.1 | Valley-spin coupling in monolayer MoS$_2$. In monolayer, the lowest-energy conduction bands and the highest-energy valence bands labelled by the z-component of their total angular momentum. The spin degeneracy at the valence-band edges is lifted by the spin–orbit interactions. The valley and spin degrees of freedom are coupled. In bilayer, spin degeneracy of the valence bands is restored by spatial inversion and time-reversal symmetries. Valley and spin are decoupled. Reprinted with permission from ref. 5. © 2012, Macmillan Publishers Limited.

Note that in bulk crystal, both inversion and time-reversal symmetry leads to spin degeneracy at each of the two valence bands: \([E_{\uparrow}(k)=E_{\downarrow}(-k)] \& [E_{\downarrow}(k)=E_{\uparrow}(-k)]\). Mak et. al. demonstrated optical control of valley-spin polarization in monolayer MoS$_2$ by helicity of incident light. The helicity parameter describes the degree of PL polarization and is defined as the following.

\[
\rho = \frac{I(\sigma_{-}) - I(\sigma_{+})}{I(\sigma_{-}) + I(\sigma_{+})}
\]

Figure 5.2 shows the PL spectra and the helicity parameter of monolayer and bilayer excited with left circularly polarized light (\(\sigma^{-}\)) right above the A exciton energy but below the B exciton energy. In monolayer without inversion symmetry, valley and spin
are coupled. $\sigma$- excitation creates excitons with electron spin down and hole spin up at the K point (Fig. 5.2c). Intravalley scattering to the hole-spin-down state is forbidden because of the giant valence band splitting of 150 meV. Intervallay scattering from the K to $K'$ point requires scattering from defects due to the large change of momentum involved. As a result, almost no PL is observed with $\sigma_+$ excitation, leading to the helicity factor reaching 1. Also, the valley-spin lifetimes for carriers is expected to be very long in monolayer. In bilayer, the spin degeneracy resulting from inversion symmetry nullifies the spin-valley polarization effect and both left and right circular excitation result in PL.

![Figure 5.2](image)

**Figure 5.2** | *a-c*, Monolayer MoS$_2$ is excited by a laser with excitation energy 1.96 eV with left circularly polarized light. *d-f*, Bilayer MoS$_2$ with same condition as (a). *Reprinted with permission from ref. 5. © 2012, Macmillan Publishers Limited.*

A previous works shows enhancement of photocurrent and photoluminescence (PL) spectra by tuning the plasmonic resonance of silica-gold nanoshells (AuNS) to the exciton energies in monolayer MoS$_2$. By dispersing on monolayer MoS$_2$ with AuNS with 60 nm-radius SiO$_2$ core and 30 nm-thick outer Au shell which shows scattering maximum in 600-700 nm range, the intrinsically low absorption cross-section of MoS$_2$
was enhanced by the plasmon resonance. Resonant light is absorbed efficiently by the AuNS, generating a local field at the surface of the MoS2, resulting in the enhanced electron-hole pair generation in the monolayer and an increased photocurrent\textsuperscript{8,9}. For both photocurrent and photoluminescence, AuNS only increase the overall signal level and has very little effect on the position of the peaks. By mapping the responsivity of the device using three different laser wavelength, the authors demonstrate that the measured photocurrent is solely from within the MoS\textsubscript{2}. The reduction in the photocurrent signal as the laser wavelength was varied from 645 nm to 680 nm to 750 nm is consistent with the intensity reduction of photocurrent in Fig. 5.3b. All photocurrent is measured between the electrodes and no signal appears to be from either gold electrodes or the substrate\textsuperscript{7}. 

![Diagram](image-url)
Figure 5.3 | a, Top: SEM image of MoS2 device coated with silica-gold nanoshells (AuNS) with inset displaying magnified image of the AuNS. Scale bar: 5 um. Bottom: schematic of the MoS2 phototransistor with inset showing nanoshells on MoS2. b, Photocurrent spectra of MoS2 monolayer before (red) and after (green) dispersing AuNS. c, Photoluminescence spectra of monolayer MoS2 with (green) and without (red) AuNS. d, SEM of Au electrodes and AuNS on MoS2 showing the laser scan area for the photocurrent maps to the right. Scale bar: 5um. A source-drain voltage of 1 V and a gate voltage of 80 V is applied as shown by the circuit illustration. Three different laser wavelengths 645 nm, 680 nm, and 750 nm are used to raster the device and map the photocurrent. Reprinted with permission from ref. 6. © 2014, AIP Publishing LLC.
5.3 Methods

5.3.1 Device fabrication

Monolayers of MoS$_2$ were grown on SiO$_2$/Si substrate as reported in Chapter 4. Numbered marker patterns were patterned on the PMMA-coated, as-grown MoS$_2$ substrate by e-beam writer. 5 nm-thick titanium adhesion layer and 30 nm-thick gold were deposited by e-beam evaporator. The sample was then lifted off in acetone. A monolayer flake of MoS$_2$ inside the marker pattern was located by optical microscope, and electrodes were designed by CAD software. The electrodes were aligned on the MoS$_2$ flake and patterned via e-beam writer. After developing, 5 nm-thick titanium adhesion layer and 50 nm-thick gold were deposited by e-beam evaporator followed by lift-off. Another alignment procedure was performed to pattern bowtie structures inside the electrodes. The bowtie patterns were developed and deposited with 50 nm-thick silver by the e-beam evaporator, followed by lift-off. After the electrodes with bowties were made, the sample was attached to the chip carrier and the electrodes were wirebonded to the pins for the electrical connections.

5.3.2 Experimental setup

Photocurrent measurements were performed with home-built chip carrier box connected to Keithley 2400 for the voltage source and Keithley 6517 electrometer for measuring the channel current. LabVIEW software was used for the data acquisition. The sample was optically excited by a continuous wave He-Ne laser at a wavelength of 633 nm through 1 mm-thick glass substrate using a home-built microscope equipped with a 60×, 0.7 NA objective (Nikon), having a spatial detection resolution of 500 nm.
5.4 Initial result and future direction

Initially, two pairs of electrodes were fabricated, one with bowtie array inside and one without, on a monolayer MoS\textsubscript{2} flake (Fig.5.5a,b). Both regions inside the two pairs of electrodes were excited by unpolarized He-Ne laser at 633 nm wavelength to measure their photocurrent. Figure 5.5c shows that the bowtie-MoS\textsubscript{2} shows higher photocurrent compared to MoS\textsubscript{2} without the bowties, indicating resonant light is absorbed more efficiently by the bowtie structures (Fig. 4.9), resulting in the enhanced electron-hole pair generation and an increased photocurrent. Both dark current spectra show almost no photocurrent with no dependency of current on the applied voltage. Although it shows increased photocurrent due to plasmonic bowtie arrays, the enhancement is not very high and the simple enhancement of photocurrent has been shown in other works as well\textsuperscript{4,7,10}.

Thus, as future work, we can optimize the electrode design, experimental setup, and overall device quality to achieve much higher photocurrent from bowtie array-incorporated monolayer or thin layer MoS\textsubscript{2} compared to the photocurrent from MoS\textsubscript{2} without bowtie arrays. Currently, three lithography steps are involved in making one device for photocurrent measurements (Methods). This is expected to degrade the MoS\textsubscript{2} sample quality, which should be checked by measuring the photoluminescence from bare MoS\textsubscript{2} area before and after each lithography steps. If we are certain that lithography steps are key factor in sample quality, sample preparation can be done differently, i.e. transferring the as-grown MoS\textsubscript{2} onto the already patterned bowtie array on SiO\textsubscript{2}/Si substrate. After we achieve higher photocurrent enhancement compared to other previous works, we can also study the systematic change in the photocurrent that may depend on...
the bowtie array design. For example, Fig. 4.10 shows various designs of bowtie arrays and their corresponding reflection spectra, showing high enhancement in PL when the dips of the reflection spectra, or lattice-LSP modes, are aligned with the excitonic transitions of MoS$_2$. Thus, from our previous studies we know the spectral position of high absorption for many designs of bowtie arrays. By utilizing this, we may study how the intensity of photocurrent relates to different design of bowties, similar to the PL study in Fig. 4.8b,c.

**Figure 5.5 | a-b.** Bright (a) and dark field (b) optical images of the electrodes patterned on monolayer of MoS$_2$. The dark field image shows patterning inside the left pair of electrodes which is bowtie array. c, Initial photocurrent measurement (I-V curves) of bowtie-MoS2 compared to that of bare MoS$_2$ excited by He-Ne laser.
It will be interesting to see how the helicity in monolayer MoS$_2$ arising from the lack of inversion symmetry (Background section) can be utilized by photocurrent spectroscopy. As one method, we suggest the use of plasmonic nanostructures with a certain geometry that can lead to circular polarization of light which will excite only one valley (K or K') in monolayer MoS$_2$ (Fig. 5.1). Figure 5.6 shows the possible schematic of the device configuration which could lead to circular polarization of light from the metal nanostructures. A rectangular metal bar will sustain two plasmonic modes depending on its geometry. One will be along the short axis and one along the long axis, termed Mode A and Mode B, respectively. The metal bar will be designed such that these two modes will not have much spectral overlap. Let's consider the excitation of the metal bar with wavelength corresponding to mode A, linearly polarized 45° with respect to the short axis as shown in Fig. 5.6b. This incident light will then have two components, one along the short axis and another along the long axis of the bar. The component along the long axis will not be resonant, as the long axis has resonant condition of mode B. However, the component along the short axis will be resonant with mode A, and thus this component will be phase-lagged with respect to the other component. This will lead to the light polarized circularly as shown by the black arrow in (b). Now, let's consider the excitation with the same wavelength that corresponds to mode A, but this time linearly polarized 135° with respect to the short axis. Or, this is polarized perpendicularly with respect to the first excitation we considered (Fig. 5.6c). In this case, the fact that the component of light along short axis resonant with mode A is phase-delayed is the same, but due to change in direction of polarization, an opposite circular polarization compared
to the case in (b) is achieved. Thus, by exciting such structures with light in two linear polarizations that are perpendicular to each other, we can achieve left and right circular polarizations of light. These two types of circularly polarized light can generate electron-hole pairs from different valleys (K or K') in monolayer MoS$_2$, which can be measured as photocurrents of opposite direction. This selective generation of photocurrent in MoS$_2$ by linear polarization can be useful in optical switching.

![Diagram](image_url)

**Figure 5.6** | **a**, Diagram of a metal bar showing excitation (red) and two plasmonic modes (blue). **b**, Resulting circular polarization (black arrow) of light when the bar is excited by incident light with the wavelength of Mode A, polarized in the direction shown. **c**, Resulting circular polarization (black arrow) of light that is opposite of (b) when the bar is excited by incident light with the wavelength of Mode A, polarized in the perpendicular direction with respect to the direction in (b).
5.5 Conclusion

In this chapter, helicity and photocurrent in monolayer MoS2 were reviewed. The initial result showed enhanced photocurrent by incorporating a bowtie array on monolayer MoS2. However, optimization of the electrode design, experimental setup, and overall device quality needs to be done as future work to achieve much higher photocurrent from bowtie array-incorporated monolayer. Also, study of how the photocurrent varies by incorporating the bowtie arrays with different lattice-LSP resonances is suggested. Furthermore, the helicity of monolayer MoS2 can be utilized for the photocurrent study, where the plasmonic metal nanostructures will convert the incident linearly polarized light into circularly polarized light, which will feed into monolayer MoS2 in order to generate electron-hole pairs from one specific valley depending on the direction of the circular polarization. Works such as this opens up a possibility to utilize the inherent helicity characteristic of monolayer MoS2 for an optical switch.
References


Chapter 6. Probing of infrared surface plasmons in patterned graphene-fluorographene nanoribbons by FTIR.

6.1 Background

Graphene is a single atomic layer of carbon in honeycomb lattice, and is a building block for all graphitic materials such as buckyballs, nanotubes, and graphite\textsuperscript{1-3}. Graphene is unique in its electronic band structure; near K point in the Brillouin zone, the E-k dispersion is linear, resulting in massless relativistic electrons called Dirac-fermions that are responsible for graphene’s ultrafast carrier dynamics\textsuperscript{1,2} (Fig. 6.1). Since the demonstration of free-standing graphene film in 2004, there has been an extensive research on graphene propelled by advances in graphene production via mechanical exfoliation and CVD growth.

![Graphene Flake Image](image1)

![Graphene Electronic Dispersion](image2)

**Figure 6.1** | a, SEM image of graphene flake showing zigzag and armchair edges. Reprinted with permission from ref. 1. © 2007, Nature Publishing Group. b, Graphene electronic dispersion. Reprinted with permission from ref. 2. © 2009, The American Physical Society.
Raman spectroscopy is useful in determining the number of layers as it identifies monolayer to bilayer graphene. Figure 6.2 shows graphene raman spectrum where G and 2D peak corresponds to doubly degenerate phonon mode, $E_{2g}$, at the brillouin zone center and the second order peak involving 2 optical phonons near K point, respectively\(^4\). Ratio of G to 2D peak is important in differentiating graphene and graphite. Also, going from monolayer to bilayer, 2D peak visibly broadens and red-shifts.

**Figure 6.2** | Raman of graphene. *Reprinted with permission from ref. 4. © 2006, The American Physical Society.*

Of particular interest is graphene in photonic and optoelectronic applications such as photodetectors, ultrafast lasers, and solar cells\(^5,14\). Optically, graphene is characterized by its constant absorption of 2.3% per layer at low intensity, a remarkably high value considering its atomic monolayer nature. Furthermore, the linear dispersion of Dirac fermions allows for broadband applications. Niu et. al. demonstrated tunable surface
plasmon resonance of gold nanoparticles by using graphene (Fig. 6.3). Due to the coupling strength change between the graphene and gold nanoparticles, induced by different thickness of oxide interlayer, the resonance wavelength shift was observed.

Figure 6.3 | Transmission spectra of a, a glass/Al₂O₃, b, glass/graphene/Al₂O₃, c, glass/Al₂O₃/particles, d, glass/graphene/Al₂O₃/particles, with various thicknesses of Al₂O₃. The insets illustrate the cross section view of the device structure. The arrow in (d) shows a shift in the resonance wavelength. Reprinted with permission from ref. 6. © 2012, American Institute of Physics.

Recent work shows tunable plasmon resonances in engineered graphene microribbon arrays across the width of ribbons. The authors demonstrated that graphene plasmon resonances can be tuned over a broad terahertz frequency range via change in microribbon width and electrical gating. The ribbon width & gating and graphene plasmon frequency exhibits power-law dependence, which is the characteristic of two-
dimensional massless Dirac electrons. In figure 6.4, as the gate voltage varies from -1.0 to -2.2eV, the plasmon resonance shifts to higher energy and gains oscillator strength with increased carrier concentration. In (d), plasmon resonance frequency shifts from 3 to 6 THz when the ribbon width decreases from 4 to 1um.

**Figure 6.4** | Control of plasmon resonance through electrical gating and microribbon width. (a) IR transmission spectra of ribbons with 4um width, as gate voltage is varied from -0.3 to -2.2eV. (b) Terahertz plasmon resonance through electrical gating. Radiation polarized perpendicular to the graphene ribbons. (c) AFM images of graphene microribbon. (d) Transmission spectra of different ribbon widths for the same doping concentration. Reprinted with permission from ref. 7. © 2011, Macmillan Publishers Limited.
In graphene, surface plasmons are expected to appear in the terahertz and infrared regime\textsuperscript{8}. By using the scattering-type scanning near-field optical microscope (scattering-type SNOM), Fei et. al. experimentally accessed these plasmons. Illuminating the tip of an atomic force microscope (AFM) with a focused infrared beam of 11.2 um wavelength launched the surface plasmons (Fig. 6.5a), which enabled direct observation of the scattering amplitude $s(w)$, a measure of the field strength inside the nanoscale gap between tip and sample (Fig. 6.5b-e). The scattering amplitudes could be manipulated with gate voltage\textsuperscript{9}, as shown in Fig. 6.5f.

![Figure 6.5 | Infrared nano-imaging of tapered graphene nanoribbon. a, Diagram of IR nano-imaging experiment of graphene on SiO2. Green and blue arrow indicate the incident and back-scattered light, respectively. Concentric circles on the surface of the graphene show plasmon waves launched by the AFM tip. b–e, Images of IR amplitude $s$ at gate voltage = 0. Interference patterns are formed near the graphene edges (blue dashed](image_url)
It has been shown that the dielectric properties of graphene can be tuned by chemical doping or applied electric bias, which change the charge density in graphene\textsuperscript{8,10}. This enables SP-based devices that can be active at different frequencies, for applications such as sensing and photodetectors. In the infrared regime, imaging plasmons using 10 µm wavelength scattering NSOM techniques has been demonstrated, revealing graphene plasmon wavelengths 50–60 times smaller than the free space wavelength\textsuperscript{11-13}. Recently, there has been a study of plasmon resonances in etched graphene nanoribbon arrays in mid-IR regime. Via FTIR with light polarized perpendicular to the nanoribbon axis, the authors showed the graphene plasmon resonance and surface-plasmon phonon polariton (SPPP) resonance\textsuperscript{13} (Fig. 6.6). The authors explain that the graphene plasmon mode corresponds to a confined plasmon excitation of graphene in a nearly constant dielectric environment. The SPPP mode represents a composite excitation of SPP on the graphene coupled to a phonon excitation in the SiO\textsubscript{2} substrate, which comes from lattice oscillations in the SiO\textsubscript{2} leading to increase in the SiO\textsubscript{2} dielectric constant below its phonon energy. The authors showed that GR and SPPP of the nanoribbon array could be tuned by applied gate voltage and width of the nanoribbons.
Figure 6.6 | Gate-induced modulation of transmission in graphene nanoribbon arrays normalized to transmission spectra at the charge neutral point (CNP). a, Nanoribbon-width dependence of optical transmission with $E_F = -0.37$ eV. Nanoribbon width is varied from 15 to 80 nm. b, Fermi level dependence of optical transmission in 50 nm-wide graphene nanoribbon array. $E_F$ is varied from $-0.22$ to $-0.52$ eV. The dotted vertical lines indicates the zone-center energy of the in-plane optical phonons of graphene. Reprinted with permission from ref. 13. © 2013, American Chemical Society.

6.2 Motivation

Graphene, as detailed previously, has ultrafast carrier dynamics and broadband tunability of light, which make it a unique 2-D plasmonic material that is an attractive alternative to conventional metals, of which the applicability is limited due to challenge in tunability and large Ohmic losses. Although investigation into graphene's plasmonic properties has been active as discussed in the previous section, it is critical to demonstrate tuning of IR plasmon modes in a controlled way, along with the design of structures that are scalable for device integration. Especially, although the work in Fig. 6.5 demonstrates
tunable plasmon-related resonances in patterned graphene, this is from a physically cut-off graphene nanoribbons with high defect concentration at the edges. Thus, it will be beneficial if an etch-free, smooth patterning of nanoribbons can be achieved; doing so may lead to stronger and smoother plasmon resonance signals compared to the previous work. In order to achieve such structures, CVD-grown graphene was fluorinated by reaction with xenon difluoride (XeF$_2$) to create fluorographene. An array structure consisting of alternating graphene and fluorographene nanoribbons was prepared to study the plasmon resonance of graphene in near-infrared regime. Preliminary data will be presented followed by future direction.

6.3 Methods

6.3.1 Device Fabrication

As-grown CVD graphene on copper foil was transferred onto SiO$_2$/Si/SiO$_2$ substrate by Johnson group. Nanoribbon arrays were patterned on the graphene substrate via e-beam lithography, followed by developing in MIBK:IPA 1:3 solution and exposing to XeF$_2$ via Xactix XeF$_2$ Silicon Etcher. PMMA was removed in Acetone to result in the final device.

Experimental setup

Transmission measurements were carried out via Fourier transform infrared (FTIR) microscopy at Murray group.
6.4 Initial result and future direction

By using a XeF$_2$ silicon etcher tool, fluorographene areas were patterned on CVD grown graphene transferred on SiO$_2$/Si/SiO$_2$ substrate. Figure 6.6 shows the optical images of fluorographene and Raman spectra of graphene vs. fluorographene. The fluorographene Raman spectrum shows no characteristic of graphene, suggesting the successful fluorination of graphene.

![Figure 6.6](image)

**Figure 6.6** | a, Optical images of fluorographene and Raman spectra of graphene vs. fluorographene. The fluorographene Raman spectrum shows no characteristic of graphene, suggesting the successful fluorination of graphene.

In order to dope the graphene, F-SAM molecules were dispersed on the sample after patterning the alternating nanoribbon arrays of graphene and f-graphene. Optical transmission from the sample was measured by FTIR spectroscopy. The transmission spectra from incident light polarized parallel to the long axis of the arrays (T$_{par}$) were used as a background. Figure 6.8a shows the transmission spectra from the 600 nm-width
arrays of graphene and fluorographene, doped with F-SAM. For the three repeated measurements, all the curves were reproducible. However, as the measurements repeated, the signal was reduced significantly due to the power reduction of IR source. Unlike shown in the previous work (Fig. 6.6), there are additional modulations in energy region $> 2000 \text{ cm}^{-1}$, located higher than optical phonon $\sim 1580 \text{ cm}^{-1}$. Fig. 6.8b shows that all the peaks from the transmission spectra of 400 nm-width sample are shifted to higher energy compared to those of 600 nm-width sample. This is consistent with aforementioned paper$^{7,13}$ in which nanoribbon arrays of narrower width produced higher SPP resonance frequency. Again, as the measurements went on, the signal became weaker and featureless. The consistency and high power of IR source is important in measuring a distinct, clear transmission spectra. With such IR source, this work can be continued with nanoribbon arrays of various widths to study the surface plasmons in graphene. We expect that smooth, undisturbed boundaries of the nanoribbon arrays created by fluorinating graphene nanoribbons, rather than physically cutting them via etching, will lead to stronger and smoother plasmon resonance signals compared to the previous work.
Figure 6.8 | a, Transmission spectra for 600 nm-width arrays of graphene and fluorographene, doped with F-SAM. The spectra were measured three consecutive times. b, Transmission spectra for 400 nm-width arrays of graphene and fluorographene, doped with F-SAM. The spectra were measured four consecutive times.
6.5 Conclusion

In this chapter, we have demonstrated fluorination of graphene by reaction with XeF₂. The arrays of alternating graphene and fluorographene nanoribbons, with varying nanoribbon widths, were patterned and the transmission spectra were measured. Although the unstable power source of FTIR spectroscope has limited more detailed studies, the initial results show modulations that seem to be the plasmonic resonances from the graphene nanoribbons. Although the shift is very small, graphene nanoribbons of narrower width shows higher energy peaks, consistent with the previous report. This can be further investigated with a consistent IR source to study the trend of SP peaks as a function of nanoribbon widths, as well as to realize sharper SP resonances from the defect-free boundaries prepared by fluorination of graphene.
References


