Photon manipulation in plasmonic crystal

Shumei Chen
Hong Kong Baptist University

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Photon Manipulation in Plasmonic Crystal

CHEN Shumei

A thesis submitted in partial fulfilment of the requirements

for the degree of

Doctor of Philosophy

Principal Supervisor: Prof. CHEAH Kok Wai

Hong Kong Baptist University

August 2014
DECLARATION

I hereby declare that this thesis represents my own work which has been done after registration for the degree of Ph. D at Hong Kong Baptist University, and has not been previously included in a thesis or dissertation submitted to this or any other institution for a degree, diploma or other qualifications.

Signature: ______________________

Date: August 2014
Abstract

Plasmonic devices, consisting of subwavelength nanostructures at optical frequency, have been widely applied to many research fields such as bio-sensing, super-resolution imaging, energy harvesting, nanolaser and so on. The strong confined electromagnetic fields in the affinity of nanostructures provides an efficient channel to guide, enhance, and modulate light energy beyond the diffraction limit. In this thesis, we first studied the plasmonic devices in linear optical regime, especially from the view of phase information in the light matter interaction; then more efforts were paid to the nonlinear plasmonics, in which the organic-plasmonic hybrid nanostructures provided a useful platform for demonstrating some interesting physical phenomena.

Firstly, we studied the fundamental optical properties of typically propagating surface plasmonic polariton (SPPs), which were generated by plasmonic gratings. Optical elliptical response of excited SPPs was studied experimentally and theoretically in both amplitude and phase domains. Then we studied the strong coupling effect from plasmonic Fabry-Perot nanocavity, in which giant Rabi splitting phenomenon with a splitting energy $\sim 148$ meV was obtained experimentally. From these studies, the interaction of SPP wave with other resonant structures were well understood from the view point of phase evolution.

Secondly, we moved from linear optics the nonlinear plasmonic optics and tried to understand how the plasmon enhancement acts on the nonlinear optical processes. In the first example, plasmon enhanced third harmonic generation (THG) on one dimensional gratings was experimentally demonstrated by integrating the nonlinear active medium into the plasmonic devices. Later, the generation of THG vortex beam was also realized by introducing hologram based plasmonic design. Lastly, we re-examined a conventional symmetry problem in nonlinear molecular optics. It was found that the metacrystal, consisting of plasmonic molecule with feature size much larger than conventional molecules, also follows the conventional selection rules.
of third harmonic generation.

We believe the knowledge we accumulated in this work also provides a strong background for our future studies on ultra-fast plasmonic switching, in which the all-optical low loss, optical switch can be realized by using the engineered optical properties of plasmonic devices.
Acknowledgements

I would like to thank my principle supervisor Prof. K. W. Cheah, for his great support and patient guidance in the past few years. I want to thank Prof. S. Zhang, who is my supervisor during my exchange study in University of Birmingham, for his great instructions, ideas and supports. Also, I would like to thank my co-supervisor Prof. S. K. So for his supports in thin film fabrication.

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Chapter 1

Introduction

In classical solid state physics, the optical properties of noble metals have been successfully described by the Drude model. In this model, the optical properties of metals such as dispersive dielectric constant, optical conductivity can be described using the physical picture of electron oscillations. [1] Plasma frequency refers to oscillation of electrons gas which corresponds to the excitation of collective longitudinal modes, and the quantized state of the plasma oscillation is defined as plasmon. [2] In most metallic materials, the plasmon excited in atomic crystal is called “volume plasmon”, which has an energy level of ~ 10 eV order. The volume plasmon can be implicated by Maxwell equations, and the study of plasmon-electron (polarons), plasmon-photon (polaritons) coupling emerged from sixty years ago.

In this thesis, we will focus on the surface plasmon which is usually excited by light at the boundary of metal/dielectric interface, and the dielectric constants of the metal and dielectric have positive and negative values. The surface plasmons can be coupled with photons to form surface plasmon polaritons (SPPs). [1,3,4] Unlike volume plasmon, which is the intrinsic property of the materials, surface plasmon excitation can be realized in artificially designed plasmonic crystals, which can be periodic nanostructures that are fabricated using state of art nanofabrication techniques. Although in the optical frequency range, bulk metallic film has a highly reflective dielectric
constant, which forbids the light transmission. However, the light propagation in plasmonic crystal can be easily manipulated and exhibits many novel properties that cannot be observed from natural materials. \cite{5, 6} These novel properties allow plasmonics devices to have many applications in such as optical communication \cite{7–9}, bio-sensing \cite{9–11} and nonlinear optics \cite{12–14} etc.

In this chapter, we review several topics on plasmonic crystals which are much related to our current research in this thesis. Firstly, the background of surface plasmon and its applications are discussed in section 1.1. Then, we review the studies of conventional Fabry-Perot cavity and plasmonic cavities, especially the Rabi splitting phenomena in section 1.2. In section 1.3, the nonlinear optical phenomena in plasmonic devices are introduced. In section 1.4, the ultra-thin plasmonic crystal (metasurface) and its applications in analogy of optical spin Hall Effect (OSHE), generation of optical vortex, three dimensional imaging will be illustrated. Finally, the outlines of the following chapters are summarized.

1.1 Surface Plasmon

Surface plasmon polaritons can be excited at the metal/dielectric interfaces if the momentum and the frequency of photon and surface plasmon have the same value and coupled together, the resonance condition is met. \cite{1} Under the resonance condition, the surface plasmon polaritons can either propagate along the interface if it is continuous, or localize inside the plasmonic nanostructures. \cite{4} For both the propagating SPPs and localized SPPs, energy of electromagnetic wave is well confined in the near field of the metal/dielectric interface or the edges of the plasmonic nanostructures. Using Maxwell’s equation, the resonant conditions of these two kinds of SPPs can be calculated and the resonance is mainly defined by the dielectric constant of metal and dielectric material and shape of the plasmonic nanostructures \cite{1}. This means the light propagation in plasmonic devices is controllable by designing the device geome-
try or changing the dielectric constants. To date, many novel optical phenomena such as extraordinary optical transmission [15], superlens [16,17], negative refraction [18] and cloak [19,20] were demonstrated using plasmonic or metamaterial nanostructure.

![Figure 1.1. T. W. Ebbesen et. al., Nature 397, 667 (1998). Typical zero-order transmission spectrum of a silver hole array. The thickness of silver is 0.2 µm, with the hole diameter t = 150 nm and period a₀ = 0.9 µm. An extraordinary optical transmission peak occurs at a wavelength λ = 1370 nm, which is due to the enhancement effect of SPPs. [15]](image)

1.1.1 Plasmonic and Phase Information

The optical properties of SPP structures can be simply observed from the transmission or reflection measurements. Thus both the field enhancement effect and environmental sensitivity properties of SPP structure application are mainly focus on the amplitude domain of the SPP waves while neglect the phase information. However, phase information of EM waves is always important for example, when we study some optical processes such as interference. Hence the phase change of the EM waves caused by SPPs excitation is another interesting topic as it provides an alternative physical picture to understand plasmon propagation and re-radiation process. [1] For
example, the constructive and destructive interference between different SPPs waves shows the Fano-type resonances and plasmon induced transparency, and it is very sensitive to the phase change of SPP waves. [21–23]

Figure 1.2. J. A. Fan et. al., Science 328, 1135 (2010). The Fano resonance from plasmonic nanoparticle clusters. The nanoparticles were tuned to support electric or magnetic resonant modes, and the interference between the two modes gives the Fano-type resonance. [22]

1.1.2 Plasmonic Sensor

Of all the applications of plasmon resonance, Surface enhanced Raman scattering (SERS) is one of the earliest and successful applications. [24–27] With selected size and shape of metallic particles on target surfaces, the signal of Raman scattering can be increased by a factor up to 1015 times for this nonlinear optical process. [25] Nowadays, SERS and tip enhanced Raman can be used to detect DNA and RNA molecules with spatial resolution down to single molecule level. [25–27]

The resonant condition of SPPs not only depends on the geometry of plasmonic structures, but also on the dielectric constant of metals and the surrounding dielectric materials. Therefore, plasmonic devices are very useful in labeling free sensing application. [28, 29] Recently, many research groups demonstrated the plasmonic sensors based on LSPR [29-31], SPPs interference [32], and metamaterial devices [33–35].
The sensing sensitivity using plasmonic nanowires up to 30000nm/RIU (refractive index per unit) was demonstrated. [35]

1.1.3 Plasmonic and Energy Harvesting

Light coupling in organic photovoltaic (OPV) device becomes an important topic in these several years. As the thickness of active layer in organic solar cell is usually very thin (comparable/less than hundreds of nanometers), efficient light absorption in such a thin film is challenging. Recently, several designs of photonic crystals (PCs) [36] have been used to enhance the light coupling efficiency in OPV cells. The patterned active layer [37,38] and textured substrate [39] have been shown to obtain enhanced light absorption using waveguide mode in PCs based OPV device. Different from the dielectric PCs discussed above [37–39], two dimensional metallic PCs [40,41] are attracting more attention. As metallic PCs show great potential to be highly transparent electrodes and may replace ITO for organic electronics application. Besides, it was reported that plasmonic effect on the metallic nanostructures can
Figure 1.4. A. V. Zayats et. al., Nat. Mater. 8, 867 (2009). The refractive index sensing application using plasmonic nanorods. A high sensitivity was achieved with the value of 30000nm/RIU. [35]

efficiently improve the power conversion efficiency of thin film solar cell [42,43]. Using field enhancement effect in plasmonic nanostructures, the one dimensional plasmonic gratings [44–47], two-dimensional dot-array PCs [48–50], two dimensional hole-array PCs [51, 52] have been integrated into the OPV device and improved photo current efficiency (PCE) were demonstrated.

1.1.4 Plasmonic and Gain Medium

Most of the demonstrated nanostructures consist of noble metals, which induce large optical loss at visible and near-infrared frequency. In order to solve this issue, quite a lot of active media have been proposed to compensate for optical loss and even obtain gain in plasmonic and metamaterial devices. For example, optically pumped fluorescent materials were used to amplify surface plasmon polariton (SPP), and \( \sim 30\% \) increase in the SPP propagation length due to stimulated emission has been observed. [53–58] For long range SPP, the propagation length is up to millimeter scale under strong optical pumping density. [59–61] As a further step to demonstrate optical gain, Xiang’s group demonstrated plasmonic nanolaser using CdS nanowire which sits
on silver surface to form a SPP cavity [62–64], and Odom’s group also demonstrated a new bowtie nanolaser with ultra-small mode volume [65]. In addition, the idea of gain medium was also introduced into the study of metamaterials [66] by doping dye molecule into the fishnet nanostructure. In 2010, a low loss active metamaterial was experimentally demonstrated by Shalaev’s group [67].

Among most of the gain media, organic semiconducting polymer is an attractive option for active plasmonics and metamaterial application. The high photoluminescence quantum efficiency and good charge transport properties of these polymers bring many applications such as polymer light emitting diode [68], organic solid state lasers [69, 70]. The combination of organic semiconducting polymer and nanophotonic device may open a new route to modulate the active plasmonic/metamaterial nanostructure optically or electrically.
1.2 Plasmonic Cavities and Rabi Splitting

As one of the main components of a laser, optical cavities are designed to have a large Q-factor and small loss by using multiple reflections for special frequencies, which provides a conventional way for controlling field enhancement in a small volume. [71] With the development of nanotechnology, microcavities and nanocavities can now be integrated with semiconductor electronic devices [71–73], quantum emitters [73] and plasmonics devices [74].

The strong coupling effect between the material emission and the cavity resonance mode provides new physical phenomenon and applications for photonic cavities. In the study of cavity-quantum electrodynamics, it is shown that when a quantum emitter, such as a two-level atom or a quantum dot, is located inside a photonic microcavity, the profile of spontaneous emission of the emitter will split into two peaks. Such strong coupling between the emission and the cavity mode is called Rabi splitting. [73]

![Figure 1.5](image_url)

**Figure 1.5.** A. Scherer et al., Nat. Phys. 2, 81 (2006). Rabi splitting of a two-level atom emitter in a microcavity. The emission spectrum splits into two peaks because of the strong coupling effect. The strength of the coupling depends on the value of $\kappa$ and $\gamma$, which are the damping coefficients of the cavity and the atom emitter respectively. [73]

The creation of Rabi splitting makes it possible to control the exciton-photon
coupling using microcavity, and a lot of important applications based on this effect have been demonstrated. For example, microcavity can be combined with quantum dots [74, 75], active organic molecular [76, 77] and electron gas [78] to modify the optical properties of the active medium. Besides, the strong coupling effect between polaritons and photons has also been demonstrated. It is shown that Rabi splitting effect can efficiently reduce the pumping threshold of polariton lasing [79, 80], based on which the first room temperature polariton laser was reported by S. Christopoulos et al. in 2007 [79]. In particular, great efforts have been devoted to explore the strong-coupling dynamics in hybrid plasmon-exciton systems [81–84], to control the energy redistribution pathways in molecules and tailor the resonant energy of exciton in semiconductor materials [75, 84, 85].

Figure 1.6. S. Christopoulos et. al, Phys. Rev. Lett. 98, 126405 (2007). (a) The structure of the first inorganic polariton laser. Reflectivity measurement (a) and calculation (b)-(c) are used to show the strong coupling effect of excited polaritons. (d) Angle resolved photoluminescence spectrum at lower energy branch (LP) and upper energy branch (UP) were also measured to characterize the emission properties of the device.

Very recently, strong coupling between localized surface plasmons and photonic cavity modes was demonstrated in coupled photonic-plasmonic systems [86, 87]. The
Rabi splitting effects from organic-plasmonic hybrid system [88,89] and THz metamaterials [78] were also observed. As one of the most common optical cavities, Fabry-Perot (F-P) cavity, which consists of two parallel mirrors and one spacer, can provide a large field enhancement with simple device configuration hence it is often used while in the plasmonic devices [87]. When the coupling effect between SPP modes and photonic cavity modes occurs, the coupled mode has both the properties of SPP and cavity modes, this means the volume of cavities can be further reduced due to light localization effect while keeping a high quality (Q) factor.

![Figure 1.7](image)

Figure 1.7. V. J. Sorger et. al., Nano Lett. 10, 3489 (2009). Demonstration of the plasmonic nanocavity. The cavity consists of two parallel vertical silver mirrors (a) with designed slit width. The SPPs could be excited by focusing white light at the surface of the silver mirrors, and coupled out by the gratings (b). [87]

In addition, the F-P cavity modes are also sensitive to the cavity length, and hence it is possible to control the modes interaction by adjusting the cavity length. [90,91] Based on the different response due to the constructive or destructive interference between SPP modes and cavity modes, applications such as high sensitive sensors [92], opto-fluidic modulators and enhanced Raman scattering devices [93] were reported by combing SPP structure and plasmonic cavities together.
1.3 Nonlinear Optics in Plasmonics

In 1960s, with the demonstration of the first laser, researches in nonlinear optics were founded. The study of nonlinear optics (NLO) started with the observation of second harmonic generation (SHG), which was caused by the second order nonlinear susceptibility ($\chi_2$) of a quartz crystal [94–96]. After that, scientists began to study many other kinds of nonlinear optical processes, such as high order frequency mixings [97], multi-photon absorption and emission [98] and optical Kerr effect [99] etc. Almost all of the nonlinear optical processes require a strong field of pumping laser. [94] To improve the efficiency of NLO processes and reduce the strict requirement of high power laser source, the strong light localization using SPP based devices provide an efficient solution. Since collective surface plasmons can provide large field enhancement near the metal/dielectric interfaces, SPP wave is important for surface nonlinear optics. In 1974, H. J. Simon’s group firstly studied the SHG signal of silver thin film on top of a quartz crystal and observed the enhancement effect due to SPP excitations. [100] Later, the enhanced SHG signal due to the SPP resonance by index matching prism scheme was also demonstrated by the same group. [101]

Figure 1.8. H. J. Simon et al., Phys. Rev. Lett. 50, 1987 (1983). The enhanced SHG reflection measurement from a silver film. The incident light was coupled to silver surface by a phase mating prism (a), and while SPPs was excited, the SHG signal has a strong enhancement (b) comparing with SHG signals from control experiment. [101]
From then application of SPP integrated nonlinear optics attracts a lot of interests. [14,102] Since SHG is very sensitive to the surface symmetry, it becomes a powerful method for analyzing the helicity and chirality of plasmonic nanostructures. [103,104] Also, surface plasmon enhanced SHG [105,108], third harmonic generation (THG) [109–112], and two-photon absorption and emission [113,114] have also been extensively investigated. Recently, SPP enhanced four-wave mixing [115,116], multipolar SHG interference [117] and nonlinear Fano resonance [118] were also investigated. As strong light localization in nonlinear optical process also induces ultrafast electron-electron and electron-phonon interactions, which result in transient change of the dielectric constants of plasmonic materials; the study of ultrafast modulation with plasmonic devices has becomes an important topic in ultrafast optics. [14]

**Figure 1.9.** V. K. Valve, Langmuir 28, 15454 (2012). The SHG microscopy images for G-shape nanostructures with different arrangement. The hot spots are due to the localized SPPs enhancement, and is sensitive to the structure symmetry. [104]

When we study the nonlinear optical efficiency of plasmonic structures, the high optical loss and the small nonlinear susceptibility of metal makes the nonlinear optical process always very weak. This limits the application of plasmonic device as optical parametric oscillator, amplifier, and harmonic generation medium, etc. One
Figure 1.10. H. Liu et al., Phys. Rev. B 84, 235437 (2011). The nonlinear Fano resonance was demonstrated using plasmonic crystal. This plasmonic structure (a) could support both SPP mode and magnetic resonance mode. While tuning the period of nanodisks, the two modes could interfere with each other and show Fano type resonance (b). This Fano-type resonance was verified in the THG process (c-d). [118]

A promising solution is integrating the active medium with high optical nonlinearity into the metallic nanostructures. The active medium could be gas, conventional optical crystal and organic complexes. It has been shown that among organic functional materials, π-conjugated polymer is a good candidate for third harmonic generation or two-photon absorption [119–121], and its third-order optical nonlinearity depends on the conjugation length of the polymer molecule, which can be further optimized from synthesis. In addition, the polymer thin film is easier to spin-cast on top of plasmonic nanostructure; this enables the fast and low cost fabrication of metal-organic hybrid plasmonic device.
1.4 Plasmonic Metasurface

Plasmonic metasurface is a new kind of plasmonic nanostructure which can introduce an abrupt phase change on an ultrathin metallic surface using artificial atoms [122–126]. The artificial atom can be nanorod, nanohole or complicated element, which exhibits strong localized plasmon resonance. Various metasurface devices have been used to demonstrate extraordinary reflection and transmission phenomena, dual-polarity imaging [124], generation of optical vortex [122, 125], and optical Spin Hall Effect (OSHE) [127–130], etc.

1.4.1 Optical Spin Hall Effect

When the current pass through a metal or semiconductor surface, if a magnetic field is applied in the surface normal direction, the separation of negative and positive charges will occur, and this is called Hall Effect. Analogous to the Hall Effect, the spin state of electrons can also be responsive to applied electric field, and this is the spin Hall Effect. 35 years after the theoretical prediction by M. I. D’yakonov in 1971 [131], spin Hall effect was experimentally observed in 2004 in Y. K. Kato’s group. [132]

Circularly polarized photon carries spin angular momentum (SAM) of $\pm \hbar$. A left circularly polarized photon ($\sigma^+$) carries a $\hbar$ momentum, whereas, the right circularly polarized photon ($\sigma^-$) have a $-\hbar$ momentum. In 2007, C. Leyder’s group demonstrated the experiments on optical spin Hall Effect, and observed the separation of $\sigma^+$ and $\sigma^-$ light after passing using a semiconductor microcavity. [133] (Fig. 1.11)

To extend study of OSHE in plasmonic devices, several types of plasmonic metasurface with optical spin properties such as plasmonic spirals [127] and nanorod rings [128] were proposed. The analogy of OSHE was also experimentally demonstrated. G. X. Li et al., designed a metasurface with Pancharatnam-Berry geometric
phase introduced by rotating rectangular nanohole in gold film. [130] They studied how this metasurface with asymmetric polarization conversions can introduce rotational transformation of the orbitals through the spin-orbit interaction. Usually, orbital rotation via natural chiral media can induce analogous rotation of orbital instead of the polarization but the effect is very weak to be observed. They demonstrated the efficient manipulation of orbitals by transporting different polarization effects to orbitals through the spin-orbit coupling. As the phase manipulation in plasmonic metasurface is very powerful for controlling the optical “spin-orbital” interaction, it should bring more applications for designing novel on-chip nanophotonic device, etc.

1.4.2 Generation of Optical Vortex

Another important topic in field of plasmonic metasurface is generating optical vortex. As we know, the light beam not only has spin angular momentum (SAM), but also has orbital angular momentum (OAM). [134] The pioneering work of OAM of photon was studied by L. Allen et al. in 1992 [135], and has attracted many interests in optical community [134, 136] and brought about a plethora of applications in macro-manipulation [137, 138] and quantum optics [139, 141]. The generation of OAM is
Figure 1.12. E. Hasman et al., Phys. Rev. Lett. 101, 043903 (2008). The plasmonic lens based on optical SHE effect. The different response between left circularly (a), right circularly (b) and linear polarized incident light was measured (d). For two circularly polarized lights, the focus points are at different positions (c). [127]

well realized by using Laguerre-Gaussian mode method [142], spatial light modulator (SLM) [143,144], spiral phase plate [145] and micro-ring resonator [146]. Among these techniques, the combination of computer generated hologram (CGH) with spatial light modulator (SLM) makes the generation of optical vortices very convenient by programming the displayed image on the SLM. Except SLM, the concept of spiral phase in plasmonic metasurface was also used to generate optical vortex. As shown in Fig 1.13, Capasso's group [122] demonstrated a metasurface consisting of eight kinds of rotating nanorod element, which can provide a phase modulation varying from 0 to $2\pi$ for the incident waves. An optical vortex beam with topological charge $l = 1$ was generated.

The study of OAM can also be realized in nonlinear optical regime. Second harmonic generation (SHG) and high harmonic generation of optical vortex have been demonstrated using nonlinear optical crystal [147–149] and gas medium [150, 151] respectively. It has been shown that the OAM of the harmonic generation depends on the OAM of the pumping laser [147–151] or the phase dislocation of the medium. One
Figure 1.13. N. Yu et al., Science 334, 333 (2011). The metasurface consists of eight kinds of nanostructures (A-B), which can provide the $0$ to $2\pi$ phase distribution as the function of phase plate. Optical vortex was generated with topological charge of $l = 1$ (C-D), which could be confirmed by interference with another Gaussian beam (E-H). [122]

of the breakthroughs in this area was made from direct fabricating phase dislocation of optical super lattice through electric field polling in ferroelectric crystal [149]; the topological charge of the phase dislocation is then involved in the nonlinear optical processes.

Another important application of metasurface is the 3-D imaging holography. Recently, we have achieved amplitude and phase controlling of metasurface by arranging different types of plasmonic elements [122–125]. Metasurface based computer generated holography (CGH) technique was developed to obtain two- and three-dimensional (2D/3D) holographic images in visible range by using rotational nanorod to record the phase and amplitude information from a CGH pattern. [126]
Figure 1.14. L. Huang et al., Nat. Commun. 4, 2808 (2013). The demonstration of a 3-D holography using metasurface. The incident circularly polarized light was converted into the opposite handedness polarization by the metasurface, and the 3-D image of airplane could be reconstructed in free space. [126]

1.5 Our Work

In this chapter, we introduced our research focused in SPPs enhancement effect, SPPs phase information and nonlinear plasmonic optics. It is obviously that the application of plasmonic structures provide us a promising way in many research fields, such as bio-medicine and optical communication.

In Chapter 2, we will introduce the basic theory of SPPs, optical vortex and nonlinear optics. An analytical model for SPPs will be built and the damping coefficients of SPPs will be discussed. Different types of Laguerre-Gaussian beams and different polarization state of light will be studied. For nonlinear optics, background of harmonic generations and the analytical polarization calculation will be discussed.

In chapter 3, the experimental methods used in this thesis, including the principle of ellipsometer, the details of nano-fabrication process and the setup of the nonlinear
optical measurement.

In chapter 4, we will study the plasmonic resonance of ellipticity using a metallic grating. The analytical model introduced in chapter 2 will be used to study different response of TE and TM waves in both phase and amplitude domain. Angle resolved ellipsometer measurements will be applied to this study.

In chapter 5, we are going to introduce the coupling effect between a propagating SPPs mode and Fabry-Perot cavity model and analyzed the coupling efficiency. The design of the structures, the simulation results as well as angle resolved reflection measurement results will be discussed in this chapter.

In chapter 6, the SPPs based hybrid plasmon structure is used to study the THG enhanced effect and nonlinear optical vortex effect. A periodic plasmonic crystal and a holography based microstructure will be fabricated, and the generation of THG vortex will be experimentally studied.

In chapter 7, the LSPR enhanced THG effect on plasmonic crystals with different symmetry types is studied. Gold nanorod structure with C2, C3, C4 symmetry were fabricated and combined with polymer thin films. Simulation and theoretical calculation are utilized analyze the experimental results.
Chapter 2

Theoretical Background

2.1 Surface Plasmon Polaritons

2.1.1 Dispersion Relation of Surface Plasmon

The electrons can perform a coherent oscillation on a metal/dielectric interface when surface plasmon polaritons are excited by electrons or photons. This oscillation can either form a localized electric field around a discrete metal medium, or propagate on a continuous metal surface. Electric field is localized at surface of metal along the z direction. The propagating surface plasmons along horizontal direction (x-axis) (Fig. 2.1) can be described using Eq. 2.1. [1]

\[
E = \pm E_0 \cdot e^{i(k_x x \pm k_z z - \omega t)}
\]  

(2.1)

According to Maxwell’s equation, the wavevector along the z direction has a dependency of the dielectric constant \(\varepsilon_1\) and \(\varepsilon_2\) of the dielectric and metal medium, respectively. Then we have the dispersion relation of \(k_x\):
Figure 2.1. Schematic diagram of the surface plasmon wave on a metal/dielectric surface. The EM wave is localized in the z direction, and propagates along horizontal direction. [1]

\[
\frac{k_{z1}}{\varepsilon_1} + \frac{k_{z2}}{\varepsilon_2} = 0 \quad (2.2)
\]

with

\[
k_{zi}^2 = \varepsilon_i (\frac{\omega}{c})^2 - k_{x}^2, \quad i = 1, 2 \quad (2.3)
\]

and finally, we obtain:

\[
k_x = k_{sp} = \frac{\omega}{c} \cdot \sqrt{\frac{\varepsilon_1 \cdot \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \quad (2.4)
\]

Eq. 2.4 describes the plasmon dispersion relation on a metal/dielectric surface. The wave vector of propagating SPPs can now be determined from the material dielectric constants. When \( k_x \) is small, \( \omega_{sp} \) is close to the incident light line \( \omega = ck_x \), and if \( k_x \) is large, \( \omega_{sp} \) approaches the value of \( \omega_p/\sqrt{1 + \varepsilon_2} = \omega_p/\sqrt{2} \) if \( \varepsilon_2 = 1 \). Here \( \omega_p^2 = 4\pi n_e e^2/m \) is the plasma frequency of metal, with \( n_e \) is the density state of electron and \( m \) is the mass of electron. The square root term in Eq. 2.4 also indicates that there always exists a momentum mismatch between the vacuum wavevector \( k_x = \omega/c \) and the wavevector of SPPs \( k_{sp} \) (Fig. 2.2), hence the SPs wave cannot radiative out directly and it is determined as “non-radiative SPs”.

There also exists another dispersion relation branch for plasmons. At high frequency, the plasmons behaves like free electron gas, therefore from Drude mode the dispersion is given as \( \omega^2 = \omega_p^2 + c^2 k_x^2 \). This indicates that there is a gap between the
Figure 2.2. Dispersion Relation of SPs. The solid black line at low frequency indicates the dispersion relation of SPPs, and the solid black line at high frequency is the dispersion relation of bulk plasmons, i.e. volume plasmons, where $\omega_p$ is the plasma frequency. Also there is a gap between SPPs and volume plasmons, and at this region the wavevector is a pure imaginary number, of which the magnitude is described by the red dash line. [1, 2]

SPs frequency and plasma frequency of the material. At this region, the wavevector becomes pure imaginary with $\varepsilon_1$ and $\varepsilon_2$ both imaginary number.

### 2.1.2 Excitation of SPPs

From the dispersion relation and the momentum conservation law of surface plasmons, we find that in order to excite SPPs, the matching condition must be required. There are mainly two experimental methods that are mostly used: prism coupling and grating coupling.

The principle of the prism coupling methods (Fig. 2.3, Kretschmann-Raether configuration [1]) is to increase the incident wave vector by using a high refractive index material $\varepsilon_2$. After passing through the prism, the incident wave vector becomes
\[ k' = k_0 \sqrt{\varepsilon_2}, \text{ and its projection in x direction is:} \]

\[ k_x = \sqrt{\varepsilon_2} \cdot k_0 \sin(\theta) \tag{2.5} \]

where \( \theta \) is the incident angle of the excitation light. And now the SPPs excitation condition can be easily satisfied using the following equation:

\[ k_x = \sqrt{\varepsilon_2} \cdot \frac{\omega}{c} \sin(\theta) = \frac{\omega}{c} \cdot \sqrt{\frac{\varepsilon_1 \cdot \varepsilon_0}{\varepsilon_1 + \varepsilon_0}} \tag{2.6} \]

where \( \varepsilon_0, \varepsilon_1, \varepsilon_2 \) are the dielectric constant of the air, metal and prism respectively.

\textbf{Figure 2.3.} Schematic diagram of the prism coupler (Kretschmann-Raether configuration). The incident wave vector is modified by the prism dielectric constant and the incident angle with a value of \( \sqrt{\varepsilon_2} \sin(\theta) \). By adjusting the incident angle, SPPs at the Metal/Air interface can now be excited.

From Eq. 2.6, we can find that the excited SPPs wave vector using Kretschmann-Raether configuration is limited by dielectric constant of the prism. To avoid this effect in SPR based applications, especially in bio-sensing area, periodic grating couplers are always used for momentum matching (Fig. 2.4). In this case, the additional momentum is provided by the reciprocal lattice vector \( G_0 \) from the grating periodicity:

\[ k_{app} = \frac{\omega}{c} \cdot \sqrt{\frac{\varepsilon_1 \cdot \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} = k_0 \sin(\theta) + mG_0 \tag{2.7} \]
where \( G_0 = 2\pi/\Lambda \), \( \Lambda \) is the period of grating and \( m \) is the order of the diffraction factor.

\[ G_0 = 2\pi/\Lambda, \Lambda \text{ is the period of grating and } m \text{ is the order of the diffraction factor.} \]

**Figure 2.4.** Schematic diagram of the grating coupler. The incident wave vector is modified by the reciprocal lattice vector of the grating and the incident angle. By adjusting the incident angle, different SPP excitation condition can be satisfied.

Eq. 2.7 indicates that the value of \( m \) can be either positive or negative, which is also described in Fig. 2.4. While \( m \) is positive, it means that \( k_{spp} \) has the same direction with \( k_0 \sin(\theta) \), and the propagating SPPs wave is defined as forward SPPs wave. While \( m \) is negative, the generated SPP wave has opposite direction with \( k_0 \sin(\theta) \), which backwardly propagates.

### 2.1.3 Damping Coefficients

When we consider to an asymmetric structure (\( \varepsilon_2|\varepsilon_1|\varepsilon_0 \), such as quartz/metal film/air structure) with finite thickness of metal layer, other parameters, the loss and skin depth of metal cannot be neglected. Taken these parameters into consideration, the wave vector \( k_{spp} \) should be modified as following:

\[ k_{spp} = k_x' = k_x^0 + \Delta k_x^{rad} \quad (2.8) \]
Here $k_0^0$ is the original SPP wavevector which is determined in Eq. 2.4, and the second term $\Delta k_{x}^{rad}$ is from the radiative damping. It means that the resonant condition of SPPs should be related to the properties of metallic film, such as thickness, surface roughness and so on.

To better understand the SPPs propagating along the interface, Eq. 2.8 is written as:

$$k_{spp} = k_0^0 + \Delta k_{x}^{rad} = k'_{x} + ik''_{x} + \Delta k'_{x} + i\Delta k''_{x}$$  \hspace{1cm} (2.9)$$

Denote the imaginary parts of Eq. 2.9 as $k''_x = \Gamma^i$ and $\Delta k''_x = \Gamma^{rad}$, the new SPP resonant position is determined by the following equation:

$$k_{spp} = k'_{x} + \Delta k'_{x} + i(\Gamma^i + \Gamma^{rad})$$  \hspace{1cm} (2.10)$$

where the imaginary parts, $\Gamma^i$ and $\Gamma^{rad}$ have the physical meaning of internal damping coefficient and radiative damping coefficient respectively.

The internal damping $\Gamma^i$ is mainly due to the absorption of the material $k''_x$. The SPPs can excite the electron-hole pairs and the re-excitation produces phonons. For the propagating surface plasmon, part of the energy will couple to the dielectric medium if the metal layer has finite thickness. This leads to the leakage radiation damping $\Gamma^{rad}$ into the substrate. This backward radiation can be experimentally observed using leakage radiation microscopy. Since the SPPs are excited by grating coupler, the radiation damping is also related to the geometry parameters of the gratings.
2.2 Nonlinear Optics

2.2.1 Nonlinear Polarization and Susceptibility

In conventional optics, the induced polarization $P(t)$ at time $t$ in material is induced by the electric field $E(t)$ at the same time, which is written as:

$$P(t) = \varepsilon_0 \chi_1 E(t)$$  \hspace{1cm} (2.11)

where $\varepsilon_0$ is the permittivity of vacuum and $\chi_1$ is the first order susceptibility of the material. From Eq. 2.11 we can see that only the linear response of is taken into consideration. In general, Eq. 2.11 can be expressed into power series:

$$P = \varepsilon_0 \left( \chi_1 E(t) + \chi_2 E^2(t) + \chi_3 E^3(t) + \ldots \right)$$ \hspace{1cm} (2.12)

with $\chi_2, \chi_3$ are the second and third order susceptibilities. Here the linear polarization term $P^{(1)}$ remains the same form as Eq. 2.11, and the additional terms $P^{(2)} = \chi_2 E^2(t)$ and $P^{(3)} = \chi_3 E^3(t)$ are defined as second and third order nonlinear polarizations. [95]

In Eq. 2.12, both polarization and E-field are written in scalar form, and all the susceptibilities are treated as different constants. However, in real case, both polarization and E-field should have vector forms. Also, even for the linear response term $P^{(1)}$, the susceptibility is a $3 \times 3$ tensor instead of a constant in anisotropic medium. When we come to the generalized vector form of Eq. 2.12, the nonlinear polarization $\vec{P}$ is written as:

$$\vec{P}_i = \varepsilon_0 \left[ \chi_{ij}^{(1)} \vec{E}_j + \chi_{ijk}^{(2)} (\vec{E}_j \cdot \vec{E}_k) + \chi_{ijkl}^{(3)} (\vec{E}_j \cdot \vec{E}_k \cdot \vec{E}_l) + \ldots \right]$$ \hspace{1cm} (2.13)

where the subscripts $i, j, k, l, \ldots$ could be $x, y$ and $z$, which represent the direction of
fields in Cartesian axes. Now the second order $\chi_{ijk}^{(2)}$ is a third rank tensor with 27 elements and the third order $\chi_{ijkl}^{(3)}$ is a forth rank tensor with 81 elements. In next section we will show that these tensors highly depend on the material symmetry.

For an electric field which consists two different frequency complex conjugate components $\omega_1$ and $\omega_2$:

$$E(t) = E_1(e^{-i\omega_1 t} + e^{i\omega_1 t}) + E_2(e^{-i\omega_2 t} + e^{i\omega_2 t}) \tag{2.14}$$

The induced linear polarization

$$\vec{P}^{(1)}(t) = \varepsilon_0 \chi^{(1)} \left[ 2E_1 \cos(\omega_1 t) + 2E_2 \cos(\omega_2 t) \right] \tag{2.15}$$

has two frequency components $\omega_1$ and $\omega_2$ independently. However, for the second order polarization, it becomes:

$$P^{(2)} = \varepsilon_0 \chi^{(2)} \left[ E_1^2 \cdot e^{\pm 2i\omega_1 t} + E_2^2 \cdot e^{\pm 2i\omega_2 t} \ldots + 2E_1E_2 \cdot (e^{\pm i(\omega_1 - \omega_2) t} + e^{\pm i(\omega_1 + \omega_2) t}) \right] \tag{2.16}$$

In this case, the frequency of induced polarization is not the same as that of fundamental electric field anymore. Hence, the second order polarization does not only depend on the susceptibilities, but also the frequencies of the fundamental electric fields.
2.2.2 Second Harmonic Generation and Third Harmonic Generation

Eq. 2.16 shows that there are four kinds of polarization with different frequencies that can be generated in second order process, which are:

\[ P_1 = P(2\omega_1) \]
\[ P_2 = P(2\omega_2) \]
\[ P_3 = P(\omega_1 + \omega_2) \]
\[ P_4 = P(\omega_1 - \omega_2) \]  

(2.17)

Here \( P_1 \) and \( P_2 \) are defined as SHG, \( P_3 \) is sum frequency generation and \( P_4 \) is the difference frequency generation. And if \( \omega_1 = \omega_2 \), the second order polarization will become pure SHG.

![Figure 2.5. (a) Geometry and (b) energy diagram of SHG process. [95]](image)

For SHG process, two photons with same frequency interacts with the nonlinear material, and then the second order polarization is induced. The radiation of this polarization gives a new photon with doubled frequency. According to Eq. 2.13, the induced polarization of SHG process is written as:

\[ \vec{P}_i(2\omega) = \varepsilon_0 \chi^{(2)}_{ijk} \left[ \vec{E}_j(\omega) \cdot \vec{E}_k(\omega) \right], \text{ where } i, j, k = x, y, z \]

(2.18)
However, while the fundamental electric field distribution is centrosymmetric: $\vec{E}_j = -\vec{E}_j$ and $\vec{E}_k = -\vec{E}_k$, the induced polarization should also be centrosymmetric and it should be changed to $-\vec{P}_i$:

$$-\vec{P}_i = \varepsilon_0 \chi^{(2)}_{ijk} \left[ -\vec{E}_j(\omega) \right] \cdot \left[ -\vec{E}_k(\omega) \right]$$

$$= \varepsilon_0 \chi^{(2)}_{ijk} \left[ \vec{E}_j(\omega) \right] \cdot \left[ \vec{E}_k(\omega) \right]$$

$$= \vec{P}_i = 0 \quad (2.19)$$

Eq. 2.19 shows the SHG polarization must be zero in this case. Hence the SHG susceptibilities $\chi^{(2)}_{ijk}$ are all zeroes in centrosymmetric materials. Now it is obvious that materials with different crystal classes will have different independent nonzero susceptibilities. [95]

![Figure 2.6.](image)

Figure 2.6. (a) Geometry and (b) energy diagram of THG process. [95]

In third harmonic generation (THG) process, if three photons with the same frequency are absorbed by the nonlinear material and then a new photon with $3\omega$ frequency will be radiated out. The polarization of THG is written as:

$$\vec{P}_i(3\omega) = \varepsilon_0 \chi^{(3)}_{ijkl} \left[ \vec{E}_j(\omega) \right] \cdot \left[ \vec{E}_k(\omega) \right] \cdot \left[ \vec{E}_l(\omega) \right], \ i, j, k, l = x, y, z$$

$$\quad (2.20)$$

Unlike SHG, for THG susceptibilities, there are non-zero elements in all crystal classes, which mean that THG process can occur in all materials.
Phase singularity was recognized by Dirac in 1930s when he discussed the requirement on magnetic monopole, and it was extended into electromagnetic regime by Nye and Berry in 1974. [152] In 1992, Allen and colleagues showed that light with azimuthal phase $e^{i\ell \phi}$ carries orbital angular momentum (OAM) that equals to $l\hbar$, where $l$ is integer, $\phi$ is the azimuthal angle.

One of the most important methods to generate OAM is to let light passes through a spiral phase plate, the azimuthal thickness of the plate is defined by: $l\lambda\phi/2\pi(n-1)$, where $n$ is the refractive index, $l$ is the topological charge and $\lambda$ is the wavelength of light. [153]

The second method is sorting the modes from a laser cavity; the cylindrical symmetric cavity can generate the Laguerre-Gaussian (L-G) beam, which is given by:

$$LG_{pl} = \sqrt{\frac{2p!}{\pi(p+|\ell|)!}} \cdot \frac{1}{w(z)} \left[ \frac{r\sqrt{2}}{w(z)} \right]^{|\ell|} \cdot L_p^{||} \cdot \left( \frac{2r^2}{w^2(z)} \right) \cdot \exp \left[ -\frac{r^2}{w^2(z)} \right] \cdot \exp \left( -\frac{ikr^2}{2R(z)} \right) \cdot \exp \left[ -i(2p + |\ell| + 1)\phi(z) \right] \cdot \exp(il\phi) \quad (2.21)$$

Where $L_p^{||}$ is the Laguerre polynomial, $w(z)$ is the beam waist at $z$ position, $r$ is radial axis, $p$ is the radial node number, $l$ is the azimuthal index, and $e^{i\ell \phi}$ term indicates the helical phase of the L-G beams.

The third way is using holography based fork gratings via computer generated hologram, in which OAM can be produced by interfering a vortex beam with a plane wave. The helical phase of light in the diffraction orders can be generated after passing the incident light through the fork grating. For a fork microstructure with binary modulation, the depth modulation of the fork grating can be described by the
following equation [153]:

\[ t(x, y) = 1 + \text{sign} \left[ \cos \left( \frac{2\pi x}{p} + l \cdot \arctan \left( \frac{x}{y} \right) \right) \right] \] (2.22)

where \( p \) is the period of a grating with line/space ratio of 1, \( l \) is the topological charge of the fork grating.
Chapter 3

Experimental Methods

3.1 Nano-fabrication

Nano-fabrication technique is important for fabricating the plasmonic nanostructures. In this work, electron beam lithography (EBL) and metal lift-off is the key prefabrication process. The feature size fabricated pattern is up to 10 nm.

Figure 3.1. Lift-off process: (a) structure patterning on the resist using EBL. (b) Develop of the pattern. (c) Metal Layer Deposition. (d) Remove the resist using acetone, and only metallic structure is left.
Fig. 3.1 shows the main procedures of EBL and metal lift-off process. Firstly, the nanostructure is patterned onto the positive resist (ZEP520A) by the electron exposure. After patterning and developing, oxygen plasma treatment was used to remove the residue to the exposed electron resist. Then the metal layer (e.g. gold or silver) is deposited onto the resist.

### 3.2 Thin Film Deposition

For most kind of metals, thermal evaporation is one of the most convenient methods to deposit the amorphous thin films. The material source is heated and vaporized by applying a large current, and then the metal atom are condensed onto the substrate. The basic structure of a standard evaporation machine is shown in Fig. 3.2a.

![Evaporation Machine](image)

**Figure 3.2.** Thermal Evaporation and QCM [10]

The thickness of the deposited thin film can be controlled by using a quartz crystal microbalance (QCM), which is based on the piezoelectricity of the quartz crystal and the acoustic impedance of the material. The voltage of the piezoelectric sensor is sensitive to the damping frequency of the crystal. Using Eq. 3.1 and Eq. 3.2,
the mass of evaporated thin film due to the piezoelectricity voltage change can be calculated and the thickness of the thin film can be obtained.

\[
\frac{\Delta f}{f} \approx \frac{i}{\pi Z_q} Z_L = \frac{2f}{Z_q} m_F
\]  

(3.1)

\[
m_F = \rho t_f
\]  

(3.2)

where \( f \) is the nature frequency of the crystal, \( \Delta f \) is the load frequency, \( Z_q \) is the acoustic impedance of the material, \( Z_f \) is the load impedance, \( m_f \) is the mass of the thin film and \( \rho \) is the density of the material.

### 3.3 Ellipsometry

Ellipsometry technique is based on the change of polarization upon reflection and transmission of the samples surface. The basic configuration of an ellipsometer is shown in Fig. 3.3.

![The configuration of Ellipsometer.](image)

Figure 3.3. The configuration of Ellipsometer. [154]

In the ellipsometer (SOPRA) measurement, the incident light from light source passes through a polarizer and becomes linearly polarized light. The polarizer rotates at a constant frequency 6 Hz, and the position of the rotating polarizer is recorded.
Then the linear polarized light is incident onto the sample and then the reflected light becomes elliptically polarized. The reflected light passes through another polarizer (analyzer), which has 45 degree angle away from the incident plane. Then separated to two linear polarized states: parallel (p-) polarized light and perpendicular (s-) polarized light to incident plane. Finally, the two polarized light is record by the detector, and the complex reflective coefficients can be calculated by the amplitude ratio of $p$ polarized waves and $s$ polarized waves ($E_p$ and $E_s$):

$$\rho = \frac{E_p}{E_s} = \tan(\varphi)e^{i\Delta}$$

(3.3)

where $\tan(\varphi)$ and $\Delta$ in Eq. 3.3 are absolute value of amplitude ratio and the phase delay of $p$ and $s$ polarized wave respectively.

### 3.4 Nonlinear Optical Experiments

The pumping laser sources for nonlinear optical experiments always used in this thesis includes optical parametric amplifier (OPA) and optical parametric oscillator (OPO), which are pumped by 800 nm femtosecond pulse laser. The femtosecond OPA system (TOPAS-C, Coherent) has a tunable wavelength from 0.5 $\mu$m to 2 $\mu$m output with a repetition frequency of 1000 Hz and pulse duration of 110 fs.

The femtosecond OPO system (Inspire HF, Spectra-Physics) has a tunable wavelength output from 0.4 $\mu$m to 2.50 $\mu$m with a repetition frequency of 80MHz and pulse duration of about 200 ts.

The power of the lasers can be controlled by using Glan-Thomas linear polarizer, while the polarization states are defined by Glan-Thomas linear polarizer, half-waveplate, and quarter-waveplate. The laser was focused onto the sample using aspherical lens or objective lens with a spot diameter of 20 $\mu$m to 100 $\mu$m. The generated harmonic generations were collected by another objective lens and sent to
PI-Acton 2300i spectrometer with photon multiplier tube and intensified CCD detector (Princeton Instruments, Intensified charge coupled device, PI-MAX II). Moreover, direct imaging of the nonlinear signals in the far field can also be recorded using charge coupled device (CCD) camera.
Chapter 4

Plasmonic Resonance of Ellipticity on Gold Grating

In this chapter, we discussed the origin of sharp plasmonic resonance on gold gratings and its application in sensing. It was shown that optical ellipticity experiences a giant change in both amplitude and phase domain, which is sensitive to the refractive index change of the surrounding medium and the incident angle of excitation. The phase difference of TE and TM waves under the resonance excitation condition is studied by analytical model, and the amplitude of the ellipticity was simulated using commercial simulation software.

4.1 Introduction

Diffraction grating has a broad application as high resolution spectrometer, beam splitter, optical coupler, and polarizer, and many of the gratings are using metal to fabricate. In metallic grating, the presence of surface plasmon polariton in free electron gas was shown by Ritchie et al. [1] However, as we mentioned in chapter 1, most of SPPs studies are focused on the amplitude domain since at most of time,
the phase information cannot be measured directly. In experiments, optical interferometer is a conventional tool to measure the phase shift under surface plasmon resonance. [155, 156] In time domain, by combining femtosecond laser with conventional interferometer technique, ultrafast plasmon excitation can be characterized using time resolved pump-probe setup. [157–159] Moreover, near field scattering technique was developed to analyze the polarization state of scattered light in near field [160–162]; this method allows us to obtain the phase resonance at subwavelength scale nanostructure. In addition, commercial ellipsometer was also introduced to characterize the photonic modes in plasmonic nanostructure in both amplitude and phase domain [118, 163], and later this technique was exploited to study plasmonic modes in metamaterial consisting of split ring resonator. [164]

In this work, we studied the sharp plasmonic resonance on one dimensional gold grating in both amplitude and phase domains using conventional ellipsometry technique. Measured ellipticity experiences a sharper plasmonic resonance for larger incident angle up to 40 deg. An analytical model was introduced to elucidate the mechanism behind sharp phase resonance. From the calculated result, it is found that the sharper plasmon resonance comes more from oblique incidence than the change of radiative damping of surface plasmon polaritons.

4.2 SPPs Resonance on Gold Grating

To excite propagating SPPs waves, we designed an one dimensional gold grating which can supported SPPs mode at visible wavelength range (Fig. 4.1). The structure was fabricated on SiO$_2$ (7 µm thick)/Silicon substrate by e-beam lithography (EBL) followed with thermal evaporation and metal lift-off process. First, the grating structure was patterned on ZEP520A resist by EBL method. After depositing 50 nm thick gold thin film onto the resist, the e-beam resist was removed by DMAC to leave the metallic grating on the substrate. Finally, a 30 nm thick gold thin film was
deposited onto the gold grating. This is to form a continuous metal surface which supports propagating surface plasmon polaritons at the gold/air interface. The gold grating has a period ($\Lambda$) of about 355 nm with modulation depth of 50 nm. The total size of the patterned area is 500 $\mu$m by 500 $\mu$m.

![Figure 4.1](image.png)

**Figure 4.1.** (a) Cross-section of one dimensional gold grating; (b) SEM image of one dimensional gold grating on $\text{SiO}_2$/Si. Period: 355 nm, line/space: 1:1. Thickness of gold layer is 30 nm and grating height is 50 nm.

### 4.2.1 Analytical Model of Ellipticity of SPPs resonance

Although the commercial software can numerically calculate the phase delay, it is not intuitive enough to capture the physical picture of sharp phase resonance. In the following, an analytical model is derived to analyze phase delay of TM and TE waves. First, the momentum matching condition of exciting SPPs on grating should be satisfied, which has been described in chapter 2 (Eq. 2.7):

$$k_{spp}(\omega) = k_0(\omega)\sin(\theta) + mG_0 \quad (4.1)$$

where $k_{spp}$ is wave vector of the surface plasmon excited at gold/air interface, $k_0$ is vacuum wave vector of incident light, $m$ indicates order of surface plasmon coupling. Since the reciprocal lattice vector $G_0 = 2\pi/\Lambda$ ($\Lambda = 360$ nm) is larger than wave vector of surface plasmon in this work, hence we have $m = -1$ which corresponds to
a backward propagating plasmon wave.

The ellipticity $E_p/E_s$ can be calculated from the ratio of reflection coefficients of TM ($r_p$) and TE waves ($r_s$) [165]:

$$\eta = \frac{E_p}{E_s} = \frac{r_p}{r_s} = \frac{|E_p|}{|E_s|} e^{i\Delta} \quad (4.2)$$

For s-polarized incident waves, SPPs cannot be excited in this case, hence the reflection coefficient $r_s^0$ at gold/air interface for s-wave can be simply calculated using Fresnel equations [165]:

$$r_s^0 = \frac{\cos(\theta_i) - n_{\text{gold}}\cos(\theta_t)}{\cos(\theta_i) + n_{\text{gold}}\cos(\theta_t)} \quad (4.3)$$

where $n_{\text{gold}}$ is the refractive index of gold, $\theta_i$ and $\theta_t$ are the incident angle and reflection angle.

Similarly, we have $r_p^0$ for this gold/air interface:

$$r_p^0 = \frac{n_{\text{gold}}\cos(\theta_i) - \cos(\theta_t)}{n_{\text{gold}}\cos(\theta_i) + \cos(\theta_t)} \quad (4.4)$$

However, while SPPs is excited by TM waves, the reflection coefficient $r_p^0$ should be modified as $r_{sp}$ in order to describe the excited SPP resonance on gold grating [1]:

$$r_{sp} = \frac{r_p^0 (G_0 - k_0\sin(\theta) + k_{sp}) - i(\Gamma^i - \Gamma^{\text{rad}})}{r_p^0 (G_0 - k_0\sin(\theta) + k_{sp}) - i(\Gamma^i + \Gamma^{\text{rad}})} \quad (4.5)$$

Eq. 4.5 describes the SPPs resonance as Lorentz type resonance which includes the phase information. In this model, $\Gamma^i$ is internal damping coefficient of SPPs and $\Gamma^{\text{rad}}$ is radiation damping coefficient which is mainly related to geometrical factor of grating as we defined in chapter 2. Due to surface roughness of gold film, the internal loss of plasmon wave $\Gamma^i$ is larger than theoretical value $k''_{\text{spp}}$ (imaginary part of $k_{\text{spp}}$), and $\Gamma^i$ is given an estimated value of $4k''_{\text{spp}}$ in the calculation.
Finally, the ellipticity (Eq. 4.2) with SPPs resonance modification becomes:

$$\eta = \frac{r_{sp}}{r_s} = \left| \frac{E_p}{E_s} \right| e^{i\Delta}$$

(4.6)

### 4.3 Ellipticity in Amplitude and Phase Domain

To measure the SPPs resonance in both amplitude and phase domain, spectra ellipsometer (SOPRA) which based on rotating polarizer technique is used. In this experiment, white light from Xenon lamp (UV-Visible-near Infrared, with wavelength of 200 nm to 2 µm) is focused onto the nanostructure by a micro-lens system with spot size of \( \sim 200 \) µm by 300 µm. Using Eq. 3.3, we can now obtain the absolute value of amplitude ratio \( \tan(\varphi = |E_p/E_s|) \) and the phase delay (\( \Delta \)) of \( p- \) and \( s- \) polarized waves from experiments.

In amplitude domain, the measured amplitude ratio \( |E_p/E_s| \) is shown in Fig. 4.2 by dashed lines. The narrow reflection dips for different incident angle are attributed to first order surface plasmon excitations. It shows that the bandwidth of these resonant dips become narrower while incident angle is increased from 50 to 75 degree. Full field simulation using COMSOL Multiphysics was performed to calculate the amplitude ratio and the calculated result agree well with experimental observations (solid lines in Fig. 4.2). The resonance in spectra of amplitude ratio of electric field comes from TM polarized SPP excitation, and this is depicted in Fig. 4.3. The reflection spectra of TM and TE polarizations at 75 degree incident angle are shown in Fig. 4.3(a), in which TE polarized light shows a slow varying response. At the resonant dip wavelength \( \lambda = 710 \) nm, magnetic distribution of electric field were calculated in a unit cell for the two polarizations (Fig. 4.3(b) and Fig. 4.3(c)).

In phase domain (Fig. 4.4), the resonance of phase delay of reflected TM and TE waves becomes dramatically sharper as incident angle increases from 50 to 75 degree. Consider 75 degree incidence, TE waves has a slow varying response in
Figure 4.2. Spectral resolved amplitude ratio of (|E_p/E_s|) for large incident angle (50 to 75 degree). Dashed lines are the experimental results and solid lines are the calculated results using COMSOL Multiphysics.

Surface plasmon resonance regime [163], the maximum phase delay at wavelength 702 nm is due to the constructive interference between direct reflection of TM wave on the grating and re-emission from surface plasmon polaritons; the minimum phase delay is at wavelength 710 nm means that incident photon is not coupled to surface plasmon. In comparison, phase delay becomes \( \pi/2 \) at resonant wavelength (705 nm) of plasmon excitation i.e. destructive interference occurs at this position (Fig. 4.4, incident angle = 75 deg). It is noted that some oscillations appearing in the measured phase and amplitude spectra, this is due to the multi-interference from the seven micron thick SiO\(_2\) layer.

Usually, the narrower the plasmon resonance, the longer lifetime the plasmon
polariton has, which corresponds to a lower radiative damping rate. In the theoretical model, with value of $0.011G_0$ was chosen to fit the experimental result (dashed lines in Fig. 4.4). The practical optical constant of gold [166] was used in these analytical equations. The calculated phase delay ($\Delta$) is shown in Fig. 4.4 (solid lines) and agrees well with the measured phase spectra, although there is a slight discrepancy for 75 degree incidence. It should also be noted that radiative damping $\Gamma^{\text{rad}}$ is assumed to be a constant for all incident angles (50-75 degree) in the calculation. This means that oblique incidence contributes more to the sharper phase resonance than the change
Figure 4.4. Measured and calculated spectral resolved phase delay between p and s wave for oblique incidence (50 to 75 degree). Dashed lines are experimental observations while solid lines represent analytical results.

4.4 Summary

In summary, in this chapter we studied the sharp plasmonic resonance on gold gratings in both amplitude and phase domains by using ellipsometry technique. When increasing incident angle, the plasmonic resonance in amplitude domain becomes narrower while in phase domain it becomes sharper. From an analytical model, it is found that the sharp phase resonance mainly comes from the large angle incidence and has less to do with the radiative damping rate of surface plasmon polaritons. In
addition, phase delay measurement using ellipsometer is less sensitive to environment vibration than conventional interferometry. This is particularly important for rapid characterization of nanophotonic devices.
Chapter 5

Efficient Energy Exchange via Rabi Splitting in Plasmonic Nanocavity

In this chapter, we experimentally and theoretically study the strong coupling between propagating SPPs and the Fabry-Perot (F-P) cavity modes in a metallic nanodot array/nanocavity hybrid system in the visible spectral range. In addition to the observation of a giant Rabi-type splitting energy of 148 meV at the strong coupling regime, we also reveal highly-efficient energy exchange between SPP and F-P modes at the low frequency dispersion branch through detailed numerical near-field studies and experimental phase delay analysis.

5.1 Introduction

Plasmonic analogy of Rabi-splitting has been extensively studied in various metallic nanosystems hybridized with semiconductor quantum dots, nanocrystals and organic molecules, with a focus on the splitting energy gap where surface plasmon polaritons (SPPs) strongly couple with excitons. Similar strong coupling also occurs for individual metallic nanoparticles locating inside a photonic microcavity or nearby
a waveguide due to the strong interaction between localized surface plasmons and photonic modes in the near-infrared wavelength range. A polariton splitting of plasmons in the near-infrared spectral range was observed. [90–92] This is very similar to the Rabi-splitting from quantum dots or molecules systems. While most of previous studies focus on the splitting energy gap [90–93], little attention has been drawn to the aspect of energy exchange between the two modes that produce the Rabi or polariton splitting.

In this work, we study the strong coupling between propagating surface plasmon polaritons, excited by a two-dimensional (2-D) metallic dot array, and the Fabry-Perot (F-P) cavity modes formed within a planar nanocavity in the visible spectral range. Under TM-polarized excitation (electric field parallel to the incident plane), we observed a large Rabi-type splitting in the surface plasmon dispersion which is absent from the dispersion under TE-polarized excitation (electric field perpendicular to the incident plane). At the strong coupling regime, there are highly efficient energy exchange and mode conversion for TM-polarized excitation, which is confirmed by near-field distributions and phase-delay analysis. Our results reveal the possibility of controlling the energy distribution channels in a hybrid plasmonic nanocavity by tuning the coupling strength of SPP and F-P modes through the excitation polarization.

5.2 Plasmonic Fabry-Perot Cavity

A basic Fabry-Perot (FP) cavity only consists two opposing plane-parallel mirror, with a separation \( d \) (Fig. 5.1). While simple, it has been commonly used as resonators in semiconductor lasers and micro-cavity lasers. In a typical metal/dielectric/metal F-P cavity, the resonance condition for having a minimum in reflection can be determined by the total phase shift \( \Delta \) accumulated by light traveling a single trip.
inside the cavity [167,168]:

\[
\Delta_{\text{cavity}} = 2\pi \frac{n_d d}{\lambda} \cos(\theta) + \Delta_{\text{res}} = 2\pi N
\]  

(5.1)

where \(d\) is the cavity length, \(\theta\) is the incident angle and \(n_d\) is the refractive index of dielectric spacer. The additional phase delay term \(\Delta_{\text{res}}\) is due to the phase loss when light is reflected by the two metal mirrors and \(N\) is the F-P mode order.

Figure 5.1. Basic Fabry-Perot cavity setup: two parallel mirrors with a spacer of distanced.

According to Eq. 5.1, a planar Fabry-Perot nanocavity consisting of silver (100 nm)/SiO\(_2\) (120 nm)/silver (30 nm) multilayers was fabricated experimentally (Fig. 5.2). The three layers were deposited on a silicon substrate by using e-beam evaporation method. The bottom silver with 100 nm thickness can be treated as a prefect mirror, while the top silver mirror with thickness of 30 nm in the fabricated structure is semi-transparent, which allows for coupling between SPPs excited on the silver surface and F-P modes in the planar cavity.
The measured reflection spectra for the bare planar cavity at several incident angles under TE and TM polarizations are shown in Fig. 5.3. The intensity minimum in the reflection spectra manifest the excitation of F-P cavity modes by the two orthogonal polarizations. A closer look into the angle-dependent reflection dip position reveals that the TM polarized mode (Fig. 5.3(a)-Fig. 5.3(c)) is less sensitive to the incident angle than TE-polarized one (Fig. 5.3(d)-Fig. 5.3(f)), which is attributed to the unidirectional coupling effect of metallic nanocavity. Theoretical results calculated by using the transfer matrix method [165] are superimposed on the experimental curves in Fig. 5.3, where good agreement between experiment and theory can be clearly seen. From the parameters of the experimental device and the measured incident angles, we can determine from Eq. 5.1 that the reflection dips observed in Fig. 5.3 are due to the excitation of the first-order F-P mode.
Figure 5.3. Measured (blue circle line) and calculated (black solid line) reflectance of a planar cavity consisting of silver (100nm)/ SiO$_2$ (120nm)/ silver (30nm) multilayers. (a)-(c) are TM-polarized reflection spectra at incident angles of 16°, 28° and 40°; (d)-(f) correspond to TE polarization.

5.3 Rabi Splitting in Plasmonic Cavity

To investigate the strong coupling behavior between SPP and F-P cavity modes, we fabricated a plasmonic grating-cavity hybrid structure consisting of a two-dimensional silver nanodot array on a planar nanocavity by using standard e-beam lithography technique. Fig. 5.4 shows a schematic cross-sectional view (Fig. 5.4(a)) and a scanning electron microscope top view (Fig. 5.4(b)) of the hybrid plasmonic system. Each silver square dot has a size of 160 nm · 160 nm · 50 nm(height). The 2-D nanoparticle array on the planar silver cavity acts as a grating coupler for exciting propagating SPPs.
along the silver/air interface.

Figure 5.4. Device structure of a plasmonic nanodot/nanocavity hybrid system; (b) Top-view SEM image of a two-dimensional silver nanodot array on a silver/SiO$_2$/silver planar Fabry-Perot nanocavity

We also calculated the dispersion mappings of the pure silver nanodot array without the presence of the underneath nanocavity at two different incident polarizations, with results shown in Fig. 5.5. It is clearly seen from Fig. 5.5(a) that a highly-dispersive SPP mode is excited by TM-polarized incident light within the wavelength range covering the spectral window of F-P cavity modes in Fig. 5.5. However, the TE-polarized incident light cannot excite any SPP modes in the observing spectral range, and the incident light was mainly reflected by the metal surface as shown in Fig. 5.5(b).
Figure 5.5. Contour plots of the calculated reflectance as a function of wavelength and incident angle for a two-dimensional silver nanoparticle array on a semi-infinite silver film under TM- (a) and TE-polarized (b) excitations. The silver nanodot array has a period of 320 nm.

When integrated this plasmonic nanostructure to the F-P cavity, the SPP mode will be first excited by the illuminated light and then coupled into the cavity mode, which is the extra-cavity coupling method (Fig. 5.6(b)). Compared to intra-cavity coupling (Fig. 5.6(a)), the extra-cavity coupling method is compatible with bottom up fabricated structures such as plasmonic circuits and other kinds of complex nanostructures.
Figure 5.6. (a) Intra-cavity coupling method: the light first becomes cavity mode and then the SPP mode is excited. (b) Extra-cavity coupling method: the SPP is first excited and then coupled into the cavity.

Once we have an in-depth understanding on the dispersion characteristic of the two isolated systems, we then turn to the metal grating-nanocavity structure for which angle-resolved reflection measurements are used to reveal the coupling behavior of SPP and F-P modes. Fig. 5.7 renders the measured and calculated dispersion mappings of the hybrid system under two different polarized excitations. As we can see from Fig. 5.7(a) and Fig. 5.7(c), only the F-P cavity mode is excited by the TE-polarized incident light. The white triangles in both figures indicate the main cavity resonant positions which are consistent with the results presented in Fig.5.3(a) and Fig. 5.3(c). This mode similarity between the bare planar cavity and the hybrid grating-nanocavity system manifests that the excitation of SPPs on the 2-D silver grating is absent under TE-polarized illumination. The other weak resonances such as the two non-dispersive modes at wavelengths of 400 nm and 450 nm (Fig. 5.7(a)) are believed to be the conventional photonic modes supported by the 2-D silver grating which are not of our interest in this work.
Figure 5.7. Contour plots of the reflection efficiency as a function of wavelength and incident angle for the hybrid system consisting of a silver nanoparticle array (the same dimensions as Fig. 5.5) and a planar cavity (the same dimensions as Fig. 5.3) under TE- ((a) and (c)) and TM-polarized ((b) and (d)) excitations. (a) and (b) are experimental results; (c) and (d) are simulation results.

For TM-polarized incident light, both SPP and cavity modes can be excited simultaneously in the hybrid system within the same spectral window, thus facilitating the mode coupling and splitting. As is shown in the measured (Fig. 5.7(b)) and calculated (Fig. 5.7(d)) dispersion mappings, the resonant wavelength of SPP mode (indicated by white circles) moves from 445 nm to 554 nm when varying the incident angle from 16 to 40 degree, while the cavity resonance (indicated by the white triangles) slightly shifts from 520 nm to 500 nm. At the incident angle of 28 degree,
the SPP and F-P modes coincide with each other, resulting in a Rabi-type mode splitting (indicated by the black dashed circle in Fig. 5.7(b) and Fig. 5.7(d) ). At the low frequency branch in Fig. 5.7(b) and Fig. 5.7(d), the originally highly-dispersive SPP mode (see Fig. 5.5(b)) surprisingly becomes insensitive to the incident angle, resembling the cavity mode character (see Fig. 5.3(b)). This sharp change in the dispersion response implies an efficient energy exchange or mode conversion between the SPP and F-P cavity resonances.

To elucidate the coupling mechanism between SPP and F-P cavity modes, the near-field distribution in the hybrid nanocavity system was calculated using the three-dimensional rigorous coupled wave approximation method (Rsoft). Fig. 5.8 renders the electric and magnetic field amplitude distributions at three relative wavelength positions (corresponding to incident angles of 16, 28 and 40 degrees) for TM-polarized excitation. At the wavelength of 520 nm corresponding to the incident angle of 16 degree, Fig. 5.8(a) and Fig. 5.8(d) show that the near-field energy (both electric and magnetic) is mainly confined in the planar cavity layer. This confirms the previous observation that the low frequency branch of the mixed dispersion is dominated by the non-dispersive cavity mode character (see Fig. 5.7(b)). However, at the wavelength of 526 nm the Rabi-type mode splitting occurs with the incident angle of 28 degree, both SPP and F-P modes were excited simultaneously, resulting in nearly-equal distribution of the near-field energy in the silver nanodot array and the planar cavity as demonstrated in Fig. 5.8(b) and Fig. 5.8(e). Further increase of the incident wavelength to 554 nm (40 degree incidence) approaches to the dispersion where the SPP mode dominates (see Fig. 5.8(b)). This is consistent with the near-field plots shown in Fig. 5.8(c) and Fig. 5.8(f) in which both the electric and magnetic field energy mainly exists on the grating surface.
Figure 5.8. Calculated near-field distribution of $|E_x|$ and $|H_y|$ at the low frequency branch of the dispersion relations in Fig. 5.7(d). The incident angle and wavelength are 16 degree and 520 nm for (a) and (d), 28 degree and 526 nm for (b) and (e), 40 degree and 554 nm for (c) and (f), respectively.

Next, we characterized the mode coupling process in phase domain by performing ellipsometry measurements of the phase delay between TM- and TE-polarized reflection beams from the hybrid grating-nanocavity system (introduced in chapter 4). From Fig. 5.9(a), the effect of the observed polariton splitting of plasmons also exits in the phase delay mapping. Compared to the theoretically calculated phase delay of TM- and TE-polarized reflection beams from a bare planar cavity (see Fig. 5.9(b)) and from a pure SPP system (see Fig. 5.9(c)), we experimentally identify an abrupt change in the phase delay at the strong coupling region (see Fig. 5.9(a)), i.e. at the incident angle of 28 degree and the wavelength of 526 nm. This sharp change in the
phase delay further evidences the occurrence of the mode conversion facilitated by the Rabi-analogue mode splitting.

![Figure 5.9](image)

**Figure 5.9.** (a) Angle-resolved phase delay mappings of reflected TM- and TE-polarized light from the hybrid silver grating-cavity system measured by a spectroscopic ellipsometer. (b) and (c) are calculated phase delay of reflection beams for the planar cavity studied in Fig. 5.3 and the silver nanoparticle array studied in Fig. 5.5, respectively.

### 5.4 Efficiency Energy Exchange Between Plasmonic and Cavity modes

The mode conversion process in the coupled plasmonic-photonic system can be mathematically described by the solution of the following Hamiltonian equation [90]:

\[
H \Psi = \begin{bmatrix} E_{\text{cavity}} & g \\ g & E_{\text{SPP}} \end{bmatrix} \begin{bmatrix} \Psi_{\text{cavity}} \\ \Psi_{\text{SPP}} \end{bmatrix} = E \begin{bmatrix} \Psi_{\text{cavity}} \\ \Psi_{\text{SPP}} \end{bmatrix} \tag{5.2}
\]

Where \( H \) is the Hamiltonian of the coupled system and \( g \) is the plasmon field coupling strength. The two eigenstates, \( E_{\text{cavity}} \) and \( E_{\text{SPP}} \) are the energy of the propagating SPPs and the F-P cavity resonance, respectively. The eigenstate \( \Psi \) of this coupled system now composes of the eigenstates of the cavity cavity and the plasmon \( \Psi_{\text{SPP}} \), creating the observed mixed dispersion of the hybrid system. The Rabi-analogue
mode splitting energy can be quantitatively estimated by $2g$ and also experimentally measured from the dispersion mappings. We can see from Fig. 5.7(b) that the strong coupling between SPP and F-P cavity modes occurs at an incident angle of 28 degree and wavelength of 526 nm where the energy gap between the two branches reach the minimum value showing a splitting energy $h\Omega_R$ of 148 meV (30 nm in spectral range).

The eigenstates of this coupled system indicate that, when the mode splitting occurs, the SPP and F-P cavity modes should possess some physical properties from each other and form a new plasmonic polariton quasi-particle, in analogy to a quantum exciton polariton in a semiconductor cavity. [71,73] In both the high and low frequency branches of the splitting dispersion, it is reasonable to assume that these new quasi-particles should have half energy from the cavity photons and half energy from surface plasmon polaritons. In fact, such Rabi-analogue mode splitting provides an efficient pathway for energy exchange between conventional cavity modes and SPP mode.

![Figure 5.10.](image)

**Figure 5.10.** Resonant dip position of the reflection efficiency for cavity and SPPs modes. The dots are the SPP resonance dip and the triangles are the cavity resonance wavelength. The Rabi splitting energy $h\Omega_R$ can be realized from the smallest splitting wavelength.

The phenomenon we observed in this work could also be explained using theory of mode hybridization. The strong modal anti-crossing is resulted from the modal
hybridization. [169, 170] Although it is a classical phenomenon, its resemblance of Rabi splitting in the quantum regime makes us call it Rabi-analogue.

5.5 Summary

In summary, we have experimentally and theoretically studied the efficient energy exchange between SPP and F-P cavity modes via a Rabi-analogue splitting in a hybrid plasmonic nanocavity. We have revealed the mechanism governing the energy exchange between the two modes by plotting the near-field distributions at respective wavelength positions identified from the angle-resolved dispersion mappings. Experimentally observed phase delay between TM- and TE-polarized reflectance also supports the observation of efficient energy exchange and mode conversion at the low frequency branch of Rabi-analogue splitting. We believe that such efficient energy exchange between SPP and cavity modes facilitated by Rabi-analogue splitting could provide new concepts for developing nanophotonic devices working in the visible spectral range, as optical losses in conventional plasmonic systems in this regime is a critical issue for efficient energy transport and coupling.
Chapter 6

Nonlinear Optics and Hybrid Plasmonic Crystals

In this chapter, we describe our work in integrated organic conjugated polymer, which has large third harmonic generation efficiency, into a gold/polymer based plasmonic crystals.

In section 1, large surface plasmon enhanced third harmonic generation in the metal-polymer hybrid plasmonic crystal was experimentally observed. The integration of organic polymer into plasmonic crystal opens a new avenue to develop novel nonlinear optical plasmonic devices.

In section 2, by combining a gold-fork microstructure with a conjugated polymer thin film with strong nonlinearity, we produced both second- and third-order harmonic generation of vortex beam with orbital angular momentum. Compared to the previously reported medium to generate nonlinear optical vortex, this approach brings great advantage in device miniaturization and provides a promising strategy for realizing on-chip nonlinear optical vortex devices.
6.1 Surface Plasmon Enhanced Third Harmonic Generation in Plasmonic Crystal

6.1.1 Introduction

Surface plasmon resonance generates strong light localization in plasmonic nanostructures which has been used to enhance various nonlinear optical processes. However, the nonlinear optical efficiency of metal itself is usually not high enough and this limits the potential application. Hence, if a material with large nonlinear optical response can be embedded within the plasmonic nanostructure, it would be possible to generate larger nonlinear response.

In this work, we studied surface plasmon enhanced THG from PFO (Poly [9,9-bis-(2-ethylhexyl)-9H-fluorene-2,7-diyl])/gold hybrid periodic plasmonic crystal, in which PFO is the \( \pi \)-conjugated polymer with high third-order optical nonlinearity. The surface plasmon enhanced THG from the gold/PFO hybrid plasmonic crystal was experimentally demonstrated when pumping laser was tuned to SPP resonant frequency. Compared to the localized plasmon enhanced nonlinear optical processes, [12, 107, 109, 111] the periodic disc array in the proposed plasmonic disc-array is useful to produce directional nonlinear optical radiation. Besides, the gold disc-array/ITO/gold layer instead of one layer of grating on bottom gold film [171,172] can be used to efficiently extract the SPP enhanced THG radiation from ITO layer. [110]

6.1.2 Gold-Polymer Hybrid Plasmonic Structure

The gold/polymer hybrid plasmonic nanostructure consists of periodic gold disc-array/ITO (indium tin-oxide)/gold quasi-three dimensional configuration, which supports propagating surface plasmon polaritons (SPPs) at gold/PFO interface. To fabricated the plasmonic nanostructure, first chromium (Cr: 20 nm)/gold (50 nm)/ITO
(40 nm) layers were coated on quartz substrate using thermal evaporation and radio frequency sputtering methods. (Fig. 6.1); then the two-dimensional (2-D) gold disc-array was fabricated on top of ITO surface by using e-beam lithography and gold lift-off process. The 300 nm thick ZEP520A was spun onto the ITO (40 nm)/gold (50 nm) coated quartz substrate. A two-dimensional hole-array was formed using e-beam lithography. The second 50 nm thick gold film was then coated on the sample using thermal evaporator. After removing the residue resist using dimethylacetamide solvent, the two dimensional gold disc arrays with period of 600 nm and diameter of 350 nm was obtained. The total area size of the patterned area is 500 µm by 500 µm.

![Figure 6.1. Cross-section of gold/ITO/gold plasmonic crystal, Thickness of ITO and gold film is 40 and 50 nm respectively, and period of the gold disc grating is 600 nm with disc diameter of 350 nm. The 20 nm thick Cr film acts as adhesion layer; (b) Scanning electron microscope image of the two-dimensional gold disc array.](image)

The PFO polymer was first dissolved in toluene with a concentration of 20 mg/ml; then the polymer with thickness of 140 nm was spin-casted on the gold/ITO nanostructure to form the hybrid plasmonic crystal (Fig. 6.2(a)).
Figure 6.2. (a) Excitation of backward propagating surface plasmon polaritons in hybrid plasmonic crystal; (b) Ellipticity spectrum of hybrid plasmonic crystal at incident angle of 52 deg. The valley at $\lambda = 1340$ nm corresponds to the SPP resonant wavelength. (c) Phase delay ($\Delta$) of TM- and TE-polarized reflected light measured using ellipsometer.

One of the advantages of 2-D disc-array design is that it allows the same momentum conservation condition even the sample is rotated by 90 deg in experiment. For the linear optical properties, we used spectroscopic ellipsometer to characterize SPP resonance on the hybrid plasmonic crystal at incident angle of 52 deg. Based on our previous studies, [163] the resonant dip in ellipticity spectrum (Fig. 6.2(b)) indicates the first-order SPP resonant wavelength (1336 nm). Because $G_0 = 2\pi/\Lambda$ ($\Lambda$ is the period) is larger than the parallel momentum ($k_0(\omega)\sin(\theta)$), it implies that the SPPs
at gold/PFO interface propagate backward.

Figure 6.3. (a) TM- and TE-polarized specular reflection spectra on PFO/-gold hybrid plasmonic crystal; (b) field distribution in hybrid plasmonic under non-resonant TM polarized light illumination with $\lambda = 1250$ nm from incident angle of 52 deg; (c) field distribution in hybrid plasmonic crystal at SPP resonant wavelength (1336 nm) from incident angle of 52 deg. The white frame indicates gold, while the blue and gray frames represent ITO and Cr layers.

The reflection efficiency (Fig. 6.3), at incident angle of 52 deg was calculated by using three-dimensional rigorous coupled wave approximation method in commercial
RSOFT software (details in Experimental and Simulation Section) the SPP excitation is clearly shown for the TM polarized (electric field is parallel to incident plane) reflection spectrum (Fig. 6.3(a)). Beyond 1600 nm, other photonic modes [15] (such as the localized plasmon resonance) should exist; however, it is out of the interests of this work. From the simulation it is observed that the reflection efficiency at is much higher than that for SPP resonant wavelength: 1336 nm; the light localization in Fig. 6.3(c) is better for third harmonic generation process. To further understand light localization in the quasi-three dimensional plasmonic crystal, field distribution for TM polarized light illumination was studied using RSOFT as well (Fig. 6.3(b) and Fig. 6.3(c)). However, it seems that the SPP field distribution in the hybrid plasmonic crystal is not clear enough compared to conventional surface plasmon enhancement, this should be due to the complex scattering, reflection, and localized resonance effect in current hybrid device.

6.1.3 Efficiency of THG

The experimental configuration of third harmonic generation is shown in Fig. 6.4. Broadband femtosecond laser (with wavelength of 1.25 µm to 1.4 µm and pulse duration of 110 femtosecond) from optical parametric amplifier (TOPAS-C, Coherent) was used to pump the hybrid plasmonic crystal at incident angle of 52 deg, and then first-order THG radiation from the PFO/gold plasmonic device was collected in the far field. The radiation direction \( \psi (\sim 2.17 \text{ deg to the surface normal of substrate}) \) is governed by the following equation:

\[
k_0(3\omega)\sin(\psi) = 3k_0(\omega)\sin(\theta) - \frac{2\pi}{\Lambda}
\]

(6.1)

In comparison, the THG signal from control device (PFO(140 nm)/ITO(40 nm)/gold(50 nm)) can only be collected at the reflection direction after filtering the pumping laser, because the planar surface has no diffraction orders as that on the hybrid plasmonic
Figure 6.4. Experimental setup of THG measurement. Ti: Sapphire femtosecond laser with wavelength of 800 nm was used to pump optical parametric amplifier, then TM polarized laser (1.25 \( \mu \textrm{m} \) - 1.4 \( \mu \textrm{m} \)) was incident on to the sample at incident angle of 52 deg. The first-order diffraction THG from hybrid plasmonic crystal and reflection direction THG from control device were collected by fiber coupled PI-Acton spectrometer with ICCD detector.

In Fig. 6.5, the THG radiation under nm excitation from the hybrid plasmonic crystal was captured by CCD (Charge Coupled Device) camera. The dark field imaging of THG at diffraction order was obtained by avoiding direct detection of THG from reflection direction of pumping laser. The THG spectrum was measured by using the PI-Acton spectrometer with Intensified CCD (Fig. 6.5(b)); the output energy of THG shows a near cubic (slope = 2.86) dependent relationship with the pumping power (Fig. 6.5(c)), which is quite close to the theoretical value (slope = 3) for third-order optical nonlinearity.
Figure 6.5. THG from PFO/gold hybrid plasmonic crystal at excitation wavelength of 1340 nm (a) THG emission spot was captured by CCD camera. (b) THG spectrum was recorded by using PI-Acton spectrometer, which is equipped with ICCD detector. (c) Power dependence of THG curve shows a cubic relation with the pumping power.

Fig. 6.6 shows the spectral responses of THG from hybrid plasmonic crystal and control device (PFO(140 nm)/ITO(40 nm)/gold(50 nm) measured by scanning the wavelength of TM polarized laser from 1.25 μm to 1.4 μm. For the hybrid plasmonic crystal device, the THG radiation at the first-order diffraction direction was collected by fiber coupled PI-Acton spectrometer with Intensified CCD detector. For the control device, the THG collection was changed to specular reflection direction of pumping laser, as there is no diffraction order on planar surface as that on hybrid
plasmonic crystal. The relative efficiency of THG from hybrid plasmonic crystal and control device: \( \eta_{THG} = \frac{I_{THG}}{I_{pumping}} \) is shown in Fig. 6.6(a) and Fig. 6.6(b) respectively. Both of the measurements were normalized to the same incident power of pumping laser \( I_{pumping} \). Besides, the solid lines in Fig. 6.6 are the calculated reflection spectra. For hybrid plasmonic crystal, THG spectrum has a peak at SPP resonant wavelength: 1340 nm, which corresponds to the calculated reflection valley. In comparison, \( \eta_{THG} \) from planar PFO/ITO/gold device (Fig. 6.6(b)) has a slow varying response with little enhancement. It should be noted that THG signal at wavelength of 1340 nm is \( \sim 3 \) times higher than that from control device at the same wavelength. Here we do not emphasize the absolute value of enhancement as the collection direction is different for the two measurements. The absence of any THG enhancement in the planar device indicates the intrinsic nonlinear optical property of the PFO/gold planar device. This also indirectly proves that the enhancement is from surface plasmon enhanced contribution. The THG process of hybrid plasmonic crystal is very complicated, however we can assume PFO take an important role in the nonlinear optical process while the contribution \( \chi^{(3)} \) from of ITO and gold should not be negligible. [95, 109] From the analysis above and other reports, we also found that the enhancement factor of THG from metal-polymer hybrid plasmonic crystal is considerably higher than that from pure plasmonic device. [112, 118] This design of PFO thin film coated hybrid plasmonic crystal is important for THG radiation.
Figure 6.6. (a) Relative efficiency of THG spectral response on hybrid plasmonic crystal. The resonant peak is centered at 1340 nm, with FWHM of 60 nm. The peak of THG spectral response matches with reflection valley (solid triangle line) which indicates the SPP resonant wavelength. (b) In control experiment, spectral resolved THG from planar PFO(140nm)/ITO (40nm)/gold(50nm) has slow varying response, and solid square line is the specular reflection spectrum.

6.1.4 Summary

In summary, we designed a nonlinear optical plasmonic crystal by integrating organic active medium into conventional plasmonic nanostructure. We experimentally demonstrated surface plasmon enhanced third harmonic generation from the metal-organic hybrid plasmonic crystal. The metal-organic hybrid configuration provides
us with new concepts to develop novel nonlinear optical devices with subwavelength electromagnetic wave confinement.
6.2 Third Harmonic Generation of Optical Vortices Using Holography Based Gold-Fork Microstructure

6.2.1 Introduction

Light with orbital angular momentum has found novel applications in macro-manipulation, quantum optics, and optical communication, etc. The generation of orbital angular momentum in nonlinear media, such as second harmonic generation and high harmonic generation, has been demonstrated using optical super lattice and gas medium.

In this work, we propose to produce the harmonic generations of optical vortices by integrating holography based gold-fork microstructure into polymer thin film with high third-order optical nonlinearity. [120] Computer generated holography technique is utilized to design gold-fork microstructure with desired topological charge, which is then fabricated on gold coated quartz substrate using focus ion beam (FIB) technique. Both second- and third harmonic generations of optical vortices are experimentally observed in the polymer thin film/gold-fork/quartz composite device. Compared to the previous work using second-order nonlinear optical super lattice, [149, 173] the integration of microstructured gold-fork into thin film organic medium is very promising in miniaturization of phase dislocation devices, on-chip integration.

6.2.2 Device Configuration

Based on the principle of hologram, fork diffraction grating has been widely used to generate or detect optical [174–176] and electron vortex beams [177, 178], and this technique becomes more attractive since the invention of spatial light modulators with which more complex vortex beams can be generated just by programming the liquid crystal pixels using computer [179, 180]. In this work, we design a gold-fork
microstructure with binary modulation, which is described by Eq. 2.22 [153,181]:

\[ t(x, y) = 1 + \text{sign} \left[ \cos \left( \frac{2\pi x}{p} + l \cdot \arctan \left( \frac{x}{y} \right) \right) \right] \] (2.22)

where \( p = 2.4 \mu m \) is the period of a grating with line/space ratio of 1, \( l = 2 \) is the topological charge of the fork microstructure. An 80 nm thick gold film is fabricated on 500 \( \mu m \) thick quartz substrate using thermal evaporation, and then the gold-fork microstructure with topological charge is fabricated using focus ion beam technique. Although the gold fork microstructure in this work cannot be actively changed as we do using SLM, the thickness of microstructure is much thinner than that of the liquid crystal. Fig. 6.7 is the scanning electron microscope image of the fork microstructure. The area size of the fork microstructure is 48 \( \mu m \) by 48 \( \mu m \).

![Image of gold-fork microstructure](image)

**Figure 6.7.** Scanning electron microscope image of gold-fork microstructure, which is fabricated on gold/quartz substrate by using focus ion beam milling method; thickness of gold film is 80 nm; period of the gold grating is 2.4 \( \mu m \).

### 6.2.3 Linear Optical Experiment

As the Fork microstructure in Fig. 6.7 has a broadband response for visible wavelength, we can choose one visible output of the laser to demonstrate its optical prop-
property in the linear regime. As shown in Fig. 6.8, a femtosecond laser pulse (pulse duration: 110 fs) with wavelength of 700 nm (which could be other wavelength, for example: 632.8 nm) from the optical parametric amplifier (OPA, TOPAS-C) is focused onto the gold-fork microstructure from quartz substrate side using aspheric lens with numerical aperture N.A. = 0.18. The diameter of the laser spot size is around 50 µm and the polarization is along Y axis.

![Figure 6.8](image)

**Figure 6.8.** Experimental setup for the measurement optical vortex using gold-fork microstructure. After passing through linear polarizer P1, the femtosecond laser was focused onto the fork microstructure by using aspherical lens (L1, N.A. = 0.18). The transmitted light was then analyzed by the analyzer (P2). The far field fourier information of transmitted light was recorded using an imaging system including: infinity corrected objective lens (L2, N.A. = 0.4), planar-convex lens (L3, focal length: f = 30 mm), and CCD camera.

The transmitted light is then collected by an infinity-corrected objective lens (Lens 2) with numerical aperture of 0.4, and sent through the analyzer (P2), of which the polarization direction is set along Y axis. The third lens (L3, focal length: 30 mm) is used to transfer the far field diffraction pattern of incident light to a color charge coupled device (CCD) camera. Fig. 6.9(a) shows real-plane image of the fork microstructure and laser spot, while the first-order far field diffraction pattern is given in Fig. 6.9(b). The optical vortex beams with topological charge $l = 2$ are generated in the first-order diffraction directions. At this wavelength, the diffraction numerical
aperture is given by the conventional diffraction equation: N.A. = λ/p ∼ 0.29, where the diffraction order m is ±1.

Figure 6.9. Generation of optical vortex beam in linear optical regime using gold-fork device. The femtosecond laser (polarization direction: Y) from the optical parametric amplifier with wavelength of λ = 700 nm is normally incident onto the gold-fork microstructure from quartz substrate to gold-fork/F8BT direction. (a) Real space imaging of the fork microstructure and laser spot. (b) Optical vortex with topological charge l = 2 was detected at first diffraction order when polarization direction of analyzer (P2) is set at Y direction. (c) Polarization direction of analyzer (P2) is set at X direction.

6.2.4 Nonlinear Optical Experiment

To enhance the efficiency of third harmonic generation, a 140 nm thick F8BT (poly [9, 9-dioctylfluorene]-co-(benzothiadiazole)] thin film is coated onto the gold fork microstructure to form the gold-fork microstructure/F8BT hybrid device. While
F8BT is usually used as fluorescent material in organic laser device, it also functions as the nonlinear optical material, with high efficiency of third harmonic generation (THG). [120] To understand the optical response of the hybrid device, a periodic configuration (inset is cross-section view in Fig. 6.10(a)) with period = 2.4 µm is used to calculate the transmission efficiency in based on Lumerical FDTD software, the polarization of incident light is set along Y direction (parallel to grating direction); it can be found that the optical response in near infrared regime is broadband which is quite flexible for choosing the excitation wavelength of the femtosecond laser.

**Figure 6.10.** (a) Calculated transmission efficiency of F8BT/gold-fork microstructure; inset: Cross-section configuration of the hybrid device; (b) Under front pumping scheme, second harmonic generation from quartz substrate was observed when polarization direction of analyzer is set at X direction; (c) Under front pumping scheme, third harmonic generation of optical vortex with topological charge \( l = 2 \) was detected at first diffraction order when polarization direction of analyzer is set at Y direction.
For the nonlinear characterization of the sample, we start with the front-pumping scheme, i.e., the pumping laser at near infrared wavelength (here we use $\lambda = 1.35 \, \mu m$, in fact, it can be other wavelength) is normally incident onto the gold-polymer hybrid microstructure from the air. The SHG and THG radiation from the F8BT/gold-fork/quartz substrate are recorded in the far field using the optical setup as shown in Fig. 6.8. An objective lens (L2) with numerical aperture of 0.25 is used to collect the harmonic generation signal. When the polarization of the incidence and detection are set at Y- (s polarization) and X- (p polarization) direction respectively, only a zero order SHG radiation (shown in Fig. 6.10(b)) is detected by the CCD after the pumping laser is filtered out by a band-pass filter and no optical vortices for SHG (red color) is observed in the imaging window. In fact, SHG from the quartz substrate only occurs for cross polarization. This is because the second order nonlinear tensor of the z-cut quartz crystal (crystal class D3) only has nonzero $\chi^{(2)}_{xxx}$ component [95], if we define there is an in-plane rotational angle ($\psi$) between the crystallographic coordinate (x-y) and laboratory coordinate (X-Y), the $\chi^{(2)}$ in X-Y coordinate is transformed to $\chi^{(2)}_{xxx} \sin(3\psi)$ for ss(in)-s(out) and $-\chi^{(2)}_{xxx} \cos(3\psi)$ for ss(in)-p(out). [38] In this work, $\psi$ is set as zero degree, so the SHG for ssp polarization (YYX) can be generated from the quartz substrate while there is no signal for sss polarization (YYY). However, when the detection polarization is set to Y-direction (Fig. 6.10(c)), two THG (blue color) vortex beams appear at the first diffraction orders (with N.A. $\sim 0.19$) of the third harmonic wavelength. This confirms that the THG vortex beams are generated in the nonlinear polymer film. As the wavelength $\lambda = 1.35 \, \mu m$ of the pump beam is less than the period of the gold grating, there exist two first diffraction orders of the pump beam inside the quartz substrate. When they propagate inside the quartz substrate, they are expected to generate third harmonic waves that are along the same directions as the pump beams. However, the nonlinear beam cannot be detected in our configuration since the first-order diffraction direction of pumping laser is at N.A. $\sim 0.56$, which is out of the detection window of the first collection lens (N.A. = 0.25). In comparison, no SHG optical vortex is observed along the
diffraction direction, this is because F8BT is a π-conjugated polymer, which has zero second-order nonlinearity due to its random molecule distribution. The radiation spot in Fig. 6.10(b) is actually from quartz when the zero-order pumping laser passes through it.

\[ \text{Figure 6.11. Second harmonic generation and third harmonic generation of optical vortex from quartz/F8BT/gold-fork device under back-pumping scheme.} \]

(a) Third harmonic generation vortex (topological charge: \( l = 2 \)) was observed when polarization direction of analyzer is set at X direction; (b) Second harmonic generation optical vortex (topological charge: \( l = 2 \)) was detected at first diffraction order when polarization direction of analyzer is set at Y direction. (c) SHG and THG of optical vortex were generated simultaneously after removing the analyzer from optical path.

We next flip the sample and investigate the nonlinear generations in the back-pumping scheme, in which the pumping laser with wavelength \( \lambda = 1350 \) nm is incident from the quartz substrate onto the fork microstructure. The collection lens
with N.A. = 0.4 is chosen to obtain a large collection angle. When the detection polarization is set at X-direction, only the SHG vortex beam is observed (Fig. 6.11(b)). It is noted that only THG vortex beam (Fig. 6.11(a)) appears if the detection polarization is switched to Y-direction. Both SHG (\(\lambda = 675 \text{ nm}\)) and THG (\(\lambda = 450 \text{ nm}\)) (Fig. 6.11(c)) are produced when the analyzer (P2) is removed from the optical path. In this case, the harmonic generation signals are produced when pumping laser is incident onto quartz substrate. Since the SHG and THG beams have different diffraction directions (\(\text{N.A.}_{\text{SHG}} \sim 0.28\), \(\text{N.A.}_{\text{THG}} \sim 0.19\)) when passing through the phase dislocation, the dual-color optical vortexes are spatially separated from each other i.e. they can be easily observed.

![Figure 6.12.](image)

**Figure 6.12.** Second- and third- harmonic generation from F8BT/quartz and F8BT/ITO glass at pumping wavelength of 1350 nm, the spectra of harmonic generations were recorded using PI-Acton spectrometer, which is equipped with Intensified CCD detector. (a) SHG spectra from F8BT/glass and F8BT/quartz devices; (b) THG spectra from glass, quartz, F8BT/glass, and F8BT/quartz devices.
We focus more on the nonlinear optical generation of vortex beam than the absolute efficiency of SHG and THG. However, to better understand the origin of the harmonic generations, we measured the (Fig. 6.12) SHG and THG from quartz, glass, F8BT/quartz, and F8BT/glass samples. The focal point was slightly moved away from the front surface of the measured sample to reduce the contribution from the quartz and glass substrate. Under this experimental configuration, we can see both F8BT and glass show higher THG efficiency than quartz, but generates weaker SHG signals than quartz. As can be expected, the quartz substrate generates efficient SHG due to the mirror symmetry breaking in the crystal lattice. For back pumping experiment (Fig. 6.11), the SHG was first generated in quartz and then pass through the fork device to generate the SHG vortex.

6.2.5 Summary

In summary, the vortex beam of SHG and THG were experimentally investigated using holography based F8BT/gold-fork microstructure hybrid device. It is demonstrated that the combination of gold-fork microstructure with organic thin film provides new platforms in producing nonlinear optical radiation of optical vortex, beam splitting of the nonlinear optical processes, etc. The thin film metal or organic-fork microstructure, which was fabricated using focus-ion-beam method, also opens new avenues for the integration of multiple optical functionalities into on chip nonlinear optoelectronic devices.

6.3 Conclusion

In this chapter, by combining a gold nanostructure with a conjugated polymer thin film with strong nonlinearity, we demonstrated surface plasmon enhanced third-order harmonic generation phenomena and produced vortex beam with orbital angular mo-
mentum using gold fork nanostructure/organic polymer hybrid crystals. Compared to the previously reported medium to study nonlinear plasmonics, this approach brings great advantage in improving the efficiency of nonlinear optical processes and provides a promising strategy for realizing on-chip nonlinear optical devices.
Chapter 7

Symmetry-Selective
Third-Harmonic Generation from
Plasmonic Metacrystals

7.1 Introduction

Nonlinear processes, particularly harmonic generations, are often governed by selection rules imposed by the symmetries of the molecular configurations. The most well-known examples are the role mirror symmetry breaking plays in the generation of even harmonic generations, and the selection rule related to rotation symmetry in harmonic generations for fundamental beam with circular polarization. The selection rule for circular polarizations is inherently linked to the angular momentum conservation. While the role of mirror symmetry breaking in second harmonic generation has been well investigated in plasmonic systems, selection rule pertaining to circular polarization of harmonic generations have been confined to crystals, i.e. symmetry in the atomic level. In this work, we demonstrate the optical spin dependent third harmonic generation from plasmonic nanorods doped isotropic media. While circularly
polarized light cannot produce third harmonic generation in isotropic media, we show that the selection rule can be imposed by the symmetry of an array of centrosymmetric plasmonic nanostructures with certain rotational symmetries into an isotropic organic nonlinear thin film. The plasmon enhanced third harmonic generation has spin dependent phenomena which was also verified in our theoretical calculations. The results presented here may open new avenues for designing spin-dependent plasmonic nanostructure with nonlinear optical responses.

In conventional nonlinear optics, the selection rules of harmonic generation and other nonlinear optical processes are mainly based on the symmetries in the most fundamental levels, such that of molecular structures and crystals [94, 95]. However, the macroscopic symmetry of photonic crystal, nanoparticles, quantum dots, liquid crystal also brings new selection rules for the nonlinear optical processes. The importance of macroscopic symmetry is especially prominent in plasmonic nanostructures, in which the plasmon excitations can be very sensitive to the shape, size, and surrounding medium [14]. In the past several years, a large number of works have dedicated to the investigation of SHG in plasmonic structures with mirror symmetry breaking, such as split ring resonator [182], L and V-type nanorods [117], G-type chiral metamolecule [102–106].

Dated back in 1970s, people have studied that the circularly polarized light induced harmonic generation is of great importance to understand the pictures of the rotational selection rules as it cannot be simply treated as the superposition of two linear polarized light in the nonlinear processes. The selection rule states that under circularly polarized light excitation, the allowed harmonic generation order $m$ is defined as: [183, 184]

$$m = nl \pm 1$$ (7.1)

where $n$ is the symmetry class of the material, the $+$ and $-$ sign corresponding to the harmonic generation with same or opposite circularly polarized state and $l$ is an integer. In conventional nonlinear optics $n > 2$ due to the anisotropic property
of the two-fold (C2) materials in z-direction. Based on these selection rules, it is well known that circularly polarized (CP) light cannot produce third harmonic generation in isotropic medium [185–189], since the spin angular momentum of light would not be conserved in such process. Further, it is very interesting that CP light induced THG also has many unique properties, which were paid little attention for a long time. One of these interesting properties is CP light produce THG with opposite handedness when it propagates along the axis of a four-fold symmetry crystal [188, 189]. This rule holds for the microscopic molecular symmetry, however, it has not been experimentally demonstrated previously at the macroscopic symmetry level of the plasmonic nanostructures.

### 7.2 Nonlinear Optics Experiments

To investigate the correlation between rotational symmetry and third harmonic generation of circularly polarized light, we design three types of plasmonic crystals consisting of an array of rectangular nanorods, two cross-nanorods, and three cross-nanorods with C2, C3 and C4 global symmetry configurations (Fig. 7.1(a)). A thin organic film (PFO) with high third-order nonlinearity was coated onto these plasmonic nanorods. The bare PFO film does not produce THG under CP light excitations as was predicted, however, the CP induced THG can be observed by introducing C4 symmetry plasmonic crystals while it cannot be observed from C3 symmetry sample. This directly proves that the selections rules of CP induced THG also works for the plasmonic nanostructures with macroscopic symmetry. Also the rectangular nanorods with C2 (two-fold) symmetry generate THG light with both circular polarizations; the C4 (four-fold) symmetry device produces THG with only the opposite circular polarization. This finding provides us with more freedom to manipulate optical spin-dependent nonlinear optical processes using plasmonic macromolecules.

The gold nanorods with C2, C3 and C4 symmetries were fabricated using electron
(a) Geometry of the C2, C3 and C4 symmetry nanorods and gold/PFO hybrid devices. The width w of these nanorods is 50 nm, and the length of C2, C3, C4 symmetry nanorods are \(d_1 = 230\) nm, \(d_2 = 115\) nm, \(d_3 = 210\) nm respectively. Right: a PFO thin film with 100 nm thickness was spin-casted onto the nanorods.

(b) Right hand circularly polarized (RCP) at fundamental frequency is incident onto the gold/PFO hybrid crystals with two- (C2), three- (C3) and four-fold symmetry, C2 symmetry sample generates both right- (RCP) and left- (LCP) hand circular polarized third harmonic generation. C3 symmetry sample does not produce any third harmonic generation signal. C4 symmetry sample generates only the opposite circular polarized third harmonic generation.

beam lithography and metal lift-off process, The center to center distance between two adjacent unit elements is 400 nm with thickness of gold film of \(t = 30\) nm. The linewidth of the nanorod is 50 nm, the length of nanorod in C2, C3 and C4 devices are \(d_1 = 230\) nm, \(d_2 = 115\) nm and \(d_3 = 210\) nm respectively. Finally, a 100 nm PFO thin film was spin-coated onto the gold nanorods from a 15 mg/mL toluene solution to form the gold-PFO hybrid plasmonic crystals. The scanning electron microscope pictures of the three samples are shown in the right row in Fig. 7.2.
Figure 7.2. Linear characterization of the metacrystals. (Right) Scanning electron microscope images of gold nanorods with C2, C3 and C4 symmetry, they are fabricated on thin ITO (15 nm) coated glass substrate using electron beam lithography and gold lift-off process. A 100 nm PFO thin film was then spin-coated onto the gold nanorods from a 15 mg/mL toluene solution to form the gold-PFO hybrid plasmonic crystals. (Left) Measured (lines and symbols) and calculated (lines) transmission spectra for the three kinds of gold/PFO plasmonic crystals. White light is normally incident on the three devices, the transmission efficiency of were measured using Fourier Transformed Infrared spectrometer (FTIR). The circle and triangle symbols represent horizontal (H-) and vertical (V-) polarized incident light.
The linear optical property of the samples is characterized by measuring the transmission spectra using Fourier transform infrared spectrometer (FTIR, BRUKER Hyperion 3000) under normal incidence. As is shown in the left row of Fig. 7.2, the transmission dips correspond to the localized plasmon resonance. For C2 device, the plasmon resonances found around at wavelength of 1269 nm under light illumination with horizontal (H-) polarization; however, using vertical (V-) polarized illumination, this localized plasmon resonance is located at visible wavelength which is not in the near infrared regime. For C3 symmetry device, the localized plasmon resonances are at 1250 nm and 1260 nm respectively for H- and V- polarizations. For C4 symmetry device, the localized plasmon resonances under H- and V- polarized light illumination should be at the same wavelength in ideal case. From the experimental measurement, they are at slightly different wavelengths (H: 1207 nm and V: 1219 nm) due to the unavoidable imperfection of fabrication processes.

The third harmonic generation measurement (Fig. 7.3(a)) was performed using a femtosecond (fs) laser output from the optical parametric oscillator at wavelength of=1.25 m, which (repetition frequency: 80 MHz, pulse duration: ~ 200 fs, averaged power: P = 8 mW) is close to the plasmon resonance wavelengths of all the three types of plasmonic metacrystals. In the measurement, the pumping laser is focused to a spot with diameter of 50 µm using an infinity-corrected objective lens (5x, N.A = 0.10) with focal length of 25.8 mm. The THG from gold/PFO composite devices is collected by a color charge coupled device (CCD) using the second infinity-corrected objective lens (5x, N.A = 0.10) after filtering out the pumping laser using band-pass filter (315 nm-710 nm).
Figure 7.3. (a) Experimental setup for the THG measurement. The polarization of the pumping laser light was controlled by the polarizer assembly which contains one linear polarizer and one quarter wave plate. The objective lens (L1, N.A = 0.10) was used to focus the light onto the plasmonic crystals. The objective lens (L2, N.A = 0.10) was used to collect the generated THG signals. Finally, THG signal was captured by a planar convex lens and charge coupled device. (b) CCD images of the THG from C2, C3, C4 and bared PFO thin film under different polarization states of pumping laser. The first two rows are the results for pumping laser with linear polarization: horizontal (H) and vertical (V), receptively. The THG signals the third and fourth rows were recorded using right hand circularly polarized (RCP) pumping laser. The third row corresponds to the THG with RCP component, and the fourth row shows the LCP component of THG.
The linear polarized measurements are first carried out to characterize the resonance features of plasmonic structures. The CCD images of THG signal from C2, C3 and C4 symmetry samples are shown in Fig. 7.3(b) and the total intensity of these THG spots are listed in Table 7.1. As expected, THG signal can be generated from all the three samples under linear polarized excitation. Compared to the THG from pure PFO thin film, localized plasmon resonance of the gold nanorods dramatically improves the efficiency of THG from gold/PFO hybrid devices due to the near field enhancement of the electric field. For C2 symmetry device, THG intensity for H polarization is much higher than that for vertical polarization, which agrees with the linear optical property of the C2 nanorod (Fig. 7.2). For samples with C3 and C4 symmetries, THG for both H and V polarizations are of similar intensities as both of the two polarized light can excite the localized plasmon resonance at the fundamental frequency. It is also observed that THG from gold nanorods is much weaker than that from bare PFO film (Supplemental Materials), and this indicates that the THG in the gold/PFO hybrid systems is dominated by the contribution from the PFO film.

We further carry out the THG measurements under circular polarized light excitation with results shown in Fig. 7.3(b). On the bare PFO thin, there is no THG signal observed when excited by a circularly polarized laser beam. This result agrees with the selection rules for THG, because the thin PFO film on glass substrate with the molecules randomly oriented can be treated as an isotropic medium [188, 189]. Once the plasmonic nanorods are embedded into the PFO thin film, they will greatly change the localized field distribution and thus alters the THG process. Besides the strong field enhancement at the fundamental wavelength, the polarization state of the local electric field in the vicinity of the nanoplasmonic structures is strongly modified by the presence of the plasmonic resonance mode and is in general not circularly polarized. This gives rise to nonzero local THG nonlinear polarization, whose emission into the far field is further mediated by the response of the plasmonic structures at the THG wavelength. Interestingly, although the local THG nonlinear polarization is nonzero, the overall THG from the C3 symmetry sample vanishes in the far field.
This is dictated by the selection rule $m = 3l \pm 1$ for C3 symmetry, according to which the allowed orders of harmonic generation with the same circular polarization as the fundamental wave are $m = 1, 4, 7...$ and those of the opposite circular polarization are $m = 2, 5, 8...$. With $m = 3$, there is no circular polarization harmonic generations.

More intriguing results come from the comparison between THG of the C2 and C4 samples. Strong optical spin dependent THG signals are observed when the circular polarized fundamental wave is incident onto the C2 and C4 symmetry samples. For the C2 symmetry sample, right circularly polarized light (RCP) excitation generates THG signals with both right hand circular polarization (RCP) and left hand circular polarization (LCP), as both are not forbidden by the selection rule $m = 2l \pm 1$. However, RCP component of THG is much stronger than LCP component, with polarization ratio: $\eta_{C2}(\text{THG}_{LCP}/\text{THG}_{RCP}) = 0.121$ (Table 7.1). This may due to the geometry of the C2 antennas, such as the length of the nanorods.

Interestingly, for the C4 symmetry sample, the LCP component dominates in the RCP induced THG signals, with an extremely weak RCP component. According to the selection rule $m = 4l \pm 1$, RCP is forbidden for C4 symmetry under RCP illuminated; However, the nonperfectness of fabrication due to the lift-off process slightly breaks the rotational symmetry. Hence, all the experimental observations are consistent with the selection rules of THG with circularly polarized light excitation in crystal optics when generalized to 2D metacrystals with twofold rotational symmetry. [189]

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**Table 7.1**: Measured normalized intensity (arbitrary unit) of the THG on C2, C3 and C4 device. "-" means the signal is too weak to be measured.
7.3 Calculation of near field Polarizations

We first performed numerical calculation of the third-order nonlinear polarization $\vec{P}^{(3\omega)}$ on C2, C3, C4 and PFO thin film devices. From theory of nonlinear optics, it is known that $\vec{P}^{(3\omega)}$ is related to the tensor of third-order susceptibility, which depends on the crystal classes. As PFO thin film is regarded as an isotropic media, the third order polarization from the PFO film is simply given by Eq. 7.2. [95]

$$\vec{P}^{(3\omega)}(\vec{r}) = 3 \cdot \chi^{(3)} E_\omega^i(\vec{r}) E_\omega^j(\vec{r}) E_\omega^k(\vec{r})$$  (7.2)

Here $\chi^{(3)}$ is the third order susceptibility of PFO, $E_\omega^i(\vec{r})$ is the electric field of fundamental wave. Eq. 7.2 tells us that circularly polarized incident light ($E_x = \sqrt{2}/2$, $E_y = -i \cdot \sqrt{2}/2$, RCP [165]) cannot generate THG signal on bare PFO thin film.

When the gold nanorods are embedded into the PFO film, the symmetry of the gold/PFO hybrid system is formed at a macroscopic level (compared to molecular scale), and it would be interesting for us to calculate the $\vec{P}^{(3\omega)}$ distribution in these three kinds of nonlinear metasurfaces with different rotational symmetry.

Fig. 7.4 shows the calculated near field distribution of the nonlinear polarization $\vec{P}^{(3\omega)}$ on C2, C3, C4 and bare PFO devices. For pumping laser with linear polarization, nonlinear polarization is enhanced along the direction that is parallel to the oscillation direction of electric field $E$. The nonlinear polarization is much stronger around the corners of the gold nanorods in these three kinds of hybrid devices. For pumping laser with circular polarization, the nonlinear polarization also has the C2, C3 and C4 symmetry distribution respectively. In comparison, the $\vec{P}^{(3\omega)}$ on bare PFO film is zero as is predicted.

To further understand the polarization properties, we also calculated the polarization state $\delta$, which is determined by:

$$|\vec{P}^{(3\omega)}| = \chi^{(3)} |\vec{E}|^3 \delta$$  (7.3)
Figure 7.4. Calculated near-field distribution of nonlinear polarizations on C2, C3, C4 and bare PFO devices. The first two rows are the results for pumping laser with linear polarization: horizontal (H) and vertical (V), respectively. The third row corresponds to nonlinear polarization using right hand circularly polarized (RCP) pumping laser.

and \( \delta \) is given by:

\[
\delta = \frac{|(\vec{E} \cdot \vec{E})|}{|\vec{E}|^2}
\] (7.4)

Hence, when \( \delta = 1 \), it means the polarization is linear polarized, and when \( \delta = 0 \), the polarization is circularly polarized. We both calculated the E-field distribution and \( \delta \) under RCP excitation and the results are shown in Fig. 7.5. It is obviously that close to the structure tips, the field is strongly enhanced and the polarization state is close to linear polarization. This gives rises to nonzero local third-order nonlinear polarizations, whose emission into the far field is further mediated by linear response of the plasmonic structures at the THG wavelength. Interestingly, although the local third-order nonlinear polarization is nonzero, the overall THG from the C3 symmetry sample vanishes in the far field, which is indicated by the selection rules.
Figure 7.5. Calculated E-field distribution and polarization state on various rotational symmetry devices. (a)-(c) Enhancement of the electric field in the near field for the C2, C3 and C4 plasmonic nanostructures. (d)-(f) The distribution of polarization state for C2, C3 and C4 structures, with blue color $\delta = 0$ and red color $\delta = 1$ denoting circular polarization and linear polarization, respectively. In all the calculations, the incident beam is RCP. In the regions close to the tips of the nanostructures, not only is the field enhancement very strong, but also the field is very close to linear polarization.

7.4 Summary

In summary, we studied localized plasmon enhanced third harmonic generation in the gold/PFO-hybrid plasmonic crystals with two-, three- and four-fold symmetries. The spin dependent third harmonic generations on the three kinds of plasmonic devices proves that the selection rules in the conventional nonlinear optics theory are still correct for macroscopic plasmonic crystals. This finding should be very important for us to develop novel spin dependent nonlinear plasmonic nanocircuits, nanochips and so on.
Chapter 8

Conclusion and Future Work

In this thesis, we have investigated both linear and nonlinear optical properties of plasmonic nanostructures. In the linear optical regime, the spectral ellipsometry techniques were developed to characterize the phase shift of plasmonic devices, for example, we demonstrate the angle resolved plasmonic resonances in phase domain, and the giant Rabi-splitting effect due to the strong coupling effect between cavity photons and SPPs by using ellipsometry measurement.

For the nonlinear plasmonics, one of our contributions is introducing nonlinear active medium into the metallic nanostructures to form a metal-organic hybrid devices. We demonstrated SPP enhanced THG process using a gold-polymer hybrid structures. For most of the nonlinear plasmonics, the plasmon enhancement is usually the key word. However, we demonstrate the vortex beam of THG can be realized by introducing hologram based modulation into the hybrid plasmonic devices.

In conventional nonlinear optics, the harmonic generations follows the selection rules which are based on the symmetry property of crystals. Very few work on the selections rules of nonlinear optical processes on plasmonic devices were reported before. We found that the THG from metacrystals with two-, three-, four- folds symmetries also follows a conventional selection rules which are applicable to con-
ventional crystals. This findings is very interesting and should be able to provide new concepts for controlling nonlinear optical processes in a unconventional ways in plasmonics and metamaterials fields.

After this work, I will move my interests to the realization the all-optical ultrafast switching using the metacrystals we studied in this thesis, and try to develop a new type of optical switch with low loss and small volume.
Bibliography


Curriculum Vitae

Academic qualifications of the thesis author, Ms CHEN Shumei:

- Received the degree of Bachelor of Science (Honours) from Hong Kong Baptist University, September 2010

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