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Linear and Nonlinear Applications of Plasmonics Based on Optical Planar Waveguides

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School of Electrical & Electronic Engineering

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LINEAR AND NONLINEAR APPLICATIONS OF PLASMONICS BASED ON OPTICAL PLANAR WAVEGUIDES

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School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

This thesis contains material from 5 papers published in the peer-reviewed journals as follows:

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T. Wu conceived of the presented idea. T. Wu and L. Wei developed the theory.
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Summary

Plasmonics is the intersection research area of science and technology which studies the behavior of surface plasmons and it seems that plasmonics is the only viable way toward the realization of nanophotonics. Plasmons are quantized charge density waves which are usually described as collective oscillations of electrons and are broadly divided into two categories: propagating surface plasmons and localized surface plasmons. Plasmons are able to localize the electric field of light to their proximity and provide accordingly high field enhancement in the immediate vicinity of the metal-dielectric interface. In this thesis, we mainly apply plasmonics in linear and nonlinear optics to study plasmonic structures and explore the advantages in them.

Nonlinear optics describe the light behavior in a nonlinear medium where the dielectric polarization depends nonlinearly on the light field and its impact on technology and industrial applications are excellent. Nonlinear optics processes have been ubiquitously used in the modern scientific and technological applications, which facilitates diverse phenomena such as ultra-short pulsed lasers, optical signal processing, imaging, sensing, and many others. However, strong nonlinear optical effects generally require giant optical fields interacting with the nonlinear media. Plasmonics can provide the giant optical fields. Theoretically, a fully nonlinear coupled mode differential equation model for lossy plasmonic waveguides is proposed and used to investigate efficient third-order wavelength conversion in various designed plasmonic structures. Specifically, two different kinds of plasmonic waveguides are studied: metallic plasmonic waveguide and graphene plasmonic waveguide. Experimentally achieved efficient third harmonic generation from a bowtie silicon hybrid plasmonic system is also presented. The obtained plasmonic enhanced third harmonic generation facilitate the future development of new frequency generators and signal processing at mid-infrared and terahertz frequencies.

Metallic plasmons possess large losses in the frequency regimes of interest which motivated us to explore other available material supporting plasmons like graphene. Graphene is a truly two-dimensional crystalline material and its tunable Fermi energy property and optical transparency have been widely utilized on optics besides its high mobility, flexibility, and environmental stability. Doped graphene supports electrically

tunable long-lived plasmons with low loss and significant wave localization. Generally, the interaction between the infrared light and the nanometric-scale molecules is very weak, the high field localization and enhancement of the graphene plasmonic device enable a tunable biosensor with high-sensitivity for label-free detection of the nanometer molecules. The doping level of graphene can be tuned to dynamically modify the plasmonic resonance so as to selectively identify the molecules. We develop three graphene plasmonic systems to detect the molecule chemical fingerprints with high accuracy. The greatly enhanced light-matter interaction and the broadband tunability of the localized graphene plasmonic resonance enable accurate label-free identification of the molecular vibrational modes at subwavelength scale. The high sensitivity may accelerate the further development of novel cost-effective biosensors with superior molecular chemical fingerprints sensitivity in an active graphene plasmonic device.

To analytically study a general class of plasmonic structures to explore the key features linking the far-field energy to the near-field energy and attaining considerable field confinement and enhancement, we introduce the transformation optics technique. Transformation optics is a technique which can be used to control the trajectories of light rays by warping space and simplify the modelling process of plasmonic devices by transforming the coordinate system. We introduce a fully analytical model with transformation optics to analytically resolve the essence of the significant enhancement of the molecule Raman emission in instability regime. The exact analytical calculations go beyond the description by the quantum-mechanical model and confirm the efficient Raman emission happens at a near constant laser blue-detuning from the plasmonic resonance for molecule vibrational frequency less than half the plasmonic linewidth. The analytical model provides a computational framework that allows the predictions of all the spectral properties of the molecule Raman emission and facilitates the experimental achievement of single molecule detection as well as other nonlinear processes.

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ε_m is the bulk metal permittivity, ω_p and γ are the metal plasma and damping frequencies, $\varepsilon_\infty = 1$, and $\beta = 3v_F^2/5$ is proportional to the Fermi velocity v_F 134

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List of Abbreviations

SERS	surface enhanced Raman scattering
SEIRA	surface enhanced infrared absorption
SEM	scanning electron microscope
SPPs	surface plasmon polaritons
TM	transverse magnetic
LSPs	localized surface plasmon resonances
EF	enhancement factor
2D	two dimensional
TO	transformation optics
THG	third harmonic generation
IR	infrared
TPA	two-photon absorption
PMC	phase-matching condition
FF	fundamental frequency
TH	third harmonic
FOM	figure-of-merit
DHPSW	double-hybrid plasmonic slot waveguide
EBL	electron beam lithography
PMMA	polymethyl methacrylate
FDTD	finite-difference-time-domain
GSERS	graphene-mediated surface enhanced Raman scattering
CVD	chemical vapor deposition
PEI	poly(ethyleneimine)
AFM	atomic force microscopy
FWHM	full-width-at-half-maximum
R6G	rhodamine 6G
MB	methylene blue

Chapter 1 Introduction

1.1 Motivation

The ability of harvesting light and concentrating the light energy into a deep subwavelength volume is highly desired for many applications¹⁻¹⁰. It seems that plasmonics is the only viable way toward the realization of nanophotonics. Plasmons are capable of confining the electric field of light to their proximity and providing high field enhancement. One major potential application of the plasmonics is in wavelength conversion. The significant electric field enhancement leads to powerful light-matter interaction strength and thus efficient harmonic generation. Other important applications of the plasmonics include surface enhanced Raman scattering (SERS), surface enhanced infrared absorption (SEIRA), plasmonic enhanced fluorescence spectroscopy, and biosensors.

For the applications of the plasmonics, we first focus on the light frequency upconversion. Efficient frequency upconversion is highly desirable for tunable lasing⁴, optical communication⁵, drug delivery⁶, bioimaging⁷, and sensing⁸ and it still remains to be a significant challenge for the development of optoelectronic devices. Third harmonic generation (THG) at nanoscale has been investigated both theoretically and experimentally in different artificial structures since the pioneering observation in a silica fiber¹¹. However, strong nonlinear optical effects generally require giant optical fields interacting with nonlinear media with large third-order nonlinear susceptibility ($\chi^{(3)}$), and phase-mismatching and large spatial overlap between fundamental and third-harmonic modes. Although it has been theoretically predicted to be possible to achieve the three requirements simultaneously, waveguide structure design still remains a major challenge. Plasmonic waveguides are ideal for nonlinear optical frequency conversion due to their extraordinary abilities of spatially confining electric field at subwavelength scale¹². Plasmonic waveguides also permit us to modify the strength of different nonlinear terms freely through tuning the waveguide geometric parameters. Since metallic plasmons bring large losses in the frequency regimes of interest, graphene plasmons are attracting more and more attention. Graphene plasmons surpass that of

metallic plasmons by properties of tighter field confinement, lower loss, and higher $\chi^{(3)}$. Since graphene plasmons mainly span infrared-terahertz range, graphene plasmons must be considered when THG at infrared or terahertz is preferred. Motivated by the advantages of plasmons in THG, we first propose nonlinear coupled mode differential equations to explore the specific critical conditions for efficient THG and design plasmonic structures to realize theoretically and experimentally high THG conversion efficiencies.

Graphene is a truly two-dimensional crystalline material^{13, 14}, which was demonstrated to have extraordinary electric and optical properties^{15, 16}. Despite the advantages for graphene's plasmons over metallic plasmons mentioned above, graphene can be doped to high values of electron or hole concentrations by applying an external gate voltage to support tunable plasmons in infrared and terahertz regimes. This is a great motivation for us to explore the applications of graphene plasmons. Since traditional optical biosensors simply detect the molecular refractive index^{17, 18} which cannot identify the type of molecules, we mainly use graphene plasmons to achieve tunable label-free biosensors to selectively identify the molecule (through detecting the molecule chemical fingerprints) with high-sensitivity and high-accuracy at subwavelength scale. We first numerically achieve mid-infrared (mid-IR) biosensors by employing tunable graphene plasmons to detect the molecular vibrational modes. We then report an experimentally achieved ultra-wideband graphene-mediated surface enhanced Raman scattering (GSERS) substrate to detect the top bonded molecules. The hybrid GSERS substrate will offer an atomically flat, thin, and chemically stable bonding interface with strongly enhanced molecule Raman signals, thereby providing a promising solution to achieve an ideal practical SERS substrate.

To rigorously study plasmonics and the corresponding applications in the future, we need a completely theoretical basis to guide us. It is difficult to use traditional methods to investigate plasmonic nanostructures, we then move to the transformation optics (TO) technique. It has been demonstrated that TO has driven the development of surface plasmons and the corresponding applications¹⁹⁻²⁴. TO can be utilized to analytically study a general class of plasmonic structures to explore the key features linking the far-field energy to the near-field energy and attaining considerable field confinement and enhancement for the exploration of applications of plasmonics. We propose a fully analytical model with TO to analytically resolve the essence of the significant enhancement of the molecule Raman emission.

1.2 Objectives

Grounded on the discussion above, the main research focus of this thesis is to extend the linear and nonlinear applications of plasmonics.

The objectives are divided into three sub-items:

(1) Nonlinear coupled mode differential equations for lossy waveguides will be proposed to explore the specific critical conditions for efficient THG. Follow these critical conditions, we will design plasmonic structures to realize theoretically and experimentally high THG conversion efficiencies.

(2) To reduce the plasmonic losses and expand the applications of plasmonics, we will present an extensive study on the graphene plasmons. We will further employ graphene plasmons to detect the molecular vibrational modes to identify the type of molecules.

(3) We will report a hybrid graphene/fragmented-gold substrate to achieve an ultra-wideband graphene-mediated surface enhanced Raman scattering substrate. The hybrid graphene/fragmented-gold substrate will be beneficial to detect the top bonded molecules and enable a wideband tracing of analytes.

(4) We will illustrate how to use the transformation optics approach to rigorously study plasmonic nanostructures that are difficult to investigate with traditional methods to provide a guideline for our future work.

1.3 Major contribution of the Thesis

Below presents the major achievements in this thesis:

(1) Nonlinear coupled mode differential equations are proposed and three designed plasmonic waveguides are used to theoretically and experimentally achieve high THG conversion efficiencies.

Nonlinear coupled mode differential equations to investigate and address the specific factors which determine the THG efficiency for lossy waveguides are proposed followed by a presentation of two designed metallic asymmetric plasmonic slot waveguides and a graphene plasmonic coupler waveguide to attain efficient THG numerically. We then present an experimentally obtained efficient THG from a hybrid silicon-plasmonic system. The papers regarding the simulation work are published as “J.

Opt. 17(2), 2015”, “Opt. Express 23(1), 2015”, “IEEE J. Lightwave Technol., 34(4), 2016”, and “Physical Review Applied, 11(1), 2019”. The manuscript regarding the experimental work is ready for submission.

(2) Graphene plasmons are explored for biosensing.

The broadband tunability of graphene plasmons makes the working wavelength cover the important molecular vibrational frequencies to identify the specific chemical fingerprints. Two numerically achieved mid-IR biosensors are presented by employing tunable graphene plasmons to detect the absorption, reflection, and transmission variations due to the protein immobilization which demonstrate the high sensitivity of the graphene nanoribbon to the complex permittivity of the nanometric-scale targeted molecule. The papers regarding the simulation work are published as “Optics Letters 42, 2066-2069 2017”, and “Opt. Express 24(23), 2017”. The manuscript regarding the experimental work is ready for submission.

(3) Transformation optics technique is used to study analytically the plasmonic amplification scenarios of SERS.

We demonstrate efficient Raman scattering can be achieved when the laser is blue-detuned to the largest slope point of the plasmonic resonance spectrum for molecule vibrational frequency smaller than half of the plasmonic decay rate and evidently close to the anti-Stokes vibrational sideband for molecular vibrations comparable or larger than half of the plasmonic decay rate to maximum the corresponding phonon population. The manuscript regarding this work is ready for submission.

1.4 Organization of the Thesis

Plasmonics can confine the electric field of light to its proximity and provide great field enhancement, which promises possibilities to control light in nanoscale. This thesis summarizes the main works during my Ph.D. period investigating theoretically and experimental on linear and nonlinear applications of plasmonics based on optical planar waveguides. Surface plasmons have made it possible to achieve efficient harmonic generation (which is generally very weak in normal media), efficient SERS, and label-free biosensing with high sensitivity by permitting strong light interactions with the free electrons in the metal. Through controlling the geometric parameters and the material

properties of the nanostructures, light can be effectively manipulated to localize within the desired region.

Chapter 1 is the thesis introduction, encompassing the motivation, objectives, and major achievements for this work.

Chapter 2 gives an overview of the basic properties of the metallic and graphene plasmons, followed by an introduction of general applications. The basic concept of transformation optics and the corresponding applications are also provided.

Chapter 3 presents the fully nonlinear coupled mode differential equation model for lossy plasmonic waveguides, efficient third harmonic generation from two different kinds of plasmonic waveguides, and experimentally achieved efficient third harmonic generation from a bowtie silicon hybrid plasmonic waveguide. We show that metallic hybrid plasmonic waveguide and graphene plasmonic coupler can significantly enhance the third harmonic generation. The effective conversion mainly comes from the combined effects of great plasmonic field enhancement, pump-harmonic phase-matching, and large third-order nonlinear susceptibility of the nonlinear media.

To reduce the plasmonic losses, we use doped graphene to excite long-lived graphene plasmons and apply the graphene plasmons to achieve chemically identification of molecules in Chapter 4. We present three critical electro-optical properties of the graphene-based device to demonstrate tunable biosensor with high-sensitivity. The Fermi energy level of graphene is tuned to dynamically tune the plasmonic resonance so as to selectively probe the molecules. From the calculation, we show that the significant spatial light confinement of graphene plasmons produces a large overlap between light and the nanometer-scale biomolecules, enabling super-sensitivity in the detection of the molecular refractive index and chemical vibrations.

Since SERS has become an attractive analytical technology to obtain the molecular specific chemical fingerprints, we further develop a novel graphene-fragmented gold nanostructure to study the ultra-wideband graphene-SERS in Chapter 5. The stimulated hot spots and their strong interaction with the top-integrated monolayer graphene make the graphene a hot surface which is beneficial for a wideband tracing of analytes by highly enhanced, stable, reproducible, and clean molecule Raman readouts.

In Chapter 6, we employ transformation optics technique to analytically resolve the exceptional backaction amplification action on the molecule Raman emission. The exact

analytical calculations confirm the efficient Raman emission in the instability region with blue-detuned laser incidence.

Chapter 7 gives a conclusion to this thesis, and propose one issue we will concentrate on in our future work, which is the Compton-like polariton scattering enhanced by localized surface plasmons.

Chapter 2 Literature Review

This chapter introduces the fundamental theory and the basic applications of surface plasmons and gives the background for Chapter 3-6. The fundamentals and theory of surface plasmon polaritons (SPPs) and localized surface plasmons (LSPs) are first introduced followed by a briefing of excitation methods of SPPs. In the third part of this chapter, general nonlinear and linear applications of plasmonics are introduced. In the fourth part, optical properties of graphene and tunable graphene plasmons are introduced. The fifth part gives a brief introduction of transformation optics. The last section gives an overview of this thesis.

2.1 Theory of plasmonics

Plasmonics come from the light interactions with the free electrons of noble metal. The negative dielectric permittivity of the noble metal induces dramatic electric field confinement in the vicinity of the metal interface. The object of this part is to provide a physical insight of surface plasmons and address the corresponding attractive and promising applications.

SPPs. SPPs were first discovered in 1902 by Wood²⁵. Theoretical interest in SPPs began to grow in the 1970s²⁶ and 1980s²⁷. But, in the meantime, corresponding possible applications were little pursued. A booming study to the SPPs was triggered by the later experimental discovery of surface enhanced Raman scattering^{28, 29} and efficient second harmonic generation from a metal surface³⁰.

A plasmon can be well described as a quantum of plasma oscillations³¹⁻³³. SPPs describe an electromagnetic wave propagating along the dielectric-metal. Maxwell's equations together with the boundary conditions are utilized to solve the surface waves. The simplest geometric structure supporting SPPs is a dielectric-metal interface as depicted in Figure 2.1. The $z > 0$ space is dielectric, and the $z < 0$ space is metal with permittivity less than 0. The surface charge and the plasmonic field which propagates along the interface (parallels to the x-axis) are shown. The electric field of SPPs is transverse magnetic (TM) polarized, and the amplitude is maximized at the interface

and decays exponentially into each medium along z direction with increased distance from the interface. The TM solutions including E_x , E_z and H_y field components follow the form

$$\begin{cases} e^{ik_x x} e^{-k_d z} & z > 0 \\ e^{ik_x x} e^{k_m z} & z < 0 \end{cases} \quad (2.1)$$

Where ε_m and ε_d are the dielectric permittivities of the metal and the dielectric, respectively. Maxwell's equations and continuous E_x and H_y yield

$$\frac{k_{zm}}{\varepsilon_m} + \frac{k_{zd}}{\varepsilon_d} = 0 \quad (2.2)$$

and

$$k_x^2 + k_{zm}^2 = \varepsilon_m k_0^2 \quad (2.3a)$$

$$k_x^2 + k_{zd}^2 = \varepsilon_d k_0^2 \quad (2.3b)$$

where $k_0 = \omega/c$ represents the free space wave vector. Due to the continuous k_x , the SPPs dispersion can be obtained

$$k_x = k_0 \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}} \quad (2.4)$$

Therefore, at small wave vector cases, k_x is close to k_0 . At large wave vector cases, the SPPs frequency approaches the metal surface plasmon frequency of $\omega_{sp} = \omega_p / \sqrt{1 + \varepsilon_m}$. Nobel metals bring relatively large losses in fact which lead to severely damped SPPs waves at a propagation length of $L = 1/[2\text{Im}(k_x)]$ (depends on the material permittivity and the light frequency). Therefore, there must be a trade-off condition between the electric field localization and the propagation loss in many practical SPPs applications.

In the modeling of SPPs, the material dispersions of the metal and dielectric are considered. The dispersion of the dielectric material is often described by a Sellmeier equation

$$\varepsilon_d(\lambda) = 1 + \sum_i \frac{B_i \lambda^2}{\lambda^2 - C_i} \quad (2.5)$$

where the wavelength λ is quoted in micrometres, and B_i and C_i are experimentally determined Sellmeier coefficients. The dielectric permittivity of the metal is described by a Drude model

$$\varepsilon_m = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega - i\gamma\omega)} \quad (2.6)$$

where ε_∞ is related to the interband transitions, ω_p is the metallic plasma frequency, ω is the light angular frequency, $\gamma = 1/\tau$ and τ is the mean relaxation time of conduction electrons. Note that, it is difficult to excite SPPs directly via far-field radiation due to the mismatch of wave vector between the incident and the plasmonic waves. One way to overcome the momentum mismatch is to couple light with SPPs at the interface with $\varepsilon_m + \varepsilon_d = 0$.

Figure 2. 1 Illustration of SPPs by a typical metal-dielectric interface.

LSPs. Through a study of the light scattering by a metallic sphere, Mie³⁴ showed that a sphere supports electromagnetic resonances at discrete frequencies which can produce significant field enhancements in the vicinity of the sphere surface. The frequencies of these resonances rely on the dielectric permittivity and the geometric size of the sphere, and the optical properties of the ambient medium. Soon afterward Fröhlich³⁵ studied these resonances in an electrostatic approximation approach under the condition that the sphere diameter is much smaller compared to the light wavelength. The concept of LSPs then came into being which describes non-propagating stationary collective excitations of free electrons in the noble nanoparticles coupling to photons, in contrast to the previously introduced SPPs. Far-field can excite LSPs with attainable conservation of energy and momentum. LSPs manifest themselves in a form of absorption and scattering resonances with subwavelength-enhanced electric fields near the metal surface. The optical response of LSPs can be described as $\mathbf{p} = \alpha \mathbf{E}$ to connect

the induced electric dipole moment ($\mathbf{p}$) and the electric field ($\mathbf{E}$), α is the polarizability. The quasi-static limit can be employed to calculate the plasmon resonances by solving for the eigenmodes of a Laplace's equation under a condition that the metallic geometry is much smaller compared to the light wavelength. In spherical polar coordinates, the eigenfunctions of a metallic sphere as described in Figure 2.2 follow

$$E_{l,m} = [Ar^l + Br^{-(l+1)}] Y_{lm}(\theta, \phi) \quad (2.7)$$

where $Y_{lm}(\theta, \phi)$ are the spherical harmonics. The corresponding resonance condition is given by

$$l\varepsilon_m = (l+1)\varepsilon_d \quad (2.8)$$

where ε_m and ε_d are the dielectric permittivities of the metal layer and the dielectric layer, respectively. Numerical simulations are needed for more complicated particle shapes or clusters of particles. A recent analytical technique which is called transformation optics has been extensively used to solve the guided modes in plasmonic systems analytically, which will be discussed in Chapter 6.

Figure 2. 2 Localized plasmon resonance of a metallic sphere.

2.2 Excitation of propagating SPPs

Phase matching is needed to excite SPPs. In general, SPPs are excited by electrons and photons. For the electrons excitation case, the component of the scattering vector of electrons can be transferred to the bulk plasma. The parallel vector results in the excitation of SPPs³⁶. For photon excitations, SPPs cannot be directly excited on the

metal-dielectric interface by incident light due to the wave vector mismatch. Certain techniques can be employed to realize wave vector phase-matching as follows.

Prism Coupling. One general method is applying a prism system to achieve momentum matching between the incident light and the SPPs as illustrated in Figure 2.3. Assume the surrounding dielectric is air with $\varepsilon_d = 1$. The prism is a dielectric medium having large electric permittivity. A light that incidents prism-metal interface can produce a sufficient in-plane wave vector to excite SPPs between the metal-air interface. SPPs cannot be excited between the metal-prism interface due to the phase mismatching.

Figure 2. 3 Typical prism system coupling to SPPs. The Kretschmann method (left panel) is the most commonly used technique to excite SPPs where a thin metal film is directly evaporated onto the top of a glass prism. While the Otto configuration (right panel) is only preferred when it is undesirable to contact with metal surface directly in which a thin air gap is introduced to separate the prism from the metal film.

Grating Coupling. A grating coupler can also phase-match the wave vectors by offering a large parallel wave vector component (depends to the grating period). Figure 2.4 depicts the typical schematic configuration using a grating structure to excite SPPs. Wave vector matching can be fulfilled as

$$k_{SPP} = k_i \sin \theta \pm \frac{2m\pi}{P}, m = 1, 2, 3... \quad (2.9)$$

Figure 2. 4 Use grating configuration to offering an increased parallel wave vector component to excite SPPs.

Near-field excitation. Near-field excitation behaves as a point source to excite SPPs³⁷. Figure 2.5 depicts the typical configuration which consists of a small probe tip illuminating a metal surface. Since the tip size is very small, the radiated light from the dip possesses a large wave vector component to attain phase-matching of wave vectors for the excitation of SPPs.

Figure 2. 5 Near-field excitation of SPPs by a typical small probe tip. The large wave vector component provided by the radiated light from the dip can realize wave vector phase-matching for the excitation of SPPs.

2.3 General applications of plasmonics

Plasmons in noble metals at optical frequencies of interest enable significant confinement of light below the fundamental diffraction limit and extremely intense electromagnetic field in a volume much smaller than the light wavelength which is very attractive for fundamental researches. A major potential application of the metallic plasmonics is in wavelength conversion. The significant electric field enhancement

leads to powerful light-matter interaction strength and thus efficient harmonic generation. Other important applications of the plasmonics include SERS, SEIRA, plasmonic enhanced fluorescence spectroscopy, and biosensors.

2.3.1 Plasmonic enhanced nonlinear response of the media

Traditionally, solid-state physics focuses on the study of equilibrium states, or on states under extreme small perturbations. The practical applications of materials, however, depends on the understanding of strongly non-equilibrium states. Such states are inherently dynamic, involving changes in material properties over a wide range of length and time scales. Recently, a large amount of ultrafast optical techniques have been employed to investigate ultrafast nonlinear optics. The recent years have witnessed a particularly vivid progress in the research of using ultrashort intense light pulses for controlling and probing ultrafast dynamics. Although ultrafast dynamics is a relative term and covers a large range of dynamical processes and timescales, we would like to define this term in this section as ultrafast nonlinear optics and process harmonic generation with an ultrafast laser source. The most common used ultrafast source for harmonic generation is the Ti:sapphire laser, due to its broad wavelength range and high power capability (the per pulse energy can reach tens of nanojoules). This high energy drive highly nonlinear light-matter interaction processes for efficient harmonic generation.

The origin of nonlinear optics is the nonlinear response of the nonlinear media to the light electric fields. The material response is manifest in a susceptibility. When intense light enters a material, its susceptibility can become nonlinear. It is usually sufficient to consider this heuristically as a Taylor expansion in the electric field as $\chi(E) = \chi^{(1)} + \chi^{(2)}E + \chi^{(3)}E^2 + \dots$, where $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ represent the linear susceptibility, second-order and third-order nonlinear susceptibilities of the medium, respectively. All higher orders beyond $\chi^{(1)}$ represent the nonlinear response of a material to the presence of intense light. The higher order terms fall off in magnitude very rapidly unless the light intensity is very high. In general, the susceptibility is a tensor and the vector component of the fields must be taken into account. A light with electromagnetic field of $\mathbf{E}(t)$ irradiates a medium, the effect of the susceptibility on the light traveling through the medium is manifest in the polarization $\mathbf{P}(t)$ which

depends nonlinearly on the electric field amplitude and can be expressed as a general form³⁸

$$\mathbf{P}(t) = \varepsilon_0 \left[\chi^{(1)} \cdot \mathbf{E}(t) + \chi^{(2)} : \mathbf{E}(t) \mathbf{E}(t) + \chi^{(3)} : \mathbf{E}(t) \mathbf{E}(t) \mathbf{E}(t) + \dots \right] \quad (2.10)$$

where ε_0 is the vacuum dielectric permittivity. The second-order nonlinearity vanishes in centrosymmetric media, while the third-order nonlinearity can occur all the time. Common second-order nonlinear effects include second harmonic generation, sum/difference frequency generation, Pockels effect, and optical rectification effect. Common third-order nonlinear effects include third harmonic generation, four-wave mixing, and Kerr effects. Nonlinear actions provide more degrees of freedom to manipulate optical field, endowing nonlinear optics more importance in optical applications such as lasers, imaging, material technology³⁹, nanomedicine^{40, 41}, photocatalysis⁴²⁻⁴⁴, and biosensing^{40, 45, 46}.

The linear, second-order and third-order polarizations can be written as

$$\mathbf{P}^{(1)} = \varepsilon_0 \chi^{(1)} \mathbf{E} \quad (2.11)$$

$$\mathbf{P}^{(2)} = \varepsilon_0 \chi^{(2)} |\mathbf{E}| \mathbf{E} \quad (2.12)$$

$$\mathbf{P}^{(3)} = \varepsilon_0 \chi^{(3)} |\mathbf{E}|^2 \mathbf{E} \quad (2.13)$$

For linear interaction as the left panel in Figure 2.6, the polarization is proportionate to the electric field strength. While the second-order and third-order polarization of the medium is proportional to the two orders of magnitude and three orders of magnitude of the local electric field strength. Plasmonics with an extremely localized electric field can greatly enhance the nonlinear polarization. Therefore, plasmonics assisted efficient nonlinear effects at nanoscale plays a crucial role in improving the light density and reducing the power consumption during the nonlinear interaction. In principle, the plasmonics assisted nonlinear effects mainly possess three main advantages: strong field localization and corresponding highly enhanced nonlinearity, scaled down geometric sizes of nonlinear components, and ultrafast response time (at femtosecond level).

Figure 2. 6 Linear (left panel) and nonlinear (right panel) interactions of waves and the media.

Critical factors to enhance nonlinear interactions. Strong nonlinear interaction is difficult to realize because of the general tiny nonlinear susceptibility of optical media and the existing phase mismatching constraints. According to our research, there are four critical factors which determine the second-order and third-order nonlinear interactions: perfect phase matching, large nonlinear susceptibility, large pump-harmonic spatial overlap, and low propagating loss. The related detailed deduction and calculation to pursue efficient nonlinear effects can be found in Chapter 3.

2.3.2 Field enhanced vibrational spectroscopy

The electromagnetic spectrum of the typical few tenths of meV of vibrational energy of molecules falls into infrared (IR) range. The energy is very specifically referring to a molecular vibrational fingerprint to realize chemical identification. Generally, two important techniques are used, i.e., Raman spectroscopy and infrared spectroscopy, to detect the molecule vibrational fingerprint. The Raman scattering intensity is very weak. One effective way to enhance the Raman signal is to perform SERS. During the inelastic light scattering process, photons interact with the molecule vibrations and produce Stokes and anti-Stokes shifts. The corresponding scattering cross-section carries the molecular vibrational information. Unlike Raman scattering, infrared spectroscopy is related to the direct excitation of molecule vibrations. The extinction spectrum is measured. The extinction cross-section can be greatly enhanced by the local hot spots when the molecules are bonded onto a nanostructured metal film or a metallic nanoparticle (called SEIRA). The enhancement of Raman scattering and infrared absorption are both associated with the local field enhancement offered by the surface plasmons. The basic idea of field enhanced spectroscopies is to locate the molecules

near the SPPs and LSPs to enhance the visible SERS and infrared SEIRA radiations so as to improve the spectroscopic signals.

SERS. SERS is first observed in 1973⁴⁷ and is correctly interpreted in 1977^{28, 29}. The observation of single-molecule SERS in 1997⁴⁸ first indicated that the Raman signal, in fact, is capable to rival the fluorescence signal of a molecule. The electromagnetic field scattered from a molecule attaching onto a rough metal surface or a metallic nanoparticle can be significantly enhanced. SERS enhancement factors of $10^6 \sim 10^{14}$ have been reported recently due to the favorable hot spots^{9, 49-51}.

In Raman scattering process, the incident photon either loses or gains energy to excite a molecular vibration. The Raman photon will have a corresponding smaller or larger energy due to energy conservation as shown in Figure 2.7. The shifts of Stokes and anti-Stokes are the spectral information which can be used to identify the molecule sidebands. For SERS, the scattering cross-section value of a molecule depends on the local field intensity at the molecule site. The final enhancement of the scattered signal comes from the combined enhancement at the excitation of $EF_1 = |E_{loc}(\omega_i)/E_i|$ and emission of $EF_2 = |E_{loc}(\omega_s)/E_i|$ as can be seen from Figure 2.8. Thus the total Raman enhancement factor (EF) reads^{52, 53}

$$EF = |E_{loc}(\omega_i)/E_i|^2 |E_{loc}(\omega_s)/E_i|^2 \quad (2.14)$$

As the molecule vibrational frequency is generally much less than the visible light frequency, the total Raman scattering enhancement factor (EF) can be rewritten as

$$EF \approx |E_{loc}(\omega_i)/E_i|^4 \quad (2.15)$$

This extreme enhancement is why SERS becomes a powerful tool in molecule spectroscopy and a single molecule identification becomes approachable.

In addition, chemical enhancements result from charge transfer in the chemisorption of a molecule to the metal surface should provide additional Raman scattering enhancement. This enhancement process is complex and there is no precise theoretical deduction to calculate this enhancement yet. An additional enhancement factor of the order 10-100 is offered.

Figure 2. 7 Schematics of Stokes and anti-Stokes. One incident photon with energy of $\hbar\omega_i$ generates or loses an energy of $\hbar\omega_{vib}$ (vibrational mode energy) and scatters a photon with energy of $\hbar\omega_s$ with smaller or larger energy.

SEIRA. SEIRA permits unified surface enhanced vibrational spectroscopy. In SEIRA, infrared light is applied and the spectral information of molecule is generally collected in transmission mode, where the obtained molecule information contains both absorption and scattering messages. The SEIRA effect has not aroused widespread concern and applications due to the insignificant enhancement compared with SERS. The SEIRA extinction cross-section is much smaller compared to that of the SERS. In fact, the absorption scales with the square power of the local field enhancement while Raman scattering strength scales with the fourth power of the local field enhancement. Thus, a considerable electric field enhancement is highly desired to attain intense signal in SEIRA process which can be achieved by using nanostructured plasmonic films or nanoparticles with infrared frequency resonances. A good example is a gold nanowire, as the scanning electron microscope (SEM) image shows in Figure 2.8a. The nanowire behaves as a linear dipole antenna with a length close to half of the wavelength and offers strong field enhancement at the wire extremities. A followed strongly enhanced infrared spectra from the adsorbed molecules can be obtained. Near the resonance, the molecule vibrations (chemical fingerprints) can be distinguished from the spectrum under the condition that the incidence is polarized parallel to the long axis of the antenna to stimulate the antenna plasmonic resonance. The two transmission peaks in Figure 2.8b indicate the molecular vibrational information. With perpendicular incidence, no resonance can be excited and no molecule vibrations will be detected. This result demonstrates the resonance effect of an antenna to overcome the detection limit in

infrared spectroscopy. Antenna-assisted SEIRA can be further optimized by more complex and advanced geometries⁵⁴⁻⁵⁹.

Figure 2. 8 SEIRA from a nanoantenna. (a) SEM image of a single gold nanowire. (b) Transmission spectroscopy of the gold nanowire with octodcanthiol molecules deposited onto the surface. Adapted from⁶⁰.

2.3.3 Plasmonic enhanced fluorescence spectroscopy

To identify the chemical and biological species, fluorescence is one of the spread optical techniques, and it has already been applied over several decades. When the fluorophore labels couple to the surface plasmons, the interaction can dramatically increase the emitted fluorescence light intensity for detecting analytes with improved detection limit and minute amounts of analytes. The interaction between the fields of SPPs and LSPs and the fluorophores at the wavelengths of molecule absorption and emission will alter the specific transitions between the ground and excited states as shown in Figure 2.9.

Figure 2. 9 (a) Schematic of SPPs and LSPs modes interact with a fluorophore. (b) Surface plasmon mediated transitions. Adapted from⁶¹.

The changed excitation rate and decay rate by surface plasmons can be obtained by solving Maxwell's equations through the fluorophore absorption and emission electric dipole moment⁶². After excitation, the fluorophore will emit a photon at lower energy as illustrated in Figure 2.9b. Under the condition that the fluorophore is near the metallic surface, the decay rate (radiative and nonradiative) is modified by the highly increased optical local density of states which can lead to a modified quantum yield η as⁶³

$$\eta = \frac{\gamma_R}{\gamma_R + \gamma_{abs} + \gamma_R^0(1 - \eta_0)/\eta_0} \quad (2.16)$$

where γ_R and γ_R^0 are the total and intrinsic radiative decay rates, $\eta_0 = \gamma_R^0/(\gamma_R^0 + \gamma_{NR}^0)$ is the quantum yield of the fluorophore, γ_{abs} is the decay rate initiated by the increased optical local density of states.

Strong quenching of the radiative decay rate can be realized for short distances of the fluorophore from the metal film which is accompanied by a metal-enhanced nonradiative decay rate and a decreased quantum yield η . For longer distance from the

metal film, the surface plasmons emission becomes dominant. The surface plasmons interact with the surface plasmons and the far-field contributes to the radiative decay rate and the quantum yield is increased as a consequence. A continuous metallic film is the general used geometry for SPPs, and metallic nanoparticles^{3, 63-65}, nanoparticle dimers^{66, 67}, nanoparticle arrays^{68, 69} are used to provide LSPs for plasmonic enhanced fluorescence.

Note the fluorescence intensity is fluorophore orientation dependent because the surface plasmons are polarization sensitivity and the fluorophores are typical random oriented. The light intensity enhancement of fluorescence produced by the surface plasmons is then averaged over all of the possible fluorescence orientations. Therefore, the large EF of the total detected fluorescence intensity through coupling between the fluorophores and the surface plasmons results from the combination of the increased excitation rate by the plasmon-enhanced field intensity at the absorption wavelength, the increased quantum yield, and the high directionality (f) of the plasmon-coupled emission which follows

$$EF \propto \frac{\gamma_E}{\gamma_E^0} \frac{\eta}{\eta_0} f \quad (2.17)$$

2.3.4 Biosensors

Recently, Label-free biosensing technologies using nanophotonic devices have been widely studied. Biosensors are devices that delivery biological information into a signal. Reliable, selective, and sensitive biosensors have become more and more attractive due to the increasing number of biological issues⁶⁹. High refractive index sensitivity of a device is the key to detect a biological molecule of interest. Among various different nanophotonic phenomena, plasmons are especially promising in biosensing. Surface plasmons assisted biosensors possess various advantages in probing biomolecules on the surface of metals, such as flexibility, rapid response, no labels needed, and versatility. Among label-free biosensing techniques, SPPs and LSPs have become a leader as they enable highly enhanced, robust, and sensitive detection. The coherence oscillation of electrons provided by the plasmonic structures can produce wavelength-selective absorption or scattering cross section as well as large electric field enhancements. The strongly subwavelength field confinement and the large field enhancement of a nanoparticle depend on the particle size and the surrounding dielectric permittivity. The

plasmons are mainly used to improve the detection limit and selectivity. Even when a very thin molecule layer is attached to the metallic nanoparticle can produce a measurable change in the spectral response.

The frequency shift upon adsorbate binding as shown in Figure 2.10(a) is described as

$$\delta\lambda = m(\delta n) \left[1 - e^{-\frac{2d}{l_d}} \right] \quad (2.18)$$

Where m represents the refractive index sensitivity, δn represents the refractive index variation, d is the molecule layer thickness, l_d is the electric field decay length. As expected, Figure 2.10(b) shows a slight increase in the reflection dip on the increased refractive index of the upper cladding region.

Figure 2. 10 (a) Scheme of coupling between a thin metal film and a prism for surface plasmon-enhanced biosensing. (b) Reflection spectra with (blue curve) and without (red curve) molecule deposited on top of the metal film.

2.3.5 Other applications

The great field localization and corresponding large field enhancement of the surface plasmons can also be applied to plasmonic waveguides⁷⁰, plasmonic lasers⁷¹, plasmonic cloaking⁷², spasers⁷³, plasmonic solar cells⁷⁴, subwavelength imaging⁷⁵, super lenses⁷⁶, etc. Plasmonics is indeed a fascinating and currently expanding field of research. The diversity of emerging and potential applications of subwavelength optics with metallic plasmons, as well as successful proof-of-concept studies, suggest that interest in the applications of plasmonics will be soaring for years to come.

2.4 Graphene plasmons and applications

Metallic plasmons possess large losses in the frequency regimes of interest which motivated us to explore other available material supporting plasmons like graphene. Graphene is a truly two-dimensional crystalline material. Recently its tunable Fermi energy property and optical transparency have been widely utilized in optics besides its high mobility, flexibility, and environmental stability. The increasing research interest in utilizing graphene in electron-optics is triggered by its fascinating optoelectronic and photonic properties. Graphene can support plasmons that are tunable with simultaneous low loss and significant field localization in infrared and terahertz regimes. We will introduce the fundamental optical properties that enable graphene to guide plasmons, followed by the methods to excite graphene plasmons, and the general applications in this part.

2.4.1 Optical properties of graphene

Graphene possesses ideal electronic and optical properties. The simple electron band structure introduces a linear energy band dispersion of $E^\pm(\kappa) = \pm\hbar v_F |\kappa|$ at the k points in the two dimensional (2D) Brillouin zone. $v_F = \sqrt{3}\gamma_0 a / (2\hbar) = 10^8$ cm/s is the Fermi velocity. Thus, the optical conductivity of graphene goes to the finite minimal of $\sigma(\omega) = e^2 / (4\hbar)$, where $-e$ is the electron charge and $\hbar$ is the reduced Planck's constant. The resulted absorption of $\pi\alpha = 2.3\%$ is only related to the fine-structure constant. Photons with energy less than twice the Fermi level will not be absorbed when incident onto the graphene layer, which is known as the Pauli blocking principle.

Bandgap (E_g). Pristine graphene is essentially a semimetal sheet with zero bandgap. Two kinds of methods of direct synthesis method and post treatment method have both been widely applied to modify the graphene bandgap. Post treatment techniques are classified into two categories: wet treatment and dry treatment. In wet treatment, acid, metal chloride, and organic material are generally utilized. P-type or n-type doped graphene is achieved via charge transfer either from graphene to dopants or vice versa. In dry treatment, electrostatic field, thermal treatment, plasma treatment, and evaporation can be carried out. One basis method to modify the graphene Fermi energy level is apply a gate voltage as shown in Figure 2.11. As the gate voltage is swept from

negative to positive values, the Fermi level moves from its initial location between the valence and conduction bands, into the conduction band.

Figure 2. 11 Use gate voltage to tune the graphene Fermi level. As the gate voltage is increased from negative to positive bias, the graphene Fermi level is increased and the carriers are excited into the conduction band.

Mobility (μ). Graphene possesses ultrahigh mobility which is one of its most wonderful advantages. The limited graphene electron mobility by the conjugated π -electrons is $2 \times 10^5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at 5K, and mobilities range from 1×10^4 to $1.5 \times 10^4 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at low temperature were measured with exfoliated graphene⁷⁷. When graphene is modified with charged impurities or ripples, a mobility up to $10^6 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ becomes achievable⁷⁸.

Conductivity. The graphene conductivity can be described by the well-known Kubo formula^{25, 79}, which consists of interband and intraband contributions $\sigma(\omega) = \sigma_{\text{inter}}(\omega) + \sigma_{\text{intra}}(\omega)$. The imaginary conductivity plays a decisive role in the excitation of surface waves. At nonzero Fermi energy level, the imaginary intraband conductivity is always positive to support TM mode. The contribution of the interband and intraband conductivities varies with the Fermi energy level and the light frequency. For pristine graphene with $E_F = 0$, no intraband contribution occurs. For low doped graphene, where $2E_F < \hbar\omega$, the dynamic conductivity is mainly determined by the interband contribution of electron transitions. The interband domain conductivity covers a broadband range (from visible to infrared), which has stimulated a wide range of research interests in communications, imaging applications and so on. Graphene conductivity of graphene is reduced to^{79, 80}

$$\sigma(\omega) = \frac{e^2 E_F}{\pi \hbar^2} \frac{i}{\omega + i\tau^{-1}} + \frac{e^2}{4\hbar} \left[\theta(\hbar\omega - 2E_F) + \frac{i}{\pi} \log \left| \frac{\hbar\omega - 2E_F}{\hbar\omega + 2E_F} \right| \right] \quad (2.19)$$

within the local limit, where $-e$ is the electron charge, $\hbar$ is the reduced Planck's constant, ω is the radian frequency, E_F is the graphene Fermi energy level, and τ is the carrier relaxation time. The carrier relaxation time accounts for losses by defect, impurity, and electron-phonon scattering which reads^{79, 80}

$$\tau = \frac{\mu E_F}{e v_F^2} \quad (2.20)$$

where the μ is the carrier mobility, and $v_F = 10^6$ m/s is the graphene Fermi velocity. When graphene is highly to $\hbar\omega < 2E_F$, the intraband contribution becomes dominant. And the corresponding conductivity is simplified into a Drude-like form

$$\sigma_{\text{intra}}(\omega) = \frac{ie^2 E_F}{\pi \hbar^2 (\omega + i\tau^{-1})} \quad (2.21)$$

Nonlinear Kerr effect. With high intensity laser radiation, graphene can provide a nonlinear phase shift by nonlinear Kerr effect. A typical z-scan measurement has demonstrated a nonlinear coefficient of 10^{-11} m²/W of graphene⁸¹ which is nine orders of magnitude greater than that of a bulk dielectric. This large nonlinear coefficient indicates that graphene can act as a powerful nonlinear medium and offers more possibilities of nonlinear applications, one important of which is the harmonic generation.

2.4.2 Graphene plasmons

In recent years, graphene plasmons have attracted considerable attention from both theoretical and experimental views. Highly doped graphene layers support similar surface plasmon effects as that of metallic thin films as shown in Figure 2.12. Graphene plasmons describe the collective oscillations of the Dirac quasi-particles which enable significant electromagnetic energy localization at subwavelength scales and can be tuned via graphene Fermi energy level modification. They have been described from terahertz up to visible regions⁸². Solutions for graphene plasmons are similar to the

metal-dielectric interface. Boundary conditions $\frac{\epsilon_{r1}}{k_{r1}} + \frac{\epsilon_{r2}}{k_{r2}} = -\frac{i\sigma(\omega)}{\omega\epsilon_0}$ are different from

Figure 2.12. The derived classically dispersion of the graphene plasmons has a form of

$$k_{sp} = \frac{\pi \hbar^2 (\epsilon_{r1} + \epsilon_{r2})}{e^2 E_F} \omega (\omega + \frac{i}{\tau_1}) . \text{ K vector mismatch impeded direct excitation of}$$

graphene plasmons. The electric field profile follows $E \sim e^{k_{sp}(ix-|z|)}$. The large wave vector of the graphene plasmons compared to the free-space wave vector $k_{sp}/k_0 = \hbar^2 (\epsilon + 1) c (\omega + i/\tau) / 4e^2 E_F$ tells the remarkable electromagnetic field localization. In fact, the light confinement in graphene can be greater than that in a metallic structure up to 2 orders of magnitude.

Figure 2. 12 Schematic of TM plasmons propagating along z direction in graphene. Adapted from⁸³.

There are some aspects on which graphene plasmons is superior to metal plasmons. First, graphene plasmons propagate along the graphene sheet and the confinement is much tighter compared with that in the conventional metallic structures due to the 2D nature of the collective plasmon excitations. Second, graphene plasmons can be modified through carrier doping which cannot be achieved in general noble metals. More importantly, SPPs in graphene hold promising applications in a wide frequency regime from the terahertz to the infrared⁸⁴⁻⁸⁷. The plasmon loss in graphene is smaller than those in normal metals as well.

Graphene Plasmon Excitation. One challenge for the excitation and application of the graphene plasmons is the wave vector mismatch between the incident light wave and the guided plasmons. According to the calculation, the guided plasmons in graphene have very large wave vector and high corresponding effective mode index. Surface plasmons in graphene have been studied to be able to launch by a variety of methods, including metal antenna⁸⁸, metalized tip⁸⁷, tapered waveguide⁸⁹, and diffractive

grating⁹⁰. One more effective and easier way to access graphene plasmons is employing large area array of graphene nanoribbons, where the graphene plasmon resonances can be excited by far field⁹¹.

2.4.3 Graphene plasmons applications

Graphene behaves as broadband and tunable optical material. Graphene has been widely employed in solar cells⁹², organic light-emitting devices⁹³, photodetectors⁹⁴, modulators⁹⁵, biosensors⁹⁶, and ultrafast lasers⁹⁷. The advantages of the graphene integrated devices are as follows: tunable optical properties, eases integration of optical circuits into optoelectronic systems, low power requirements due to the small amount of graphene for graphene-integrated devices, and device fabrication can be performed in complementary metal-oxide-semiconductor (CMOS) foundries.

2.5 Transformation optics

To analytically study the plasmonic structures, we introduce the transformation optics technique in this section which can be used to predict the critical features to link the far-field energy to near-field energy, and explore the plasmonic field confinement and enhancement.

2.5.1 General theory of transformation optics

Transformation optics technique is proposed by Ward and Pendry⁹⁸ in 1996. This specific method can analytically solve Maxwell's equations to obtain the electromagnetic fields by a finite-difference computer code in a transformed space where only the permittivity and permeability tensor are modified. With coordinate system transformation, Maxwell's equations are rewritten in a form-invariant manner which ensures the TO method being a powerful tool to manipulate electromagnetic fields.

2.5.2 Permittivity and permeability transformation

TO method reveals that a distorted system carries all the associated fields and guides the trajectory of light. Only a distortion of the coordinate system is needed. The permittivity and permeability in the transformed space are desirable. In the Cartesian system, Maxwell's equations are written as

$$\begin{aligned}\nabla \times \mathbf{E} &= -\mu \frac{\partial \mathbf{H}}{\partial t} \\ \nabla \cdot (\varepsilon \mathbf{E}) &= \rho \\ \nabla \times \mathbf{H} &= \varepsilon \frac{\partial \mathbf{E}}{\partial t} + \mathbf{J} \\ \nabla \cdot (\mu \mathbf{H}) &= 0\end{aligned}\tag{2.22}$$

where ε and μ are the electrical permittivity and magnetic permeability, respectively.

Now consider general transformations on the form

$$\begin{aligned}x' &= x'(x, y, z) \\ y' &= y'(x, y, z) \\ z' &= z'(x, y, z)\end{aligned}\tag{2.23}$$

The scalar electric potential is preserved during the transformation. The vector fields in the original (unprimed) and transformed (primed) spaces must be related by the Jacobian matrix $\mathbf{J} = \frac{\partial(x', y', z')}{\partial(x, y, z)}$ according to $\mathbf{E}' = \mathbf{J} \cdot \mathbf{E}$ and $\mathbf{H}' = \mathbf{J} \cdot \mathbf{H}$. Thus through

rewriting Maxwell's equations in the transformed space, the related physical quantities in term of $\mathbf{J}$ in the transformed space can be obtained. Accordingly, the permittivity and permeability in the transformed space can be deduced

$$\begin{aligned}\varepsilon' &= \det(\mathbf{J})^{-1} \mathbf{J} \varepsilon \mathbf{J}^T \\ \mu' &= \det(\mathbf{J})^{-1} \mathbf{J} \mu \mathbf{J}^T\end{aligned}\tag{2.24}$$

Therefore, in 2D transformation, the dielectric constant of each material is conserved which is called conformal transformation.

2.5.3 Applications of TO method

One famous TO method application is the electromagnetic invisibility cloak^{99, 100} through space distortion. TO method has been well extended to the field of plasmonics recently to control the surface plasmon waves as desired such as SPPs adapter¹⁹, and

plasmonic Luneburg and Eaton lenses²⁰. Other applications of TO in plasmonics is to analytically study the plasmonic devices²¹⁻²⁴. TO approach also offers a route to quantitatively understand the interaction between a molecule and its surrounding plasmonic field which facilitates the further study on the molecule scattering spectrum and the corresponding molecule fingerprints identification.

Chapter 3 Plasmonic Structures for Efficient Third Harmonic Generation

Efficient light frequency upconversion is highly desirable and still remains to be a significant challenge for the development of optoelectronic devices¹⁻³. Coherent light conversion has been extensively exploited to achieve tunable lasing⁴, optical communication⁵, drug delivery⁶, bioimaging⁷, and sensing⁸. Particularly, THG developed by Armstrong et al¹⁰¹, which is induced by the third-order nonlinear optical susceptibility $\chi^{(3)}$ in optical materials, has attracted much attention¹⁰²⁻¹⁰⁵. THG has been investigated both theoretically and experimentally since the pioneering observation in silica fiber¹¹. Among the efforts made for THG¹⁰⁶⁻¹¹¹, approaches of on-chip integration with various platforms, such as silicon nitride microring resonators¹¹⁰, photonic crystal cavities¹¹², and germanium nano-disks¹¹³ are mainly limited by the trade-off between phase-matching and pump-harmonic mode overlap. Due to the large wavelength difference between the pump and harmonic waves, the phase-matching between the fundamental mode of pump light to higher order mode of harmonic light leads to a small mode overlap. And these structures are not nanoscale. Extremely strong mode confinement is one key aspect of deep subwavelength THG operation of a device. Plasmonic structures allow optical signals to be concentrated into a deep subwavelength volume³². This nanoscale confinement not only facilitates compact frequency upconversion which is suitable for planar optical circuitry but also enhances the optical intensity, thus increasing THG conversion efficiencies. However, the limitation of the small $\chi^{(3)}$ of the interactive nonlinear material^{111, 114}, phase-mismatching, and the small spatial overlap between the interacted modes^{110, 115, 116} have prevented the practical application of THG-based devices. Therefore, there is a need to explore new waveguide structures which enable the summarized critical factors simultaneously.

Plasmonic waveguides are ideal for nonlinear optical frequency conversion due to their extraordinary abilities of spatially confining electric field in subwavelength scale¹². Another advantage of utilizing plasmonic waveguides is that the strength of different nonlinear terms can be engineered freely through modifying the waveguide geometric

parameters. A variety number of metallic plasmonic waveguide structures have been proposed and investigated¹¹⁷⁻¹²¹. Since mid-IR and terahertz also serve as an ideal test-bed for next-generation plasmonic architectures and it is difficult to use metal to achieve plasmons in this range. Graphene plasmons can be employed to extend efficient THG to the mid-IR and terahertz regimes. Furthermore, graphene plasmons surpass that of metallic plasmons by properties of tighter field confinement and lower loss.

This chapter presents the proposed nonlinear coupled mode differential equations to explore the specific critical conditions for efficient THG, and the designed plasmonic structures to realize theoretically and experimentally high THG conversion efficiencies. We start with nonlinear coupled mode differential equations to investigate and address the specific factors which determine the THG efficiency followed by a presentation of two designed metallic asymmetric plasmonic slot waveguides and a graphene plasmonic coupler waveguide to attain efficient THG numerically. We then present an experimentally obtained efficient THG from a hybrid silicon-plasmonic system with gold bowtie nanoantennas integrated onto the surface of a silicon substrate. We believe our studies in this chapter not only offers the guidance for both fundamental understandings and further developing of efficient and practical achievable THG through plasmons-based waveguides with extraordinary electric field enhancement but also reveals potentials of employing the efficient obtained THG for a broad range of applications.

3.1 Nonlinear coupled mode differential equations

To model the THG process in lossy plasmonic waveguides, the nonlinear coupled mode differential equations describing the interaction between the fundamental and the generated third-harmonic waves are highly needed. Light traveling in waveguides can be described with Maxwell's curl equations

$$\nabla \times \mathbf{E}(\mathbf{r}, t) = -\mu \frac{\partial \mathbf{H}(\mathbf{r}, t)}{\partial t} \quad (3.1)$$

$$\nabla \times \mathbf{H}(\mathbf{r}, t) = \varepsilon \frac{\partial \mathbf{E}(\mathbf{r}, t)}{\partial t} + \frac{\partial \mathbf{P}_{NL}}{\partial t} \quad (3.2)$$

where ε and μ are the linear permittivity and permeability. $\mathbf{P}_{NL}$ is the induced nonlinear polarization vector and $\partial \mathbf{P}_{NL} / \partial t$ behaves as a source term results from the nonlinear

interaction. Assume only two different propagating modes in a plasmonic waveguide (pump mode at frequency ω_1 and generated third harmonic mode at ω_3), and neglect the linear propagation loss at first, the electric field $\mathbf{E}$ and magnetic fields $\mathbf{H}$ at any location $\mathbf{r}$ of the waveguide can be described as^{122, 123}

$$\mathbf{E}(\mathbf{r}, t) = \frac{1}{2} \sum_j \tilde{A}_j(z) Z_0^{1/2} \mathbf{F}_j(\mathbf{r}_\perp) \exp[i(\beta_j z - \omega_j t)] + c.c. \quad (3.3)$$

$$\mathbf{H}(\mathbf{r}, t) = \frac{1}{2} \sum_j \tilde{A}_j(z) Z_0^{1/2} \mathbf{G}_j(\mathbf{r}_\perp) \exp[i(\beta_j z - \omega_j t)] + c.c. \quad (3.4)$$

where $n_{eff}(\omega_j)$ is the effective mode index, $\beta_j = \omega_j n_{eff}(\omega_j)/c$ is the propagation constant, $\tilde{A}_j(z)$ is the slowly-varying mode amplitude, $\mathbf{F}_j(\mathbf{r}_\perp)$ and $\mathbf{G}_j(\mathbf{r}_\perp)$ are the mode profiles which have been normalized by $\iint_{A_{NL}} (\mathbf{F}_j \times \mathbf{G}_j^* + \mathbf{F}_j^* \times \mathbf{G}_j) \cdot \hat{z} dx dy / 4 = 1$, where $j=1$ and $j=3$ are related to the fundamental and the third harmonic modes. $Z_0 = \sqrt{\mu_0/\epsilon_0}$ is applied to simplify the calculation process. $\mathbf{r}=(x, y, z)$ and $\mathbf{r}_\perp=(x, y)$. Under the normalization, electric field power reads $P_j(z) = |A_j(z)|^2$.

Reciprocity theorem is applied to calculate $d\tilde{A}_j/dz$

$$\frac{d\tilde{A}_j}{dz} = -\frac{Z_0^{1/2}}{2} \iint_{A_{NL}} \left\langle \exp[-i(\beta_j z - \omega_j t)] \mathbf{F}_j^* \cdot \frac{\partial \mathbf{P}_{NL}}{\partial t} \right\rangle_t dx dy \quad (3.5)$$

where $\langle \dots \rangle_t$ means time averaging, A_{NL} represents the nonlinear cross-section, and the nonlinear polarization is described as¹²⁴

$$\mathbf{P}_{NL} = \epsilon_0 \chi^{(3)}(\mathbf{r})(\mathbf{E}(\mathbf{r}, t) \cdot \mathbf{E}(\mathbf{r}, t)) \mathbf{E}(\mathbf{r}, t) \quad (3.6)$$

With propagation loss, the complex propagation constant can be written as $\beta = \beta_j + i\alpha_j/2$, where β_j (phase propagation constant) and α_j (linear propagation loss coefficient) are both real and positive. We define

$$A_j = \tilde{A}_j \exp\left(-\frac{\alpha_j z}{2}\right) \quad (3.7)$$

and substitute it into Eq. (3.6), the nonlinear polarization is rewritten as

$$\mathbf{P}_{NL}' = \epsilon_0 \chi^{(3)}(\mathbf{r})(\mathbf{E}'(\mathbf{r}, t) \cdot \mathbf{E}'(\mathbf{r}, t)) \mathbf{E}'(\mathbf{r}, t) \quad (3.8)$$

where $\mathbf{E}(\mathbf{r}, t) = \frac{1}{2} \sum_j A_j(z) Z_0^{1/2} \mathbf{F}_j(\mathbf{r}_\perp) \exp[i(\beta_j z - \omega_j t)] + c.c.$. We then can obtain the following nonlinear coupled-wave equation

$$\frac{d\tilde{A}_j}{dz} = -\frac{Z_0^{1/2}}{2} \exp\left(\frac{\alpha_j z}{2}\right) \iint_{A_{NL}} \left\langle \exp[-i(\beta_j z - \omega_j t)] \mathbf{F}_j^* \cdot \frac{\partial \mathbf{P}_{NL}}{\partial t} \right\rangle_t dx dy \quad (3.9)$$

Note that the THG nonlinear process is based on $\chi^{(3)}$. And $\chi^{(3)}$ is accompanied by two-photon absorption (TPA) process. The real part and the imaginary part of $\chi^{(3)}$ are related to the nonlinear refractive index n_2 and the TPA coefficient α_2 by $\frac{\omega}{c} n_2 + \frac{i}{2} \alpha_2 = \frac{3\omega}{4\epsilon_0 c^2 n_0^2(\omega)} \chi^{(3)}$ ¹²⁵, where $n_0(\omega)$ is the linear refractive index.

With continuous wave incidence, the electric field amplitudes at fundamental and third harmonic waves follow

$$\frac{\partial \tilde{A}_1}{\partial z} = i[(I_1 |A_1|^2 + I_2 |A_3|^2) A_1 + I_3 (A_1^*)^2 A_3 e^{i\delta\beta z}] \exp\left(\frac{\alpha_1 z}{2}\right) \quad (3.10)$$

$$\frac{\partial \tilde{A}_3}{\partial z} = i[(3I_4 |A_1|^2 + I_5 |A_3|^2) A_3 + I_6 (A_1)^3 e^{-i\delta\beta z}] \exp\left(\frac{\alpha_3 z}{2}\right) \quad (3.11)$$

where $\delta\beta = \beta_3 - 3\beta_1$ is the phase-mismatch, α_j is the linear propagation loss coefficient, and the nonlinear parameter related overlap integrals I_1, I_2, I_3, I_4, I_5 , and I_6 are defined as

$$I_1 = \frac{1}{12} \oint\!\!\!\oint_{A_{NL}} (2|\mathbf{F}_1|^4 + |\mathbf{F}_1^2|^2) \cdot n_0^2(\omega_1, \mathbf{r}_\perp) \cdot [k_I n_2(\mathbf{r}_\perp)] dS \quad (3.12)$$

$$I_2 = \frac{1}{6} \oint\!\!\!\oint_{A_{NL}} (|\mathbf{F}_1|^2 |\mathbf{F}_3|^2 + |\mathbf{F}_1 \cdot \mathbf{F}_3|^2 + |\mathbf{F}_1 \cdot \mathbf{F}_3^*|^2) \cdot n_0^2(\omega_1, \mathbf{r}_\perp) \cdot [k_I n_2(\mathbf{r}_\perp)] dS \quad (3.13)$$

$$I_3 = \frac{1}{4} \oint\!\!\!\oint_{A_{NL}} (\mathbf{F}_1^* \cdot \mathbf{F}_3)(\mathbf{F}_1^* \cdot \mathbf{F}_1^*) \cdot n_0^2(\omega_1, \mathbf{r}_\perp) \cdot [k_I n_2(\mathbf{r}_\perp)] dS \quad (3.14)$$

$$I_4 = \frac{1}{6} \oint\!\!\!\oint_{A_{NL}} (|\mathbf{F}_1|^2 |\mathbf{F}_3|^2 + |\mathbf{F}_1 \cdot \mathbf{F}_3|^2 + |\mathbf{F}_1 \cdot \mathbf{F}_3^*|^2) \cdot n_0^2(\omega_3, \mathbf{r}_\perp) \cdot [k_I n_2(\mathbf{r}_\perp) + i \frac{\alpha_2(\mathbf{r}_\perp)}{2}] dS \quad (3.15)$$

$$I_5 = \frac{1}{4} \oint\!\!\!\oint_{A_{NL}} (2|\mathbf{F}_3|^4 + |\mathbf{F}_3^2|^2) \cdot n_0^2(\omega_3, \mathbf{r}_\perp) \cdot [k_I n_2(\mathbf{r}_\perp) + i \frac{\alpha_2(\mathbf{r}_\perp)}{2}] dS \quad (3.16)$$

$$I_6 = \frac{1}{4} \oint\!\!\!\oint_{A_{NL}} (\mathbf{F}_1^* \cdot \mathbf{F}_3)(\mathbf{F}_1^* \cdot \mathbf{F}_1^*) \cdot n_0^2(\omega_3, \mathbf{r}_\perp) \cdot [k_I n_2(\mathbf{r}_\perp) + i \frac{\alpha_2(\mathbf{r}_\perp)}{2}] dS \quad (3.17)$$

where $k_1 = 2\pi/\lambda_1$ is the fundamental wave number. By substituting Eq. (3.7) into Eqs. (3.10) and (3.11), we finally obtain the nonlinear coupled mode equations describing the THG process in a lossy plasmonic waveguide as

$$\frac{\partial A_1}{\partial z} = -\frac{\alpha_1}{2} A_1 + i[(I_1 |A_1|^2 + I_2 |A_3|^2) A_1 + I_3 (A_1^*)^2 A_3 e^{i\delta\beta z}] \quad (3.18)$$

$$\frac{\partial A_3}{\partial z} = -\frac{\alpha_3}{2} A_3 + i[(3I_4 |A_1|^2 + I_5 |A_3|^2) A_3 + I_6^* (A_1)^3 e^{-i\delta\beta z}] \quad (3.19)$$

Using the substitution of $A_1 = \sqrt{P_1} e^{i\varphi_1}$ and $A_3 = \sqrt{P_3} e^{i\varphi_3}$, and defining the pump-harmonic phase difference during the THG process as $\Psi = \delta\beta z + \varphi_3 - 3\varphi_1$, Eqs. (3.18) and (3.19) can be rewritten as

$$\frac{dP_1}{dz} = -\alpha_1 P_1 - 2I_3 P_1^{\frac{3}{2}} P_3^{\frac{1}{2}} \sin \Psi \quad (3.20)$$

$$\frac{dP_3}{dz} = -\alpha_3 P_3 + 2I_6 P_1^{\frac{3}{2}} P_3^{\frac{1}{2}} \sin \Psi \quad (3.21)$$

$$\frac{d\Psi}{dz} = \delta\beta + 3(I_4 - I_1) P_1 + (I_5 - 3I_2) P_3 + (I_6 P_1^{\frac{3}{2}} P_3^{-\frac{1}{2}} - 3I_3 P_1^{\frac{1}{2}} P_3^{\frac{1}{2}}) \cos \Psi \quad (3.22)$$

3.1.1 Critical conditions of efficient THG

Eqs. (3.18) (3.19) indicate that efficient THG in a lossy plasmonic waveguide depends on three critical conditions:

- 1) The interactive nonlinear medium should have large third-order nonlinear susceptibility $\chi^{(3)}$ since the induced nonlinear polarization vector $\mathbf{P}_{NL} = \varepsilon_0 \chi^{(3)} (\mathbf{E} \cdot \mathbf{E}) \mathbf{E}$ and the nonlinear source term $\partial \mathbf{P}_{NL} / \partial t$ depend on the $\chi^{(3)}$. In fact, THG efficiency is proportional to the square of $\chi^{(3)}$ ¹²⁶.
- 2) The pump-harmonic mode overlap in the waveguide should be sufficiently large in conjunction with reasonable linear propagation loss. THG efficiency is proportional to the square of the spatial mode overlap as well.
- 3) Phase-matching between the fundamental and the generated third harmonic waves should be satisfied. Phase-matching condition (PMC) represents the ideal state that the fundamental frequency (FF) power continuously transfers to the third harmonic (TH) power. Under PMC, the FF and TH waves can propagate at a same phase velocity, and accordingly, TH signal energy is able to accumulate continuously along its propagation. For phase-mismatch case, the build-up continuity of the TH

power is limited to the coherence length L_c ($L_c = \pi / \text{Re}(3\beta_1 - \beta_3)$ for the case that no loss is present, and β_1 and β_3 are the propagation constants of FF and TH modes), over which a phase difference of π accumulates between the FF and the TH waves, and correspondingly the TH power is transformed back to the FF reducing the generated TH. When PMC is satisfied, the effective nonlinear interaction length can also be greatly increased.

3.2 Asymmetric hybrid Plasmonic slot waveguide for efficient THG

Although it has been theoretically predicted to be possible to meet the above three critical conditions simultaneously for efficient THG, designing corresponding appropriate waveguides is still a major challenge. We provide a comprehensive study (numerically) on two designed metallic asymmetric hybrid plasmonic slot waveguides to develop guidance for efficient THG. One is a metal-hybrid-metal asymmetric plasmonic slot waveguide, the other one is a double-hybrid plasmonic slot waveguide. These two specific asymmetric slot waveguide structure aims to significantly enhance the pump-harmonic mode overlap in addition to the permission of PMC and high $\chi^{(3)}$.

3.2.1 Metal-hybrid-metal asymmetric plasmonic slot waveguide

According to our calculation, in plasmonic slot waveguides, the three critical conditions can be fulfilled or optimized simultaneously by employing special nonlinear materials and adjusting the geometrical parameters of the waveguide. In fact, in addition to the PMC (which can be achieved by inter-mode phase-matching technique through tuning the plasmonic waveguide geometrical parameters) and the nonlinear material with large $\chi^{(3)}$, a large enough pump-harmonic mode overlap aiming at improving the contributions of the two interactive modes to THG is highly necessary. According to Eq. (3.17), the pump-harmonic mode overlap is influenced by the field distributions of the FF and the TH, especially the TH since the FF is always assumed to propagate at fundamental mode. Due to the low pump-harmonic mode overlap in common planar waveguide structures¹²⁴, it is difficult to fully take advantage of the inter-modal phase-matching technique. To enlarge the mode overlap, one effective method is to reduce the negative contribution of the higher-order mode at TH. Asymmetric plasmonic slot waveguide structures can

meet this requirement^{127, 128}. Due to the asymmetric geometry, the asymmetry of the higher-order field is greatly enhanced and the counteraction effect of its negative field components can be greatly reduced. We would emphasize the significance of the asymmetric structure here because the pump-harmonic mode overlap in common symmetric planar waveguide structures is very small.

Waveguide structure. The schematic diagram of our designed metal-hybrid-metal symmetric plasmonic slot waveguide structure is shown in Figure 3.1 with silicon nanocrystal (Si-nc) and silicon integrated into the slot region. The whole waveguide is surrounded by air. The width and height of the Si-nc slot are $5r$ and h , respectively. The silicon slot width is r . Metal is defined to be silver (Ag, due to the relatively low loss) with a Lorentz-Drude permittivity dispersion given by $\varepsilon_{Ag} = \varepsilon_{\infty} - f_p / [f(f + i\gamma)]$, with $\varepsilon_{\infty} = 5$, $f_p = 2175$ THz, and $\gamma = 4.35$ THz¹²⁹. Material dispersions for accurately modeling the refractive indices of Si-nc and silicon are considered^{124, 130}. The PMC and the corresponding pump-harmonic mode overlap integral related I_6 will be evaluated to explore the THG conversion efficiency.

Figure 3. 1 Cross-section view of the proposed metal-hybrid-metal asymmetric (along x-axis) plasmonic slot waveguide. Light propagates along the z-axis.

PMC. To find the required phase-matching waveguide geometric parameters, the commercial COMSOL software for full-vector finite-element mode analysis is used to study the characteristics of the guided modes. We choose the fundamental mode at FF to phase-match the first mode at TH since the pump-harmonic mode overlap for the other modes is very small due to the mode symmetry. We first set a fixed slot height $h = 20$ nm and adjust the slot width r to fulfill PMC. Figure 3.2 shows the dependence

of the effective mode indices of the two guided modes on r . The intersection point indicates the phase-matching point.

Figure 3. 2 Effective mode indices of the fundamental mode at FF and the first-order mode at TH as a function of r . ‘0th’ stands for the fundamental mode, while ‘1st’ stands for the first-order mode.

Field distribution. Figure 3.3 shows the electric field E_y distributions. For the two guided modes, electric fields are tightly confined in the subwavelength metallic slot region. The first-order mode at TH results from the coupling between the fundamental mode in the Si-nc slot region and the opposite fundamental mode in the silicon slot region which forces the counteractive electric field part into the silicon part. This essential field-guiding mechanism differentiates the proposed metal-hybrid-metal asymmetric plasmonic slot waveguide from the previously reported metal-insulator-metal waveguide. Due to the silicon, the field confinement and enhancement of the negative fundamental mode are greatly reduced compared with the positive field in the Si-nc region. Therefore, the counteract contribution of the first-order mode at TH to the pump-harmonic mode overlap is greatly reduced, which will yield high corresponding THG conversion efficiency where the contribution of the negative part of the first-order mode at TH to THG becomes almost negligible in the integration domain as depicted in Eq. (3.17). The principle of the sufficient large mode overlap can be seen more clearly in Figure 3.3(c), where plots of the one dimensional normalized E_y distributions along the x cutline of $y=0$ (as the horizontal dash lines plotted in Figures 3.3(a) and 3.3(b)).

Figure 3. 3 Electric field distributions of (a) fundamental mode at FF, (b) first mode at TH. (c) One dimensional normalized electric field distributions along the x cutline of $y=0$ (as the horizontal dash lines shown in (a) and (b)).

Figure-of-merit (FOM). Then we carried out an optimization of the waveguide geometrical parameters to further enhance the pump-harmonic mode overlap. We analyze the influence of the slot height h at PMCs on the mode overlap performance. In Figure 3.4(a), the silicon slot width to satisfy PMC and the corresponding mode overlap related integral $|I_6|$ are plotted as a function of h . With increased h , the silicon slot width required to ensure PMC increases and $|I_6|$ decreases correspondingly due to the weaker field confinement. When the slot height is increased, the electric field distribution at TH gradually distorts horizontally with more and more electromagnetic energy concentrates in the silicon slot region, which significantly reduces the pump-harmonic mode overlap. It can be summarized here that the proposed asymmetric plasmonic waveguide has better THG property with a narrower slot. However, too narrow slots cannot be considered due to the fabrication feasibility. On the other hand, reducing the slot width can also increase the linear propagation loss. Since less power of FF can be transferred to TH with higher loss, we define a figure-of-merit (FOM) parameter for the phase-matched THG to evaluate the overall waveguide performance as $FOM_{FF,TH} = |I_6|/\alpha_{FF,TH}$ where α_{FF} and α_{TH} are the linear propagation loss

coefficients at FF and TH, respectively. FOM as a function of h are plotted in Figure 3.4(b). Both FOMs at FF and TH decrease with increasing h , indicating that the most promising slot height for efficient THG is 20 nm.

Figure 3. 4 (a) Silicon slot width r along with the mode overlap related $|I_6|$, and (b) FOMs of FF and TH as a function of the slot height h at different PMCs.

THG conversion efficiency. Now we calculate the THG conversion efficiency by solving Eqs. (3.18) and (3.19) in MATLAB for the case of Figure 3.3 in which the fundamental mode at FF is converted into the first-order mode at TH. The THG conversion efficiency is defined as $\eta = P_3(L_p)/P_1(0)$, where $P_1(0)$ is the pump power injected into the waveguide, $P_3(L_p)$ is the maximum output power of the generated third harmonic wave, and L_p is the corresponding waveguide length, respectively. Figure 3.5(a) reports the THG conversion efficiency contour map with different initial detuning constants. It is found that a maximum THG conversion efficiency is achieved at an optimized initial detuning. This optimized initial detuning constant (negative value) $\delta\beta$ is used to compensate for the nonlinear phase-shift during the THG process. It has been demonstrated experimentally achievable by perturbing the waveguide geometry with pump-harmonic mode overlap almost unchanged¹³¹. We further calculate the conversion efficiency at different waveguide geometries to verify that the optimized geometry in Figure 3.4(b) can generate the most efficient THG. Figure 3.5(b) shows the conversion efficiency with respect to the slot height at different PMCs at a fixed pump power of 1 W and initial detuning of 0. It is obviously found that slot height of 20 nm under the PMC can lead to higher conversion efficiency. Fix the slot height to be 20 nm with initial detuning $\delta\beta = 0$, the maximum output TH powers with different input pumping powers are also investigated as illustrated in Figure 3.5(c). The cubic

dependence on the pumping power of the output TH power represents a significant advantage of THG in terms of nonlinear signal processing¹⁰², material processing¹⁰³, scanning microscopy¹⁰⁴, and optical performance monitoring¹⁰⁵.

Figure 3. 5 (a) Contour map of the conversion efficiency with different initial detuning constants. (b) Conversion efficiency as a function of the slot height at PMCs. (c) Maximum output power $P_3(L_p)$ versus the pumping power.

Note that, we have excluded the THG process both at the metal surfaces and in the metal layers during our calculation though metal benefits from strong third-order nonlinearity at optical frequencies. Since the electric field is tightly confined in the slot region, does not penetrate deeply inside the metal layers and decays exponentially with distance from the metal-dielectric interfaces, the generation of the nonlinear response in the silver layers or at the silver surfaces can be rationally neglected.

In this section, we have reported three crucial conditions dependence of efficient THG in lossy waveguides. In addition to PMC and high third-order nonlinear susceptibility of the silicon nanocrystal, large enough pump-harmonic mode overlap along with moderate linear propagation loss in the proposed metal-hybrid-metal asymmetric plasmonic slot waveguide are achieved, which result in efficient THG. In the geometry optimized plasmonic waveguide, we get a THG conversion efficiency of $\eta = 2.79 \times 10^{-4}$ at the waveguide length of $L_p = 4.5 \mu\text{m}$ with input pump power of 1 W.

3.2.2 Double-hybrid plasmonic slot waveguide

This part presents a proposed double-hybrid plasmonic slot waveguide (DHPSW) with Si-nc integrated into the two parallel slots acting as the main interactive nonlinear material for efficient THG. The effect of nonlinear loss, which is contributed by the TPA effect, on the THG conversion efficiency is fully investigated. The calculation results reveal that the THG conversion efficiency can be greatly enhanced by the field

confinement and enhancement, whereas it is greatly impeded in the presence of the TPA effect.

Waveguide geometry and TPA effect. The proposed DHPSW is composed of Ag/Si-nc/Si/Si-nc/Ag layer stack and its cross-section view is depicted in Figure 3.6. By means of this DHPSW, we study THG conversion from 3600 nm to 1200 nm with the effect of nonlinear loss. We chose these two specific wavelengths so that we can just focus the nonlinear loss effect on the generated third harmonic wave for the sake of simplicity.

The nonlinear refractive index n_2 and the TPA coefficient α_2 of Si-nc, Si, and SiO₂ are taken from the previous publications¹³²⁻¹³⁴. Nonlinear loss caused by TPA effect may act as an additional loss mechanism. With the consideration of the TPA effect, the power evolution of the generated third harmonic wave $P_3(z)$ along the propagation z direction follows

$$\frac{dP_3(z)}{dz} = -\alpha_3 P_3(z) + 2 \text{Im}\{\gamma\} P_3^2(z) + 2I_6 P_1^{\frac{3}{2}}(z) P_3^{\frac{1}{2}}(z) \sin \Psi \quad (3.23)$$

where $P_3(z)$ is the generated third harmonic wave power by the waveguide, γ is the nonlinear coefficient, $\text{Im}\{\gamma\}$ refers to the nonlinear loss, and $\Psi = \delta\beta z + \varphi_3 - 3\varphi_1$ where $\varphi_{1,3}$ are the initial phase of the two guided modes. Note that we ignore the free-carrier absorption effect since the waveguide has very weak carrier effect compared with TPA^{132, 135}. The input pump intensity is sufficiently low and the nonlinear loss caused by 3PA effect does not contribute appreciably to the THG¹³³.

Figure 3. 6 Schematic of the proposed DHPSW: $W_{Ag}=200$ nm, $w=50$ nm, $h=500$ nm, $h_{SiO2}=500$ nm.

Guided field distribution. To get an intuitionistic understanding of the benefits of the double-hybrid structure, we plot the one-dimensional E_x distributions at $y=0$, as shown in Figure 3.7. The guided electric fields at FF and TH are strongly confined in the two nanoscale plasmonic slot regions. Here, the supported fundamental mode at FF results from the coupling between the SPPs mode in the Si-nc slot and the TM_{00} dielectric mode in the Si slab. While the second-order SPPs-like mode at TH comes from the coupling between the SPPs mode and the TM_{02} dielectric mode. The tail of the second-order mode distributed in the Si slab layer undergoes two signs of change, and it is clear that the sign change only occurs in the high-index Si slab part. In the main interactive slot areas, the two modes are nearly sharing the same field distribution. As a consequence, the pump-harmonic mode overlap is greatly enhanced. Furthermore, by taking advantage of the properties of the hybrid waveguide structure, the negative component of the second-order mode at TH is forced into the Si slab part with reduced mode confinement and lower $\chi^{(3)}$ leading to a significantly enhanced THG nonlinear coefficient $|I_6|$. It is interesting to point out that the THG nonlinear coefficient $|I_6|$ between these two different orders modes is larger than that of two fundamental modes at FF and TH in the proposed DHPSW structure.

Figure 3. 7 One-dimensional E_x distributions of the two guided modes along the x-cutline at $y = 0$.

TPA effect on THG efficiency. The THG conversion efficiency of the DHPSW is related to the third harmonic fields generated from the Si-nc slot, the Si slab, and the SiO_2 substrate. For reference, the relationship between the third harmonic power and the pump power is plotted in Figure 3.8. The conversion efficiency is higher in the case of

only considering the linear propagation loss. A cubic dependence of the generated third harmonic wave power on the pumping power without the effect of nonlinear loss can be seen. The deviation from the cubic behavior, as the red dash line, is attributed to the TPA damping. A larger reduction will occur as the pump power increases, resulting in a severer reduction on the conversion efficiency.

Figure 3. 8 The generated third harmonic power value versus the input pump power with and without TPA effect.

In addition, we emphasize the geometry flexibility of the proposed DHPSW taking the nonlinear loss into account. The phase matching tolerance can be evaluated with $|\delta\beta| < \delta\beta_c = 2\pi/L_p$. Figure 3.9(a) gives the phase mismatch trend versus the slot width w . It can be seen that the condition $|\delta\beta| < \delta\beta_c$ can be satisfied under a wide range of slot width (from 37 nm to 65 nm). Figure 3.9(b) shows the phase mismatch versus the slot height h . The condition $|\delta\beta| < \delta\beta_c$ is also satisfied for a wide range of slot height (from 470 nm to 530 nm). These results are due to the strong mode confinement and the short needed waveguide length for high THG conversion efficiency of the DHPSW.

Figure 3. 9 Phase mismatch versus (a) the slot width w and (b) the slot height h .

We further optimize the waveguide geometrical parameters to achieve maximum FOM of the DHPSW to realize corresponding maximum THG efficiency. We perform an optimization of the DHPSW cross-section parameters by maximizing the FOM which is defined as $FOM = |I_6|$, α is the total loss coefficient. The total loss coefficient consist of two parts, which can be expressed as $\alpha = \alpha_0 + \alpha_{NL}I$, where α_0 is the linear coefficient, α_{NL} is the nonlinear loss coefficient, I is pumping light intensity. For FF, the nonlinear loss coefficient is considered to be 0. For TH, the nonlinear loss coefficient is assumed to be the TPA coefficient of the materials. We neglect the non-degenerate TPA effect since the degenerate TPA effect is much more significant. Figure 3.10(a) shows the silicon slab width versus the slot width under different PMCs. With a wider slot, the silicon slab width decreases accordingly to obtain phase matching condition since more third harmonic field is concentrated into the silicon slab while the pump field distribution is much less influenced. Accordingly, the third harmonic generation efficiency also reaches the maximum value. Since these two slot layers are relatively thin, increasing the slot width causes very little changes for both FOM and THG conversion efficiency.

Figure 3. 10 (a) Silicon slab width w_{Si} and (b) FOM and the corresponding THG conversion efficiency as a function of the slot width w at different PMCs with “1” referring to the pump wave and “3” referring to the third harmonic wave.

In this section, we numerically demonstrate the possibility of achieving efficient THG in a DHPSW with the consideration of the nonlinear loss effect. Analysis shows that even the nonlinear loss by TPA greatly impairs the nonlinear property of the waveguide, a key observation during the simulation process is that the large $\chi^{(3)}$ of Si-nc and the large mode overlap enable the host waveguide to have a two orders of magnitude increment in the THG conversion efficiency compared to other reported nanoscale plasmonic waveguides. The capability of generating efficient THG within short waveguide length and small fabrication-error sensitivity under TPA effect enable the realization of THG based applications of the proposed DHPSW in nanophotonics.

3.3 Efficient THG in a graphene plasmonic coupler

The three critical conditions can be fulfilled by the combination of metallic plasmons with efficient nonlinear dielectrics where the metallic plasmons exhibit large electric field strength and the nanostructured structures can be designed carefully to achieve PMC to enhance THG conversion. In this section, we move on to the graphene plasmons to extend efficient THG to the mid-IR region. Since mid-IR also serves as an ideal test-bed for next-generation plasmonic architectures and it is difficult to use metallic plasmonic resonance to achieve plasmons at mid-IR range. Graphene enables tunable mid-IR plasmons (graphene plasmons also surpass metallic plasmons by properties of tighter field confinement and lower loss) and at the same time possesses very much high

$\chi^{(3)}$. This section presents our designed graphene plasmonic coupler waveguide to pursue highly efficient tunable THG numerically with: (1) phase-matching of graphene plasmons at fundamental and third harmonic frequencies, and (2) peak $\chi^{(3)}$ of doped graphene. The significantly enhanced nonlinear optical responses in the graphene plasmonic coupler make this configuration an ideal platform to develop new frequency generators, and signal processing at mid-IR or terahertz frequencies.

3.3.1 Graphene plasmonic coupler

Figure 3.11(a) illustrates the three-dimensional configuration of the proposed graphene plasmonic coupler where FF beam at ω_1 incidents from the left graphene nanoribbon and TH wave at ω_3 is generated from the other side. The two-dimensional cross-section is illustrated in Figure 3.11 (b). During the third-order nonlinear process, the excited pump plasmons in nanoribbon a act as the nonlinear transformer that converts the guided evanescent mode energy to the stimulated TH mode in nanoribbon b. Graphene sections with fixed Fermi level of $E_{F0}=1$ eV are taken as background states possessing little contribution to the THG. $\epsilon_1=2$ and $\epsilon_2=1$ are the permittivities of the nondispersive silica substrate and the surrounding air. ϵ_3 is to be determined to obtain PMC. The fixed background Fermi level of $E_{F0}=1$ eV aims to increase the evanescent mode component while the small distance C of 2 nm between the two graphene nanoribbons enables a strong coupling between the two propagating modes, thus increasing the pump-harmonic mode overlap for efficient THG. Considering the practical achievement, we recommend doping the background graphene to be 0.6 eV or larger and the separation C to be as small as possible for efficient THG, which will be discussed later.

Figure 3. 11 The configuration of the graphene plasmonic coupler. (a) Three dimensional schematic illustration. FF wave at a frequency of ω_1 (red arrow) illuminating from the left side nanoribbon is converted to TH wave at frequency of ω_3 (blue arrow) in the right side. (b) Two dimensional configuration consisting of parallel graphene nanoribbons with different doping levels sandwiched between dielectric media with relative permittivities of ϵ_1 , ϵ_2 , and ϵ_3 .

3.3.2 PMC effect

We use nonlinear coupled mode theory as presented in section 3.1 to model the power transfer between the FF and TH waves. Under PMC and lossless conditions, the generated TH intensity I_3 in a bulk sample from an incident beam with irradiance I_1 can

be described by
$$I_3 = \frac{(2\pi)^4 (3\omega)^2}{n_1^3 n_3 c^4} |\chi^{(3)}|^2 I_1^3 L^2 \rho^{126}.$$
 n_1 and n_3 are the refractive indices of

the nonlinear matter at FF and TH frequencies, L is the interaction length, and ρ is the pump-harmonic spatial overlap. This TH intensity expression indicates the crucial roles of $\chi^{(3)}$ and pump-harmonic spatial overlap for efficient THG.

To characterize the THG conversion with plasmonic wave propagation along the graphene coupler, we first investigate the PMC property. PMC represents the ideal state that the FF power transfers to the TH power continuously. Finite element method calculations for fundamental and third harmonic mode profiles and their mode indices based on commercial COMSOL Multiphysics are performed. Graphene is modeled as a thin layer with a thickness of 0.5 nm by a dielectric permittivity of $1 + i\sigma(\omega)/(\omega\epsilon_0 t_g)$, where $\sigma(\omega)$ is the linear surface conductivity described by the Kubo formula,^{136, 137} ω is the light frequency, and t_g is the graphene layer thickness. We set the carrier relaxation

time to be $\tau = 0.1$ ps during the calculation according to the experimental limited $\mu \approx 10000 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ^{14, 77, 138}. Larger relaxation time (i.e., lower degrees of propagation loss) can be used to further enhance the harmonic generation efficiency. Since the nonlinear conductivity of graphene is 17 orders of magnitude smaller compared to the linear conductivity, the nonlinear conductivity is not considered during the calculation. For a single graphene sheet surrounded by two dielectrics with dielectric permittivity of ϵ_1 and ϵ_2 , the surface plasmon dispersion is modeled by ⁷⁹

$$\frac{\epsilon_1}{\sqrt{\beta^2 - \epsilon_1 \omega^2 / c^2}} + \frac{\epsilon_2}{\sqrt{\beta^2 - \epsilon_2 \omega^2 / c^2}} = j \frac{\sigma(\omega)}{\omega \epsilon_0}$$

where β is the propagation constant, ω is the angular frequency, c is the free space light speed, $\sigma(\omega)$ is the graphene conductivity, and ϵ_0 is the vacuum permittivity. Effective mode index is defined as $\text{Re}(\beta)/k_0$, where k_0 is the corresponding wavenumber in free space. Modifying the dielectric permittivity of the surrounding media will change the plasmonic wave-vector. This suggests phase-matching between the FF and TH plasmonic modes in the graphene plasmonic coupler through tuning the surrounding permittivity.

For a thin graphene layer, due to the small thickness, the accumulated phase-mismatch normal to the film plane is negligible and the requirement of matched wave-vector normal to the film is unnecessary. For propagating THG along the graphene film, perfect phase-matching is essential to ensure the continuous increment of the generated harmonic power. The Fermi levels of the two graphene nanoribbons are set to be $E_{F1}=E_{F2}=0.5$ eV at first. FF wavelength is fixed to be $\lambda_1=6 \mu\text{m}$ during the calculation. Quantitative analysis of the phase-matching-assisted THG is presented in Figure 3.12. The excited graphene plasmons provide strongly localized and highly enhanced electromagnetic field. Ideally, we would like to use fundamental modes for both of the FF and the TH waves, simply because of the high field enhancement. However, the dramatically localized field impairs pump-harmonic spatial overlap due to the lack of evanescent mode component. It hence needs to equilibrate the field enhancement and mode localization to boost the pump-harmonic spatial overlap and therefore permit efficient THG. We thus examine three different PMC pairs with different guided mode orders (two fundamental (0th) modes pair, first-order (1st) FF and 0th TH modes pair, and 0th FF and 1st TH modes pair).

The electromagnetic field of the plasmonic modes shown in Figure 3.12 emphasizes the high level of nanoscale localization. As shown in Figure 3.12, higher-

order mode possesses lower intensity enhancement and larger evanescent mode component. Figures 3.12(c), 3.12 (f), and 3.12(i) depict the effective mode index at FF and TH waves and the corresponding THG conversion efficiency as a function of ϵ_3 . The effective mode index tendencies reflect the achievable of PMC for different FF and TH modes pairs. The trade-off between the field enhancement and the evanescent mode component for FF and TH waves results in a larger pump-harmonic spatial overlap and a higher corresponding THG efficiency for the 0th FF and 0th TH modes pair as can be seen in Figure 3.12(c). We study the mode-order effect here to emphasize modulating the coupling strength between the fundamental and third harmonic modes by controlling the guided mode-order. Concurrently, different higher-order modes can phase-match the pump wave to the third-harmonic wave, most of them are unavailable for THG because of the corresponding small field enhancement and poor pump-harmonic spatial overlap. Figures 3.12(f) and 3.12(i) reveal that the THG efficiencies of the 1st TH and 0th FF PMC pair and the 0th FF and 1st TH PMC pair exceed 3 orders of magnitude compared to the value in a freestanding graphene. A relatively noticeable increment of 10^4 -fold is achieved for the PMC pair between 0th FF and 0th TH. The three different PMC pairs produce identical results that PMC can greatly enhance the THG strength. Carefully controlling the guided mode-order is necessary as well to optimize the third-order nonlinear process.

Figure 3. 12 THG assisted by PMC with stimulated plasmons producing high electric field enhancement. Electric field profiles of E_z in the x - y plane under PMC pairs between (a) 0th FF and (b) 0th TH modes, (d) 1st FF and (e) 0th TH modes, and (g) 0th FF and (h) 1st TH modes. (c), (f), (i) Effective mode index (n_{eff}) at FF and TH, and the THG conversion efficiency (η) for the corresponding three PMC pairs as a function of the dielectric permittivity ϵ_3 . Black: FF mode, red: TH mode, and blue: conversion efficiency.

Figure 3.13 depicts the THG conversion efficiency over propagation distance along the graphene plasmonic coupler. For non-PMC conditions, the ϵ_3 value for the different mode pairs is set to be half of the corresponding value at which PMC is satisfied. Due to the phase-mismatch, the buildup continuity of the TH power is limited to the coherence length, over which a π phase difference accumulates between the FF and the TH waves. With PMC, the FF and TH waves can propagate with same phase velocity, and accordingly, TH signal energy is able to accumulate continuously along its propagation as depicted by the black lines in Figure 3.13. More than 2 (4) orders of

magnitude improvement in the THG conversion is achieved for the 1st FF and 0th TH modes pair (0th FF and 1st TH modes pair), and over 6 orders of magnitude improvement for the 0th FF and 0th TH modes pair. This is due to the greatly increased effective nonlinear interaction length under PMC and the light energy from the pump wave is continuously transformed to the signal third-harmonic. The peak THG conversion efficiency is caused by the interplay between the propagation loss and the converted third harmonic power (per unit length). The intrinsic graphene layer is considered as the primary source of loss due to the interband absorption and intraband transition. No Landau damping is considered. The plasmon damping induced by the interband excitation can be greatly suppressed when the graphene Fermi level is larger than the plasmon energy. We only consider the loss due to intraband transitions during the calculation.

Figure 3.13 THG conversion efficiency over the propagation distance under PMC (black, left y-axis) and non-PMC (blue, right y-axis) conditions for (a) 0th FF and 0th TH modes pair, (b) 1st FF and 0th TH modes pair, and (c) 0th FF and 1st TH modes pair.

3.3.3 Peak $\chi^{(3)}$ effect

An analytical formalism of $\chi^{(3)}$ for doped graphene based on Genkin-Mednis nonlinear conductivity theory has been reported¹³⁹, indicating the dependence of graphene $\chi^{(3)}$ magnitude on the carrier concentration and the working frequency. The static limit ($\omega \rightarrow 0$) of the THG susceptibility of graphene can be described as

$$\chi^{(3)}(0) = \frac{33}{20} \frac{e^2 (\hbar v_F)^2}{\pi \epsilon_0 d_g (2E_F)^5} \quad (139)$$

where $v_F = 10^6 \text{ ms}^{-1}$ is the graphene Fermi velocity, ϵ_0 is

the vacuum permittivity, and $d_g = 0.5 \text{ nm}$ is the effective thickness of the graphene layer.

For ω being nonzero, $\chi^{(3)}$ of graphene can be obtained by

$$\chi^{(3)}(-3\omega; \omega, \omega, \omega) = \chi^{(3)}(0) \left\{ \left[\frac{10}{11} F_{inter}^1(Z) + \frac{40}{33} F_{comb}^1(Z) \right] + i\delta \left[\frac{10}{11} F_{inter}^2(Z) + \frac{40}{33} F_{comb}^2(Z) \right] \right\} \quad (2.24)$$

The dimensionless functions $F_{inter}(Z)$ and $F_{comb}(Z)$ are used to describe the Fermi level and frequency dependence of the nonlinear optical process. $Z = \hbar\omega/E_F$ and $\delta = \hbar\Gamma/E_F$ represent the photon energy and the broadening parameter normalized to the Fermi level. Table 3.1 shows the values of all parameters involved to calculate $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ at different Fermi levels. Graphene possesses a resonant peak in $\chi^{(3)}$ when the light frequency equals to two-thirds of the Fermi level. Peak graphene $\chi^{(3)}$ can be pursued when the Fermi level is set to be 0.31 eV for FF wavelength fixed at 6 μm .

TABLE 3. 1 Z , δ , A and B values at different graphene doping levels to calculate $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ at 6 μm pump wavelength.

E_F (eV)	0.31	0.4	0.5	1
Z	$\frac{2}{3}$	0.5177	0.4141	0.2071
δ	$\frac{1}{31}$	$\frac{1}{40}$	$\frac{1}{50}$	$\frac{1}{100}$
$A_1(Z)$	0.0136	0.0131	0.0129	0.0126
$A_1(2Z)$	0.0187	0.0155	0.0143	0.0129
$A_1(3Z)$	0.0700	0.0230	0.0175	0.0134
$A_2(Z)$	0.0036	0.0026	0.0020	9.4027e-04
$A_2(2Z)$	0.0145	0.0074	0.0049	0.0020
$A_2(3Z)$	1.3958	0.0272	0.0116	0.0032
$B_1(Z)$	0.0160	0.0145	0.0137	0.0128
$B_1(3Z)$	-0.4927	0.0650	0.0319	0.0154
$B_2(Z)$	0.0061	0.0041	0.0031	0.0014
$B_2(3Z)$	26.8155	0.0990	0.0282	0.0054
F_{inter}^1	0.6169	0.1937	0.1443	0.1083
F_{inter}^2	12.5586	0.2425	0.1026	0.0283
F_{comb}^1	-33.1696	3.9090	1.9961	1.0659
F_{comb}^2	3.3168×10^3	11.6600	3.3048	0.6436

We study three peak $\chi^{(3)}$ cases in the plasmonic coupler for efficient THG conversion: left peak $\chi^{(3)}$ case ($E_{F1}=0.31$ eV, $E_{F2}=0.5$ eV), right peak $\chi^{(3)}$ case ($E_{F1}=0.5$

eV, $E_{F2}=0.4$ eV), and two peak $\chi^{(3)}$ case ($E_{F1}=0.31$ eV, $E_{F2}=0.4$ eV). The real and imaginary $\chi^{(3)}$ values with different graphene doping levels are depicted in Figure 3.14. For the right peak and two peak $\chi^{(3)}$ cases, the Fermi level of the nanoribbon b is set to be 0.4 eV, because when E_{F2} is set to be 0.31 eV, it becomes difficult to stimulate TH plasmons in nanoribbon b and it is unlikely to realize PMC by only tuning ϵ_3 . For the left peak $\chi^{(3)}$ case, THG efficiency at a level of 10^{-4} is achieved between the 0th FF and the 0th TH, as can be seen from Figure 3.15.

Figure 3. 14 Total (black line), real (Re, red line) part and imaginary (Im, blue line) part of the graphene $\chi^{(3)}$ at 6 μm under different doping levels.

The electric field enhancement of the FF wave is further increased for different PMC pairs because lower Fermi level value corresponds to smaller wave-vector for graphene plasmons. Due to the trade-off between field enhancement and mode localization, pump-harmonic mode overlap reaches its maximum value under two fundamental modes pair. The obtained highest conversion efficiency of 6.3051×10^{-4} is more than 10 orders of magnitude larger than that in a freestanding monolayer graphene.

Figure 3. 15 THG conversion efficiency along the propagation distance for 0th FF and 0th TH (black line), 1st FF and 0th TH (red line), and 0th FF and 1st TH (blue line) PMC pairs.

For the right peak $\chi^{(3)}$ case as shown in Figure 3.16, the highest conversion is provided by the 1st FF and 0th TH PMC pair. Even the nanoribbon b is the main interaction nonlinear matter, and its $\chi^{(3)}$ is larger compared with the left peak $\chi^{(3)}$ case, it is still difficult to achieve higher THG efficiency. The electric field distribution for the three different PMC pairs shows that reduced evanescent mode components lead to smaller pump-harmonic spatial overlap. For the two peak $\chi^{(3)}$ case as shown in Figure 3.17, the plasmonic coupler offers higher nonlinearity, while suffers from large propagating loss and strong nonlinear phase-modulation. The nonlinear interaction length is reduced to be less than 20 nm. Although pump-harmonic spatial overlap is noticeable in this case, the generated TH power drops too quickly to obtain efficient THG.

Figure 3. 16 Electric field profiles of E_z in the x-y plane under different PMC pairs for right peak $\chi^{(3)}$ case between (a) 0th FF and (b) 0th TH modes, (d) 1st FF and (e) 0th TH modes, and (g) 0th FF and (h) 1st TH modes. (c), (f), and (i) THG conversion efficiency along the propagation distance for the three different PMC pairs.

Figure 3. 17 Electric field profiles of E_z in x - y plane under different PMC pairs for two peak $\chi^{(3)}$ case between (a) 0th FF and (b) 0th TH modes, (d) 1st FF and (e) 0th TH modes, and (g) 0th FF and (h) 1st TH modes. (c), (f), and (i) THG conversion efficiency along the propagation distance for three different PMC pairs.

Considering the practical availability, we provide the background Fermi level E_{F0} and the separation C dependences of the THG conversion at PMC in Figure 3.18. As shown in Figure 3.18(a), although 60% decrement of the THG efficiency is induced when decreasing the background Fermi level to be 0.6 eV, the corresponding conversion efficiency is still over 9 orders of magnitude larger than that from bare graphene. Further decreasing the background Fermi level to be less than 0.6 eV makes it difficult to obtain PMC by only tuning the permittivity of the top cladded layer. Since PMC guarantees the continuous transformation of the pump power to the third harmonic power, we recommend doping the background graphene to be 0.6 eV or larger. From Figure 3.18(b), THG efficiency at separation of 8 nm is decreased to be 0.82% of that from the coupler at separation of 2 nm due to the weakening of coupling strength. Even so, the THG efficiency is 7 orders of magnitude higher than that from a bare monolayer graphene.

Therefore, our proposed graphene plasmonic coupler can be used to pursue efficient THG in practical applications. The quantum size and nonlocal effects, and the temperature effect are not included in our current calculations. These effects may change the quantitative values of the results we obtain, while the idea of using phase matching and peak $\chi^{(3)}$ still remains valid. Further investigations of the quantum effects and temperature dependence are beyond the scope of this work. We will leave these investigations to our future study.

Figure 3. 18 Normalized THG conversion efficiency of left peak $\chi^{(3)}$ case at PMC for 0th FF and 0th TH versus (a) background graphene Fermi energy level E_{F0} with fixed $C=2$ nm, and (b) separation C at $E_{F0}=1$ eV.

Therefore, the combination of PMC and peak $\chi^{(3)}$ provided by the graphene plasmonic coupler leads to the significantly enhanced THG. THG efficiency more than 10 orders of magnitude higher than that of a bare monolayer graphene is achieved. The plasmonic modes at FF and TH modes provide high field enhancement, and the PMC ensures the continuous transformation of the FF power to the TH power. The peak $\chi^{(3)}$ of the doped graphene offers intense nonlinearity and thereby remarkable nonlinear response. Our calculation represents a theoretical evidence of extraordinary THG from a nanoscale graphene plasmonic coupler structure at the mid-IR regime, which ensures further exploration of tunable sub-wavelength nonlinear coherent sources, and ultra-compact signal processing in mid-IR and terahertz spectral regimes.

3.4 Efficient THG from a hybrid silicon-plasmonic system

Nonlinear optical metasurfaces are promising structures for optical switching^{140, 141}, upconverting tunable laser¹⁴², and fast label-free imaging¹⁴³. Continuing efforts have

been made to investigate third harmonic generation (THG) by metallic plasmons. To achieve high THG conversion at nanometre scale, an ITO nanoparticle decorated with a plasmonic nanorod dimer structure¹⁴⁴ is proposed. To realize coherent confinement of the electric field to pursue higher THG conversion, a silicon/gold (nanodisk/nanoring) hybrid structure¹⁴⁵ is proposed to combine metallic and high-index dielectric nanoparticle. A more recent nonlinear metasurface¹⁴⁶ is designed to have a giant third-order nonlinear susceptibility for efficient THG in the mid-infrared region. Although a plasmonics-enhanced harmonic generation has been widely studied, these devices usually exhibit high intrinsic losses which severely limit the corresponding conversion efficiency. An appropriate solution would be the metal-silicon hybrid plasmonic devices since silicon possesses large nonlinear susceptibility and relatively small dissipation losses at infrared frequencies. In this section, we propose and experimentally demonstrate a hybrid silicon-plasmonic system with gold bowtie nanoantennas integrated onto the surface of a silicon substrate to couple the LSPs into the silicon for efficient THG which is desirable for CMOS-compatible applications of hybrid silicon-plasmonic systems, such as silicon amplifiers and silicon laser sources. This hybrid system employs the gold bowtie arrays to produce large field enhancements and the silicon substrate as the third-order nonlinear element thereby offers the advantages of low-loss and compact on-chip dimensions. Benefitting from the large intrinsic density, large third-order nonlinearity, and high electric field enhancement, the hybrid silicon-plasmonic system is a promising platform for efficient THG. The experimental outcomes expand contemporary knowledge on localized plasmonic modes to control the nonlinear properties of the bulk silicon, revealing important properties for the development of efficient frequency upconversion metasurfaces. Moreover, the exploitation of the optical nonlinear response of nanometre-scale plasmonic structure integrated with macroscopic silicon substrate provides new degrees of freedom to improve the already remarkable performance of silicon photonics. It also has great potential for further miniaturization in future on-chip applications.

3.4.1 Third-order upconversion mechanism

Figure 3.19(a) depicts the schematic of the third-order nonlinear upconversion mechanism of the hybrid silicon-bowtie plasmonic system where pump light is incident normally and the generated harmonic beam is detected from the reflection. The gold

bowtie arrays can confine the far-field incidence to its vicinity, and the supporting silicon substrate acts as a transmitter converting three incident photons at frequency of ω to one emission photon at frequency of 3ω . Each bowtie antenna consists of two identical equilateral triangles (flare angle $\theta=60^\circ$) opposing tip-to-tip and separated by a nanoscale gap. The side length and thickness of each equilateral triangle are set as $L=220$ nm and $t=30$ nm, respectively. The gap between the triangles in the bowtie arrays varies from 30 nm to 44 nm. The gap between the triangles in the bowtie arrays varies from 30 nm to 44 nm. The horizontal and vertical center-to-center spacing (i.e. pitch period Λ) is $1\ \mu\text{m}$ (corresponding to a surface coverage of 4.2%) to avoid plasmonic cross-coupling. We fabricated 4 patches of bowtie arrays. Each patch has an area of $100\ \mu\text{m}\times 100\ \mu\text{m}$. Figure 3.19(b) shows a representative SEM image of the gold bowtie arrays.

Figure 3. 19 Nonlinear frequency upconversion hybrid plasmonic system. (a) Schematic of THG characterization from a hybrid silicon-bowtie plasmonic system composed of gold bowtie arrays integrated onto the top of a silicon substrate. L is the side length, t is the thickness, θ is the flare angle, g is the gap size, and Λ is the pitch size. (b) SEM micrograph of an array of gold bowties. Scale bar: $1\ \mu\text{m}$.

Structure Fabrication. The bowtie antenna is fabricated onto the silicon wafer by means of electron beam lithography (EBL) and a standard lift-off process as shown in Figure 3.20. A polymethyl methacrylate (PMMA, 950K molecular weight, 1.67% in anisole) layer was spin-coated onto a silicon substrate, and baked on a hot plate at 180°C for 120 s. The bowtie array was defined with EBL. Development of the PMMA was carried out with a 1:3 MIBK/IPA solution at a temperature of -15°C for 10 s, followed by a subsequent e-beam evaporation of a 2 nm-thick chromium adhesion layer and a 30

nm-thick gold film layer. Lift-off was performed *via* immersion in the n-methylpyrrolidone solvent at 70 °C.

Figure 3. 20 Schematic representation of the fabrication process for the hybrid silicon-plasmonic system.

3.4.2 Linear characterization

We first measure the linear optical response of the hybrid plasmonic systems with bowtie gaps of 30, 35, 40 and 44 nm. Figure 3.21 plots the experimental reflectivity and simulated extinction cross-section spectra. The reflection peaks in Figure 3.21(a) (peak extinction cross-sections in Figure 3.21(b)) correspond to the stimulated LSPs by the gold bowtie arrays. The overall shapes and trends of the reflectivity and the extinction cross-section are in good agreement at all gap sizes. The slight differences between the resonance peaks may arise from the defects related to the structural imperfections (such as the metal surface roughness in nanofabrication). The linear measurement is performed via a commercial Fourier transform infrared spectroscopy (FTIR, Bruker Vertex 70) in reflection mode (normal incidence, 36× objective) while numerical calculations are carried out by three-dimensional finite-difference-time-domain (FDTD) method. Note that, InGaAs detector is used during the characterization. The experimentally observed red shift of the resonance with reduced gap follows the expected trend from the simulations.

Figure 3. 21 Linear characterizations of the hybrid plasmonic system. (a) Experimental reflectivities of the hybrid silicon-bowtie plasmonic system with gap sizes of 30, 35, 40, and 44 nm. (b) Corresponding calculated extinction cross-section spectra.

3.4.3 THG characterization

THG measurements were carried out as the experimental setup illustrated in Figure 3.22. A mode-locked Ti:sapphire laser (Coherent Libra and OPERA Solo optical parametric amplifier, pulse duration of 50 fs, repetition rate of 1 KHz) with excitation wavelength at 1390 nm and 1500 nm was focused on the hybrid plasmonic system after passing through a 20 $\times$ /0.9 NA objective from Nikon. The THG signal was collected in a backscattering regime by the same objective. After going through the beamsplitter, the third-harmonic signal was coupled into the monochromator to obtain the THG spectrum.

Figure 3. 22 Schematic of the THG characterization setup.

Figure 3.23(a) shows the third-harmonic spectrum produced by the bare silicon substrate when excited with a 1390 nm femtosecond laser, which results in a third harmonic wave centered at 463 nm (one-third of the incident wavelength). Figure 3.23(b) shows the third-harmonic emission from the hybrid plasmonic system with 44-nm-gap bowtie arrays, at different pump laser intensities. The THG intensity provided by the hybrid plasmonic system is much stronger than that measured from the bare silicon substrate. Note that the same laser polarization was used during the THG intensity measurements for bare silicon and the hybrid plasmonic system. The inset in Figure 3.23(b) shows the corresponding pump intensity dependent integrated third-harmonic intensity which shows an excellent agreement with $I^{3.03}$, where I is the pump intensity and 3.03 is the harmonic order.⁹ This trend highlights the THG nature, i.e., a process as a third-order nonlinear volumetric phenomenon, and that no saturation or damage to the silicon-bowtie system has occurred (harmonic emission from the bare silicon and the hybrid plasmonic system behave reversibly under the pumping conditions they were subjected to during the measurements). Due to the strongly confined electric field in the vicinities of the bowtie gaps, a large laser diameter ($\sim 20\ \mu\text{m}$ using a $20\times/\text{N.A. } 0.9$ objective, follows a detection surface away from focal point) was used to make sure that the hybrid plasmonic system is not damaged and that the laser beam can simultaneously excite enough bowtie units to make an appropriate estimation of the THG enhancement.

Figure 3. 23 THG intensity characterization. (a) THG spectrum of a bare silicon substrate with an excitation wavelength of 1390 nm at normal incidence. The average laser fluence is 52.9 mJ/cm². (b) Pump intensity dependence of the THG intensity for the hybrid plasmonic system. Inset: integrated third-harmonic intensity of the plasmonic system versus the excitation power. Black diamonds depict the experimental data. Redline is a numerical fit with a third-order power function. The error bars indicate the standard deviation of the measurements.

THG intensity enhancement is then quantified for four bowtie arrays with different gap sizes under different incidences to characterize the capability of the hybrid plasmonic system. Figures 3.24(a), 3.24(b) show the THG intensity for four different bowtie gaps (30, 35, 40, and 45 nm) with laser incidence at 1390 nm and 1500 nm. The corresponding pump laser fluences are 26.5 mJ/cm^2 and 29.1 mJ/cm^2 , respectively. The highest THG emission occurs at $g=40 \text{ nm}$ with 1390 nm excitation and $g=30 \text{ nm}$ with 1500 nm excitation, respectively. The excitation wavelength of 1390 nm is closest to the plasmon resonance of the bowtie arrays at a gap of 40 nm, which leads to the largest THG enhancement for this array at 1390 nm excitation. A corresponding 23.3-fold increment in THG emission compared with that from pure silicon is obtained. This nonlinear signal intensity increment comes essentially from the large excitation intensity enhancement resulting from the electric field hotspot generated at the bowtie gap at plasmon resonance¹². When the incident laser wavelength is tuned to 1500 nm, away from all of the resonance peaks of the four bowtie arrays, bowtie arrays with larger gaps were found to have weaker THG signals due to the reduction in the plasmonic hotspot intensity for larger gaps as Figure 3.24(b) depicted. In this case, the highest field enhancement is attained in the plasmonic system with 30 nm gap size, and the largest achieved THG intensity enhancement is 17.1. Both the experimentally measured and numerically calculated THG intensity enhancements are presented in Figures 3.24(c), 3.24(d). The solid/patterned black and red columns represent the experimental/calculation results at excitation wavelengths of 1390 nm and 1500 nm, respectively. The numerical predictions fit the experimental results very well for all cases.

Figure 3. 24 Probing the THG enhancement. Third-harmonic signal intensity of the hybrid silicon-plasmonic system for various bowtie gap sizes with an excitation wavelength of (a) 1390 nm (average pump laser fluence is 26.5 mJ/cm²), and (b) 1500 nm (average pump laser fluence is 29.1 mJ/cm²). Experimental measurements and numerical simulations of the THG enhancement with different gap size under an excitation wavelength of (c) 1390 nm, and (d) 1500 nm. The solid and patterned columns represent the experimental measurements and simulations. (e) SEM images of individual bowtie antennas with various gap sizes and the simulated electric field enhancements at 1 nm below the silicon surface at 1390 nm and 1500 nm excitation wavelengths.

Therefore, under certain excitation conditions, the interaction strength between the pump laser and the generated third-harmonic in the hybrid plasmonic system is

limited by the bowtie gap size because the interaction is very sensitive to the pulse peak intensity. On the other side, the incident field can be greatly enhanced under the condition that the laser central wavelength is close to the plasmon resonance. Bowtie arrays with larger gap size can lead to a larger THG intensity enhancement when the central wavelength of the laser is tuned to its plasmon resonance, as confirmed by the $\lambda_{pump}=1390$ nm measurement of the hybrid plasmonic system. To get a better understanding of the enhanced THG of the plasmonic system, we also calculate the electric field enhancement ($|E|/|E_0|$ at 1390 nm and 1500 nm) at 1 nm below the silicon surface (as the surface oxide film thickness in air is typically 1 nm^{33,34}) as shown in Figure 3.24(e). Strong electric field confinement is observed. The field enhancement spatial distribution in silicon for distances of 1 to 20 nm below the silicon surface in Figure 3.24 reveals the variation of the electric field enhancement with depth and confirms the high THG from the silicon is due to the plasmonic enhancement.

In this section, the viability of a silicon-bowtie hybrid plasmonic system under different excitation wavelengths to achieve efficient THG is experimentally and numerically demonstrated. The plasmonic system provides a third-order nonlinear upconversion enhancement factor of up to 23.3, where localized plasmons drive efficient harmonic generation from the underlying silicon substrate. The hybrid silicon-plasmonic system enables practical subwavelength on-chip applications such as wavelength conversion, imaging, biosensing, and information processing.

Figure 3. 25 Calculated electric field enhancements ($EF = |E|/|E_0|$, $|E|$ is the local field of the plasmonic system, and $|E_0|$ is the incident electric field strength) maps along the cut planes below the silicon surface of 1 nm, 2 nm, 3 nm, 4 nm, 5 nm, 10 nm, 15 nm, and 20 nm with light polarized along the bowtie long axis.

3.5 Conclusions

To conclude, the specific designed plasmonic waveguides in this chapter offer guidance to investigate efficient THG numerically and experimentally. The typical research steps are as follow: we start with a nonlinear coupled mode differential equations to find out the critical factors for effective THG and then design specific plasmonic waveguides to achieve efficient THG numerically and experimentally. We have demonstrated the viability of plasmonic hybrid plasmonic systems and graphene plasmonic coupler for efficient THG where the plasmons drive effective harmonic generation from the nonlinear media under PMC. Our findings deepen the understanding of the THG process

by using metallic and graphene plasmons incorporated with high third-order nonlinear susceptibilities.

Chapter 4 Graphene Plasmons for Biosensing

The previous chapter has shown that the metallic and graphene plasmons are able to significantly increase the nonlinear third-order wave conversion efficiency where the coupled mode differential equations offer good guidance on the design of the plasmonic systems. However, metallic plasmons possess large losses in the frequency regimes of interest. To reduce the plasmonic losses and expand the applications of plasmonics, in this chapter, we present our extensive study on the graphene plasmons. Atomically thin graphene has been recently proposed as a promising alternative to noble metals for highly integrated active plasmonic devices in infrared and terahertz ranges with tunable Fermi energy levels^{86, 147, 148}. When the Fermi energy level is tuned away from the k-point, graphene exhibits metal-like responses and thus can guide plasmons induced by the two-dimensional collective Dirac quasi-particles oscillations. Compared with metals, graphene plasmons possess higher electric field confinement and enhancement, larger external tunability, longer lifetimes, and lower loss^{88, 149, 150}. Active plasmons in graphene allow external control of the incident light confined around graphene at deeply subwavelength dimensions, thereby producing strong light-matter interactions¹³⁸. Furthermore, the broadband tunability of graphene plasmons can easily make the working wavelength to cover the important molecular vibrational modes to identify the specific chemical fingerprints.

We employ graphene plasmons for biosensing in this chapter because traditional optical biosensors simply use resonance shift to detect the change in the refractive index of the adjacent materials^{17, 18}, but cannot identify the type of molecules. Detecting the molecules structural vibrational modes is one strategy to tackle the problem and the molecules vibrational modes are commonly located in the infrared regime and produce specific spectral features that precisely identify their chemical properties^{147, 151}. The broadband tunability of graphene plasmons can easily make the working wavelength to cover the important molecular vibrational frequencies to identify the specific chemical fingerprints. One pioneer work has utilized active graphene plasmons to detect the molecular vibrational modes¹⁵². However, due to the large coupling between the localized graphene plasmons and the substrate phonons¹⁵³, the near-field enhancement

and the corresponding molecular chemical fingerprints sensitivity are limited. To further improve the nanometric molecular vibrational modes sensitivity, we employ two numerically achieved mid-IR biosensors through tunable graphene plasmons to detect the absorption, reflection, and transmission variations due to the protein immobilization at different graphene Fermi levels. Our results show that the resonant reflection or transmission spectrum as a function of graphene Fermi level is sufficient to provide accurate chemical identification of the nanometric molecules.

4.1 Tunable resonant graphene plasmons for mid-IR biosensing

In this part, tunable SPPs based on a graphene nanoribbon are studied to detect nanoscale protein molecules in mid-IR region. Biosensing in mid-IR is a research area where graphene plasmons can fully utilize its unique tunability and light localization. The two-dimensional nature of the collective oscillations of Dirac quasi-particles result in strong electric field confinement of graphene plasmons and lead to a large light overlap with the nanoscale biomolecules, which plays an essential role in the demonstrated high sensitivity in the detection of the refractive index of the nanometric-scale targeted protein molecule. Resonant spectra of the device are acquired by finite-element method with incident electric field polarized perpendicular to the nanoribbon plane. The tunable localized resonant SPPs in graphene nanoribbon structure with mid-IR excitation are then employed to probe the protein chemical vibrations. The strong optical field confinement provided by the tunable resonant SPPs with extremely small mode volume enhances the light-protein interaction, leading to the high molecule sensitivity.

4.1.1 Plasmon resonance modes of the graphene nanoribbon

The spectra of individual graphene SPPs can be stimulated in the mid-IR regime. The optical conductivity of graphene determines the corresponding plasmonic properties. Under the condition that the absolute value of the Fermi level is tuned above the threshold value, i.e., $|E_F| > \frac{0.25117(\varepsilon_1 + \varepsilon_2)\hbar\omega}{\sqrt{\varepsilon_1 + \varepsilon_2 + 1} - 1}$ ^{87, 90, 154}, graphene exhibits metallic

optical response and supports TM polarized SPPs. ε_1 and ε_2 are the relative permittivity of two sides cladded layers, ω is the angular frequency of the incident light.

Therefore, as long as $|E_F|$ is larger than 0.24 eV, it is possible to excite TM SPPs in graphene cladded by silicon ($\varepsilon_1 = 11.7$) and air ($\varepsilon_2 = 1$) at a fixed incident wavelength of 6 μm . Taken the permittivity of the substrate ε_1 and the above surface layer ε_2 into consideration, the effective index of the guided plasmon mode in graphene can be evaluated as^{87, 90, 154, 155}

$$n_{\text{eff}} = \frac{(\varepsilon_1 + \varepsilon_2)\hbar\omega}{4\alpha|E_F|} \quad (4.1)$$

which scales with ε_1 , ε_2 and $|E_F|^{-1}$. $\alpha = e^2/(4\pi\varepsilon_0\hbar c) = 1/137$ is the fine structure constant.

To understand the physical mechanisms of the guided graphene SPPs and their strong light localization and high field enhancement in the mid-IR regime, we first calculate the electric field intensity distribution with different nanoribbon widths and Fermi levels. The excitation wavelength is fixed to be 6 μm in this part. We study the plasmon properties of the graphene nanoribbon with different widths on a silicon substrate surrounded by air as the structure schematic shown in Figure 4.1. For the sample fabrication, first, monolayer graphene grown by chemical vapor deposition (CVD) technique on a copper foil can be transferred onto a commercially purchased silicon substrate. Second, the electron beam resist can be spin coated on the surface of the graphene and then exposed the chip using EBL followed by a resist development and an oxygen plasma cleaning. Resist stripping is done in acetone, followed by IPA and DI water rinsing. The metalized tip is used to launch the graphene SPPs and the silicon substrate offers high dielectric permittivity to significantly enhance the field localization from Eq. (4.1). We use TM polarized incident light by means of finite element method for the 2D cross section geometry as indicated in Figure 4.1. During the simulation, the complex permittivity of the graphene layer is modeled with complex conductivity from Kubo formula¹⁵⁵ by considering monolayer thickness of 0.5 nm. The complex refractive index of the silicon¹⁵⁶ is also taken into consideration. According to Eq. (4.1), with large Fermi level (larger than the threshold value of 0.24 eV at 6 μm), graphene plasmon modes emerge.

Figure 4. 1 Schematic of the graphene nanoribbon with width of W on a silicon (Si) substrate. The protein layer is immobilized on top of graphene. Cross section is depicted.

The near-field intensity images for different ribbon widths with $EF = -0.3$ eV is shown in Figures 4.2(a)-4.2(d), indicating the guided mode features at wide and narrow ribbons. The near-field intensity amplitude is a direct measurement of the square of the z -component field amplitude ($|E_z^2(\omega)|$). Stronger field intensity occurs close to the boundary regions which is due to the constructive interference between multiple boundary-reflected SPPs. The induced plasmons are scattered by the graphene edges, which produce reflected fields. The stronger intensity close to the edge can also be attributed to the strong concentration of electromagnetic field included in the local density of optical states model⁸⁷. The graphene SPPs confined in the ribbon is equivalent to a Fabry-Perot model with $-\pi$ phase reflection¹⁵⁷. The decay field intensity inside the ribbon is caused by the mode damping effect, which results from a combination of substrate loss and intrinsic graphene loss. The intrinsic graphene layer acts as a primary source of loss due to interband absorption. The plasmon damping induced by the interband excitation occurs at small carrier densities and could be suppressed when $|E_F| > E_p$, E_p is the SPPs energy. As the ribbon width W decreases, the total number of distinct intensity peaks reduces and consequently the two edge peaks move close to each other. Strongest enhancement of the plasmon intensity occurs when the two principal peaks move inward and merge at the ribbon center, as depicted in Figure 4.2(c). This mode is regarded as a localized plasmonic mode (first-order resonance) with high resonant enhanced near-field intensity. Its field amplitude appears to be the sum of the two principal peak amplitudes close to the boundaries, and the corresponding maximum plasmon intensity is about four times larger than that of the two separately boundary peaks in wider ribbons. In Figure 4.2(d), we provide another resonant near-field

intensity image where the ribbon width is $W=8$ nm. This mode is a zeroth-order localized resonant plasmonic mode. We define the wavelength of maxima interference of forward and backward propagating SPPs to be λ_p , which can be directly obtained by measuring two adjacent peaks from the field intensity image. We can numerically find resonant plasmon mode in a graphene ribbon at wavelength $\lambda_p = \lambda_0/n_{\text{eff}}$, which is about n_{eff} times smaller than the wavelength of free-space excitation. The remarkable strong reduction in the guided plasmon wavelength can be directly attributed to the 2D nature and the unique conductance properties of graphene. Based on our calculation, $n_{\text{eff}}=375.57+5.0777i$ and $326.17+5.8709i$ are obtained for the zeroth-order resonant SPPs mode in Figure 4.2(d) and first-order resonant SPPs mode in Figure 4.2(c).

With a fixed Fermi level, the SPPs resonance in graphene nanoribbon depends on the incident wavelength λ_0 and ribbon width W . We observe the peak enhancements for the two lowest-order resonant SPPs modes at $W=8$ nm and $W=16.5$ nm in Figure 4.2(e), when the incident wavelength is fixed to be $6 \mu\text{m}$ with increasing W . Figure 4.2(f) indicates the ribbon width as a function of the absolute value of the Fermi level for the two lowest-order resonant SPPs modes. By increasing $|E_F|$, the two resonances still exist for wider nanoribbons. At resonant condition, the wavelength λ_p of the two plasmonic modes in Figure 4.2(e) and the corresponding value of ribbon width W normalized to the λ_p are depicted in Figure 4.2(g). We extract the resonant conditions to be $W \approx 0.5 \lambda_p$ and $0.9 \lambda_p$ for the zeroth- and the first-order resonant SPPs modes, respectively. For the two resonant modes, the calculated λ_p and the corresponding ribbon widths with different Fermi levels as shown in Figure 4.2(g) are in reasonable agreement with the theoretical prediction from Eq. (4.1) and the field intensity image distribution in Figures 4.2(a)-4.2(d). Note that, the optical conductivity of the graphene ribbon layer used here for the dispersion calculation is obtained with the random phase approximation method where the Fermi level is the only variable.

Figure 4. 2 Near-field intensity image of the guided resonant graphene SPPs in the nanoribbon graphene-silicon waveguide with ribbon width of (a) 100 nm, (b) 50 nm, (c) 16.5 nm and (d) 8 nm under TM polarization illumination. (e) The maximum intensity enhancement distribution at different ribbon width conditions with a fixed incident light wavelength of $6 \mu\text{m}$ and Fermi level of -0.3 eV. (f) Nanoribbon width distribution of the two SPPs modes as a function of Fermi level to satisfy the resonant condition. (g) λ_p and W/λ_p with different Fermi levels at resonances. Solid lines correspond to λ_p . Dashed lines correspond to W/λ_p . Black lines denote the zeroth-order resonant SPPs mode and red lines denote the first-order resonant SPPs mode in (f) and (g). We use COMSOL to obtain the mode profiles. During the calculation, graphene is modeled as a thin layer with a thickness of 0.5 nm by a dielectric function of $1 + i \sigma(\omega) / (\omega \epsilon_0 t_g)$, where $\sigma(\omega)$ is the linear graphene surface conductivity described by the Kubo formula^{136, 137}, ω is the light frequency, and t_g is the graphene layer thickness.

4.1.2 Protein permittivity sensing

For the graphene nanoribbon, the guided SPPs in the atomic-thick structure leads to significant field confinement and large spatial overlap with the above-cladded analyte. As known to all, protein molecules are the primary material of life which enable most of the biological functions. Here, we use recombinant protein A/G and goat anti-mouse immunoglobulin G (IgG) bilayer to act as the sensing analyte. The protein layer is induced as an 8 nm thick layer possessing Lorentzian complex permittivity¹⁵². To validate the proposed nanoribbon graphene-silicon waveguide as a highly sensitive mid-IR biosensor, we prefer to utilize guided plasmonic mode with high electric field enhancement. We then assume that the ribbon response is dominated by the two lowest-order resonant modes, i.e., 0-th and 1-st order resonant SPPs modes, since these two modes possess higher electric field enhancement as stated above.

Figure 4. 3 (a) Maximum intensity enhancement of the zeroth-order resonant SPPs mode at $W=8$ nm and the first-order resonant SPPs mode at $W=16.5$ nm as a function of the incident wavelength before (solid curves) and after (dashed curves) protein layer formation. (b) At resonant conditions, the wavelength shifts for the two SPPs modes with different absolute value of Fermi levels.

The maximum intensity enhancements of the two resonant SPPs modes at $W=8$ nm and $W=16.5$ nm of the graphene ribbon with various incident wavelengths are presented in Figure 4.3(a) before (solid curves) and after (dashed curves) protein formation, showing significant changes upon protein immobilization. The first observed prominent effect in Figure 4.3(a) is the red shift of the plasmonic resonance as a consequence of the variation in the refractive index at the sensor surface. Despite the nanometric-scale protein layer, wavelength red shift of 78 nm and 99 nm for the zeroth-

($W=8$ nm) and first-order ($W=16.5$ nm) resonant SPPs modes are achieved, upon protein immobilization above with Fermi level of -0.3 eV. The second prominent effect is the severe decrement of the field intensity resulting from the non-perfectly resonant condition and the loss induced by the protein. We expect that this decrement can be utilized to reveal the chemical vibrational modes of the protein. We set the incident wavelength to be $6\text{ }\mu\text{m}$ and turn the Fermi level merely to achieve tunable refractive index sensitivity as plotted in Figure 4.3(b). The wavelength shift decreases as the Fermi level increases for both of the two resonant conditions. As a result, the sensitivity decreases with increasing Fermi levels. Table 4.1 summarizes the effective mode indices of the two resonant plasmonic modes without protein layer, which indicates that narrow graphene ribbon is favorable to confine light down to an extremely small volume. The strongest reduction in the guided plasmon wavelength occurs at $\lambda_p \approx \lambda_0/375.6$, when $E_F = -0.3$ eV and $W=8$ nm. This strong electromagnetic field concentration offers increased near-field signal intensity, enhanced forward and backward reflected plasmon interaction and therefore better sensing performance.

TABLE 4. 1 Effective mode index distribution of the guided resonant graphene SPPs with different absolute values of Fermi level.

$ E_F $ (eV)	Effective mode index n_{eff}	
	0-th, $W=8$ nm	1-th, $W=16.5$ nm
0.3	$375.57+5.0777i$	$326.17+5.8709i$
0.4	$261.54+3.097i$	$227.28+3.5785i$
0.5	$202.59+2.2636i$	$176.06+2.6148i$
0.6	$165.89+1.7975i$	$144.14+2.0772i$
0.7	$140.72+1.4967i$	$122.28+1.729i$

To extract the capability of graphene SPPs in controlling the nanoscale molecule sensing *in situ*, we set the ribbon width to be 8 nm and 16.5 nm and engineer the Fermi level from -0.3 eV to -0.7 eV at first. For the 0-th order resonant SPPs mode at $W=8$ nm in Figure 4.4(a), with increasing $|E_F|$ from 0.3 eV to 0.7 eV, the resonant wavelength is turned continuously from $6\text{ }\mu\text{m}$ to $3.794\text{ }\mu\text{m}$. And the wavelength shift (due to the immobilized protein layer) decreases from 78 nm to 54 nm accordingly. For the first-order resonant SPPs mode at $W=16.5$ nm in Figure 4.4(a), the resonant wavelength is

turned continuously from 6 μm to 3.782 μm and the corresponding wavelength shift decreases from 99 nm to 52 nm. Therefore, the resonant wavelengths of the two resonant SPPs modes can both be tuned continuously and the sensitivity reaches to the maximum with a Fermi level of -0.3 eV for the first-order resonant SPPs mode. The above dynamic tunability enables a broad spectrum of biosensing applications over a single graphene ribbon at mid-IR regime by precisely tuning the Fermi levels of graphene.

Figure 4.4 Resonant wavelength (solid line) and the corresponding wavelength red shift (dash line, due to the above-immobilized protein layer) as a function of $|E_F|$ with dimensions of (a) $W=8$ nm, and 16.5 nm and (b) $W=17.6$ nm and 36.2 nm. (c)/(d) The distribution of ratio $|E'_{\text{max}}/E_{\text{max}}|^2$ between the two maximum intensity enhancements with and without protein immobilization for the two resonant modes in (a)/(b) at different Fermi levels.

Then we further study the sensitivity of the protein chemical vibrations upon the tunable graphene SPPs. The ribbon width of $W=8$ nm, and 16.5 nm with Fermi level tuned from -0.3 eV to -0.7 eV can only probe the amide II band of the protein. Therefore, we set the Fermi level to be -0.5 eV and the incident wavelength to be 6.5 μm , and calculate the yielded resonant ribbon width of $W=17.6$ nm (zeroth-order resonant SPPs mode), and 36.2 nm (first-order resonant SPPs mode) to meet the resonant graphene SPPs. With ribbon width of 17.6 nm and 36.2 nm, Figure 4.4(b) gives the distributions of the resonant wavelengths and the corresponding wavelength shifts due to the protein

formation at different Fermi levels. The variation trend of the resonant wavelength and the corresponding wavelength shift with various Fermi levels are consistent in Figures 4.4(a) and 4.4(b). To probe the protein vibrational modes, we take advantage of intensity decrement induced by the resonant coupling between the resonant graphene SPPs and the molecular vibrations. Figures 4.4(c) and 4.4(d) show the ratio between the maximum intensity enhancement with and without the protein immobilization for the two resonant SPPs modes in Figures 4.4(a) and 4.4(b), respectively. In Figure 4.4(d), two apparent dips of intensity enhancement ratio occur at $|E_F|$ of 0.5 eV and 0.6 eV which correspond to the resonant wavelengths (with protein) of 6.56 μm and 5.956 μm for $W=17.6$ nm and $W=36.2$ nm, as shown in Figure 4.4(b). These two additional decrements are induced by the protein vibrational modes as a result of the resonant coupling between the resonant graphene SPPs and the molecular vibrations. The two dips at 6.56 μm and 5.956 μm match the amide I (6.527 μm) and II (5.995 μm) bands of the protein,¹⁵² explicitly revealing the presence of the protein compounds in a chemically specific manner. Figure 4.4(c) also confirms that the chemical manner of the protein layer can be detected through slightly tuning the Fermi level of the graphene nanoribbon. The intensity enhancement ratio dip at $|E_F|$ of 0.3 eV in Figure 4.4(c) reproduces the amide II band of the protein. Therefore, the proposed resonant graphene SPPs biosensor recognize unique protein chemical specificity in mid-IR spectroscopy and provide an extra degree of freedom in the design of graphene-enabled electron-optical tunability for biomolecule sensing.

In this work, we propose a graphene nanoribbon based tunable mid-IR biosensor and demonstrate its high sensitivity for detecting the optical properties of the protein. The Fermi level is modified to realize resonant localized graphene plasmons with both high electromagnetic confinement and enhancement. The Fermi level controlled resonant plasmons in graphene nanostructure provide a unique capacity to control light in nanoscale to probe the protein chemical vibrations. Tunable resonant spectra combined with the super ambient condition sensitivity promise the graphene plasmons based device exciting prospects in future nanoscale biosensing.

4.2 Mid-infrared sensing of molecular vibrational modes with tunable graphene plasmons

The former section has utilized active graphene plasmons to detect the molecular vibrational modes¹⁵². However, due to the large coupling between the localized graphene plasmons and the substrate^{153, 158}, the near-field enhancement and the corresponding molecular chemical fingerprints sensitivity are limited. To further improve the nanometric molecular vibrational modes sensitivity, in this part, we employ a continuous graphene film integrated above a patterned gold grating substrate to detect the vibrational modes of nanometric molecules at different graphene Fermi levels. The greatly enhanced light-matter interaction and the broadband tunability of the localized graphene plasmonic resonance enable accurate label-free identification of the molecular vibrational modes at subwavelength scale. The calculations results show that the resonant reflection or transmission spectrum as a function of graphene Fermi level is sufficient to provide accurate chemical identification of the nanometric molecules.

4.2.1 Biosensor geometry and the reflection/transmission spectra

Figure 4.5(a) depicts the schematic of graphene plasmonic biosensor with a continuous graphene layer immobilized on top of a gold grating with a periodical array of patterned narrow air slots. Quartz is the substrate, and the device is surrounded by air. The grating is used to compensate the wave-vector mismatch between the graphene plasmons and the free space light. For normal-incident light with linearly polarized electric field along the grating period, the guided resonance is excited. FDTD calculations are performed on a unit cell of such device with periodic boundary conditions. Compared with patterned graphene, the graphene layer of our biosensor is continuous, which suppresses the edge scattering and the deterioration on the graphene mobility. On the contrary, the free-carriers motion in the micrometer or nanometer dimension patterned graphene is restricted and the guided resonant oscillation modes are associated with bound electrons.

Figure 4. 5 (a) Geometry of the graphene plasmonic biosensor with 8 nm-thick protein monolayers immobilized by 1 nm on top of the graphene film. Continuous graphene film is integrated onto the gold (Au) grating. $P=3\ \mu\text{m}$ is the grating period, $W=2.92\ \mu\text{m}$ is the gold channel width, and $t=40\ \text{nm}$ is the gold thickness. (b) Guided near-field E_x and E_z profiles at the plasmonic resonant frequency when the Fermi level (EF) of graphene is fixed at 0.5 eV. The inset shows that the electric field is mainly confined inside the air slot. The horizontal dashed white line represents the graphene layer, and the vertical dashed white line represents the gold and air interface. (c)/(d) Reflection (R)/transmission (T) spectra without the protein immobilization for graphene EF varies from 0.5 eV to 0.9 eV.

4.2.2 Probe the molecular vibrational frequencies

We use 8 nm-thick recombinant protein A/G and goat anti-mouse immunoglobulin G bilayer as the sensing analyte. The protein layer is modeled as Lorentzian complex permittivity¹⁵² $\varepsilon(\omega)=2.08+\frac{213^2}{1668^2-\omega^2-i78.1\omega}+\frac{200^2}{1532^2-\omega^2-i101\omega}$, where the unit of ω is cm^{-1} . The nanometric protein monolayers can be achieved through physisorption. By adjusting gold grating geometry and graphene Fermi levels, the structure working from mid-IR to terahertz wavelength range can be realized. FDTD method is used in this work. According to our calculation, the plasmonic resonance can be tuned to the frequencies of the mid-IR molecular vibrational modes with feasible grating periodic size P (several micrometers) and graphene Fermi levels (less than 1 eV).

To ensure the working wavelength region can cover the target vibrational fingerprints, we set $P=3\ \mu\text{m}$, $W=2.92\ \mu\text{m}$, and $t=40\ \text{nm}$. Graphene is modeled as a thin layer with complex conductivity from Kubo formula^{136, 137}. The complex permittivity of the graphene is modeled as $1+i\sigma(\omega)/(\omega\varepsilon_0t_g)$, where $\sigma(\omega)$ is the frequency-dependent surface conductivity, ω is the light frequency, and t_g is the graphene thickness.

In the practical configuration, it is more interesting to probe a thin molecule layer placed over a distance above the graphene film to suppress the quenching and blocking effect¹⁵⁹. Therefore, we consider 8 nm-thick protein monolayers separated by 1 nm above from the graphene film, as shown in Figure 4.5(a). Since higher quality graphene leads to better sensitivity and spectral resolution with reduced absorption loss, we set electronic mobility of graphene to be $\mu = 30,000\ \text{cm}^2/(\text{Vs})$ ¹⁶⁰. Note that, the Fermi level pinning effect at the graphene-gold interface¹⁶¹ is ignored and zero contact resistance between graphene and gold is assumed in the calculation. The metal regions contacted with graphene are considered as a capacitance to accumulate charges and the graphene acts as an inductance, enabling strong interaction with the incident radiation. The resonance spectral width decreases inversely with graphene mobility and reaches a plateau at relatively high mobility. The localized graphene plasmonic wavelength scales with E_F ^{138, 147} and therefore can be tuned by controlling the Fermi energy level through varying the device charge carriers. Figures 4.5(c) and 4.5(d) show the reflection and transmission spectra for the graphene integrated gold grating without the top protein layer. High quality plasmonic resonance is observed, whose resonant wavelength can be tuned continuously over a wide wavelength range from $7\ \mu\text{m}$ to $5.2\ \mu\text{m}$ with a small change in the graphene Fermi level from 0.5 eV to 0.9 eV. The graphene absorption is greatly suppressed due to the high graphene electronic mobility. At the resonance frequencies with different Fermi levels, transmission through the device all reaches about 90% with negligible reflection. This indicates that the corresponding absorption is approximately 10%. When the incident light couples to the graphene plasmons, the resonance leads to a sharp notch/peak in the reflection/transmission spectra. The resonance spectral width also decreases inversely with the Fermi level as shown in Figures 4.5(c) and 4.5(d). The local electric field profile at graphene plasmon resonance is shown in Figure 4.5(b), which illustrates the extremely high field confinement and enhancement in the narrow air slots.

The mid-IR spectrum absorption of the protein bilayer is dominated at two main vibrational modes at photon wavelengths 5.995 μm and 6.527 μm as shown in Figure 4.6(a). Figure 4.6(b) presents the reflection and transmission spectra with biomolecule monolayers incubated on the sensor surface at a fixed graphene Fermi level of 0.9 eV. Since the plasmonic resonance possesses a high quality factor and the plasmonic resonance peak is away from the molecular vibrational modes, two reflection dips/transmission peaks due to the coupling between the graphene and protein molecules are almost undetectable. Through tuning the graphene Fermi level, the reflection and transmission variations can become progressively more intense with increasing spectral overlap in which the plasmonic resonance positions can coincide with the two molecular vibrational modes.

Figure 4. 6 (a) Imaginary part of the protein permittivity as a function of wavelength. Yellow vertical strips indicate the two protein vibrational modes. (b) Reflection (dark curve) and transmission (red curve) spectra with biomolecule monolayers at a specific graphene Fermi level of 0.9 eV. The plasmonic resonance peak is away from the molecular vibrational modes.

4.2.3 Tunable graphene plasmons to enhance sensitivity

Figures 4.7(a) and 4.7(b) show the reflection and transmission spectra of the plasmonic device with protein at different graphene Fermi levels. Two distinct reflection peaks/transmission dips are observed due to the greatly enhanced coupling between the graphene plasmons and the molecular vibrations. Since the absorption at resonance of the graphene layer keeps at around 10% for different graphene Fermi levels without protein, the two greatly enhanced resonant absorptions are purely induced by the vibrational modes of the thin protein layer. The two reflection peaks/ transmission dips occur at Fermi level of 0.68 eV and 0.8 eV, and the corresponding resonant wavelengths

are 6.573 μm and 5.987 μm , which are exactly the resonance frequencies of the two protein vibrational modes. One important feature of the reflection/transmission spectra in Figures 4.7(a) and 4.7(b) is that there is a one-to-one correspondence between the molecular resonant photon energies and the graphene Fermi levels when the broadband tunable plasmonic spectra overlap with these two molecular resonances. Therefore, it is convenient to reveal the molecular chemical fingerprints using graphene integrated gold grating plasmonic device by tracking the reflection or transmission spectra. Figure 4.7(c) gives the resonant transmission and reflection values with and without protein formation. Two resonant transmission dips with transmission variation value of 61.42 % (at $E_F=0.68$ eV, from 91.7 % without protein to 30.28 % with protein) and 68.34 % (at $E_F=0.8$ eV, from 89.14 % without protein to 20.8 % with protein) and two resonant reflection peaks with reflection variation value of 7.91 % (at $E_F=0.68$ eV, from 3.17 % without protein to 11.08 % with protein) and 18.2 % (at $E_F=0.8$ eV, from 3.16 % without protein to 21.36 % with protein) can be observed when the graphene plasmons couple to the two main protein vibrational modes. The detection of the vibrational modes of the nanometer-size protein layer is greatly enhanced compared with the previous works^{152, 159}.

Figure 4. 7 (a)/(b) Reflection/transmission spectra under different graphene Fermi levels with protein monolayers immobilized by 1 nm on top of the graphene film. (c) Transmission (solid curve) and reflection (dashed curve) values at resonance with (red curve) and without (black curve) protein layer in terms of the graphene Fermi energy level.

Therefore, for the graphene integrated gold grating plasmonic device, the dependence of the reflection/transmission spectra on the molecular resonant photon energies is sufficient to identify the molecular chemical fingerprints. An important practical aspect of the proposed plasmonic sensor is the control of the graphene Fermi level. We envisage a gated device in which the bottom gate is connected with graphene.

Electrical connections can be provided by a thin transparent insulating layer as demonstrated by Zheyu Fang and his colleges¹⁶².

Figure 4. 8 Graphene electronic mobility is set to be $\mu = 10,000 \text{ cm}^2/(\text{Vs})$. Transmission (solid curve) and reflection (dashed curve) values at resonance before (black curve) and after (red curve) protein immobilization for graphene Fermi energy level various from 0.5 eV to 0.9 eV.

Then we set the electronic mobility of graphene to be $\mu = 10,000 \text{ cm}^2/(\text{Vs})$ with structure geometry remains the same to explore the sensitivity of the proposed graphene integrated gold grating device under low graphene quality condition.¹⁶⁰ As can be seen from Figure 4.8, due to the reduced electronic mobility of the graphene film, the absorption of the graphene film at resonance is increased compared with $\mu = 30,000 \text{ cm}^2/(\text{Vs})$ condition. Still, we can obtain two reflection peaks and transmission dips at resonance induced by the protein layer. These two reflection peaks/transmission dips occur at Fermi level of 0.68 eV and 0.78 eV, and the corresponding resonant wavelengths are $6.58 \text{ }\mu\text{m}$ and $6.1 \text{ }\mu\text{m}$, respectively, which can also correctly meet the two protein vibrational modes. When the graphene plasmons couple to the two main protein vibrational fingerprints, the transmission variations at the two dips change to be 43.61 % (at $E_F=0.68 \text{ eV}$, from 69.85 % without protein to 26.24 % with protein) and 45.33 % (at $E_F=0.78 \text{ eV}$, from 70.6 % without protein to 25.27 % with protein), and the corresponding reflection variations at the two peaks change to be 14.1 % (at $E_F=0.68 \text{ eV}$, from 0 without protein to 14.1 % with protein) and 15.06 % (at $E_F=0.78 \text{ eV}$, from 0 without protein to 15.06 % with protein), respectively.

The above results demonstrate that the proposed graphene integrated gold grating biosensor with an extra degree of freedom provided by the graphene electro-optical

tunability offers unique molecular chemical identification at mid-IR region. Clearly, the dynamic graphene tunability and the corresponding greatly enhanced electric field in the air slots are the distinctive advantages for surface plasmons enhanced mid-IR light-matter interaction, allowing biosensing on the molecule vibrational modes over a wide wavelength range by a single active device. It indicates the ability of tunable graphene plasmons to accurately resolve the chemical fingerprints of target molecules. Graphene plasmons, therefore, may find more applications by the large electro-optical tunability, and particularly, the label-free chemical identification.

4.3 Conclusions

In conclusion, tunable resonant graphene plasmons of two graphene plasmonic waveguides possess strong optical field localization and confinement which induce large spatial overlap between the mid-IR SPPs and the biomolecules are proposed to realize accurate detection of molecular chemical features in this chapter. To be specific, the large resonant spectral shifts and intensity enhancement ratio dips confirm the high sensitivity of the graphene nanoribbon biosensor to the complex permittivity of the nanometric-scale targeted protein molecule. The ability of one-to-one correspondence between the molecular photon energies and the graphene Fermi levels (when the broadband tunable plasmonic spectra overlap with molecular resonances) of the graphene integrated gold grating plasmonic device makes it convenient to reveal the molecular chemical fingerprints by only tracking the reflection or transmission spectra. Fermi level controlled graphene plasmons, therefore, provide a solution to facilitate the design and miniaturization of the future development of nanoscale biosensing devices with enhanced sensitivity, and may find more applications by the label-free chemical identifications.

Chapter 5 Ultra-Wideband GSERS Substrate

Conventional SERS substrate is well-known for its supreme electromagnetic enhancement and the corresponding ultra-high sensitivity in detecting molecules at low concentrations. However, the existing problems like limited stability and reproducibility, fluctuant SERS response, and severely subjected to the fluorescence interference should be overcome before practical application. Graphene makes up this deficiency by its homogeneous surface, chemical inertness, biological compatibility, and capability of quenching the molecules fluorescence, and therefore offers a more stable, more reproducible, and cleaner molecule Raman spectrum. On the other hand, most commercial SERS substrates only work at individual excitation wavelengths¹⁶³⁻¹⁶⁵. Multiple excitation wavelengths and different corresponding substrates will be required to identify mixed samples¹⁶⁶⁻¹⁶⁸, which consumes more chemical materials, substrates, and causes a waste of time. This is an obvious disadvantage for the conventional SERS substrates. SERS enhancement is proportional to the field intensity enhancements at both excitation and scattering wavelengths. To realize higher SERS enhancement, double-resonance SERS substrates were proposed to realize strong field enhancements at both excited and scattered signals¹⁶⁴. Due to the narrowband absorption spectra for both resonances, the enhanced SERS signal is limited within narrow spectral regions. To address this problem, broadband resonant nanostructures are highly desired. When a single substrate can work for a wide range of excitation wavelengths, it will become particularly useful for sensing a broad spectrum of chemicals on one single chip¹⁶⁷⁻¹⁶⁹. Furthermore, more analytes can be detected on the same chip where broadband SERS is available.

We report a hybrid graphene/fragmented-gold substrate to achieve ultra-wideband GSERS substrate in this part. Through a controllable fragmentation of a gold nanofilm by cold-drawing, a two-dimensional fragmented gold substrate is achieved with periodically distributed gold nanoscale tips. The localized surface plasmon resonance created by the fragmented gold tips passes through the top integrated one-atom-thick graphene layer, leading to strong GSERS. Furthermore, the hybrid graphene/fragmented-gold substrate is beneficial for sensing the top bonded molecules, enabling a wideband tracing of analytes. The experimentally demonstrated hybrid

GSERS substrate offers an atomically flat, thin, and chemically stable bonding interface with strongly enhanced molecule Raman signals, thereby providing a promising solution to achieve an ideal SERS substrate.

5.1 Graphene/fragmented-gold substrate

Figure 5.1(a) shows the experimental steps to fabricate the graphene/fragmented-gold substrate. A thin gold film is first deposited onto the poly(ethyleneimine) (PEI) surface using e-beam evaporation. PEI is chosen to be the stretchable substrate, due to its insensitivity to acetone to facilitate the following graphene wet transfer. Cold-drawing along the x -axis is first performed to obtain 1D fragmented-gold film. The gold film is brittle while the PEI substrate is ductile. With a homogeneous x -axial extension, neck forms and then propagates at a constant speed. A large amount of strain localizing in the necking region reduces both the width and the thickness of the PEI film which acts as a tool to fragment the gold film. Then, a second cold-drawing is performed along the y -axis to achieve 2D fragmented-gold film. Atomic force microscopy (AFM) is used to characterize the surface morphology of the deposited gold film. Figure 5.2 shows AFM images of the 10 nm, 20 nm, and 30 nm gold film deposited onto a silicon substrate covered with 285 nm oxide ($\text{SiO}_2(285 \text{ nm})/\text{Si}$). The surface of the gold film with different deposition thicknesses is smooth with a surface roughness of $\pm 2 \text{ nm}$. Figures 5.1(b)-5.1(g) show the SEM images of the 1D and 2D fragmented-gold films at different gold deposition thicknesses (10, 20, and 30 nm), respectively. Thicker gold film results in larger sized fragmented tips. We can control the y -axial extension length to ensure the PEI is 120% drawn (the drawn length along y -axis equal to 1.2 times of the length before being drawn). After multiple attempts, we find that small y -axial drawn length results in small amount fragmented tips, while large drawn length leads to overlapping of the fragmented tips along the x -axis. Therefore, we choose 120% drawn length along the y -axis as the optimal extension length, which offers the densest fragmented gold tips aiming to provide the strongest enhancement on localized plasmons in a wide wavelength range. Next, monolayer graphene sheet grown by CVD is wet transferred onto the top of the 2D fragmented-gold film.

We consider three main parameters, i.e., the gold film thickness, the cold-draw dimension (1D or 2D), and the excitation wavelength, to investigate the optimized

condition to maximize GSERS enhancement. 10 different samples are prepared: monolayer graphene sheet integrated onto (1) a $\text{SiO}_2(285 \text{ nm})/\text{Si}$ substrate (hereafter g-Si), (2) 10 nm-thick, 20 nm-thick, and 30 nm-thick gold films which are deposited by e-beam evaporation onto PEI (hereafter g-film), (3) 10 nm-thick, 20 nm-thick, and 30 nm-thick 1D fragmented-gold film (hereafter g-1D), and (4) 10 nm-thick, 20 nm-thick, and 30 nm-thick 2D fragmented-gold film (hereafter g-2D).

Figure 5. 1 Fabrication and characterization of the hybrid graphene/fragmented-gold substrate. (a) Schematic of the fabrication procedure. SEM micrographs of 1D fragmented-gold substrate with the gold film thickness of (b) 10 nm, (c) 20 nm, and (d) 30 nm. SEM micrographs of 2D fragmented-gold nanostructure with gold film thickness of (e) 10 nm, (f) 20 nm, and (g) 30 nm. The second and fourth columns depict the magnified SEM images. The dashed cyan circles highlight the fragmented nanoscale tips aiming to stimulate electromagnetic hot spots.

Figure 5. 2 Upper panel: AFM topography image with gold thickness of (a) 10 nm, (b) 20 nm, and (d) 30 nm. Lower panel: corresponding line trace along the solid white line in the upper panel. The scanning area is $5 \times 5 \mu\text{m}$.

5.2 GSERS characterization

Periodically distributed gold nanoscale tips are formed with a simple mechanical stretching process. The plasmonic resonance nanoscale tips and the enhanced graphene Raman signal provided by the hot spots from the fragmented gold tips under 532 nm, 633 nm, and 785 nm incidences is fully characterized in this part.

5.2.1 Localized surface plasmon resonance

Due to the formation of nanoscale fragmented tips via cold-drawing as the SEM images shown in Figures 5.1(b)-5.1(g), the plasmonic hot spots can be excited by normal light incidence. The linear experimental characterization of the fabricated structures is performed by a UV/Vis/NIR spectrometer. The reflectivity spectra of the graphene/fragmented-gold substrate with gold film thickness of 10 nm, 20 nm, and 30 nm are presented in Figure 5.3. The g-1D nanostructures possess nearly same resonance peak position (Figure 5.3(a)). It can be seen from Figure 5.3(b) that strong absorption appears from 575 nm to 975 nm (a very wide wavelength range) for the three g-2D nanostructures. The extreme wideband operation is induced by the non-uniform sized gold tips per unit area by cold-drawing. The greatly enhanced absorption relies on the stimulated transverse/longitudinal collective localized plasmon resonances by a large number of fragmented tips. Note that, the linear optical properties are sensitive to the geometric parameters.

Figure 5. 3 Localized surface plasmon resonance of the hybrid graphene/fragmented-gold substrate. Visible/near-infrared reflectivity spectra of the graphene integrated (a) 1D and (b) 2D fragmented-gold substrates with 10 nm, 20 nm, and 30 nm gold film thicknesses. Gray vertical strips indicate the reflectivity at laser wavelengths of 633 nm, and 785 nm.

5.2.2 Graphene Raman intensity

A lot of graphene/metallic plasmonic hybrid systems have been explored as GSERS substrates for sensitive molecule detection. It was suggested that the enhanced bio-sensitivity of the GSERS substrates can be verified by the enhanced graphene Raman intensity. Before discussing the capacity of the graphene-fragmented gold system in biosensing, we present the typical studies on the interactions between graphene and the fragmented gold substrate by Raman spectroscopy, i.e., graphene is employed as a target analyte. Raman scattering spectra of the 10 samples are recorded with a commercial Renishaw Raman system at 532 nm, 633 nm, and 785 nm. The laser beam is illuminated onto the sample after a 20 $\times$ objective. Large beam size is used to cover a sufficient amount of fragmented gold tips, so as to minimize the variation of hot spots numbers in parallel characterizations. Figures 5.4(a) and 5.4(b) depict the Raman scattering spectra of the 10 samples at 633 nm and 785 nm. Each Raman scattering spectrum is obtained with 10 s detector exposure time. GSERS enhancement is clearly observed in both g-1D and g-2D samples compared with that from g-Si sample, which is mainly induced by the stimulated localized surface plasmons (electromagnetic mechanism) where the gold nanostructure localize the incident laser and produce hot spots near the graphene surface.

Figure 5. 4 Raman spectrum of the graphene layer on 10 different substrates with laser excitation at (a) 633 nm, and (b) 785 nm. The Raman spectra of g-Si and g-film are magnified 10 times. All spectra are displayed with background subtraction. Yellow vertical strips indicate the graphene Raman G and G' bands. Histogram of the GSERS enhancement factor at (c) 633 nm and (d) 785 nm. Since graphene Raman is not detectable with 785 nm excitation for the g-Si substrate, we compare the G and G' Raman intensity at 785 nm of each hybrid graphene/fragmented-gold substrate to that at 633 nm of g-Si to quantify the GSERS enhancement factor at 785 nm.

Figure 5.5 gives the Raman scattering spectrum of the graphene layer from 10 different substrates with laser excitation at 532 nm. The exposure time is 10 s. No significant enhancement of the graphene/metallic plasmonic hybrid systems is achieved.

Figure 5. 5 Raman spectrum of the graphene layer from 10 different substrates with laser excitation at 532 nm. The Raman spectra from g-Si/ g-Au are magnified 5/10 times.

GSERS enhancement factor. EF is defined as $EF = I_{GSERS}/I_{Raman}$ ($\sim E_{loc}^2(\omega_I)E_{loc}^2(\omega_R)/E_{inc}^4(\omega_I)$, E_{loc} and E_{inc} are the local and incident field strengths, ω_I and ω_R represent the incident and Raman frequencies), where I_{GSERS} and I_{Raman} denote the GSERS and normal (from g-Si) Raman intensities. Figure 5.4(c) depicts the GSERS enhancement factor distribution of g-1D and g-2D substrates at 633 nm. g-2D 20 nm possesses the highest EF for graphene G (44.5-fold enhancement) and G' (59-fold enhancement) bands. The significant enhancement is attributed to the high intensity enhancement created by plasmonic coupling³³ which agrees well with the reflectivity spectrum in Figure 5.4(b). Figure 5.4(d) shows the enhancement factor for each hybrid substrate at 785 nm. To evaluate the GSERS performance at 785 nm, we compare the GSERS intensity at 785 nm for each hybrid sample with normal Raman intensity at 633 nm from g-Si. This is because the GSERS enhancement factor at 785 nm cannot be determined since no band is observed in the normal Raman spectrum (from g-Si)¹⁷⁰. Figure 5.4(d) indicates larger GSERS EF at 785 nm (further 4.75/3.3-fold enhancement for G/G' bands at 785 nm compared with GSERS EF at 633 nm can be achieved for g-2D 20 nm), which is because 785 nm is closer to the plasmon resonance (see Figure 5.3b). Moreover, the small Raman spectrum of graphene from the g-film substrates indicates no resonance effects offered by the smooth gold film. Also, we characterize

the GSERS at 532 nm, no enhancement is observed. From Figure 5.4, for both g-1D and g-2D structures, the optimized gold film thickness possessing highest GSERS EF is 20 nm, followed by 10 nm and 30 nm. Normally, thinner gold film possesses denser fragmented tips which will provide more hot spots for higher GSERS EF. However, too small fragmented gold tips lose much of their spectral features due to the broadening of plasmon bands by size effects. 20 nm is the optimized gold film thickness for hybrid graphene/fragmented-gold substrate according to our measurements.

For the g-2D substrates, the GSERS EF correlates well with the linear optical response. However, there is no consistent correlation between the GSERS EF (Figure 5.4) and the conventional reflection characterization for the g-1D substrates (Figure 5.3(a)), i.e., extinction peak occurs at 508 nm and GSERS EF at 785 nm is the largest. This is because multiple collective localized surface plasmon resonances are stimulated at 633 nm and 785 nm.

To demonstrate the superiority of our proposed graphene/fragmented-gold GSERS substrate, Table 5.1 lists the graphene Raman intensity enhancements of the recently reported GSERS substrates. Among them, a graphene gold-void platform¹⁷¹ and a graphene-nanopyramid system¹⁷² are able to provide remarkable graphene Raman response enhancements up to 700-fold and 600-fold due to the extremely dense electromagnetic hot spots and the sharp gold tips, respectively. However, the fabrication process of the nonflexible nanopyramid¹⁷¹ is complicated which includes a self-assembly monolayer of colloidal spheres followed by an electrochemical deposition, and a final dissolution. And the corresponding full-width-at-half-maximum (FWHM) of the plasmon resonance is very small (~40 nm). For the graphene-nanopyramid system¹⁷², the non-uniform distributed gold tips lead to poor reproducibility and uniformity, polarization-dependence of Raman spectroscopy. The very sharp gold tips also induce sharp graphene folds near the nanopyramid extremities where graphene is inclined to crack. This will result in reduced reusability of the GSERS substrate. In contrast, our proposed flexible graphene/fragmented-gold substrate, which is easily fabricated at the scale of manufacturing, can provide very large GSERS EF, at the same time uniform and reproducible, reliable GSERS EF in parallel characterizations. Therefore, the proposed graphene/fragmented-gold substrate should be considered as one of the ideal SERS substrates.

TABLE 5. 1 Compare the maximum achievable enhancement factors (max EF) of G peak and G' peak of graphene from our graphene/fragmented-gold substrate to other recent reported GSERS substrates. For the GSERS substrates possessing high graphene SERS enhancement factors, corresponding FWHM of the localized surface plasmon resonance is also provided.

Max EF (G peak)	Max EF (G' peak)	FWHM [nm]	Morphology
2		-	Graphene on Au gratings ¹⁷³
7	7.5	-	Graphene on Au dimers ¹⁷⁴
<10		-	Au nanoparticles (NPs) on graphene ¹⁷⁵
~12	<10	-	Graphene on Ag nanoantennas ¹⁷⁶
9	13	-	Graphene to rough Ag films ¹⁷⁷
15.5		-	Reduced graphene oxide sandwiched between Ag and Au nanostructures ¹⁷⁸
<20	<10	-	Au NPs on graphene ¹⁷⁰
10-20	10-20	-	Graphene-veiled Au substrate ¹⁷⁹
<20		-	Graphene on Au/Ag NPs ¹⁸⁰
20	20	-	Graphene on Au nanoholes ¹⁸¹
22	27	-	Au dots on graphene ¹⁸²
	<50	-	Graphene on Au hemispheres ¹⁸³
50	15	-	Graphene-nanospheres(NS), NS-graphene-film, and NS-graphene-NS ¹⁸⁴
10	10	-	Graphene on Ag nanoholes ¹⁸⁵
~40 ^a	~40 ^a	-	Crumpled graphene – Au NPs ¹⁸⁶
87.44 ^b	87.44 ^b	-	
600	700	100	Graphene on Au nano-pyramid ¹⁷²
700	700	40	Graphene on Au nanovoid arrays ¹⁷¹
44.5 ^c	58.9 ^c	200	e
211.4 ^d	194.3 ^d	200	e

a: experimental EF; b: theoretical upper bound of EF; c: 633 nm excitation; d: 785 nm excitation; and e: hybrid graphene fragmented-gold substrate. For the cases with mark

‘-’, the FWHM values are not important for us due to the small graphene Raman scattering enhancements. We will not report them here.

3D FDTD method using total-field scattered-field source is performed to understand the extinction spectrum, GSERS EF, and the corresponding electric field distribution in the g-2D 20 nm substrate (provides the largest GSERS EF as shown in Figure 5.4) as shown in Figure 5.6. The geometrical model is generated from the magnified SEM image presented in Figure 5.1(f). Figure 5.6(a) presents the simulated extinction spectrum, and Figure 5.6(b) shows the calculated enhancement factor at 633 nm and 785 nm. The extinction shape agrees well with the experimental measurement expect a slight red shift of the resonance. Each calculated GSERS EF is also smaller than the experimental results. We believe this is because: (1) some defects and variation exist in the deposited gold film such as thickness and surface roughness, and (1) the detailed fragmented tip pattern cannot be effectively captured by SEM. Figure 5.6(c) and 5.6(d) show the spatial distribution of the electric field intensity in the graphene layer of the GSERS substrate, informing that hot spots is mainly induced by the fragmented gold tips.

Figure 5. 6 FDTD simulation of the g-2D 20 nm substrate. (a) Simulated extinction cross-section. (b) GSERS enhancement factor ($EF = \int |E / E_0|^4 dS / S_0$, with E being the maximum local electric field, and E_0 being the incident electric field. S is the GSERS region, and S_0 is the total GSERS area) at 633 nm and 785. Electric field (logarithmic scale, i.e. $\log_{10}(|E|)$) distribution in the graphene layer at (c) 633 nm and (d) 785 nm.

5.3 Biosensing

Although it has been widely accepted that a rough surface can achieve strong SERS signals, a relatively flat surface is preferable for many analytical situations^{171, 175, 187, 188}. Graphene, as an ideal building block to achieve a flat SERS surface, is atomically flat and thin, and chemically stable to act as a seamless adhesion layer^{189, 190}. Here, we use g-2D 20 nm and 2D 20 nm (only 2D fragmented-gold film without graphene integrated on top) substrates to analyze molecules at 785 nm to confirm the possible superiorities of the graphene/fragmented-gold system for SERS. We prepare 10 μM rhodamine 6G (R6G), 0.1 μM R6G, and 0.1 mM methylene blue (MB) molecular solutions. Figure 5.7 depicts the Raman scattering spectra of the R6G and MB molecules assembled on top of the GSERS and SERS (2D 20 nm) substrates. The insets illustrate the possible bonding states of molecules. For the SERS substrate, molecules possess various orientations which follow the rough morphology of the fragmented-gold film resulting in complicated molecular Raman signals. While the atomically flat surface in GSERS can arrange the molecules in a controllable way. The GSERS substrate presents clear peaks at 611, 781, 1183, 1310, 1360, 1450, 1507 cm^{-1} for R6G and 1036, 1128, 1181, 1304, 1325, 1394, 1439, 1504, 1621 cm^{-1} for MB. The 1590 cm^{-1} peak is the graphene G band. In contrast, Raman spectra enhanced by the SERS substrate show some inconsistent extra peaks as the “#” marks (701, 860, 1241, 1380 cm^{-1} for 10 μM R6G, 701, 862, 1241 cm^{-1} for 0.1 μM R6G, and 1078, 1154, and 1280 cm^{-1} for 0.1 mM MB). As a result, it is difficult to identify each molecular vibration.

Figure 5. 7 Sensitivity comparison of probing molecular fingerprints between the GSERS (g-2D 20 nm) and SERS (2D 20 nm, only 2D fragmented-gold film) substrates. Raman spectra of (a) 10 μM R6G, (b) 0.1 μM R6G, and (c) 0.1 mM MB on GSERS and SERS substrate at 785 nm. The peaks labeled by “*” are from the corresponding molecules. The peaks marked by “+” are the G band of graphene. The peaks labeled by “#” are the extra peaks in the fragmented-gold substrate which results from the interaction between the gold and the top bonded molecules.

Furthermore, Raman signal in GSERS substrate provides a cleaner baseline. For example, the photo-carbonization background (photo-induced damage) at 1330~1430 cm^{-1} (for R6G, Figures 5.7(a), and 5.7(b), 1450~1550 cm^{-1} (for MB, Figure 5.7(c)) is not observed in the GSERS spectra. Carbonization background is normally induced by

the surface adsorbates of the gold film from the atmosphere¹⁹⁰. For GSERS substrate, graphene prevents the direct contact of the molecules with the fragmented-gold film to minimize the gold catalytic activity, producing clean and stable Raman signals of adsorbates with comparable enhancement factor. Note that, the Raman intensity of R6G and MB on GSERS substrate is slightly weaker than that on SERS substrate. This is because of the existing nanoscale gap (due to the excited nanobubbles¹⁹¹) between graphene and the fragmented-gold surface which prevents the high Raman intensity. Also, weak photoluminescence background can be observed in GSERS substrate because graphene can quench the fluorescence from the dyes and the photoluminescence from the gold film^{189, 192}. Moreover, the top bonded molecules on GSERS can be removed after multiple washing, leaving a clean graphene surface, which is suitable for real-time characterization and monitoring.

The plasmon resonant frequency (which can be tuned through tuning the morphology of the fragmented tips) and intensity (higher electromagnetic field enhancement can be achieved when hot spots couple with each other in smaller gap sizes) can further be modified by selecting appropriate stretchable polymer films and metal deposition thicknesses, or heating the hybrid graphene/fragmented-gold substrate to restore the polymer dimensions.

5.4 Conclusions

In this chapter, we fabricated an ultra-wideband GSERS substrate by integrating monolayer graphene on top of a fragmented-gold film *via* cold-drawing. Leveraging on this simple fabrication method, periodically/evenly distributed gold nanoscale tips are achieved through a controllable two-axial fragmentation of a gold nano-film. The two-dimensional fragmented-gold film possesses ultra-wideband plasmon resonance with significant electromagnetic field enhancement. By tuning the morphology of the fragmented nanostructure through tuning the gold film thickness and fragmented dimension, detailed GSERS enhancement activity is investigated. This novel GSERS substrate is flexible and can provide greatly enhanced, uniform, more reliable, and reproducible molecule SERS readout. Furthermore, it is resistant to metal degradation and can be cleaned after each test. Undoubtedly, the proposed hybrid structure is

expected to one of the promising reliable choices to meet the future GSERS practical applications.

Chapter 6 Backaction Enhanced Raman Scattering with Transformation Optics

To analytically study the plasmonic structures, we introduce the transformation optics technique in this chapter. Transformation optics technique provides the ability to bend light or electromagnetic waves and energy for prospective applications in any preferred or desired manner. Since Maxwell's equation sustains the same form, it is the permittivity and permeability that vary though coordinates transform and can be controlled at will due to the spatial gradients independence. The precise degree of electric and magnetic response in the original space can be maintained in the transformed space. Therefore, TO becomes a very effective technique to study novel and unique plasmonic devices to guide us the waveguide design to attain the inclined properties.

In this chapter, we utilize TO technique to study analytically the backaction amplification scenarios of SERS. Raman scattering intensity is greatly enhanced on a nanostructured metal surface^{47, 193}, known as surface enhanced Raman scattering (SERS)^{8, 194}. It is well accepted the combined enhancement at excitation and emission contributes to the fourth power of the electromagnetic enhancement of giant SERS^{28, 48, 49, 193, 195-199} until a recent quantum explanation^{200, 201} and a followed phenomenological semi-classical model²⁰² account for the dynamical backaction amplification action. Kippenberg and his colleagues suggest that an analogy could be found between the interaction between molecular vibrations and plasmons in SERS and the optomechanical backaction in an optical cavity. In an optomechanical cavity, when one of the mirrors is allowed to move freely, the radiation pressure induced by the circulating photons can be harnessed. The mechanical motion of the mirror shifts the cavity resonance which modifies the circulating light and the corresponding radiation pressure. This 'backaction' effect acts as a feedback mechanism which can, in turn, quench or amplify the mirror vibrations depending on the laser illumination. It has been demonstrated that a blue-detuned illumination will amplify the mirror vibrations. The quantum explanation by Kippenberg and his colleagues^{200, 201} suggests that the molecular vibrations can be

greatly amplified in SERS with a blue-detuned laser. Correspondingly, a significant enhanced Raman signal is expected. We demonstrate that efficient Raman scattering can be achieved when the laser is blue-detuned to the largest slope point of the plasmonic resonance spectrum for molecule vibrational frequency smaller than half of the plasmonic decay rate and evidently close to the anti-Stokes vibrational sideband for molecular vibrations comparable or larger than half of the plasmonic decay rate to maximum the corresponding phonon population.

6.1 Geometric transformation

In this part, we introduce TO technique to address the local field upon the Raman-active molecule located at the gap center of a spherical dimer. We consider one of the commonly used plasmonic structure, a silver spherical dimer to study the backaction amplification effect. The dielectric separating the silver spheres is taken to be vacuum. The whole spherical dimer system is illuminated by a plane wave polarized along z' -axis. Figure 6.1 shows the geometric transformation between a dimer system to an annulus system. 3D transformation of

$$\mathbf{r}' = \frac{R_T^2}{\mathbf{r} - \mathbf{R}_0} \quad (6.1)$$

is applied. R_T is an arbitrary constant. Different from the 2D conformal transformation, the 3D transformation action transform both the plasmonic geometry and material properties of the plasmonic system. All homogeneous permittivities in the original space are transformed as $\varepsilon(\mathbf{r}) = \varepsilon'(\mathbf{r}') R_T^2 / |\mathbf{r} - \mathbf{R}_0|^2$ to non-homogeneous in the transformed space.

Figure 6. 1 Geometry of transformation. Transformation by $\mathbf{r}' = \frac{R_T^2}{\mathbf{r} - \mathbf{R}_0}$ links the dimer system with the annulus system. The red point demotes the Raman-active molecule. R_T is an arbitrary transformation parameter. Coordinates for the original space are primed. All homogeneous permittivities in the original space are transformed as $\varepsilon(\mathbf{r}) = \varepsilon'(\mathbf{r}') R_T^2 / |\mathbf{r} - \mathbf{R}_0|^2$ in the transformed space.

6.2 Solution to the plasmonic resonances

Scalar electric potential is conserved during the transformation and the scattered electric field can be achieved by differentiating the scattered electric potential. To find the electric potential in the dimer system, we calculate the potential in the annulus system first by solving Laplace's equation in spherical coordinates where the Laplacian is given as

$$\nabla = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (6.2)$$

To solve Laplace's equation $\nabla \varphi = 0$, method of separation of variables is used to attain the electric potential thus to get the local electric field at the site of the molecule. The electrical potential in each region of the annulus can be written as²⁰³

$$\begin{aligned}
\varphi &= |\mathbf{r} - \mathbf{R}_0| \sum_{l=0}^{\infty} \sum_{m=-l}^l a_{lm}^{in} \left(\frac{r}{R_0} \right)^l Y_{lm}(\theta, \phi) & r < R_1 \\
&= |\mathbf{r} - \mathbf{R}_0| \sum_{l=0}^{\infty} \sum_{m=-l}^l \left[(a_{lm}^+ + a_{lm}^{S+} + a_{lm}^{R+} + a_{lm}^{M+}) \left(\frac{r}{R_0} \right)^l + a_{lm}^- \left(\frac{r}{R_0} \right)^{-(l+1)} \right] Y_{lm}(\theta, \phi) & R_1 < r < R_0 \quad (6.3) \\
&= |\mathbf{r} - \mathbf{R}_0| \sum_{l=0}^{\infty} \sum_{m=-l}^l \left[a_{lm}^+ \left(\frac{r}{R_0} \right)^l + (a_{lm}^- + a_{lm}^{S-} + a_{lm}^{R-} + a_{lm}^{M-}) \left(\frac{r}{R_0} \right)^{-(l+1)} \right] Y_{lm}(\theta, \phi) & R_0 < r < R_2 \\
&= |\mathbf{r} - \mathbf{R}_0| \sum_{l=0}^{\infty} \sum_{m=-l}^l a_{lm}^{out} \left(\frac{r}{R_0} \right)^{-(l+1)} Y_{lm}(\theta, \phi) & R_2 < r
\end{aligned}$$

where $a_{lm}^{S\pm}$, $a_{lm}^{R\pm}$, and $a_{lm}^{M\pm}$ are the expansion coefficients of the (l, m) harmonics which are related to the laser source, the radiative damping correction, and the molecule dipole moment, respectively. Radiative damping is included to extend the validity of the transformation optics approach to a larger dimer dimension (generally larger than 20 nm). $a_{lm}^{\pm}$ are to be solved by applying boundary conditions at $r = R_1$ and $r = R_2$ and exploiting the induced dipole moment of the plasmonic system and the molecule.

Boundary conditions. The $|\mathbf{r} - \mathbf{R}_0|$ in Eq. (6.3) couples the lower and higher angular momentum together. Accordingly, the boundary conditions can be provided as

$$a_{lm}^{in} \left(\frac{R_1}{R_0} \right)^l = (a_{lm}^+ + a_{lm}^{S+} + a_{lm}^{R+} + a_{lm}^{M+}) \left(\frac{R_1}{R_0} \right)^l + a_{lm}^- \left(\frac{R_1}{R_0} \right)^{-(l+1)} \quad (6.4a)$$

$$a_{lm}^{out} \left(\frac{R_2}{R_0} \right)^{-(l+1)} = a_{lm}^+ \left(\frac{R_2}{R_0} \right)^l + (a_{lm}^- + a_{lm}^{S-} + a_{lm}^{R-} + a_{lm}^{M-}) \left(\frac{R_2}{R_0} \right)^{-(l+1)} \quad (6.4b)$$

$$\begin{aligned}
&\sum_{l=1}^{\infty} \sum_{m=-l}^l \varepsilon_m a_{lm}^{in} \left[\left(l+1+l \frac{R_0^2}{R_1^2} \right) \frac{R_1^{l+1}}{R_0^l} - (2l+1) \frac{R_1^l}{R_0^{l-1}} \cos \theta \right] Y_{lm}(\theta, \phi) \\
&= \sum_{l=1}^{\infty} \sum_{m=-l}^l \left\{ \left[\left(l+1+l \frac{R_0^2}{R_1^2} \right) (a_{lm}^+ + a_{lm}^{S+} + a_{lm}^{R+} + a_{lm}^{M+}) - \left(l+1+l \frac{R_1^2}{R_0^2} \right) a_{lm}^- \frac{R_0^{2l+3}}{R_1^{2l+3}} \right] \frac{R_1^{l+1}}{R_0^l} - \right. \\
&\quad \left. (2l+1) \left(a_{lm}^+ + a_{lm}^{S+} + a_{lm}^{R+} + a_{lm}^{M+} - a_{lm}^- \frac{R_0^{2l+1}}{R_1^{2l+1}} \right) \frac{R_1^l}{R_0^{l-1}} \cos \theta \right\} Y_{lm}(\theta, \phi) \quad (6.4c)
\end{aligned}$$

$$\begin{aligned}
&\sum_{l=1}^{\infty} \sum_{m=-l}^l \varepsilon_m a_{lm}^{out} \left[\left(l+1+l \frac{R_2^2}{R_0^2} \right) \frac{R_0^{l+3}}{R_2^{l+2}} - (2l+1) \frac{R_0^{l+2}}{R_2^{l+1}} \cos \theta \right] Y_{lm}(\theta, \phi) \\
&= \sum_{l=1}^{\infty} \sum_{m=-l}^l \left\{ \left[\left(l+1+l \frac{R_2^2}{R_0^2} \right) (a_{lm}^- + a_{lm}^{S-} + a_{lm}^{R-} + a_{lm}^{M-}) - \left(l+1+l \frac{R_0^2}{R_2^2} \right) a_{lm}^+ \frac{R_2^{2l+3}}{R_0^{2l+3}} \right] \frac{R_0^{l+3}}{R_2^{l+2}} - \right. \\
&\quad \left. (2l+1) \left(a_{lm}^- + a_{lm}^{S-} + a_{lm}^{R-} + a_{lm}^{M-} - a_{lm}^+ \frac{R_2^{2l+1}}{R_0^{2l+1}} \right) \frac{R_0^{l+2}}{R_2^{l+1}} \cos \theta \right\} Y_{lm}(\theta, \phi) \quad (6.4d)
\end{aligned}$$

Different angular momenta can be coupled together with $\cos \theta$ by

$$\cos \theta Y_{lm}(\theta, \phi) = p_l^m Y_{l-1,m}(\theta, \phi) + p_{l+1}^m Y_{l+1,m}(\theta, \phi) \quad (6.5)$$

$$\text{where } p_l^m = \begin{cases} \sqrt{\frac{l^2 - m^2}{4l^2 - 1}} & |m| < l \\ 0 & |m| \geq l \end{cases}.$$

Spherical harmonic expansion of a plane wave. With z' -polarized plan wave incidence, all modes except those with $m=0$ vanish. It is convenient to treat the electrical potential in terms of a spherical harmonic function basis. The potential of the uniform electric field source in the transformed annulus system has the form

$$\varphi^S = |\mathbf{r} - \mathbf{R}_0| \sum_{l=0}^{\infty} \left[a_{l0}^{S+} \left(\frac{r}{R_0} \right)^l + a_{l0}^{S-} \left(\frac{r}{R_0} \right)^{-(l+1)} \right] Y_{l0}(\theta, \varphi) \quad (6.6)$$

The term inside the square bracket of Eq. (6.6) is a solution of Laplace's equation. The corresponding expansion coefficients in spherical harmonics are

$$a_{l0}^{S+} = -2E_0 \frac{R_T^2}{R_0^2} (l+1) \sqrt{\frac{\pi}{2l+1}} \quad (6.7)$$

$$a_{l0}^{S-} = 2E_0 \frac{R_T^2}{R_0^2} l \sqrt{\frac{\pi}{2l+1}} \quad (6.8)$$

Therefore, to determine all the unknown coefficients in Eq. (6.3), we need another two equations relating $a_{l0}^{R\pm}$, $a_{l0}^{M\pm}$ to $a_{l0}^{\pm}$.

Spherical harmonic expansion of the radiative correction dipole. $a_{l0}^{R\pm}$ account for the radiative damping to extend the validity of the TO technique to a plasmonic system with a larger dimension. Since dipole and field exchange roles under transformation, the radiation in the transformed coordinate can be modelled as a fictional absorbing particle in the original space²⁰⁴. The electrical potential takes the form

$$\varphi^R = \lim_{r \rightarrow R_0} |\mathbf{r} - \mathbf{R}_0| \sum_{l=0}^{\infty} \left[a_{l0}^{R+} \left(\frac{r}{R_0} \right)^l + a_{l0}^{R-} \left(\frac{r}{R_0} \right)^{-(l+1)} \right] Y_{l0}(\theta, \varphi) \quad (6.9)$$

In the transformed annulus system, the expansion coefficients take the form

$$a_{l0}^{R+} = -i \frac{k_0^3 p^{R+}}{3\sqrt{\pi} \varepsilon_0} \left(\frac{g}{R_0} \right)^2 (l+1) \sqrt{\frac{1}{2l+1}} \quad (6.10)$$

$$a_{l0}^{R-} = i \frac{k_0^3 p^{R+}}{3\sqrt{\pi} \varepsilon_0} \left(\frac{g}{R_0} \right)^2 l \sqrt{\frac{1}{2l+1}} \quad (6.11)$$

where $\mathbf{p}^{R'}$ is the radiative dipole moment related to $m = 0$ and the magnitude can be obtained at $\theta' \rightarrow 0$.

We can get now

$$\begin{bmatrix} |a^+\rangle \\ |a^-\rangle \end{bmatrix} = \mathbf{R} \begin{bmatrix} |a^{S+}\rangle + |a^{M+}\rangle - i \frac{k_0^3 p^{R'}}{3\sqrt{\pi}\epsilon_0} \left(\frac{g}{R_0}\right)^2 (l+1) \sqrt{\frac{1}{2l+1}} \\ |a^{S-}\rangle + |a^{M-}\rangle + i \frac{k_0^3 p^{R'}}{3\sqrt{\pi}\epsilon_0} \left(\frac{g}{R_0}\right)^2 l \sqrt{\frac{1}{2l+1}} \end{bmatrix} \quad (6.12)$$

Spherical harmonic expansion of the molecular dipole moment. Assume the molecule location in the original dimer is

$$\mathbf{r}^{M'} = \mathbf{z}' b \quad (6.13)$$

where, $\mathbf{z}'$ is the unit vector in the original space corresponding to the $\mathbf{z}'$ direction. The induced molecular electric potential in terms of the transformed geometrical parameters is

$$\varphi^M = |\mathbf{r} - \mathbf{R}_0| \sum_{l=0}^{\infty} \left[a_{l0}^{M+} \left(\frac{r}{R_0}\right)^l + a_{l0}^{M-} \left(\frac{r}{R_0}\right)^{-(l+1)} \right] Y_{l0}(\theta, \varphi) \quad (6.14)$$

whose expansion coefficients are:

$$a_{l0}^{M+} = K^{M+} p^{M'} \quad (6.15)$$

$$a_{l0}^{M-} = K^{M-} p^{M'} \quad (6.16)$$

with

$$K^{M+} = -\frac{R_0}{4\pi\epsilon_0} \left[2\sqrt{\frac{\pi}{2l+1}} \frac{(R_0 b)^{l-1} (R_0 b + l R_T^2)}{(R_0 b - R_T^2)^{l+2}} \right] \quad (6.17)$$

$$K^{M-} = \frac{R_0}{2\pi\epsilon_0} \sqrt{\frac{\pi}{2l+1}} \frac{(R_0 b - R_T^2)^{l-1} [R_0 b - (l+1) R_T^2]}{(R_0 b)^{l+2}} \quad (6.18)$$

The stimulated molecular dipole moment $\mathbf{p}^{M'} = \alpha_M \mathbf{E}'$ can be obtained from the local electric field $\mathbf{E}'$.

Eq. (6.12) can be rewritten as

$$\begin{bmatrix} |a^+\rangle \\ |a^-\rangle \end{bmatrix} = \mathbf{R} \begin{bmatrix} |a^{S+}\rangle + |a^{R+}\rangle + K^{M+} p^{M'} \\ |a^{S-}\rangle + |a^{R-}\rangle + K^{M-} p^{M'} \end{bmatrix} \quad (6.19)$$

Therefore, for molecule moves perpendicular to the symmetric axis z' , a_{l0}^+ and a_{l0}^- can be obtained by solving Eqs. (6.4)(6.12)(6.19).

With known a_{l0}^+ and a_{l0}^- , the scattered electric potential reads

$$\varphi^{sca} = |\mathbf{r} - \mathbf{R}_0| \sum_{l=0}^{\infty} \left[a_{l0}^+ \left(\frac{r}{R_0} \right)^l + a_{l0}^- \left(\frac{r}{R_0} \right)^{-(l+1)} \right] Y_{l0}(\theta, \phi) \quad (6.20)$$

And the local electric field at any position of the dimer can be obtained as the gradient of the scattered electric potential

$$E^{sca'} = -\cos \theta' \left(\langle t^+ | a^+ \rangle + \langle t^- | a^- \rangle \right) \quad (6.21)$$

where

$$a^+ = a_{l0}^+ \quad (6.22)$$

$$a^- = a_{l0}^- \quad (6.23)$$

$$t^+ = \frac{R_T^2}{rr'^2} Y_{l0}(\theta, \phi) \left\{ \begin{aligned} & \left[\frac{R_T^2}{r'} \cos \theta' + R_0 (\sin^2 \theta' - \cos^2 \theta') \right] \left[|\mathbf{r} - \mathbf{R}_0| \frac{l}{r} + \frac{r - R_0 \cos \theta}{|\mathbf{r} - \mathbf{R}_0|} \right] \left(\frac{r}{R_0} \right)^l + \\ & \frac{1}{r \sin \theta} \left[(\cos^2 \theta' - \sin^2 \theta') \left(1 - \frac{R_0 \cos \theta}{r} \right) + \frac{R_T^2 \cos \theta' \cos \theta}{rr'} \right] \cdot \\ & \left[-|\mathbf{r} - \mathbf{R}_0| \frac{(l+1)}{r} + \frac{r - R_0 \cos \theta}{|\mathbf{r} - \mathbf{R}_0|} \right] \left(\frac{r}{R_0} \right)^{-(l+1)} \end{aligned} \right\} \quad (6.24)$$

$$t^- = \frac{R_T^2}{rr'^2} \left[\frac{r R_0 \sin \theta}{|\mathbf{r} - \mathbf{R}_0|} Y_{l0}(\theta, \phi) + |\mathbf{r} - \mathbf{R}_0| \frac{\partial Y_{l0}(\theta, \phi)}{\partial \theta} \right] \cdot \left\{ \begin{aligned} & \left[\frac{R_T^2}{r'} \cos \theta' + R_0 (\sin^2 \theta' - \cos^2 \theta') \right] \left(\frac{r}{R_0} \right)^l + \\ & \frac{1}{r \sin \theta} \left[(\cos^2 \theta' - \sin^2 \theta') \left(1 - \frac{R_0 \cos \theta}{r} \right) + \frac{R_T^2 \cos \theta' \cos \theta}{rr'} \right] \left(\frac{r}{R_0} \right)^{-(l+1)} \end{aligned} \right\} \quad (6.25)$$

$$\frac{\partial r}{\partial r'} = -\frac{R_T^2}{rr'^2} \left(\frac{R_T^2}{r'} - R_0 \cos \theta' \right) \quad (6.26)$$

$$\frac{\partial \theta}{\partial r'} = -\frac{R_T^2}{r'^2} \frac{1}{r \sin \theta} \left[\cos \theta' + \frac{\cos \theta}{r} \left(\frac{R_T^2}{r'} - R_0 \cos \theta' \right) \right] \quad (6.27)$$

Note that, with z' -polarized incidence (uniform electric field $\mathbf{E}_0'$), all modes expect those with $m = 0$ vanish. The corresponding local field in the dimer system is $\mathbf{E}' = \mathbf{E}_0' + \mathbf{E}^{sca'}$.

6.2.1 Electric field enhancement

First, we calculate the plasmon resonance of the dimer system. The metal is taken as silver and the permittivity is taken from the Palik experimental data²⁰⁵. During the calculation, mode orders up to $l = 60$ is included to ensure convergence. Figure 6.2 present the plasmonic field enhancement of the spherical dimer at gap $g'=1$ nm at $R_1'=R_2'$ with different radius calculated with Eq. (6.21) and numerical simulations. There are two resonance peaks induced by the dipole coupling. The excellent agreement demonstrates the validity of the TO technique for small plasmonic dimensions (less than $\lambda/10$). For structures with large physical sizes, the numerical results are red-shifted from the theoretical predictions, which is due to the neglected retardation effects in the analytical treatment. The retardation effect becomes significant on the plasmons in large dimensions, i.e., larger than $\lambda/10$, and plasmon frequencies are red-shifted accordingly²⁰⁶. In these regimes, transformation optics approach is no longer valid and this approach which based on the electrostatic limit will produce significant errors. Weber and Ford²⁰⁷, and Citrin²⁰⁸ first noticed that retardation had a significant impact on the plasmonic bandstructure and resulted in radiative shifts of the quasistatic dispersion relation. The retardation effects cause a spatial-temporal coupling. Retardation is the effect of the phase difference between the fields propagating from two different regions of the plasmonic system during the study of large size coupled plasmons, and it is related to the effects of re-radiation. Transformation optics solves Maxwell's equations and provides accurate predictions of the properties of plasmonic systems in the quasistatic limit (without including the effects of retardation in the far field). To obtain reasonable and accurate optical properties for the plasmonic system with large dimensions, it is desirable to consider retardation.

Figure 6. 2 Theory compared with simulations. Electric field enhancement without molecule inside the gap at different radius of the silver spherical dimer system with fixed gap $g'=1$ nm. The radius of the sphere dimer is increased from 10 nm to 50 nm. Numerical simulations (open square) which are performed by COMSOL are compared with the analytical calculations (solid lines). Optimal geometry allows large electric field enhancement and small retardation effect at the same time.

6.3 Backaction enhanced Raman scattering

Feedback radiation force had been demonstrated to be able to trigger dynamical backaction amplification on plasmonic enhanced Raman scattering, which holds an important potential of ultrasensitive single molecule detection. However, the recently proposed linearized Hamiltonian is restricted to a single plasmon mode picture and cannot be solved analytically easily under arbitrary pumping detuning conditions. Here, we utilize TO technique to precisely calculate the significant enhancement of the molecule Raman emissions with plasmonic dimer system to offer both physical insight and mathematical certainty into the Raman signal intensity.

Plasmon damping can either be positive (damping the vibration) or negative (amplifying the vibration), depending on the laser detuning. The laser detuning determines which scattering process is dominant in the interaction. When the laser is red-detuned, the anti-Stokes enhancement is larger than the Stokes, the plasmon damping is positive. Conversely, when the laser is blue-detuned, the Stokes enhancement is larger than the anti-Stokes, the plasmon damping is negative²⁰⁰. For sufficiently high pump intensities, the blue-detuned laser induced backaction amplification is able to create instability.

Denoting by the molecular Raman tensor, the molecule dipole moment can be written as $\mathbf{p}^M = \alpha_0 \mathbf{E}' + \frac{1}{2} \alpha_s \mathbf{E}_s' + \frac{1}{2} \alpha_{as} \mathbf{E}_{as}'$, α_0 is the Rayleigh polarizability, α_s and α_{as} are the Stokes and anti-Stokes polarizability, respectively. $\mathbf{E}'$, $\mathbf{E}_s'$, and $\mathbf{E}_{as}'$ are the electric field at pump, Stokes, and anti-Stokes frequencies. Single normal mode of typical vibration of frequency $f_M=30$ THz and dissipation rate $\Gamma_M=0.06$ THz of a molecule is focused for calculation. The loss of mechanical energy is described by the mechanical dissipation rate which is assumed to be frequency independent. According to our calculation, the instability threshold occurs close to the phonon sideband. Figure 6.3 shows the significant stiffing and strengthening of Stokes and anti-Stokes scattering cross-sections under blue-detuned laser incidence with intensity increases to near the intensity instability threshold.

Figure 6. 3 Backaction enhanced Raman scattering. Additional enhancement for (a) Stokes and (b) anti-Stokes scattering cross-section under various pumping intensity. For selected molecular vibration of $f_M=30$ THz, efficient scattering occurs when the pump is blue-detuned to near the anti-Stokes sideband ($\Delta \sim f_M$). Stokes and anti-Stokes emissions reveal a similar laser intensity dependence.

6.4 Raman scattering instability

The backaction between the molecule vibration and the plasmon resonance leads to the modification of the molecular vibrational dissipation rate which can induce high enhancement on scattering. With blue-detuned incidence, the backaction damping rate is negative to amplify the vibrational mode²⁰⁹. Instability begins when optomechanically induced damping rate is negative and the magnitude equals to the molecule dissipation

rate. Instability intensity threshold depends on the laser detuning and the electric field enhancement factor at laser, Stokes and anti-Stokes sidebands. With pump intensity increase to near the threshold value, as shown in Figure 6.4, the Stokes and anti-Stokes scattering cross-sections, and the corresponding anomalous anti-Stokes/Stokes ratio depend on the intensity superlinearly and possess tangent enhancement.

Figure 6. 4 Super-nonlinear enhancement of Raman scattering at large pump intensity with backaction amplification induced by blue-detuned incidence. Additional enhancement factor for Stokes, anti-Stokes, and anomalous anti-Stokes/Stokes ratio (aS/S, which is divided by the ratio value under no backaction) versus the laser intensity. The tangent increment indicates scattering instability. The corresponding intensity value is the instability intensity threshold.

6.5 Molecule vibrational frequency effect

Different molecule vibration should correspond to different laser detuning to achieve efficient Raman emission under backaction amplification. We apply our theoretical model and calculate the laser blue-detuning as a function of the molecule vibration (range from 0.1 terahertz to 150 terahertz, almost covers all of the commonly experimentally relevant molecule vibrations ²¹⁰) as shown in Figure 6.5. When the molecule vibrational frequency is less than half of the linewidth of the plasmonic resonance, the laser incidence should be blue-detuned to the highest slope point of the plasmon resonance spectrum. Laser detuning can exceed the molecule vibrational frequency to produce the largest non-equilibrium phonon population, which is induced

by the second plasmonic resonance peak. This large detuning aims to further suppress the phonon annihilation by anti-Stokes.

Figure 6. 5 Molecule vibrational frequency dependent laser detuning at a fixed laser intensity 20 GW/cm^2 for efficient Raman scattering. The blue solid curve describes the optimal laser detuning versus molecule vibrational frequency. The black solid curve describes a condition when the laser blue-detuning is forced to equal to the molecule vibrational frequency.

6.6 Nonlocal effect

The first attempt to include the nonlocal effect in transformation optics was made by Fernandez-Dominguez *et. al.*²¹¹. For the specific spherical dimer in our calculation, the nonlocal effect can be included as shown in Figure 6.6. Quantum tunnelling effect cannot be included in the transformation optics approach due to the inhomogeneous permittivity of the gap media²¹².

Figure 6. 6 Schematics of a dimer system within nonlocal description. The surface charge smearing is mapped into a dielectric cover layer (green) by the local analogue model. The dielectric layer thickness t and the dielectric constant ϵ_t of this layer obeys

$$\frac{\epsilon_t}{t} = \frac{\epsilon_b \epsilon_m \sqrt{\omega_p^2 / \epsilon_\infty - \omega(\omega + i\gamma)}}{\beta(\epsilon_m - \epsilon_b)}^{213}, \text{ where } \epsilon_b \text{ is the dielectric constant of the background,}$$

ϵ_m is the bulk metal permittivity, ω_p and γ are the metal plasma and damping frequencies, $\epsilon_\infty = 1$, and $\beta = 3v_F^2/5$ is proportional to the Fermi velocity v_F .

6.7 Conclusions

We provide an analytical framework based on transformation optics to elucidate the physical ground under backaction amplification in SERS under blue-detuned incidence. The calculation is done by using 3D transformation optics where the electrostatic potential in each coordinate system are preserved and the mode calculated in the initial frame can be found in the other frame through transformation. We expect the theoretical study here will guide future experimental characterization of significantly SERS. These insights permit SERS system designs with backaction amplification for more sensitive Raman spectroscopy. Note that, we neglect the quantum and nonlocal effects during the calculation. For small gap geometry, the consideration of quantum and nonlocal effects of the metal^{214, 215} may become necessary to further improve the TO model.

Chapter 7 Conclusion and Recommendations

7.1 Conclusion

In this thesis, we have developed the high performance of planar plasmonic waveguides to study the metallic and graphene plasmons. Throughout the course of this thesis, four specific designed plasmonic waveguides have been employed both numerically and experimentally to achieve efficient third harmonic generation. Tunable resonant graphene plasmons possess strong optical field localization and provide corresponding large spatial overlap between the mid-IR graphene plasmons and the biomolecules to realize accurate detection of molecular chemical features. Two graphene plasmonic biosensors are proposed to detect the unique molecular chemical identification at mid-IR region with high accuracy. We also fabricated an ultra-wideband GSERS substrate to provide highly-enhanced, stable, and reproducible molecule Raman signals. In addition, we employ TO technique to analytically calculate the backaction amplification effect on SERS.

At the beginning of this thesis, the motivation, objectives, and major achievements for this work are introduced.

Chapter 2 gives an overview of the plasmonics, followed by an introduction of the basic properties and general applications of plasmonics. The basic concept of transformation optics and the corresponding applications are also provided.

Chapter 3 concludes three critical conditions for efficient THG based on the nonlinear coupled mode differential equations. Accordingly, two asymmetric plasmonic waveguides and a graphene plasmonic coupler are proposed and fully studied for efficient THG where the plasmons drive effective harmonic generation from the nonlinear media (with large $\chi^{(3)}$) under PMC. Since metallic plasmonic devices exhibit high intrinsic losses, we fabricate a hybrid silicon-plasmonic system with gold bowtie nanoantennas integrated onto the surface of a silicon substrate to couple the localized plasmons into the silicon and efficient THG is obtained experimentally.

According to our study, graphene plasmons surpass that of metallic plasmons by properties of tighter field confinement and lower loss. In chapter 4, we propose two

graphene plasmonic systems to detect the molecular vibrational frequencies. The strong light-molecule coupling leads to accurate identification of the molecular chemical fingerprints. High sensitivity is confirmed by the large resonant spectral shifts and intensity enhancement ratio dips of the graphene nanoribbon biosensors. The ability of one-to-one correspondence between the molecular photon energies and the graphene Fermi energy levels makes it convenient to reveal the molecular chemical properties by only tracking the reflection or transmission spectra.

In chapter 5, we fabricated an ultra-wideband GSERS substrate by integrating monolayer graphene onto the top of a fragmented-gold film. With a simple cold-etching process, periodically distributed gold nanoscale tips are formed, and greatly enhanced graphene Raman signal of the hybrid graphene fragmented-gold substrate is achieved. The stimulated hot spots and their strong interaction with the top-integrated monolayer graphene make the graphene a hot surface which is beneficial for a wideband tracing of analytes by highly enhanced, stable, reproducible, and clean molecule Raman readouts. We anticipate our results benefit the fabrication of a desirable practical GSERS platform.

In Chapter 6, we provide an analytical framework of transformation optics to elucidate the physical ground under backaction amplification in SERS with blue-detuned laser incidence. With transformation optics technique, the electrostatic potential in the original coordinate system can be achieved from the potential in the transformed system and the mode calculated in the initial frame can be found in the other frame through transformation.

7.2 Recommendations for further research

Investigations of plasmonic enhanced Compton-like scattering by transformation optics.

Compton scattering describes the scattering process of a photon by a charged particle. The scattered light wavelength is less than the incident radiation. The variation of the light's wavelength is called the Compton shift. A recent study on the enhanced Compton-like scattering in a hyperbolic photonic media has been processed²¹⁶. In a plasmonic system, the photon momentum can be significantly enhanced to be much larger than that in the free space. Therefore, under the condition of energy and momentum conservations, the plasmon-plasmon scattering by the free electrons in the

plasmonic system can lead to a giant Compton-like shift and dramatic scattering cross section enhancement.

Author's Publications

Journal Papers

1. **T. Wu**, Y. Luo, and L. Wei, "Phase-matching and peak nonlinearity enhanced third-harmonic generation in graphene plasmonic coupler," *Phys. Rev. Applied* 11(1), 2019.
2. **T. Wu**, Y. Luo, and L. Wei, "Mid-infrared sensing of molecular vibrational modes with tunable graphene plasmons," *Optics Letters* 42, 2017.
3. **T. Wu**, and L. Wei, "Tunable Resonant Graphene Plasmons for Mid-infrared Biosensing," *Opt. Express* 24(23), 2017.
4. **T. Wu**, P. P. Shum, Y. Sun, T. Huang, and L. Wei, "Third Harmonic Generation with the Effect of Nonlinear Loss," *IEEE J. Lightwave Technol.* 34(4), 2016.
5. **T. Wu**, P. P. Shum, X. Shao, Y. Sun, T. Huang, and L. Wei, "Efficient phase-matched third harmonic generation in a metal-clad plasmonic double-slot waveguide," *J. Opt.* 17(2), 2015.
6. **T. Wu**, Y. Sun, P. P. Shum, X. Shao, and T. Huang, "Study on the crucial conditions for efficient third harmonic generation using a metal-hybrid-metal plasmonic slot waveguide," *Opt. Express* 23(1), 2015.
7. S. Ma, T. Ye, **T. Wu**, Z. Wang, Z. Wang, S. Ramakrishna, C. Vijila, and L. Wei, "Hollow rice grain-shaped TiO₂ nanostructures for high-efficiency and large-area perovskite solar cells," *Solar Energy Materials and Solar Cells* 191, 2019.
8. **T. Wu**, W. Chen, J. Ho, Z. Xu, J.K.W. Yang, T. C. Sum, Y. Luo, and L. Wei, "Efficient third-harmonic generation from a hybrid silicon-plasmonic system," to be submitted.
9. **T. Wu**, K. Li, N. Zhang, J. Xia, Q. Zeng, X. Wen, U. S. Dinish, M. Olivo, Z. Shen, Z. Liu, Q. Xiong, S. A. Maier, Y. Luo, and L. Wei, "Ultra-Wideband Surface Enhanced Raman Scattering in Hybrid Graphene Fragmented-Gold Substrate via Cold-Etching," to be submitted.
10. **T. Wu**, L. Wei, and Y. Luo, "Controlling Raman emission with transformation optics," to be submitted.

Conference Presentations and Posters

1. **T. Wu**, Y. Luo, and L. Wei, “Ultra-Wideband Surface-Enhanced Raman Scattering in Hybrid Graphene/Fragmented-Gold Substrate via Cold-Drawing,” MRS, 2018.
2. **T. Wu**, Yu Luo, Lei Wei, “Mid-infrared molecular refractive index and vibrational modes sensing,” CLEO, 2017.
3. **T. Wu**, P. P. Shum, Y. Sun, T. Huang, and L. Wei, “Two-photon absorption effect on the third harmonic upconversion,” ICMAT15-A-2394 (H), 2015.

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