Alternative approaches for enhancing plasmonic sensor performance

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**ALTERNATIVE APPROACHES FOR ENHANCING
PLASMONIC SENSOR PERFORMANCE**

ALANA MAULUIDY SOEHARTONO

SCHOOL OF ELECTRICAL AND ELECTRONIC ENGINEERING

2020

**ALTERNATIVE APPROACHES FOR ENHANCING
PLASMONIC SENSOR PERFORMANCE**

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School of Electrical and Electronic Engineering

A thesis submitted to the Nanyang Technological University

in fulfillment of the requirement for the degree of

Doctor of Philosophy

2020

STATEMENT OF ORIGINALITY

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

July 6, 2020

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Alana Mauluidy Soehartono

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July 6, 2020

Date

Assoc Prof Yong Ken-Tye

AUTHORSHIP ATTRIBUTION STATEMENT

This thesis contains material from three papers published in peer-reviewed journals, where I was the first and/or corresponding author.

Chapter 3 is published as Soehartono AM, Mueller AD, Tobing LYM, Chan KK, Zhang DH, Yong K-T. Ultra-small v-shaped gold split ring resonators for biosensing using fundamental magnetic resonance in the visible spectrum. *Nanotechnology*. 2017;28:405305.

The contributions of the co-authors are as follows:

- I proposed to conduct a study on biosensing with magnetic resonance.
- Dr. Tobing fabricated the samples and conducted SEM measurements.
- Dr. Mueller and I developed the framework for numerical analysis.
- I conducted optical characterization, biosensing experiments, and simulations.
- Kok Ken Chan prepared the solutions used for bulk sensing characterization.
- Dr. Mueller and I wrote the manuscript; Dr. Tobing contributed to the results analysis, and all authors made revisions.
- Prof. Yong and Prof. Zhang supervised the work.

Chapter 4 is published as Soehartono AM, Tobing LYM, Mueller AD, Zhang DH, Yong K-T. Hybrid Transverse-Longitudinal Modes for High Figure-of-Merit Localized Plasmonic Refractometric Sensing in the Visible Spectrum. *Advanced Optical Materials*. 2020.

The contributions of the co-authors are as follows:

- I proposed the study and characterized optical and sensing performances for all electrodeposited vSRR structures.
- Dr. Tobing and Dr. Mueller performed nanopatterning and electrodeposition.
- Dr. Mueller and I conducted full- wave simulations.
- Dr. Tobing, Dr. Mueller, and I contributed technical discussions on the mode analysis of hybrid LSP- waveguide modes.
- I wrote the manuscript with inputs from Dr. Tobing and Dr. Mueller. All authors read and revised the manuscript.
- Prof. Yong and Prof. Zhang supervised the work.

Parts of Chapter 4 and 5 are published as Soehartono AM, Tobing LYM, Mueller AD, Yong K-T, Zhang DH. Resonance Modes of Tall Plasmonic Nanostructures and Their Applications for Biosensing. *IEEE Journal of Quantum Electronics*. 2019; 56(2).

The contributions of the co-authors are as follows:

- I proposed the idea and characterized optical responses and sensing performance for all the electrodeposited vSRR structures.
- Dr. Tobing and Dr. Mueller performed nanopatterning and electrodeposition.
- Dr. Mueller and I conducted full- wave simulations.
- Dr. Tobing, Dr. Mueller, and I contributed technical discussions.
- I wrote the manuscript with inputs from Dr. Tobing and Dr. Mueller. All authors read and revised the manuscript.
- Prof. Yong and Prof. Zhang supervised the work.

July 6, 2020

Date

Alana Mauluidy Soehartono

Dedicated to my daughters, Ariani and Alia.

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With gratitude,

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ABSTRACT

Strong light localization near metal nanostructures occurs by collective oscillations of plasmons in the form of electric and magnetic resonances. The high susceptibility of such localized surface plasmons (LSP) to refractive index changes has made it an excellent platform for rapid and label-free sensing, particularly in the development of low-cost sensing platforms in the visible spectrum. However, the linear relationship between sensitivity and resonance wavelength indicates that sensitivity decreases for shorter wavelengths. In this thesis, alternative plasmon resonance mechanisms are explored to address the challenges of plasmonic sensing in the visible frequency range. The numerical and experimental investigation of the magnetic-type LSP resonance is contrasted with the electric-type used in conventional LSP-based sensing. The role of geometry, especially height, on the resonance mechanisms is also studied, in which it is found that higher aspect ratio structures, realized by a cost-effective electrodeposition process, support waveguide-like modes which outperform typical planar resonances by up to 3X in the sensitivity and 10X in the figure of merit for the bulk and surface aspects. Furthermore, the practical implications of the work are discussed.

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NOMENCLATURE AND ABBREVIATIONS

BSA	Bovine serum albumin
EBL	Electron beam lithography
IgG	Immunoglobulin G
ITO	Indium tin oxide
FDTD	Finite difference time domain
FWHM	Full width at half maximum
FOM	Figure of merit
FOM _B	Bulk figure of merit
FOM _S	Surface figure of merit
LSPR	Localized surface plasmon resonance
LSP	Localized surface plasmons
NSL	Nanosphere lithography
PBS	Phosphate buffered saline
PDMS	Polydimethylsiloxane
SAM	Self-assembled monolayer
S _B	Bulk refractive index sensitivity
S _S	Surface sensitivity
SiO ₂	Silicon dioxide

SEM	Scanning electron microscopy
SPR	Surface plasmon resonance
SPP	Surface plasmon polaritons
SRR	Split-ring resonator
ν SRR	v-shaped split ring resonator
u SRR	u-shaped split ring resonator
ZDMAC	N,N-dimethylacetamide

Chapter 1 INTRODUCTION

1.1 Motivation

Diagnostic assays are indispensable tools in the detection and treatment of many diseases. Gold standard methods like the enzyme-linked immunoassay (ELISA) are nevertheless burdened with laborious processes, long turnaround times, and high costs (logistics/transportation, skilled technicians) [1–3]. Early intervention has been shown to improve patient outcomes [4], but the trace concentration of molecules in early disease stages make detection challenging. With rising disease prevalence amid a growing global population, decentralizing and streamlining the testing process without compromising on value and performance remains a key issue to be addressed. Miniaturized biosensors can potentially improve conventional diagnostic assays in terms of portability, high-throughput, and reduced sample and reagent consumption. To this end, plasmonics are among the technologies which can realize sensitive, real-time integration with microfluidic architecture as point-of-care devices.

Known for its characteristically strong light localization at the nanoscale, localized surface plasmon resonance (LSPR) is an attractive candidate for rapid, label-free, and noninvasive interrogation through colorimetric or spectroscopic (vibrational or refractometric) means. In particular, its susceptibility to the local dielectric medium enables the recognition of minute refractive index changes from molecular adsorption and binding events within the nanoscale environment. LSPR can be implemented as a direct or sandwich assay, and can be colloidally-suspended or substrate-supported. The implementation of arraying becomes important when considering multiplexing as a

means for high-throughput parallel testing, and for improving disease precision in point-of-care settings [5][6]. A well-known commercial application of plasmonics is for off-the-shelf home pregnancy testing kits as a lateral-flow sandwich-type assay. Upon nanoparticle binding with human chorionic gonadotropin in the sample, a colorimetric change arises from particle aggregation on the surface [7] in a chromographic manner which can be observed with the naked eye. This unique property can similarly be applied to detect the presence low concentrations molecules.

The basis of plasmonic sensing arises from the coherent oscillation of free electrons as surface plasmon polaritons (SPP) propagating on a thin metal film, or localized surface plasmons (LSP) around metallic nanostructures whose resonance conditions are determined in part by the permittivity of the metal and dielectric. The changes in the medium refractive index from molecule adsorption modifies the resonance conditions of the plasmons as a measurable shift. Typical surface plasmon resonance (SPR) setups for SPP detection employ a prism-coupled Kretschmann configuration, which is non-trivial considering the precise and tedious optical alignment (angle-resolving, prism, laser). Furthermore, the larger evanescent field (~ 300 nm) leads to a greater susceptibility to bulk effects such as temperature sensitivity, necessitating additional components for compensation [8]. By contrast, typical sensing volumes of LSPR are confined around the nanostructure (~ 30 nm) and it can be conducted with standard optical transmission geometry at normal incidence with a broadband source. Because of the fractionally smaller contribution of the background, it is less susceptible to bulk effects.

The broad scope of this work is to investigate localized surface plasmon resonance (LSPR)-based optical transduction methods for biochemical applications which are in line with a high performance, cost effective, miniaturized rapid sensor. In particular, we

investigate resonance mechanisms and strategies for spectral engineering which be used to improve sensing benchmarks where general requirements of biosensors are selectivity, reliability, stability, sensitivity, and linearity. Furthermore, within the context of practical sensing, measurement complexity and cost are factors also influence the adoption of a technology. In the interest of maintaining the simplest optical detection setup, our work aims to work limit the sensing region within the visible spectrum, allowing for the use of low-cost detectors and sources. As a comparative example, mid-infrared wavelength range components are costly, with temperature-regulated detectors (for example, cooled InGaAs detectors) and laser sources, making them unsuitable for point-of-care applications.

1.2 Objective

The key objective of this thesis is to investigate alternate LSP-based plasmonic resonance mechanisms and their impact on biosensing performance, which encompasses both bulk and surface effects. The study is guided by three main design considerations: the ability to support visible wavelength range operation, routes of improvement for one or more aspects of its sensing parameters (such as figure of merit, bulk and surface sensitivity, and Q-factor), and robustness in terms of biological compatibility, stability, and suitability for functionalization.

1.3 Major Contributions

The major contributions of this thesis are outlined as follows:

1. The fundamental magnetic resonance is proposed for sensing biological molecules in the visible region using planar (height of 30 nm) v-shaped split ring resonators. Magnetic resonances are observed due to electric field coupling resulting charge accumulation across the resonator gaps. The bulk and analyte sensing performance of the magnetic mode was found to outperform that of the electric mode. The structures were characterized and used to quantify the monolayer thickness of biomolecules (cytochrome *c* and bovine serum albumin) and observe the specific binding of protein A/G with immunoglobulin G.

2. Hybrid transverse-longitudinal modes in tall vSRRs are proposed for attaining high *Q* resonances to improve the figure of merit (FOM) while maintaining the resonance region within the visible spectrum (400-700 nm). Localized plasmon modes are limited by a proportionality with resonance wavelength, such that shorter resonances (e.g. visible) lead to lower sensitivity. To overcome this, height is introduced as a strategy to blue-shift the resonances and support modes along the out-of-plane vertical axis. The mode is associated with longitudinal oscillations along the height of the nanostructure and transversal LSP modes. When structures are sufficiently tall ($h \sim 150$ nm), the experimental FOM increases by 10X compared to the planar FOM of ~ 2 , which is consistent with LSP resonances. Height-dependent resonance regimes are identified as the planar, intermediate, and waveguiding according to the respective spectral features. The study focuses on the intermediate regime, for which localized plasmon modes are found to saturate. Surface sensing was experimentally verified with alkanethiol layers for resonance modes under investigation.

3. The concept of the transversal-longitudinal modes is extended to capacitively and conductively coupled square disk dimer geometries. For the latter, the addition of a conductive bridge is used to explore guided charge transfer plasmons and LC magnetic

resonances of a conventional u-shaped geometry. The onset of plasmon decoupling is found to be geometry-dependent. The longitudinal-associated mode is comparatively evaluated for bulk and surface sensing for three dimer variants, for which the center-connected dimer exhibited the highest FOM and bulk sensitivity.

4. Plasmon decoupling and longitudinal oscillations associated with increased nanostructure height were studied for engineering resonance application in surface sensing where short LSP evanescent tails (~ 30 nm) are insufficient. Multiple functionalization layers in specific binding can be problematic when functionalization layers consume and saturate the resonant response before any binding event can take place. It was found that the hybrid-longitudinal mode provides a strategy to overcome pure LSP-mode limitations by extending the evanescent tail. Additionally, the resonance of some narrow waveguided modes emerged conditional with dielectric medium. The selective onset is identified as a strategy to facilitate surface sensing and demonstrated experimentally.

1.4 Organization of the Thesis

The thesis is organized into six chapters as outlined below:

Chapter 1 provides the motivation behind the work and outlines the objective and major contributions and findings of the work. The summary of chapters is also provided.

Chapter 2 details the basis for plasmonic sensing, pertaining to optical properties and material properties. The chapter introduces quality measures used to benchmark performance of the nanostructures in the study. An overview of the methods in the work is given, as well as practical biosensor considerations.

Chapter 3 demonstrates the biosensing application of magnetic resonance in the visible range. Simulated and experimental results of v-shaped split ring resonators on quartz substrate are investigated as a function of its structures' geometric parameters. Nonspecific and specific binding experiments are carried out for varied molecular weight molecules.

Chapter 4 is investigates the characteristics of employing height to manipulate the spectral response of the planar vSRRs from Chapter 3. An inherently different resonance mechanism is observed due to non-negligible Fabry-Perot reflections, which are referred to as longitudinal or waveguiding modes. Improvements in the sensitivity, Q-factor, and FOM are reported. The experimental data is supported by numerical analysis.

Chapter 5 builds upon strategies of the previous chapter to explore resonance modes of disk dimers modified by coupling and symmetry conditions. Where the previous chapter pertains to the waveguide-like mode, the work in this chapter explores the LSP-dominated waveguide modes. The effects and origins of the emergence of waveguided resonances are considered in the context of visible range biosensing.

Chapter 6 provides a conclusion of the presented work and outlines future avenues of research to serve as a follow-up to the present study.

Chapter 2 BACKGROUND

In this section, a brief background on plasmonics is given, encompassing surface and localized plasmonic resonances. Quality measures of plasmonic sensing used throughout the thesis are discussed. Finally, practical considerations and experimental methods are given.

2.1 Plasmonics

Early adopters of plasmonics employed the striking dichroic effects of nanoparticles in stained glass fixtures and, most famously, the Lycurgus Cup out of 4th Century Roman Empire. The colors due to particle dichroism changed between green and red based on direction of light transmission, but its mechanism was not well understood at the time. The notable visual changes were later attributed to colloidal gold and silver nanoparticle alloys [9], leading to the eventual contextualization of the nanoscale light-matter interaction to become the field known as plasmonics. Plasmonics has been used across disciplines for sensing [10–12], imaging [13–15], photodetection [16–19], and energy applications [20–22]. In terms of sensing, plasmonics has been implemented in vibrational spectroscopy or refractometric sensing. For the former, this includes surface enhanced Raman spectroscopy (SERS), or surface enhanced infrared absorption spectroscopy (SEIRA) capitalizing on highly confined and enhanced electric fields in noble metal nanostructures to boost molecular vibration signals. In the latter,

which is the focus of this work, changes are detected in the dielectric medium within vicinity of the coherently oscillating surface plasmons. The use of surface plasmons for refractometry was demonstrated as early as 1983 to observe both gas concentrations and antibody adsorption on a thin metal film [23]. It would only be in 1998 when localized surface plasmons of colloidal gold nanoparticles were investigated for antibody binding studies [24].

Figure 2.1. The Lycurgus Cup in (a) reflected and (b) transmitted light. Image adapted from [9].

With coherent oscillations of electrons at the interface of two materials, localized plasmons can resemble dipoles, quadrupoles, or other more complex localized modes. It will be shown later that a requirement for this phenomenon to be observed is that the real part of the material permittivity should be changing in sign across the interface. After discussing the electromagnetic theory behind the various types of plasmons, we will explore some resonance characteristics as they relate to size and shape, followed by the application background and some experimental methods.

2.1.1 Electromagnetic Theory

We begin our study with an overview of the electromagnetic wave propagation that can be described by the well-known Maxwell's equations, in the so-called macroscopic formulation, which accounts for the bulk properties of the matter in which the waves may occur, and in differential form (vectors in bold):

$$\nabla \cdot \mathbf{D} = \rho_f \quad (2-1)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (2-2)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (2-3)$$

$$\nabla \times \mathbf{H} = \mathbf{J}_f + \frac{\partial \mathbf{D}}{\partial t}, \quad (2-4)$$

where $\mathbf{D}$ is the electric flux density in C/m², $\mathbf{B}$ is the magnetic flux density in T, $\mathbf{E}$ is the electric field intensity in V/m, $\mathbf{H}$ is the magnetic field intensity in A/m, and ρ_f [C] and $\mathbf{J}_f$ [A/m²] are the free (not bound) charge density and current density, respectively. If we assume time-harmonic fields with time dependence $e^{-j\omega t}$, then we may replace the time derivatives in Equations (2-1) – (2-4) with multiplication by $-j\omega$, where ω is the radian frequency and $j = \sqrt{-1}$, so that, for example, $-\partial \mathbf{B} / \partial t$ becomes $j\omega \mathbf{B}$. For a linear, isotropic, homogeneous medium, the constitutive relations which relate the field intensities to their corresponding flux densities are given by

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0(1 + \chi_e) \mathbf{E} = \varepsilon_0 \varepsilon_r \mathbf{E} \quad (2-5)$$

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) = \mu_0(1 + \chi_m) \mathbf{H} = \mu_0 \mu_r \mathbf{H} \quad (2-6)$$

where $\varepsilon_0 \cong 8.854 \times 10^{-12}$ F/m is the free space permittivity, $\mathbf{P}$ is the induced dielectric polarization density in C/m², χ_e is the electric susceptibility of the medium, ε_r is the relative permeability of the medium, $\mu_0 = \frac{1}{4\pi} \times 10^{-7}$ H/m is the free space permeability,

$\mathbf{M}$ is the magnetization of the material in A/m, χ_m is the magnetic susceptibility of the medium, and μ_r is the relative permeability of the medium, usually taken to be unity for non-magnetic materials. The relative permittivity and permeability are related to the phase velocity of light in a medium as $v_p = c/\sqrt{\mu_r \epsilon_r} = c/n$, where $c = 1/\sqrt{\mu_0 \epsilon_0}$, is the speed of light in free space, and n is the refractive index for a lossless medium.

In addition to Maxwell's equations and the above constitutive relations, another crucial relation between the electric field and the current density is given by Ohm's Law, $\mathbf{J} = \sigma \mathbf{E}$, where σ is the conductivity, in S/m, of a resistive material. Note that material resistivity $\rho = 1/\sigma$, and we could write $\mathbf{E} = \mathbf{J}\rho$, similar to the familiar Ohm's Law of circuit analysis, $V = IR$. To include the contributions of displacement and conduction current responses of the electric field, we may reformulate Equation (2-4), in time-harmonic form, as

$$\nabla \times \mathbf{H} = -j\omega \epsilon_0 \epsilon(\omega) \mathbf{E}, \quad (2-7)$$

in which we have defined the frequency-dependent complex dielectric function to be

$$\epsilon(\omega) = \epsilon' + j\epsilon'' = \epsilon_r + j\sigma/\epsilon_0\omega. \quad (2-8)$$

We may think of the real and imaginary parts of this dielectric function to represent the polarization due to bound charge and the current due to free charge, respectively, although this distinction may be less accurate at optical frequencies [25]. The real and imaginary parts of the complex dielectric function and the complex refractive index $\tilde{n} = n + j\kappa$, where n determines the phase velocity and κ determines the loss, are inter-related by the following equations:

$$\epsilon' = n^2 - \kappa^2 \quad (2-9)$$

$$\epsilon'' = 2n\kappa \quad (2-10)$$

$$n = \sqrt{(|\varepsilon| + \varepsilon')/2} \quad (2-11)$$

$$\kappa = \sqrt{(|\varepsilon| - \varepsilon')/2}, \quad (2-12)$$

where $|\varepsilon| = \sqrt{\varepsilon'^2 + \varepsilon''^2}$ is the modulus of the complex dielectric function. Finally, we may combine the curl equations to arrive at

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{r}, \omega) = \omega^2 \varepsilon_0 \varepsilon(\omega) \mu_0 \mathbf{E}(\mathbf{r}, \omega) \quad (2-13)$$

for the electric field (with an analogous version for the magnetic field). Using the vector identity $\nabla \times \nabla \times \mathbf{E} = \nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E}$, in the absence of external stimuli and with negligible change in the dielectric function over distances on the order of wavelength, we can rewrite Equation (2-13) as

$$\nabla^2 \mathbf{E}(\mathbf{r}, \omega) + \omega^2 \varepsilon_0 \varepsilon(\omega) \mu_0 \mathbf{E}(\mathbf{r}, \omega) = 0, \quad (2-14)$$

which is a starting point for the solution of wave propagation in many approaches.

2.1.2 Optical Properties of Metals

Many optical properties of metals can be understood in terms of a plasma model (also called the Drude dispersion model), in which stationary ions are surrounded by a moving cloud of conduction electrons with density n_e , mass m_e , and charge q_e . The characteristic resonance frequency of this system is known as the plasma frequency, given by $\omega_p = q_e \sqrt{n_e / \varepsilon_0 m_e}$. It is the spectral location of this frequency, typically in the ultraviolet (UV) for metals (respectively determined by their n_e), that gives metals their shiny, reflective appearance. The plasma model assumes that m_e accounts for some of the metal band structure, and that the electron motion is damped with a damping frequency $\gamma = 1/\tau$, where τ is the relaxation time, on the order of 10 fs at room

temperature. With these assumptions, we can write the Drude dielectric function for metals as

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + j\gamma\omega} , \quad (2-15)$$

where ε_{∞} is the high frequency permittivity, usually set to unity. The plasma frequencies (with corresponding wavelengths) and damping frequencies for some common metals are given below in Table 2.1.

Table 2.1 Plasma frequencies and corresponding wavelengths from some metals,
from model-fitting, from [26]

Metal	Ag	Al	Au	Cu
Plasma frequency, ω_p	2.18 PHz	3.57 PHz	2.18 PHz	1.79 PHz
Plasma Wavelength, λ_p	138 nm	84 nm	137 nm	168 nm
Damping frequency, γ	4.35 THz	19.8 THz	6.45 THz	2.19 THz

Light at frequencies below the plasma frequency, i.e. in the visible (wavelength roughly 400-700 nm) and infrared (IR, $\sim 700\text{nm}$ - $100\ \mu\text{m}$) is reflected due to screening, whereby the free electrons near the surface oscillate out of phase with the incoming electric field of the light. At frequencies above the plasma frequency, the electrons cannot react quickly enough for the incoming electric field, and the light is transmitted. When approximately all the visible light is reflected, we see a silver color, as is the case with silver, aluminum, platinum, etc. However, some metals, such as gold and copper, do not reflect all visible light, with interband transitions (light absorption) starting for wavelengths below $\sim 500\ \text{nm}$ and $\sim 600\ \text{nm}$, respectively, leading to their characteristic colors. The complex permittivities and dielectric constants of some of these metals are plotted below in Figure 2.2.

Figure 2.2. Permittivities and refractive indexes of several metals around the visible range, (a) permittivity, solid lines $\text{Re}(\epsilon)/10$, dashed lines $\text{Im}(\epsilon)$, and (b) solid lines n , and dashed lines $\kappa/10$, taken from [27] .

As seen in Figure 2.2(a), the real part of the complex permittivity for metals is negative in the visible (and longer) wavelength range. We will see in the next section that this is necessary for plasmon excitation at the surface of a metal and dielectric.

2.1.3 Surface Plasmons

Plasmons can be categorized as bulk (or volume) plasmons, surface plasmons, or localized surface plasmons. Because of their preferred use in refractometric sensing, we will focus only on the latter two.

The first type, surface plasmons (SPs), also known as surface plasmon polaritons (SPPs), may be excited at the interface between a flat metal surface and a dielectric. They propagate (with non-negligible loss) along this plane. To see how these waves follow from Maxwell's equations, we may start from the wave equation, Equation (2-14), with the substitution of the free space wavenumber $k_0 = 2\pi/\lambda = \omega/c = \omega\sqrt{\epsilon_0\mu_0}$,

$$\nabla^2 \mathbf{E}(\mathbf{r}, \omega) + k_0^2 \epsilon \mathbf{E}(\mathbf{r}, \omega) = 0, \quad (2-16)$$

commonly known as the Helmholtz equation. Without loss of generality, we assume the surface at $z = 0$, with dielectric (permittivity ϵ_d) for $z > 0$ and metal (ϵ_m) for $z < 0$,

with a wave which is independent of y and propagating in the x direction with wavenumber $\beta = k_{SPP}$, as shown in Figure 2.3. In this case we can write the spatial variation of our electric field as $\mathbf{E}(x, y, z) = \mathbf{E}(z)e^{j\beta x}$, and wave equation is

$$\frac{\partial^2 \mathbf{E}(z)}{\partial z^2} + (k_0^2 \varepsilon - \beta^2) \mathbf{E} = 0, \quad (2-17)$$

with a similar equation for the magnetic field $\mathbf{H}$.

Figure 2.3. Geometry for SPP propagation

To find explicit expressions for the field components, we may use the curl equations (2-3) and (2-4) which yields two sets of uncoupled equations, known as transverse electric (TE) and transverse magnetic (TM). The TM modes have only E_x , E_z , and H_y components which are nonzero, and the TE modes have only H_x , H_z , and E_y components which are nonzero. The TM equations are

$$E_x = -j \frac{1}{\omega \varepsilon_0 \varepsilon} \frac{\partial H_y}{\partial z}, \quad (2-18)$$

$$E_z = -\frac{\beta}{\omega \varepsilon_0 \varepsilon} H_y, \quad (2-19)$$

$$\frac{\partial^2 H_y}{\partial z^2} + (k_0^2 \varepsilon - \beta^2) H_y = 0, \quad (2-20)$$

which yield solutions in both half spaces

$$H_y(z) = A_i e^{j\beta x} e^{-k_i z}, \quad (2-21)$$

$$E_x(z) = jA_i \frac{1}{\omega \epsilon_0 \epsilon_i} k_i e^{j\beta x} e^{-k_i z}, \quad (2-22)$$

$$E_z(z) = -A_i \frac{\beta}{\omega \epsilon_0 \epsilon_i} e^{j\beta x} e^{-k_i z}, \quad (2-23)$$

where $i = 1, 2$ represents the medium. Matching the boundary conditions that tangential components of $\mathbf{D}(= \epsilon \mathbf{E})$ and $\mathbf{H}$ should be equal at $z = 0$, which requires that $A_1 = A_2$ and that $k_2/k_1 = -\epsilon_2/\epsilon_1$, meaning, importantly, that the two materials must have permittivities of opposite signs, or that if one region is dielectric ($\epsilon > 0$), then the other must be plasma/metal-like ($\epsilon < 0$). After a little more work, we can arrive at the dispersion relation of the propagating wave:

$$\beta = k_{SPP} = k_0 \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}}. \quad (2-24)$$

This is shown in Figure 2.4(a) for a Drude metal for two cases of dielectric material, air and silica. It can also be shown that there is no non-zero solution for the TE modes when we attempt solution in the same matter. Thus, only TM polarized light can excite SPPs. Of course, the wavevector cannot become infinitely large as suggested in Figure 2.4(a). When finite metal losses are considered, as for gold in Figure 2.4(b), we can see that the SPP wavevector indeed reaches a finite maximum.

Figure 2.4. Dispersion relation of Equation (2-24) for (a) the interface of a Drude metal with two dielectrics: silica (black) and air (gray). Solid (dashed) curves represent the real (imaginary) part of β . The straight lines are the light lines, i.e. propagation of light in the respective homogeneous media, reproduced from [25], and (b) the same but with material data for gold from Johnson and Christy [28]

Looking at the propagation constants $\beta = k_{SPP}$ (solid lines) for air ($\epsilon_d = 1$) and fused silica ($\epsilon_d = 2.25$) in Figure 2.4(a), we note that due to the bound nature of SPPs, the dispersion relations lie to the right of the respective light lines, meaning they have a larger wavenumber than in the bulk dielectric medium. Thus, in order to excite them, special phase-matching methods are required, such as a grating or a prism. Two common configurations for excitation with a prism include the Otto configuration [29][30], and the Kretschmann configuration [31], in which the SPP is excited between the prism and metal film or on the opposite side of a metal film in contact with a prism, respectively, as shown in Figure 2.5.

Figure 2.5. SPP excitation mechanisms: (a) grating coupled, (b) prism-coupled Otto configuration, and (c) prism-coupled Kretschmann configuration. Reproduced from [32]

The second type of plasmons considered here, known as localized surface plasmons (LSP) occur in metallic nanoparticles smaller than the wavelength of light. They consist of coherent oscillations of free electrons in such subwavelength particles. The resonance characteristics of the nanostructures, dependent on the permittivity of the metal and that of the surrounding dielectric medium, are also highly tunable through particle geometry. Particle geometries like nanospheres [33], nanorods [34], nanorings [35], and nanoholes [36] have been previously studied. The properties arise from the changing light absorption and scattering at different wavelengths. These properties form the basis of our investigation and are engineered for applications in biochemical sensing. A schematic of the basic concept of LSPR is shown in Figure 2.6.

Figure 2.6. LSPR concept - oscillation of electron cloud in a metal sphere with impinging electric field. Reproduced from [37]

In LSPR, the electron cloud of a metallic (or other plasma-like material) nanoparticle is resonantly excited at certain wavelengths due to the increased particle polarizability. These resonances give rise to enhanced near fields which are confined much more closely to the metal surface than SPPs, on the order of tens of nanometers as opposed to hundreds of nanometers in the optical frequency range. The simplest geometry to consider for LSPR is that of a spherical nanoparticle of radius a with dielectric function $\epsilon_m(\omega)$ embedded in a dielectric with dielectric function ϵ_d .

Assuming a radius much smaller than the wavelength of incident light ($k_0 a \ll 1$), the solution for the resonance frequency may be obtained in the quasi-static limit, solving Laplace's equation

$$\nabla^2 \Phi = 0, \quad (2-25)$$

where Φ is the electric potential with $\mathbf{E} = -\nabla\Phi$, subject to the boundary conditions at the surface of the particle:

$$\Phi_{in}|_a = \Phi_{out}|_a \text{ and } \epsilon_m \frac{\partial \Phi_{in}}{\partial r} \Big|_a = \epsilon_d \frac{\partial \Phi_{out}}{\partial r} \Big|_a, \quad (2-26)$$

The dipole moment of the particle can be written in terms of its polarizability α and the incident plane wave electric field intensity $\mathbf{E}_0$: $\mathbf{p} = \alpha \mathbf{E}_0$. It can be shown that the polarizability for such a nanoparticle is given by the expression

$$\alpha = 4\pi a^3 \epsilon_d \frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d}. \quad (2-27)$$

Moreover, the scattering and absorption cross sections can be determined as [38,39]:

$$\sigma_{sc} = \sigma_{geom} Q_{sc} = \sigma_{geom} \cdot \frac{8}{3} q^4 \left| \frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d} \right|^2, \quad (2-28)$$

$$\sigma_{abs} = \sigma_{geom} Q_{abs} = \sigma_{geom} \cdot 4q \operatorname{Im} \left[\frac{\epsilon_m - \epsilon_d}{\epsilon_m + 2\epsilon_d} \right], \quad (2-29)$$

where $q = k_0 a$ is a dimensionless size parameter, $\sigma_{geom} = \pi a^2$ is the geometric cross section of the sphere, and Q_{sc} and Q_{abs} are known as the scattering and absorption efficiencies. The resonance occurs when the denominator of Equations (2-27)-(2-29) is a minimum, i.e. when $\epsilon_m = -2\epsilon_d$, resulting in maxima for the scattering and absorption. For larger spherical particles, with size on the order of wavelength, Mie

theory may be used to obtain exact expressions for the scattering and absorption which include higher order (quadrupolar, octupolar, etc.) modes [40,41].

Few analytical expressions for resonant frequency or scattered spectrum exist for finite geometries other than spheres. Much experimental work has been done to determine general design rules for other structures such as nanodisks, with resonance wavelength dependent mainly on aspect ratio and with slight redshifting due to size-dependent retardation effects [42], and spherically-capped nanorods' resonance dependence on radius and total length [43], for example. A notable exception for the existence of exact analytical solutions other than spheres is oblate and prolate spheroids [44,45]. An expression for the axis-dependent dipolar polarizability similar to Equation (2-27) can also be obtained for ellipsoidal particles with semimajor axis half-lengths $j = a, b, c$ ($a > b \geq c$), namely [39]

$$\alpha_j = 4\pi \frac{abc}{3} \varepsilon_d \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_d + L_j(\varepsilon_m - \varepsilon_d)}, \quad (2-30)$$

where the geometrical factor $L_j = \frac{abc}{2} \int_0^\infty \frac{dq}{(j^2+q) \sqrt{(a^2+q)(b^2+q)(c^2+q)}}$, which is equal to $1/3$ when $a = b = c$.

The effects of elongation on the scattering efficiency of a prolate spheroid is illustrated in Figure 2.7(a). The main effects are a blueshift (inferred from larger $k_0 a = 2\pi a/\lambda$) and an increase in the maximum of the first, lowest order peak. The higher order maxima, due to constructive interference, are separated by $\sim 2\pi$. For reference, for visible light ($\lambda \sim 400 - 700\text{nm}$), $a = 150\text{nm}$ corresponds to $k_0 a$ values in the range of 1.35 to 2.36, whereas $a = 1000\text{nm}$ corresponds to $k_0 a$ values of 8.98 to 15.7. In Figure 2.7(b), the effect of prolateness on the resonance condition for excitation on both the long and short axes is shown. We note that these are the same for sphere, which has

$L_j = 2$ and a resonance condition of $\text{Re}\{\epsilon_m\}/\epsilon_d = 2$. Thus, we see that the resonance is strongly dependent on both geometry (aspect ratio) and material.

Figure 2.7. (a) The effect of prolateness on the scattering efficiency of spheroids for incidence angle of 0° (along major axis) with $\epsilon_m/\epsilon_d = 1.5$, reproduced from [44] and (b) Resonance condition as a function of L_j for prolate and oblate spheroids, reproduced from [46]

However, for larger particles, e.g. spherical particles with radius much larger skin depth $\delta = [\text{Im}\{k_0\epsilon_m\}]^{-1}$ (around 25-42 nm for gold and silver in the visible range) [47], the modes may behave more like surface modes than volume modes. They begin to behave more like SPPs, travelling over the surface. For example, for a silver sphere embedded in glass, considering the multipolar modes as SPPs quantized around the circumference (i.e. $2\pi r = m\lambda_{SPP}$) yields strikingly similar resonance wavelengths to that obtained via Mie theory for the higher order modes, as shown in Figure 2.8.

Figure 2.8. Comparison of Mie theory with quantization to an integer number of SPP modes propagating around the circumference of a silver sphere in glass. Reproduced from [48]

When considering substrate-supported nanostructures with height (away from substrate) comparable to incident wavelength λ , or even to λ_{SPP} , it is important to consider that the distance between the top (‘air’) side and the bottom (‘substrate’) is enough to support SPPs that travel up and down the structure, experiencing reflection at both the air and substrate interfaces, analogous to a Fabry-Perot (FP) cavity, illustrated in Figure 2.9. With the amplitude transmittances and reflectances shown, total amplitude transmittance is given by

$$t = e^{j\phi} t_1 t_2 \sum_{i=0}^{\infty} (r_1 r_2 e^{j2\phi})^i = \frac{e^{j\phi} t_1 t_2}{1 - r_1 r_2 e^{j2\phi}}, \quad (2-31)$$

where $\phi = k_0 n d$ in the general case and, in the case of SPP, $\phi = k_0 n_{eff} d = (\frac{2\pi}{\lambda_{SPP}} + j \frac{1}{\delta_{SPP}}) d$, where n_{eff} is the effective modal index and δ_{SPP} is the loss per unit length for the SPP. The transmittances t_1 and t_2 in the plasmonic case correspond to the (lossy) coupling coefficients from air into the nanostructure and from the nanostructure into the substrate, respectively. The reflectances r_1 and r_2 correspond to the complex reflection phases at the nanostructure-air and nanostructure-substrate boundaries. For a given

structure above a certain height, certain incident wavelengths should satisfy the phase-matching condition (constructively or destructively), yielding peak and dip features in the transmission spectrum. Similar results for in-plane SPPs have been observed in, for example, gold [49]. The FP resonances are part of the strategies for improving sensing in Chapter 4 and 5.

Figure 2.9. Fabry-Perot resonance (a) light enters the cavity through a mirror with amplitude transmittance t_1 , undergoing multiple round trips between mirrors with amplitude reflectances r_1 and r_2 , and exiting with transmittance t_2 , (b) phasor addition to final amplitude, and (c), intensity transmittance as a function of round-trip phase, adapted from [50]

As stated above, very few structures yield exact solutions for scattering spectra and resonance peaks. Simple structures such as nanorods and disks have some design guidelines, but changing the substrate, superstrate, or coating may cause drastic changes, which are difficult to analytically determine. As such, for modeling the LSPR properties of more complex geometries, computational methods are needed as well. These include the finite element method (FEM) [51], the discrete dipole approximation (DDA) [52], and the finite difference time domain (FDTD) method [53], which is used in this work. A good comparison of these techniques and more is found in [54].

2.2 Plasmonic Biosensing

In this section, we outline the performance metrics relevant to LSPR sensor design considerations, namely, bulk and surface sensitivity, and figure-of-merit.

Figure 2.10. Schematic representation of localized surface plasmon-based refractometric sensing. The attachment of analyte on the surface of a nanoparticle induces a change in the resonance wavelength, reproduced from [55].

2.2.1 Sensitivity

Sensitivity is a measure of the spectral resolution from an optical parameter (such as transmission or reflection) change caused by a refractive index shift of the dielectric medium. A higher sensitivity is understood to be a finer discrimination of dielectric medium changes. The bulk refractive index sensitivity (S_B) assumes a medium of infinite thickness surrounding the nanostructure, and is characterized by the linear relation:

$$S_B = \frac{\Delta\lambda}{\Delta n} \quad (2-32)$$

where S_B denotes the bulk sensitivity parameter, $\Delta\lambda = \lambda_n - \lambda_{ref}$, where λ_n is the resonance at refractive index n , λ_{ref} the resonance wavelength at reference, and Δn for the medium index changes. From the relation, $S \propto \lambda$, structures resonating in the longer wavelengths are expected to have higher S value. The origins of the relations can be found from the condition that the electric field excitation bound to metal nanoparticles satisfies the wave equation, Equation (2-13). With a medium change of $\Delta\epsilon$, the electric

field term is re-written as $\mathbf{E} = E_0 + E_1$ and a modified resonance frequency of $\omega = \omega_0 + \Delta\omega$. When solving for the surface integral at the quasistatic limit as a function of wavelength, S is simplified to [56]:

$$S_{Qs}^\lambda = \frac{\Delta\lambda_0}{\Delta n} = \frac{\lambda_0}{n} f \frac{2}{1+q} \quad (2-33)$$

where λ_0 refers to the resonance wavelength, n the refractive index of a dielectric bulk volume, f the ratio of energy within the sensing volume to the dielectric bulk (fill factor), and q the ratio of energy stored in the metal and dielectric. This establishes that LSPR sensitivity is only dependent on the resonance wavelength, independent of the nanoparticle geometry. Given the condition, the simplest strategy for which the LSPR sensor can be improved is to select geometries where the fill factor is maximized and resonating at longer wavelengths.

In terms of absolute numbers, the S_B of LSPR which can be on the order of 800 nm/RIU [57] appears unimpressive compared to SPR which can reach up to 10,000 nm/RIU. Yet because of the lower surface sensitivity of SPR, the magnitude of change at the surface for the two strategies is comparable [12,42,58], which is attributed to the variation in fractional occupation of molecules within the evanescent field. The tighter confinement of LSPs lowers its susceptibility to the background environment such as buffer conditions and temperature, which are more relevant for SPP.

Nevertheless, the bulk metric has been found insufficient in fully characterizing surface binding events. Instead of bulk, the spectral resolution is characterized with respect to the thin dielectric coating on the nanostructure surface with the surface sensitivity, expressed as [10]:

$$S_s = \frac{\Delta\lambda}{\Delta t} \quad (2-34)$$

where Δt refers to changes of the dielectric coating thickness. The expression assumes a homogeneously coated surface of constant refractive index, such as the n value for the biological molecule. However, surface coatings are more complex in practice. In addition to capture and target analytes, additional layers are typically included to increase specificity of the binding event. Differences in analyte (adsorbate) thickness layers are also attributed to the varying molecule size, which would also change the surface sensitivity value. Given the additional variable dependencies, Li et al. proposed the second order derivative of the spectral shift of an exponentially-decaying field [59] expressed as $S'' = \frac{\delta^2 \Delta \lambda}{\delta n_a \delta t} = \frac{2m}{l_d} e^{-2t/l_d}$ with n_a referring to the refractive index of the adsorbate layer, t the thickness of the adsorbate layer, m bulk sensitivity, and l_d the decay length of the evanescent field. The expression originates from the mathematical formulation to approximate the spectral shift from an adsorbate layer: $\Delta \lambda = m(n_a - n_{ref})(1 - e^{2t/l_d})$ [60]. The prefactor $2m/l_d$ refers to conditions when the adsorbate layer thickness is zero and the inverse proportionality indicates that the second order surface sensitivity is largest when bulk sensitivity is largest with the smallest decay length.

2.2.2 Linewidth, Q-Factor, and Figure-of-Merit

Whereas sensitivity does not take into account the spectral feature being tracked, a dimensionless figure-of-merit (FOM) is used to account for the spectral linewidth, taken as the full width at half maximum (*FWHM*), where a smaller *FWHM* value is preferable for determining the resonance shifts. This measure is expressed as the ratio of sensitivity with the linewidth:

$$FOM_B = \frac{S_B}{FWHM} \quad (2-35)$$

Due to the strong radiative damping of metals, plasmon resonances typically exhibit broad linewidth, effectively reducing the Q-factor as well [61]. Q-factor, defined as $\lambda_0/FWHM$ is a measure of a resonator quality, where a higher Q-factor value corresponds to lower damping and longer oscillatory behavior.

As with differences in bulk and surface sensitivity, the FOM can be adapted to consider its performance within the analyte region as $FOM_S = S_S/FWHM$. The parameters as shown contribute to the considerations of an LSP-based plasmonic sensor design.

2.2.3 Practical Biosensor Considerations

Several methods have been demonstrated for realizing plasmonic nanostructures, such as with colloiddally synthesized nanoparticles [8,62]. Early LSP sensing works typically studied the geometrical dependence and effects of field localization on the sensitivity resulting in comprehensive studies of solution-based spheres [63,64], rods [65–68], cubes [69–71], rice [72–74] and stars [75–78] demonstrated, amongst others. Wet chemistry (colloidal synthesis) methods are attractive for their simplicity, good performance, cost-effectiveness, and scalability. Notably, because of the availability of the entire sensing volume for analyte-binding, solution-suspended nanoparticles have been reported to achieve sensitivities of up to 408 nm/RIU in the visible range [79]. For sensing, substrate-supported nanoparticles or structures are preferred from a practical point-of-view. Nanoparticle suspensions, owing to their thermodynamic instability, are susceptible to aggregation with changing solution conditions [80]. These condition changes, such as in pH, ionic equilibrium, or temperature, are inevitable in both specific

and non-specific molecular binding events of analytes or other molecules. In turn, aggregation-induced near-field coupling of suspended nanoparticles modifies the optical response which would adversely affect the refractometric sensing performance on two fronts. First, the stochastic nature of aggregation can introduce significant size dispersion to the resonance wavelength and therefore, attainable sensitivity, where refractive index sensitivity is linearly related to the resonance wavelength. Secondly, near-field interactions introduce spectral broadening of the linewidth [81,82]. The repercussions would then be reflected in the Q-factor and FOM. By contrast, smaller linewidths are necessary, in pursuit of a high performance sensing platform, to obtain higher Q-factors and FOM. Although this aggregation may not be suitable for refractometry, this feature has been exploited for colorimetric aggregation-based sensors [83].

On this basis, the scope of this work is limited to substrate-supported nanostructures, where planar sensors can facilitate in-flow type assays, binding kinetic analysis, surface regeneration, and multiplexed analysis. Substrate-supported nanostructures tend to have lower sensitivities compared to colloidal nanoparticles, known as the substrate effect, due to lower surface contact area and substrate refractive index [84]. The extent of sensitivity reduction is dependent on the fractional contact area of the structure with the substrate, where larger contact lowers the sensitivity more, owing to a reduced sensing volume. However, considering its merits, the shortcomings of substrate effects and can be compensated by appropriate nanostructure engineering.

Finally, an important consideration in plasmonic sensing is the specificity and selectivity of the analyte detection. Specificity refers to the affinity of the biological species used to bind the analyte. While affinity is an intrinsic molecular characteristic, the evanescent decay length should be sufficiently long to prevent signal saturation

before analytes can be introduced. For example, antibodies are typically 14.5 nm x 8.5 nm x 4 nm [85] in size. Immobilization can be achieved by covalent bonding, where the surface is modified with thiol- or amine groups, with high affinity to gold, attached on the substrate [86]. In the second case, selectivity refers to the confinement of bioactivity to be within the functional sensor area. In analysis of mixed media, as is the nature of biological media, non-specific binding may occur due to methodological reasons which amplify undesired background signals. These arise from protein-protein interactions, denaturation, adsorption of background molecules, or non-specific electrostatic binding on the surface. Refractometric sensing does not discriminate between analyte and background signals, therefore prevention of non-specific adsorption is necessary to attain high selectivity and reduce false positive signals [87]. In other words, inactive sensor areas should be inert to non-specific binding. This can be accomplished by using anti-fouling agents such as bovine serum albumin (BSA, dimensions: 14 nm x 4 nm x 4 nm [88]), by inhibiting adhesion of certain molecules (e.g. water-soluble molecules like antibodies) using polymer layers (ranging in length between 0.35 nm – 6 nm [89] according to density), or self-assembled layers [90]. For all cases, the immobilization procedure should take into account the surface conditions of the nanoparticle and substrate. As such, the plasmonic structure should account for these layers which contribute crucially to its overall detection performance.

2.3 Methods

2.3.1 Numerical Analysis

Numerical analysis was employed to approximate the near- and far-field optical responses of complex structures which cannot be solved analytically. For this work, the

finite difference time domain (FDTD) method was employed using a commercial simulation software (Lumerical, Inc.). The basis of the FDTD method is to solve a set of Maxwell's curl equations in the time domain, corresponding to field components based on a discrete spatiotemporal grid. Each field component is solved in a different position of the grid cell, termed the Yee Cell. The six components of the electric and magnetic field components are solved for in slightly different positions of the Yee cell, shown in Figure 2.11 with collected data interpolated to the grid point origin. The process is iterated until convergence is reached.

Figure 2.11. The Yee cell used in Lumerical FDTD, with various field components calculated at slight offsets from the grid point origin. Reproduced from [91]

Examples of the computational domain used in the study are shown in Figure 2.12, consisting of plane (Bloch/periodic or BFAST) or TFSF source, sample, boundaries, monitors, and analysis groups. The sample consists of a single unit cell of on a substrate. Following the experimentally characterized structures, all structures are simulated as periodic in the x and y directions, with simulation region x and y spans set to the respective periodicities. If the structure exhibits symmetry with respect to the source, then (anti-)symmetric boundary conditions are used appropriately to reduce the simulation time by a factor of two to four. This is shown in Figure 2.12 for the case of

the 150nm height dimer simulations for an x -polarized (polarization angle of 0°) source, where the x boundaries are set to be anti-symmetric (AS) and the y -boundaries are set to be symmetric. In all cases, the FDTD region has a z -span defined such that, at a minimum, moving the z boundaries farther away from the nanostructure has no effect on the obtained results. In general, for measuring transmission, a plane wave Bloch/periodic source is launched in the $-z$ direction from above the structure, with transmission measured by a z -normal monitor in the substrate. For measuring absorption and scattering cross sections (and hence extinction cross sections and radiation efficiency), a normally-incident total-field scattered-field (TFSF) plane wave broadband source is used along the z -direction, with the launch and absorb planes each surrounded by monitors belonging to an analysis group to calculate the cross sections. This is similar to the cross-section analysis group available in the software; however, since these structures are periodic, there is no need for lateral faces for the absorption and scattering boxes, only for the tops and bottoms, which extend to the boundaries of the FDTD simulation region. Generally, a conformal graded mesh, with maximum mesh size set to $dx=dy=dz=2$ nm, is used, while a refined mesh override region is applied in smaller sections of the unit cell, such as narrow regions (V-shape apex, dimer gap), and set to $dx=dy=1$ nm. A perfectly matched layer (PML) of standard profile was used in the z -direction for all cases as an absorbing boundary to minimize unwanted reflections. The simulation time was set to either 600 fs (default) or 1000 fs.

Figure 2.12. Examples of simulation in Lumerical FDTD for a 150 nm-tall square dimer using symmetric (labelled S) and anti-symmetric (labelled AS) boundary conditions, (a) measuring transmission and (b) measuring cross sections

The materials used in the simulation consisted of gold (Au), silicon dioxide (SiO_2), and generic dielectric. The gold material used 6 coefficients to fit the Johnson and Christy [28] data with a fit tolerance of 0.1. This material data fit, rather than other material models such as plasma, was found to correlate the best with experimental results. The silicon dioxide was modelled as a lossless nondispersive dielectric ($\epsilon=2.14$) based on the data from Palik [92]. Generic dielectric material (with various indexes n) was used to model both bulk analyte and surface analyte materials, with the latter set to extend a thickness t from all exposed nanometallic surfaces, for bulk and surface sensing simulations. The FDTD region was set to have a background index of 1 (air).

Throughout this work, transmission measurements are used to characterize sensing performance features akin to the experimental process. A rectangular superstrate is used to model immersion of the structure in dielectric medium of refractive index n , as with bulk sensing. For surface sensing, a uniform analyte layer of n with thickness t , is conformal to the unit cell. In the computation domain, this is represented as a dielectric layer in the shape of the structure. The numerical assessment of sensing performance models an ideal case of a uniform layer. It should be noted that practical sensing consists

of a number of layers (functionalization, capture, blocking, and analyte layers) of differing refractive indices and thicknesses whose parameters are dependent on the targeted analyte species. In practice, practical variations may arise from molecular binding efficiency (target binding per particle) and molecule characteristics like geometry, molar mass, or dielectric properties which are not represented in the simulation. Sub-optimal layers from non-uniform coating or binding would affect the observed performance. For example, antibodies which are routinely used as capture agents, are Y-shaped proteins that need a specific orientation to maximize antigen-binding sites at tips (epitopes). Experimentally, site-specific orientation onto target surfaces is highly process-dependent on factors such as pH of buffer solution used [93].

2.3.2 Optical Characterization

Scanning electron microscopy (SEM) using the Raith e-Line was used to characterize nanostructural features such as width, length, height using normal and oblique incidences ($25^\circ, 45^\circ$). For insulating substrates, a conductive polymer (ESPACER) coating was used prior to scanning. Structures were probed using a 10 keV beam at magnification between 50,000X-150,000X. After imaging, the conductive polymer coating was rinsed with DI water and dried using a nitrogen gun when applicable.

Figure 2.13 A schematic diagram of the hyperspectral optical characterization setup. A broadband source is used, with 10X or 50X objective lens.

The transmission measurements were conducted with a microscope system based on bright-field geometry for optical characterization measurements. The sample was illuminated from the bottom by a broadband halogen lamp focused through a condenser and actuated using a piezo-controlled stage. Polarization-resolved measurements were carried out by placing a polarizer before the condenser (for the source) and an analyzer before the hyperspectral imaging system (for the detector). The scattered light was collected through an objective lens (10X, NA=0.3; 50X, NA = 0.55) into a hyperspectral imaging system (Cytoviva) creating a spectroscopic image of various plasmonic nanostructures within the field of view. Spectroscopic information was recorded through the diffraction grating for line scans of the sample. The spectrum was averaged with a 10 x 10 or 20 x 20 window. Transmittance was obtained by normalizing the transmitted signals of the plasmonic nanostructures with that of the substrate. A diagram of the setup is shown in Figure 2.13. ENVI 4.4 software was used to collect spectral information.

2.3.3 Nanofabrication

In this subsection, the nanofabrication approaches used for this work are introduced. All nanopatterning are conducted by electron beam lithography (EBL), followed by metal deposition. For the planar structure in Chapter 3, electron beam evaporation is used, while for tall structures in Chapter 4 and 5, electrodeposition is used. To this end, we collaborated with the group of Professor Zhang Dao Hua, whose nanofabrication capability helped realize the nanostructures used in this work.

Nanopatterning was conducted by electron beam lithography (EBL) for sub-100 nm resolution and more precise spatial and geometrical control. The prevailing cost-effective nanofabrication technique is recognized as nanosphere lithography for its ability to achieve wafer-scale templating, as demonstrated circular split-ring resonator geometries [94]. Nevertheless, as shown previously, control of position, size, and geometry remains challenging. This exploration is included in the Appendix. The nature of serial patterning, as with EBL and FIB, will always be slower than physical mask-based processes. To address concerns on the cost-effectiveness and throughput of the method, an optimized patterning process has been developed and demonstrated to realizing sub-15 nm patterning capability with the possibility of writing up to 250,000 elements in 5 mins [95,96]. The small footprint used for the arrays minimizes the long e-beam writing process where for our application, large areas are not required. Typically, higher e-beam doses and longer writing times are required with sub-30 nm feature sizes [97]. A cold-sonicated development process was used to circumvent this, facilitating low e-beam dosage (400 pC/cm^2). The typical area of the nanostructure arrays is $100 \text{ }\mu\text{m} \times 100 \text{ }\mu\text{m}$. The writing time of 25 patterns of this area requires about 6

minutes, including markers. The writing time of a $10\ \mu\text{m} \times 10\ \mu\text{m}$ footprint array of moderately-complex nanostructures can be deduced to be approximately 15 seconds. To further reduce the resource burden of EBL-based methods, several strategies can be implemented to reduce the cost of the EBL-based process towards practical applications in the future. For example, nanoimprint lithography may be used. Due to resource limitations, the exploration of such strategies is beyond the scope of the current work.

After patterning the resist, deposition of gold film in this work is achieved using either (a) e-beam evaporation or (b) electroplating. Schematics of the two deposition methods are shown below in Figure 2.14.

Figure 2.14. Methods of metal deposition. (a) e-beam evaporation and (b) electrodeposition

E-beam evaporation is a physical vapor deposition process atomically depositing materials within a vacuum chamber [98]. The target material inside a crucible is bombarded by an electron beam with an accelerating voltage of a few kV and a beam current of tens of mA. The sample is inverted and affixed to a rotating chuck inside a vacuum chamber, which must pump down to a sufficient level, less than 10^{-5} torr, before the electron gun is turned on. The sublimation of the material transforms it into the gas phase, and the atoms precipitate on a surface to deposit a thin layer of material. The beam current determines the deposition rate, which in turn determines the final

deposited thickness, for a given time, and the size and shape of the deposited material grains. Although it is a prevailing deposition method, evaporation has inherent limits on the achievable structural height. Typically, the height cannot exceed $\sim 1/3$ of the resist thickness; otherwise, lift-off, i.e. subsequent removal of the resist covered with metal, may be unsuccessful due to the lack of discontinuity between the respective metal films on the substrate and resist.

Electroplating, also known as electrochemical deposition (or electrodeposition for short), is the other method used metal deposition in this work. At a minimum, it requires two electrodes, separated by an aqueous electrolyte solution containing ions of the metal to be deposited. The anode is made of metal that oxidizes and goes into solution when current or voltage is applied to it, while at the cathode, which is to be coated, the following general reaction takes place [99]:

where M is any metal with valence z , and the subscripts (aq) and (s) denote the aqueous metal ions in the electrolyte and the solid metal in the deposited coating, respectively. In our case, the anode is a platinized titanium mesh, and the cathode is the EBL-patterned ITO-coated glass substrate.

Some electroplating setups make use of a third electrode, known as a reference electrode, which has a standard potential against which other metal ion electrochemical reactions are measured. This is especially useful for potentiostatic (constant potential) electroplating, where the total overpotential required to force the reaction may increase between the anode and cathode to effects such as charge transfer, diffusion, reactions, and crystallization [99]. The electroplating done in this work utilizes pulsed

galvanostatic (constant current) deposition, for which a reference electrode is not required.

For a constant current, if we assume that each (single if $z = 1$, pair if $z = 2$, etc.) electron passing through the electrodes translate to a metal ion deposited on the anode, then we can write the mass of metal deposited as

$$m = \frac{Q M}{F z} , \quad (2-37)$$

where Q [C] is the total amount of passed charge, M [g/mol] is molar mass, $F = 96485$ C mol⁻¹ is the Faraday constant, and z is the metal valence as above. If we pass a known current I for a time t , then we can replace Q with It . Moreover, rewriting mass as the product of density ρ and plated volume V , or more specifically as the product of density and plated area A times plated thickness d , $m = \rho V = \rho A d$, we can write the theoretical maximum plating rate, for example in units of nm/s, in terms of thickness for a given time, as

$$rate = d/t = J \left(\frac{M}{F z \rho} \right) , \quad (2-38)$$

where $J = I/A$ is the current density, for example, in units of mA/cm².

For gold, which is the metal used in this work, the molar mass is 196.97 g/mol, its valence is 1, and its density is 19.32 g/cm³. From Equation (2-38), this means that the plating rate is given by current density times 1.0567×10^4 cm³/C, equivalent to about 1.06 nm/s per mA/cm². We note that this rate is only approximate. In this work, the structures to be electrodeposited occupy a footprint on the order of μm^2 , rather than cm², meaning that the required current should be on the order of nA or pA. In order to have

better control over the current density, the nanopatterns were deposited in parallel with a bare sacrificial “dummy” substrate of a known area $A_{dummy} \gg A_{nano}$, such that

$$J = \frac{I}{A_{dummy} + A_{nano}} \cong \frac{I}{A_{dummy}} , \quad (2-39)$$

It was found that a current density of 3mA/cm² and square pulses with period 0.4 s and duty cycle 25% yielded the best structures and the parameters used in the work.

Chapter 3 MAGNETICALLY-RESONANT SPLIT RING

RESONATORS IN THE VISIBLE SPECTRUM

Strong light localization within metal nanostructures occurs by collective oscillations of plasmons in the form of electric and magnetic resonances. This so-called localized surface plasmon resonance (LSPR) has gained much interest in the development of low-cost sensing platforms in the visible spectrum. However, demonstrations of LSPR-based sensing are mostly limited to electric resonances due to the technological limitations for achieving magnetic resonances in the visible spectrum. In this work, we report the first demonstration of LSPR sensing based on fundamental magnetic resonance in the visible spectrum using ultrasmall gold v-shaped split ring resonators. Specifically, we show the ability for detecting adsorption of bovine serum albumin and cytochrome c biomolecules at monolayer levels, and the selective binding of protein A/G to immunoglobulin G.

3.1 Introduction

Split-ring resonators (SRRs) have been implemented in sensing applications for their versatility in exhibiting magnetic and electric resonances which are directly tunable based on their geometrical parameters. Conventionally, SRRs are represented by as an open loop with a single slit, akin to u-shape, where the arm tips behave as parallel plate capacitors. The magnetic mode is the fundamental resonance mode of an SRR induced from the generation of circulating current around the SRR, arising from tip-to-tip dipole oscillations of the arms under excitation [100]. Despite the stronger electric field

enhancement and the higher sensitivity of the magnetic resonance, most LSPR sensing experiments are done with electric resonance modes. This is because the electric modes, as higher order resonances, are typically located in the visible spectrum, which is the recommended spectrum for biosensing experiments as most optical interrogation phenomena occur within this spectrum. In addition, working in the visible spectrum aligns with low-cost sensing platforms that utilize low-cost light sources and detectors.

The magnetic resonances, on the other hand, are typically located in the infrared region [95,101,102]. Recently, LSPR sensing based on magnetic resonance has been demonstrated in the near-infrared spectrum [103], but scaling SRRs to the visible spectrum has been difficult due to its stringent requirements of the resonator critical dimensions on the order of tens of nanometers. In this work, we demonstrate magnetic resonance-based LSPR sensing in the visible spectrum using ultra-small gold v -shaped SRR (v SRR) structures, as shown in Figure 3.2(a). The v SRR structures were fabricated by electron beam patterning followed by a sonicated cold-development process that has been developed previously to fabricate ultra-small resonators at low exposure dose [97]. The resonance characteristics of a v SRR are tunable by its opening angle and arm length, and further demonstrate its sensing capability at 131 nm/RIU sensitivity in the visible spectrum.

Generally for SRR structures, there exists magnetic and electric modes, whose excitation is determined by the incident electric field. The magnetic mode refers to the magnetic field localization within the SRR opening area and strong E -field across the SRR tips, while the electric mode refers to the E -field localization at all three vertices. SRRs can be understood via an “ LC -circuit” analogy [26], where the capacitance (C) and inductance (L) are defined by the SRR gap and metal wire, respectively Figure 3.1. An incident electric field can couple to the LC resonance when it has a component

normal to the capacitor plates, or if the magnetic field vector has a component normal to the plane of the coil. The coupling of the incident electric field is polarization dependent. As such, when the incident field is parallel to the gap, charges can accumulate on either side of the gap, and a circulating current is induced in the loop. This circulating current induces a magnetic field perpendicular to the plane of the SRR, generating an LC resonance in which the magnetic dipole moments are the product of a circulating current, coil, and plate capacitor. Meanwhile, when the incident electric field is polarized perpendicular to the gap, there is an absence of LC resonance, as the electric field cannot couple to the capacitance. There is, however, still resonant behavior occurring; it is simply the plasmon resonance [104].

Figure 3.1 (a) Schematic of a typical u-shaped split ring resonator and (b) analogy of LC circuit resonance observed for magnetically-resonant nanostructures.

Based on the equivalent circuit analysis, the magnetic mode is analogous to the oscillation frequency (ω_0) of the LC circuit, $\omega_0 \approx 1/\sqrt{LC}$. By this, for higher frequency resonances towards visible range wavelengths, the inductance and capacitance parameters should be reduced. If we consider a simplified model of a conventional u-shaped loop (u-SRR) as parallel plate capacitor it is found that the $L \propto \text{arm length}$, while $C \propto 1/\text{gap distance}$ [105]. Linear geometric scaling is applicable when metals behave as ideal conductors (e.g. microwave frequencies) and electron kinetic energy is

negligible. At high frequencies, the effects of electron kinetic energy (kinetic inductance) dominate over inductive energy and lead to saturation of the magnetic response [106][107]. Fundamentally, the upper frequency limit arises from the bulk plasma frequency of the metal. As linear scaling breaks down, the magnetic resonance with respect to scaling saturates is dependent on the characteristics of the particle geometry, such as number of gaps which modify the total capacitance [106].

3.2 Methods and Materials

3.2.1 vSRR Fabrication and Characterization

For the v-shaped structures in Figure 3.2(a), the unit cells were designed with opening angles of $\theta = 30^\circ, 40^\circ, 60^\circ$, and 90° , and arm lengths of $s = 50, 60, 70, 80$ nm. The range of opening angles considers the magnetic-electric mode, as opposed to angles at the extremities $\theta = 0^\circ$ and $\theta = 180^\circ$ (as with nanorods), where the mode is purely electric with weak electric field confinement. Due to the proximity of the arms with the smallest angular opening of $\theta = 30^\circ$, a lateral offset of $d = 12$ nm and $d = 14$ nm was included in the cell design to compensate for fabrication limitations in the lithographic process which, for decreasing feature sizes, subjects the pattern to a higher degree of proximity effects.

Although vSRRs based on aluminum have been previously fabricated with fundamental magnetic resonance covering the entire visible spectrum [108], gold was instead chosen as the constituent material due to its biocompatibility, chemical stability, and ability to attach biomolecules [109]. A series of periodic vSRR arrays were

fabricated using electron-beam lithography (EBL) for pattern definition and e-beam evaporation for metal deposition, followed by lift-off. Each square lattice iteration had a $100 \mu\text{m}^2$ footprint, with all patterns within a $100 \mu\text{m} \times 100 \mu\text{m}$ space. The lattice constant a_{xy} denotes the periodicity of the structures and was fixed as $a_{xy} = 2s$. The total writing time for all the resonator designs within the footprint (including reference markers) was approximately 4 minutes. A cold-sonicated process was used during the development step. Then, using e-beam evaporation, a 30-nm-thick Au film was deposited with a 2-nm-thick titanium film as an adhesion layer. The process was followed by lift-off pattern transfer where the sample was soaked in N,N-dimethylacetamide (ZDMAC) solution for 10 minutes at 70°C . Characterization was conducted using a hyperspectral imaging system as shown in Figure 3.3. Microscope images of the vSRR array reflection and transmission under orthogonal polarizations are shown.

Figure 3.2 (a) Schematic of vSRRs and SEM images for design variations. The bottom shows a larger-scale view of 30 nm gold $\theta_{60}s_{70}$ vSRR structures and nominal period of 140 nm . Scale bars are 100 nm . (b) Simulated (top) and experimental (bottom) spectra for $\theta_{60}s_{60}$ vSRR structures excited with a normally incident broadband source x- (blue) and y-polarized (red). Simulated resonance wavelengths were observed at 597 nm and 733 nm for the electric and magnetic modes respectively, while experimental resonances were 572 nm and 661 nm . The simulated resonances are with insets showing corresponding H_z fields and dipolar coupling.

Figure 3.3 (a) A schematic diagram of the hyperspectral microscope used for characterization and (b) post-scan images of the vSRR arrays using x - and y -polarized illumination in reflection and transmission mode.

3.2.2 Bulk Sensing Characterization

To determine bulk sensing performance, the experimental sensitivity was characterized by $S = \frac{\Delta\lambda}{\Delta n}$. Shifts for λ_R were obtained for different refractive index claddings and the sensitivity parameter is given by the slope of the best fit line to these points along with the reference point ($\Delta n = 0, \Delta\lambda = 0$). The sensor was immersed in a custom polydimethylsiloxane (PDMS) holder with varying glycerin–water mixtures ($n = 1.3370, 1.3539$) and immersion oil ($n = 1.510$) and the corresponding transmission dip shift $\Delta\lambda$ determined with respect to reference measurement. The x -polarization, corresponding to the magnetic resonance, was used for all measurements with an exposure time of 25 ms. Surfaces were cleaned with isopropyl alcohol. Prior to measurements, the resonance wavelength of the cleaned surfaces was re-measured in air, with the as-fabricated resonance used as the reference.

3.2.3 Biosensing

Adsorption of biomolecules to the sensing surface was measured to estimate the analyte thickness. Bovine serum albumin (BSA, MW: 65 kDa) and cytochrome *c* (cyt *c*, MW: 12 kDa), recombinant protein A/G (MW: 50.46 kDa), and human IgG protein (MW: 150 kDa) solutions were reconstituted in phosphate buffered saline (PBS) according to manufacturer instructions. The stock solutions were serially diluted (BSA: 15 μ M, 75 μ M, 150 μ M; cyt *c*: 833 pM, 83.3 nM, 83.3 μ M), drop-cast over the sensor surface and allowed to dry in ambient temperature. All measurements were taken in air.

For specific binding measurements, the surface was cleaned using a 3:1 ratio of piranha solution (sulfuric acid, H₂O₂; hydrogen peroxide, H₂SO₄) and rinsed in DI water. For functionalization of protein A/G (1 mg/ml) and IgG (1 mg/ml), the sample was loaded in a custom-built mesh holder, submerged in the solution and suspended over a stirrer bar to introduce a gentle stirring. After each step the sample was thoroughly rinsed with PBS and allowed to dry in ambient temperature before measuring in air.

3.2.4 Numerical Analysis

The ν SRR structures were numerically studied by finite difference time domain (FDTD) simulations, where silicon dioxide (SiO₂) was used as the substrate with ν SRRs of 20 variations based on the half-angle opening and arm length. The lateral dimensions of the FDTD region were twice the ν SRR arm length, and periodic boundary conditions were used. Transmission below the structures were recorded from a normally-incident plane wave source above the structures. Dielectric functions of gold (Au) and SiO₂ were based on the experimental data of Johnson, Christy and Palik, respectively.

3.3 Results and Discussion

3.3.1 Plasmonic Characterization of Magnetically-Resonant Structures

Magnetic resonances have been reported in various geometries in the literature include shapes such as u-shapes, and cut ring resonators [100,110]. In this study, v-shaped geometries are used for spectral simplicity and tunability. The geometry can be considered a special case of u-SRR, instead with a bottom arm length of zero and angled vertical arms of mirror symmetry functioning as an open loop. The capacitance can be tuned by adjusting the opening angle, where smaller angles are associated with lower capacitance and higher electric field confinement. In addition to reducing resonator dimensions, the absence of a bottom arm lowers inductance (blue-shifting the resonance) and prevents the excitation of higher order magnetic modes in the region of interest. This simplifies the response to a single mode, which is preferred for biosensing. By contrast, the u-SRR magnetic resonance includes higher order modes attributed to the bottom arm (see Appendix). Considering high frequency target range, feature sizes were chosen to be larger than 45 nm, which is in line with observation of kinetic inductance saturation at optical frequencies [111].

The spectrally-unique arrays can be seen in Figure 3.3(b) for reflection and transmission measurements qualitatively convey the differences of x - and y -polarization modes. Scanning electron microscopy (SEM) images of the experimental vSRR structures are shown in Figure 3.3(a), along with angular variants. The fabricated patterns generally demonstrated good pattern fidelity with uniform periodicity. The arm widths w of the fabricated patterns was between $\sim 27 - 31$ nm, while s values were

between $\sim 48 - 75$ nm. These figures fall within the expected range, accounting for fabrication process variability. The variations in the dimensions are expected to contribute to some inhomogeneous broadening in the spectrum.

The electric dipole coupling along the two arms of the vSRR results in two resonance modes. In the magnetic mode (x -polarization, 0°), the antisymmetric dipolar coupling results in a circulating current due to capacitive interactions between SRR edges, leading to the occurrence of a magnetic dipole. On the other hand, the symmetric dipolar coupling with y -polarization (90°) leads to an oscillatory behavior along the arms that has a zero-net magnetic moment, resulting in the electric mode. Practically, this anisotropic behavior translates to a shorter resonance wavelength λ_R (characterized by the transmission dip in the spectrum) for the electric mode, compared to the magnetic mode, as seen in Figure 3.2(b), and is consistent with the simulated spectra. To understand the localized field enhancement, the field distributions from the numerical simulations are observed. The so-called “lightning-rod effect” gives rise to electric fields are strongest at sharp features such as tips and corners. The proximity of such sharp features can further increase the localization enhancement, generating electric field “hot-spots”. In the context of vSRRs, this property is tunable by narrowing the opening angle. The intensity distributions shown in Figure 3.4(a) indicate that at smaller opening angles, tighter electric field confinement is observed as there is a reduction in the capacitive impedance. The higher electric field confinement further corresponds to an increase in the magnetic dipole strength. At $\theta = 30^\circ$, the magnetic field H_z is confined within the inner gap of the vSRR. As the opening angle widens towards $\theta = 90^\circ$, the field distribution expands from its gap confinement and is observable at the inner apex and edges of the longitudinal arms. The intensity at the edges in the E_y fields tend toward the outer boundaries and minimally contributes to the spectrum. The

intensity distribution of E_x follows, where the confinement is no longer within the bounds of gap as θ widens. Thus, we can conclude that the larger field confinement permits the dominance of a magnetic mode. In all cases of $\theta = 30^\circ$ - 90° , the magnetic moment is supported. With widening θ , the electric mode takes over and as the structure approaches a pure nanorod, and the magnetic dipole is no longer supported.

Figure 3.4. Optical characterization of vSRRs in the x-polarization. (a) The numerically-obtained electric field distribution of components with respect to opening angle indicates greater field confinement within the gap of smaller opening angles. Experimental transmission spectra of θ_{60} structures for s values red-shifts the resonance wavelength with (b) longer arm length and (c) greater opening angle.

Tracking λ_R with respect to the resonator size and opening angle (for $\theta > 30^\circ$) shows a linear relationship. As seen in Figure 3.4(b), as s increases, λ_R accordingly red-shifts. The experimental trends agree with theoretical results which show a red-shifting trend with increasing s and wider θ . One noticeable spectral difference between the polarization configurations is that the y-polarization exhibits a smaller dynamic range of λ_R than the x-polarization. The most prominent resonance differences occurred with structures of larger angular openings such as $\theta = 60^\circ$ and $\theta = 90^\circ$ in x-polarization, with a difference of up to 66 nm. The shortest resonance occurred for $\theta_{40}s_{50}$ at 565.6 nm, while the longest was found to be 835 nm for $\theta_{90}s_{80}$. Figure 3.4(c) shows that for a longer s and widening θ , a longer λ_R can be expected, indicating tunability offered by structures. According to the trends, with θ_{30} structures having the smallest opening angle, these structures would have shortest resonance wavelength. However, the addition of a lateral offset affects the intrinsic resonance characteristic of the vSRR, and

does not follow the linearity of the vSRRs without a lateral offset. The lateral offset effectively yields a permutation of the conventional u-shape SRR, having an additional magnetic resonance not seen with strictly v-shaped SRRs. Thus, $\theta_{30}d_{12}$ is seen to have longer wavelengths than θ_{40} structures, despite the smaller opening angle. This spectral characteristic was seen in both experimental and simulation results. Experimentally, there is a minimal difference in the resonance characteristics of $\theta_{30}d_{12}$ and $\theta_{30}d_{14}$, suggesting that the fabricated structures bear close resemblance due to the limits of our fabrication process.

In addition to λ_R , we also consider the spectral contrast of the resonance dip in the transmission spectrum. The contrast describes the signal-to-noise ratio of the sensor and is defined as $C = T_{peak} - T_{dip}$, where T_{peak} is the lower of the local maxima surrounding the absolute minimum T_{dip} . The spectral responses for y-polarized light consistently yielded lower contrasts than for the corresponding x-polarizations, both experimentally and in simulations, as exemplified in Figure 3.2(b). Furthermore, increasing s was marked by a decrease in C , as seen in Figure 3.4(b). This arises from the decrease in surface number density of structures due to the periodicity constraint and fixed array dimensions imposed.

3.3.2 vSRRs for Sensing

For biosensing applications using vSRR structures, the x-polarization is preferred over y due to the larger contrast and higher sensitivity afforded, which can be attributed to the dominance of the magnetic mode. To observe the effects of magnetic resonance on sensing, we compare the simulated sensitivities of two structures with similar resonances operating in the magnetic and electrical resonance. The first structure is the as-simulated $\theta_{60}s_{60}$ with a thickness of 30 nm, with a magnetic resonance wavelength

of 733 nm in air. The second structure, $\theta_{60}s_{60}f_{2.6}$ (where f refers to a dimensional scaling factor) is scaled by a factor of 2.6 in the lateral dimensions and is observed in the electric mode with a resonance wavelength of 735 nm in air. Bulk sensitivity was determined from the resonance wavelength of structures in cladding with refractive indices from $n = 1 - 1.5$, in increments of 0.1 (Figure 3.5(a)). Analyte sensitivity is determined for $n = 1.4$ with coating thickness $t = 0 - 25$ nm, in increments of 5 nm (Figure 3.5(c)). Despite the marginally shorter wavelength, the former structure (in magnetic mode) outperforms the electrically-resonant $\theta_{60}s_{60}f_{2.6}$ in both bulk and analyte sensitivity, with bulk sensitivities of 366 nm/RIU and 252 nm/RIU respectively as seen in Figure 3.5(b). The sensitivity-improved magnetic resonance is due to a different dependence on the resonance. Moreover, the spectra under x -polarization exhibit visible range resonances overlapping with the region of highest permittivity-limited Q-factor, about 600—700 nm [112]. Thus, all subsequent measurements were performed using x -polarized illumination corresponding to the magnetic mode.

Figure 3.5 Simulated spectra for $\theta_{60}S_{60}f_{2.6}$ (top) and $\theta_{60}S_{60}$ (bottom) for (a) varying refractive index claddings from $1 < n < 1.5$ and (c) analyte thickness of $0 < t < 0.25$ nm and. (b) Bulk sensitivity comparison of $\theta_{60}S_{60}f_{2.6}$ (red) and $\theta_{60}S_{60}$ (blue) shows the sensitivity improvement when sensing in magnetic mode. (d) Magnetic mode also provides a higher dynamic range for analyte sensitivity. Here, the solid lines are best-fit second order polynomials for illustration purposes only

The contribution of capacitive impedance on refractometric sensing is observed for two structures resonating at ~ 733 nm for $\theta_{60}S_{60}$ and $\theta_{40}S_{68}$ numerically. In terms of bulk sensing, $\theta_{40}S_{68}$ exhibits greater bulk sensitivity (366 nm/RIU 407 nm/RIU) and a wider dynamic range which can be attributed to the greater field localization for a narrower opening angle at the expense of thickness for a given refractive index. The linear region on analyte sensing is reduced by approximately half suggesting that the appropriate selection should the target analyte thickness and functionalization layers.

Table 3.1 Resonance characteristics and sensitivities of selected arrays

Structure		Resonance Wavelength, λ_R (nm)	Linewidth (nm)	Q-Factor	Sensitivity (nm/RIU)
θ_{60}	s_{50}	611.9	102.3	6.0	72.0
	s_{60}	645.6	103.7	6.2	106.3
	s_{70}	690.1	117.5	5.9	131.2
θ_{40}	s_{50}	565.6	81.6	6.9	50.8
	s_{60}	565.7	74.7	7.6	77.3
	s_{70}	579.5	81.6	7.1	83.4
	s_{80}	593.7	82.9	7.2	96.4
$\theta_{30}d_{12}$	s_{50}	588.1	85.7	6.9	47.8
	s_{60}	595.3	92.6	6.4	54.9
	s_{70}	595.6	100.9	5.9	57.1
	s_{80}	626.5	147.9	4.2	61.3
$\theta_{30}d_{14}$	s_{60}	597.0	85.7	7.0	59.2
	s_{70}	599.4	98.2	6.1	65.2
	s_{80}	617.9	130.0	4.8	80.6

The experimental resonance characteristics and bulk sensitivities of some of the resonator arrays are tabulated in Table 3.1. The sensitivities were found to range from 48 nm/RIU to 131 nm/RIU. A plot of the sensitivity vs. resonance wavelength in air is shown in Figure 3.6(a). As seen with θ_{60} and θ_{30} structures, the plot indicates that sensitivity is linearly related with the resonance wavelength, where a shorter wavelength corresponds to an intrinsically lower sensitivity. ν_{40} data is not consistent with this due to behavior similar to that of a nanoparticle and not a SRR. Measurements for ν_{90} were excluded from sensitivity measurements due to transmission grating inefficiency beyond 800nm inherent in the Cytoviva system, which is optimized for the visible

spectrum [111]. The shift in resonance with changing refractive index for the $v_{60}s_{60}$ array can be seen in Figure 3.6(b). The sensitivity S for this structure, 131 nm/RIU, is the slope of the best fit line. There is a performance trade-off with visible-range sensing, where sensitivities are expected to be lower in comparison to those in a longer-wavelength region.

Figure 3.6 (a) Experimental sensitivity of resonators with respect to its corresponding resonance wavelength in air shows a positive correlation. (b) Resonance wavelength shift $\Delta\lambda$ (reference is air) with respect to refractive index of bulk liquid. Experimental sensitivity determined from the slope of the plot. (c) Resonance wavelength shift $\Delta\lambda$ (reference is air) as a function of estimated thickness for cytochrome c and BSA. (d) Estimated analyte thickness vs. concentration (color online).

Subsequently, the non-specific adsorption of two biomolecules was investigated using the $v_{60}s_{60}$ array. For an equal mass per volume concentration of 1 mg/ml, BSA was found to have a shift of 32.67 nm while that of cyt c was 25.51 nm, illustrating the influence of molecular weight on wavelength shift. This is consistent with the results of different BSA (15 μM , 75 μM , 150 μM) and cyt c (833 pM, 83.3 nM, 83.3 μM) concentrations tested where the shift $\Delta\lambda$ increased accordingly with concentration. The observed shifts were used to estimate the layer thickness of the biomolecules for various concentrations of BSA and cyt c by inverting the approximate relation, illustrated in Figure 3.6(c), $\Delta\lambda = S \Delta n [1 - \exp(-2d/l_d)]$, where d represents the molecule thickness, l_d the plasmon decay length, and Δn the refractive index of the molecule less unity. The decay length l_d was estimated to be 25 nm based on simulations of

resonator arrays uniformly coated with a dielectric. With a mean refractive index of 1.602[113], the BSA layer thickness is approximately 9 nm for lower concentrations and about 12 nm for the highest concentration, translating to slightly more than a monolayer and slightly less than a bilayer based on the BSA molecule Stokes radius $r_s = 3.48$ nm. For cytochrome *c*, having a mean refractive index of 1.49 [114], the layer thicknesses for the studied concentrations are estimated to be between 5.5 nm and 8.6 nm. This corresponds to thicknesses ranging from 1.5 to 2.5 monolayers, given that cyt *c* is an approximately spherical molecule with a hydrodynamic radius $R_H = 1.7$ nm. The estimated thickness as a function of concentration is shown in Figure 3.6(d) for both molecules.

To demonstrate the specific binding ability of the sensor, protein A/G and IgG were used as the model receptor-analyte system. Protein A/G is a 50.46 kDa molecular weight recombinant fusion protein that binds selectively with the Fc regions of immunoglobulins such as protein IgG (molecular weight 150 kDa). Protein A/G is attached onto the gold surface via physisorption, selectively binding to gold [115]. A protein IgG layer is formed, where IgG binds to protein A/G. The yellow, blue, and red lines in Figure 3.7 correspond to the spectrum of air, protein A/G, and IgG binding respectively. The spectrum red-shifts for each molecular binding event, with transmission dips occurring at 620.45 nm, 630.14 nm, and 642.44 nm. We note that convective effects from stirring result in a thorough cleaning of the structures, resulting in a blue-shift of the reference (air) resonance compared to that of the as-fabricated measurements. A 12.3 nm resonance shift was seen upon IgG binding onto protein A/G, and demonstrates the utility of such a biosensor for specific binding.

Figure 3.7 The observed spectrum red-shifting upon binding with biomolecules protein A/G and IgG and (inset) schematic of biomolecule adsorption process.

3.4 Conclusion

We have reported the fabrication and implementation of magnetically-resonant subwavelength vSRR arrays in the visible spectrum as a planar biosensing substrate with sensitivities up to 131 nm/RIU. The magnetic resonance can be excited when the structure supports a circulating current, and in the case of the vSRR is polarization-dependent. Furthermore, we numerically demonstrate that, when the structure is normalized to the resonance wavelength of 733 nm, the magnetic resonance outperforms the electric resonance by 114 nm/RIU. To the best of our knowledge, these experiments are the first demonstrations of such a resonance in the visible region using ultra-small split ring resonators being implemented to detect biomolecules and estimate layer thickness. With spectrally-unique responses which are tunable, such plasmonic sensor provides a coupler-free alternative to existing platforms and is promising for use in multiplexed real-time and label-free assays.

Chapter 4 STRATEGY FOR HIGH FIGURE-OF-MERIT

PLASMONIC SENSING IN THE VISIBLE SPECTRUM USING

HYBRID TRANSVERSE-LONGITUDINAL MODES

Localized surface plasmon (LSP) resonance has emerged as an excellent platform for rapid and label-free sensing due to its strongly confined electric fields which are highly susceptible to refractive index changes. However, the performances of an LSP-based sensor are dictated by the LSP resonance mechanism that limits its sensitivity and figure of merit (FOM). The linear relationship between sensitivity and resonance wavelength indicates a decreasing sensitivity for shorter wavelength, rendering the FOM for a given spectral region mainly dependent on the achievable Q-factor of the LSP resonance. This leads to a typical sensitivity of $\sim 100\text{-}300\text{ nm/RIU}$ and FOM of $\sim 2\text{-}3$ in the visible frequency range, which presents a dilemma for the realization of practical sensing platform that requires high sensitivity and high FOM in the visible spectrum. In this work, we propose the use of a hybrid mode resulting from an interaction between the transverse LSP and the longitudinal Fabry-Perot (FP) modes, which is capable of improving the sensitivity and Q-factor, and hence FOM, simultaneously. We realize this hybrid mode in tall v-shaped split ring resonators fabricated via seedless pulsed gold electrodeposition, and demonstrate plasmon-based sensing with FOM as high as 24 in the visible range. In addition to these significant improvements in bulk sensing, we also demonstrate a nanofabrication technique based on a combination of nanopatterning and seedless electrodeposition for realizing plasmonic resonators with much higher Q-factor

due to their much better surface morphology than those fabricated by physical deposition.

4.1 Introduction

Plasmon-based sensing has emerged as an attractive candidate for rapid and label-free interrogation in biomedical diagnostic and environmental monitoring due to its nanoscale light confinement which is highly influenced by changes in refractive index [10,42,116]. Importantly, in contrast to their integrated optics counterparts which require complex configurations with stringent optical alignments [117], the excitation scheme for the localized surface plasmon (LSP) modes can be done in a microscope setting, making LSP-based sensing practical and cost-effective. The performance of a plasmon-based sensor is gauged by the sensitivity (S) and the figure of merit (FOM), with the former describing the susceptibility of the plasmonic confinement to the refractive index changes and the latter, dependent on the resonance Q-factor, describing the sensing resolution. The sensitivity has been shown to increase linearly with the resonance wavelength [56,118], indicating that sensitivity progressively decreases towards the visible frequency range. This presents a dilemma in the realization of practical and cost-effective sensing platform, where high sensitivity and high FOM are the desirable parameters for visible frequency operation.

Various types of planar resonators, including split ring resonators (SRR) [119] nanorods [120,121] crescents [122], and pyramids [123] have been reported to have sensitivities of 100-300 nm/RIU and FOM of ~ 2 in the visible frequency range. Higher sensitivity is achievable in self-assembled metal nanoparticles due to their lower damping loss and negligible interaction with the substrate [81,124]. However, this

approach is not preferable in the context of a practical sensing platform that requiring precise control of nanoantenna dimensions and placements. Another approach for improving sensing parameters is through planar multi-cavity configurations that allow bright and dark modes to interfere and produce a narrow Fano resonance [125–128], where the cancellation of radiative loss gives rise to linewidth reduction and consequently higher Q-factors. Sensing based on Fano resonance with FOM of 5.7 has been reported in gold disk heptamers [129]. However, owing to its mode interference requirements, the excitation of Fano resonance is typically achieved only under certain incidence angle and polarization. In addition, background resonances which often accompany the realization of the Fano resonance can complicate spectral interpretation in sensing.

The sensing performance of standard planar metal nanostructures is limited by their material properties and their resonance mechanism. The Q-factor of localized surface plasmon (LSP) resonance is dictated by the complex permittivity of the given metal [112], which limits the achievable figure of merit. The sensitivity is shown to be limited by the resonance wavelength, regardless of resonator geometry [56,130]. Therefore, further improvement in sensing performance can only be achieved when an alternative resonance mechanism is introduced. In this Chapter, we demonstrate that both the sensitivity and figure of merit can be simultaneously improved in moderate aspect ratio v-shaped split ring resonators (vSRRs) fabricated by a seedless electrodeposition method. We demonstrate the existence of a hybrid waveguide-LSP mode emerging from a retardation effect introduced via the vSRR height, which exhibits up to ~6x higher Q-factor than those achievable in the planar counterparts. A much higher sensing performance in the visible range based on a hybrid waveguide-LSP mode is observed, with ~10x higher figure of merit (FOM ~ 24) compared to its planar counterparts.

4.2 Methods and Materials

4.2.1 Nanofabrication

The high aspect ratio vSRRs were realized by electron-beam lithography patterning on 120-nm thick ZEP520A (Raith e_LiNE, 20 keV energy, 30 pA current) on ITO-coated glass (~20 ohms surface resistance), followed by a sonicated cold development process. The patterns were then subjected to gold pulsed electrodeposition in $\text{K}[\text{Au}(\text{CN})_2]$ plating solution at $J = 3 \text{ mA/cm}^2$ with $T = 400 \text{ ms}$ period (25% duty cycle), corresponding to ~6.5 nm/pulse deposition rate [131]. Afterwards, the samples were rinsed in deionized water, followed by resist removal in *n*-methyl pyrrolidone (NMP) and final isopropanol rinse. The gold nanostructures were arranged in a periodic square lattice occupying a $10 \times 10 \text{ }\mu\text{m}$ footprint, with a fixed period of three times the arm length, $p = 3s$.

4.2.2 Characterization

For transmission measurements, a broadband halogen lamp was focused onto the sample from the bottom through a condenser and the transmission signals were collected through 10x objective lens ($\text{NA} = 0.3$) into a hyperspectral imaging system (Cytoviva). The transmission mapping was obtained by scanning the sample via piezo-controlled stage. Polarization-resolved measurements were carried out by placing polarizer before the condenser (for the source) and analyzer before the hyperspectral imaging system (detector). The transmission was obtained by normalizing the transmitted signals with that of the bare ITO substrate.

The lateral and vertical sizes of the ν SRRs were characterized from normal- and oblique-incidence SEM inspection, respectively, in the same EBL system at 10 keV. The statistical analysis for the SRR height was carried out using image processing software.

4.2.3 Sensing Measurements

To conduct bulk sensitivity characterization, the samples were dropcasted with refractive index liquids of different refractive indices ($n = 1.300 - 1.380$, Cargille Instruments, USA), followed by transmission measurements. Between each measurement, the sample was cleaned with toluene and rinsed in deionized water. Cleaned samples were re-measured to ensure that the transmission spectrum returned to that of the as-fabricated ν SRRs.

For surface sensing characterization, alkanethiols of varying carbon chain lengths were prepared in ethanol. Samples were immersed in the ethanolic solution for 24h to ensure monolayer formation, and the background air was purged with nitrogen. Prior to measurement, the samples were rinsed copiously with ethanol and dried using nitrogen gun. Samples were cleaned using oxygen plasma which followed with measurement to ensure return to the as-fabricated resonance.

4.2.4 Numerical Simulation

All the numerical simulation in this work were performed by a commercial finite difference time domain software (FDTD Solutions, Lumerical Inc) based on top illumination ($-z$ direction) of x - and y -polarizations, and (anti)symmetric and periodic boundary conditions in the x and y directions, respectively. The permittivity of gold was taken from Johnson and Christy model [28]. For the curve fitting in Fig. 3, we model

the ITO substrate as a dielectric with a constant refractive index $n = 1.5-1.75$, where smaller refractive index is used for resonances located at shorter wavelength due to the dispersive properties of the ITO glass. The lower spectral contrast in the experimental transmittance is attributed to the non-ideal mode excitation where the plasmonic nanoantenna is not just excited under normal incidence, but also from other incident angles dictated by the numerical aperture of the condenser. In order to take this into account, we adjust the spectral contrast of the numerically simulated transmittance to match those of the experimental transmittance.

4.3 Results and Discussion

4.3.1 Characterization of electrodeposited nanostructures

The fabrication of the ν SRRs was based on the combination of nanopatterning and pulsed gold electrodeposition. Nanopatterning was carried out by electron beam lithography (EBL) on indium tin oxide (ITO) coated glass substrate, followed by a sonicated cold development process for achieving sub-15 nm resolution at lower exposure dose [132]. ITO was chosen as the substrate due to its transparency and its suitable conductivity which allows the electrodeposition process. Larger surface resistance values ($2\text{k}\Omega/\square$) could not support a continuous solid growth but instead, yield granular nanoparticles that do not extend vertically. Pulsed electrodeposition was used instead of physical evaporation to overcome the thickness limitation in the lift-off transfer, in addition to improving the surface morphology of the gold film.[131,133] Based on this technique, ν SRRs were successfully fabricated with feature sizes such as width in the sub-30 nm range and height comparable to the resist thickness. An example

of the fabricated ν SRR in this work is shown in Fig. 1c for ν SRR with $\theta = 60^\circ$, arm length $s = 80$ nm and height $h = 150$ nm (denoted for simplicity as $\theta_{60}s_{100}h_{150}$ ν SRR).

Figure 4.1 (a) Representative SEM micrograph for height characterization (red lines). (b) Characterization of pulse with respect to nanostructure height, with fitted line to determine the deposition rate.

To determine the relation of pulse width to nanostructure height in the electrodeposition process, an oblique SEM micrograph (at $\alpha = 45^\circ$ tilt angle) was used to measure heights of the ν SRR using the relation $h = l/\sin(\alpha)$, where l is the length of the red lines in Figure 4.1 and α is the tilt-angle. The average height is tabulated in Table 4.1. Figure 4.1(b) presents the linear relation of the average ν SRR height with the number of pulses (n_p), with the error bars representing the standard deviation from the statistical height measurements. The deposition rate is determined by the slope of the linear fitting, which was found as ~ 6.5 nm/pulse. It should be noted that this deposition rate is based on deposition with an ITO dummy substrate. In our experiments, the dummy substrate was reused for the subsequent electrodeposition process, meaning that subsequent dummy samples had a gold coating on the ITO. We observed that the deposition rate is higher for the first sample in the batch, which corresponds to a fresh ITO substrate.

Table 4.1 Height characterization results from structures in Figure 4.1(a)

Average height [nm]	Std. Dev [nm]	Number of pulses, n_p	Sampling, n
33.07	3.41	15	37
113.57	7.08	27	31
150.01	7.1	33	70

4.3.2 Resonance characteristics of planar and tall vSRRs

We first begin with the analysis of a planar vSRR whose magnetic and electric modes have been studied in our previous works [108,111,119]. The magnetic mode (m_0) is excited when the incident light is polarized across the SRR gap (x polarization), which is associated with a strong electric dipole across the SRR gap (x direction) and a strong magnetic dipole perpendicular to the SRR plane (z direction). The surface charge configuration for the m_0 mode is depicted in Figure 4.2(a), which illustrates the accumulation of opposite charges at the SRR tips that gives rise to a circulating current, leading to localized H_z -field for the magnetic dipole. The electric mode (e_0) is associated with electric dipole oscillations along the SRR arms, which is excited when the incident light is polarized along the y direction. The surface charge distribution for the e_0 mode is shown in Figure 4.2(b), with opposite charges accumulated at both ends of the SRR arms. The hybrid magnetic-electric characteristics of the m_0 mode have been shown to be dependent on the SRR opening angle (θ) [108]. At large opening angle, the m_0 mode behaves more as an electric resonance with the E -fields localized at the SRR tips, resembling that of a nanorod. As the opening angle is decreased, the E -field and H_z -field localizations shift towards the vSRR gap area, resembling the behavior of a magnetic

resonance. Based on this, we focus mainly on the $vSRR$ with $\theta = 60^\circ$ where the m_0 mode is predominantly magnetic.

Figure 4.2 Resonance properties of tall vSRR. Transverse surface charge distribution for (a) the m_0 and (b) the e_0 modes, illustrated by E_z -field distribution at the vSRR top surface. (c) False-colored SEM of the tallest fabricated vSRR ($h = 150$ nm). The scale bar represents 100 nm. (d)-(e) Spectral height mapping of the m_0 and e_0 modes for $v_{60}s_{100}$ vSRR structures, with the dashed curves indicating the resonance modes and dashed vertical lines denoting planar, intermediate, and waveguide regimes.

In order to observe the evolution of the resonance modes at increasing height, we numerically simulated the transmission spectra of $\theta_{60}s_{100}$ vSRRs for the m_0 and e_0 modes as the height is varied from 10 nm to 1000 nm, where the resonance positions are identified from transmission dips. Starting from the m_0 mode under x polarization (Figure 4.2(d)), we observe that the resonance mode blue shifts from ~ 1000 nm to ~ 750 nm as the height increases until ~ 80 nm. The blue shift, however, does not occur indefinitely and appears to saturate at ~ 700 nm as the height reaches ~ 80 nm,

accompanied with the emergence of another mode at ~ 620 nm. Such a split resonance is also observed for the e_0 mode under y polarization (Figure 4.2 (e)), where the resonance position asymptotically approaches ~ 600 nm as the height passes ~ 80 nm, accompanied with the emergence of another mode at ~ 550 nm. As the height is increased further (up to ~ 300 nm), while the positions of the split resonances appear unchanged for the m_0 and e_0 modes, there is yet another mode emerging from the e_0 mode (under y polarization) that red shifts as the height increases. The repeated emergence of similar modes is observed at ~ 300 nm, ~ 500 nm and ~ 700 nm as the height is increased beyond 300 nm, whose characteristics resemble the dispersion characteristics of optical waveguide modes [134,135]. The resonance mechanism in the tall plasmonic nanostructures can thus be classified according to the dependence of the mode position on the resonator height. The first resonance mechanism is the transverse resonances known as the localized surface plasmon modes, which blue shift as the height is increased. The second mechanism is the longitudinal resonance associated with waveguide mode, which red shifts as the height is increased. Based on their dominant resonance mechanisms, the transmission mappings can thus be divided into planar ($h < 80$ nm), intermediate (80 nm $< h < 300$ nm), and waveguiding ($h > 300$ nm) regimes.

In the planar regime, where the localized plasmon resonance is the dominant mechanism, both the m_0 and e_0 modes blue-shift with increasing height. The cause for such a blue shift has been discussed by Henson et al [136], where increasing height leads to the increase of charge induced by the incident optical field at both sides of the resonator, translating to a larger restoring force and consequently, higher resonance frequency. A more quantitative explanation for the blue shift is by interpreting the plasmonic nanoantenna from the LC -model perspective [137], which analyzes the effect

of increasing height in reducing the plasmonic damping loss. In this case, increasing the resonator height translates to a decrease in resistance due to the larger wire cross-sectional area. As the resonance frequency (ω_0) in the presence of loss is $\omega_0 = \sqrt{1/LC - (R/L)^2}$, it is thus clear that a reduction in the resistance gives rise to a resonance blue shift (higher ω_0). The planar regime holds when the surface plasmons at the top and bottom of the resonator oscillates synchronously. However, the phase retardation introduced via the ν SRR height can no longer be ignored when the height becomes comparable to the effective wavelength, leading to decoupling of the two surface plasmon oscillations. In this intermediate regime, the delocalization of modes in the longitudinal direction allows for mode interference which results in resonance splitting. This is illustrated in the mapping of the $|E_y|$ -fields in the XZ plane near the SRR tips for the m_0 and e_0 modes, as shown in Figure 4.3(b). The plasmonic fields are equally localized at the top and bottom ν SRR surfaces at split resonances of shorter wavelengths (m_{01} and e_{01} modes), while the plasmonic fields are mostly localized at the bottom ν SRR surface at split resonances of longer wavelengths (m_{02} and e_{02} modes). It is worth noting that the top and bottom plasmonic fields appear to be more continuous for the e_{01} mode than for the m_{01} mode. This is attributed to the dependence of the phase retardation on the wavelength, which suggests that the e_0 mode experiences more phase retardation due to its shorter wavelength. As will be shown later, we attribute the significant improvement of sensitivity arising from height to the extended interaction length made possible by the hybrid LSP-waveguide properties of the resonance modes.

Meanwhile, the resonance mode associated with the vertical Fabry-Perot (FP) reflections can be observed in the transmission dip that progressively red shifts from the background LSP resonance along with the increasing height. The trace of this mode is denoted by the dashed curve (Figure 4.2 (e)), which also indicates that the guided mode

emerges just as the resonance splitting occurs due to the phase retardation. The emergence of other guided modes is also observed at different heights in a manner similar to the dispersion characteristics of an optical waveguide. This situation is referred to as the waveguiding regime, which has been investigated in high aspect ratio gold nanostructures on metal and dielectric substrates [138,139]. The resonance mode characteristics under the waveguiding regime are illustrated in the E_y -field mapping of the ν SRR with $h = 700$ nm (Figure 4.3 (c)), where multiple longitudinal guided modes exist at locations denoted by the red circles in Figure 4.2(e). As expected, these longitudinal guided modes exhibit standing wave patterns associated with vertical FP reflections. In fact, a qualitative difference can be found between the FP-like field localization of the mode “4” (at ~ 590 nm, Figure 4.3(c)) and the bottom field localization of the e_{02} mode (at ~ 592 nm, Figure 4.3(b)), despite their similar spectral positions. This means that for taller heights, the resonance mode no longer behaves as localized plasmon modes, but as vertical FP resonances.

Figure 4.3 Electric field distributions of transverse and longitudinal resonances in tall vSRR. (a) The schematic for the front and back XZ planes. (b) $|E_y|$ -field distributions (front XZ plane) for the split m_0 resonances at ~ 618 nm (m_{01}) and ~ 720 nm (m_{02}); and the split e_0 resonances at ~ 554 nm (e_{01}) and ~ 592 nm (e_{02}) in the intermediate regime ($h = 120$ nm). The substrate is denoted by the dashed lines. (c) E_y -field distributions of the longitudinal guided modes in the waveguiding regime ($h = 700$ nm) at (1) ~ 842 nm, (2) ~ 747 nm, (3) ~ 653 nm, and (4) ~ 590 nm.

The onset height for the decoupling of the top and bottom plasmon modes is related to the transverse resonance wavelength, which is dependent on resonator size. This means larger height would be required for the emergence of longitudinal guided modes in larger resonator sizes. This can be seen in the vertical FP resonances at $h > 500$ nm in resonator of hundreds of nanometer sizes, whose localized plasmon resonances are typically located in the near infrared [139] or longer [140] wavelength range. Smaller

onset height is thus expected when the transverse resonances are in the visible spectrum. In this work, we demonstrate the emergence of longitudinal modes in moderately high aspect ratio SRR structures. We realize this using v -shaped SRR design, which has been shown to push the magnetic resonance into the visible spectrum due to its smaller inductance area compared to that of the conventional u -shaped design [111]. Figure 4.5 presents the experimental transmission spectra of $v_{60}s_{100}$ v SRRs in the planar and intermediate regimes under x and y polarizations. The scanning electron micrographs (SEM) of v SRRs with different heights are shown in Figure 4.5(b)-(d), with the top-view SEM (Figure 4.5(b)) demonstrating good pattern fidelity of the fabricated v SRRs with their original designs.

Figure 4.4. (a) Effect of periodicity on resonance wavelength of x - (blue) and y -polarized $v_{60}s_{100}h_{150}$ with period ranging from 2s – 8s. The resonances were characterized for the LSP resonance. (b) Transmission spectra for 2s – 8s.

The periodicity of the v SRRs were chosen to be three times the arm length in order to have sufficient optical contrast without much impact of inter-resonator near-field interactions in broadening the resonance linewidth. This is essential for reducing the coupling loss responsible for resonance broadening in dense resonator array, and

consequently for the design of a high FOM sensing platform. These periodicities are much smaller than the resonance wavelength of the nanoantenna, making the far-field interaction between neighboring antennas negligible compared to the near-field interaction [141]. Periodicity effects are shown in Figure 4.4 for lattice constants between $2s$ to $8s$ for $v_{60}s_{100}$ in the x - and y -polarization. Up to $5s$ ($4s$), the resonant behaviour of x - (y -) polarization is consistent with nondiffractive arrays, which blue-shifts with decreasing interparticle distance. The trend breaks down at periods larger than $5s$ and $4s$ respectively, due to interactions with higher order diffraction [142]. The transmission spectrum with larger distances exhibit linewidth narrowing and interactions with the far-field (Figure 4.4 (b)).

Figure 4.5 Experimental transmission spectra of $v_{60}s_{100}$ vSRR as the height is varied to $h = 50$ nm (top), $h = 85$ nm (middle), and $h = 120$ nm (bottom) under (a) x and (e) y incident polarizations. The inset shows the electric-field distribution $|E|$ in the XY plane at $z = h/2$. (b)-(d) Scanning electron micrographs of the fabricated vSRR: (b) top-view, (c) oblique-view (45°) for $h = 50$ nm, and (d) oblique-view (45°) for $h = 120$ nm. The scale bars represent 100 nm.

The evolution of the x -polarized and y -polarized transmission as the height is increased from $h = 50$ nm to $h = 120$ nm are shown in Figure 4.5(a) and (e), respectively. In the planar regime ($h = 50$ nm), for x -polarized transmission, we observe a single resonance mode at ~ 863 nm associated with the magnetic mode (m_0). In the transition between planar and intermediate regimes ($h = 85$ nm), we observe a weak transmission dip at ~ 600 nm and a strong m_0 resonance which has blue shifted to ~ 808 nm due to the increase of height. As the height is further increased to $h = 120$ nm, which brings the v SRR into the intermediate regime, we observe split resonances located at ~ 644 nm (m_{01} mode) and ~ 731 nm (m_{02} mode). The same is observed for the y -polarized transmission, where the split resonances are observed at ~ 533 nm (e_{01} mode) and ~ 628 nm (e_{02} mode). Both the simulated (dashed) and measured (solid) transmissions are in good agreement, and the resonance splitting for both polarizations can be reproduced by our numerical simulations. The differences in the spectral contrast and mode positions are likely due to the dispersive properties of the conductive ITO film, which exhibits free carrier loss in the near infrared. The resistance of the ITO film across for 1×1 cm² is measured to be 20Ω , a sufficient resistance to ensure a satisfactory seedless electrodeposition process [133]. Other factors also contribute to the differences, such as the rounding caused by e -beam proximity effects and thickness non-uniformity of the electrodeposition process (particularly for the tall v SRRs).

4.3.3 Bulk sensing characterization of tall v SRRs

In order to characterize bulk sensing performance of the hybrid LSP-waveguide mode in the tall v SRRs, we focused our experiment on the $v_{60}s_{100}h_{150}$ and $v_{60}s_{80}h_{150}$ v SRRs. Experimentally, the tallest experimental structures were limited to 150 nm due to the mushrooming occurring at the top of the structures during growth as they exceed

the resist height, which itself is limited by the desired lateral feature size and available e -beam accelerating voltage. The transmission spectra of the $v_{60}s_{100}h_{150}$ under x and y incident polarizations are shown in the Appendix; they are similar to those of $v_{60}s_{100}h_{120}$ (Figure 4.5), but with red shifted m_{02} mode at ~ 755.7 nm. The polarization-resolved bulk sensitivity characteristics of $v_{60}s_{100}h_{150}$ vSRR are presented in Figure 4.6(a). The bulk sensitivity was obtained from the slope of the best-fit linear regression of the resonance shift as a function of cladding refractive index, which was varied by drop-casting refractive index liquids (Cargille Labs) of different indices ($n = 1.3 - 1.38$). The bulk sensitivity under x polarization (solid circle markers) is deduced as $S_{x,exp} = 327nm/RIU$, in agreement with the simulated bulk sensitivity of $S_{x,sim} = 318nm/RIU$ (hollow circle markers). By comparing the sensitivity at similar resonance wavelength, we note that this sensitivity is $\sim 2.5x$ higher than that of the planar vSRR whose sensitivity is $S = 131nm/RIU$ at 690 nm resonance wavelength [119]. Likewise, the resonance mode for the y -polarized transmission is observed as a weak transmission dip at ~ 679.8 nm, located far from the background resonance of stronger contrast at ~ 550 nm (Appendix). This resonance is dominated by the longitudinal guided mode characterized by its low spectral contrast and a resonance position that is far detuned from the background resonance. The corresponding sensitivity of this mode is $S_{y,exp} = 402nm/RIU$ (solid triangle markers), in agreement with the simulated sensitivity of $S_{y,sim} = 366nm/RIU$ (hollow triangle markers). Meanwhile, the sensitivity for the LSP-dominant mode at ~ 550 nm was measured to be $234nm/RIU$. The resonance shifts for different cladding refractive indices for all the above resonance modes are summarized in Table 4.2.

Table 4.2 Resonance wavelength shifts at different refractive index change for $v_{60}s_{100}h_{150}$ vSRR

$x - pol$		$y - pol$	
n	λ_R [nm]	$\lambda_{R,m=1}$ [nm]	$\lambda_{R,m=0}$ [nm]
1.00	755.7	553.5	679.8
1.30	852.6	626.3	804.7
1.32	863.3	633.4	810.3
1.34	866.9	635.3	813.8
1.36	873.3	636.0	822.2
1.38	879.1	639.8	834.2
S [nm/RIU]	327	234	402

Figure 4.6 Bulk sensing characteristics of tall vSRR structure. (a) Numerical (triangle markers) and experimental (circle markers) sensitivity properties of $v_{60}s_{100}h_{150}$ vSRR for the x and y

incident polarizations. The results for the x and y incident polarizations are shown in the hollow and filled markers, respectively. (b) The (S, λ_R) mapping of $vSRR(\theta, s, h)$ with $h = 50$ nm (blue) and $h = 150$ nm (red). The resonance modes are denoted by the square (for x polarization) and triangle (for the y polarization) markers. The variation of the SRR size (s) and opening angle (θ) are: $s = 60$ nm, 80 nm, and 100 nm; and $\theta = 40^\circ$, 60° , and 90° . The $S \propto \lambda_R$ relation of the planar nanostructure is denoted by the dashed line. (c)-(d) Experimental transmission spectra of $v_{60}S_{80}h_{150}$ $vSRR$ structures under x and y incident polarizations is shown as a representative spectra, with the LSP-like and waveguide-like modes, respectively. The cladding refractive index is varied from 1 to 1.38, with the corresponding resonance modes indicated by the arrows.

It is interesting to note that in terms of absolute values, the highest sensitivity is not found in the resonance mode with the longest resonance wavelength. This conflicts with the $S \propto \lambda_R$ dependence in planar plasmonic nanostructures [56,118], which clearly illustrates the fundamental difference in the resonance mechanisms of the planar and tall plasmonic nanostructures. The reason for the improved sensitivity lies in the dependence of the resonance condition of the longitudinal guided mode on the $vSRR$ height, which is more highly susceptible to the refractive index changes in the cladding. This is because the oscillation of the top and bottom plasmon modes along the $vSRR$ height leads to the significant increase in the interaction volume with the analyte or cladding. Note that the vertical oscillation characteristic is also present in the x -polarized mode, which explains its much higher sensitivity compared to that of the planar $vSRR$. However, the x -polarized m_{02} mode is more dominated by the LSP mode, as evident from its strong transmission dip and its spectral proximity to the background resonance. The y -polarized mode, on the other hand, exhibits low spectral contrast and is located far from the background resonance, indicating that the mode behaves more as a longitudinal guided mode. Based on this, it can be concluded that the higher sensitivity in the y -polarized mode (despite its shorter resonance wavelength) is attributed mainly to its more waveguide-like characteristic.

The sensitivity mapping (S, λ_R) of $vSRR$ in planar ($h = 50$ nm) and intermediate ($h = 150$ nm) regimes are presented in Figure 4.6 Bulk sensing characteristics of tall $vSRR$

structure. (a) Numerical (triangle markers) and experimental (circle markers) sensitivity properties of $v_{60}s_{100}h_{150}$ vSRR for the x and y incident polarizations. The results for the x and y incident polarizations are shown in the hollow and filled markers, respectively. (b) The (S, λ_R) mapping of vSRR(θ, s, h) with $h = 50$ nm (blue) and $h = 150$ nm (red). The resonance modes are denoted by the square (for x polarization) and triangle (for the y polarization) markers. The variation of the SRR size (s) and opening angle (θ) are: $s = 60$ nm, 80 nm, and 100 nm; and $\theta = 40^\circ$, 60° , and 90° . The $S \propto \lambda_R$ relation of the planar nanostructure is denoted by the dashed line. (c)-(d) Experimental transmission spectra of $v_{60}s_{80}h_{150}$ vSRR structures under x and y incident polarizations is shown as a representative spectra, with the LSP-like and waveguide-like modes, respectively. The cladding refractive index is varied from 1 to 1.38, with the corresponding resonance modes indicated by the arrows. (b). The dashed line denotes the $S \propto \lambda_R$ relation of the planar plasmonic nanostructures, which in our case is obtained from the linear fitting of sensitivities of the planar vSRRs. The position of the sensitivity in the $S(\lambda_R)$ mapping relative to the $S \propto \lambda_R$ line illustrates the dominant resonance mechanism in the sensing measurements. It can be seen that most of the achieved sensitivities for the tall vSRRs are located far from the $S \propto \lambda_R$ line, which indicates that the resonance modes are more waveguide-like. As these sensitivities are based on both polarizations, this confirms that both the x -polarized and y -polarized modes are hybrid LSP-waveguide modes. The cases where the resonance modes are more LSP-like can be seen at sensitivities located along the $S \propto \lambda_R$ line. The transmission spectra of the LSP-like and waveguide-like hybrid modes for different cladding refractive indices are presented for the $v_{60}s_{80}h_{150}$ vSRR with its x -polarized LSP-like mode (at $\lambda_R = 658\text{nm}$) and y -polarized waveguide-like mode (at $\lambda_R = 651\text{nm}$), as shown in Figure 4.6 Bulk sensing characteristics of tall vSRR structure. (a) Numerical (triangle markers)

and experimental (circle markers) sensitivity properties of $v_{60}s_{100}h_{150}$ vSRR for the x and y incident polarizations. The results for the x and y incident polarizations are shown in the hollow and filled markers, respectively. (b) The (S, λ_R) mapping of vSRR(θ, s, h) with $h = 50$ nm (blue) and $h = 150$ nm (red). The resonance modes are denoted by the square (for x polarization) and triangle (for the y polarization) markers. The variation of the SRR size (s) and opening angle (θ) are: $s = 60$ nm, 80 nm, and 100 nm; and $\theta = 40^\circ$, 60° , and 90° . The $S \propto \lambda_R$ relation of the planar nanostructure is denoted by the dashed line. (c)-(d) Experimental transmission spectra of $v_{60}s_{80}h_{150}$ vSRR structures under x and y incident polarizations is shown as a representative spectra, with the LSP-like and waveguide-like modes, respectively. The cladding refractive index is varied from 1 to 1.38, with the corresponding resonance modes indicated by the arrows. (c) and (d), respectively.

The broad resonance and strong spectral contrast characteristics of the LSP-like mode is observed under x incident polarization in Figure 4.5(c), with the resonance mode positions denoted by the colored arrows and sensitivity measured as $S = 227\text{nm}/RIU$. The Q-factor of the LSP-like mode is measured as $Q = 7.3$, yielding a figure of merit of $FOM = 2.5$. In terms of the position in the sensitivity mapping (Figure 4.6 (b)), the corresponding (S, λ_R) is close to the $S \propto \lambda_R$ line, thereby confirming the LSP-like characteristic of the x -polarized mode. Meanwhile, the narrow resonance and weak spectral contrast characteristics of the waveguide-like mode are observed under y -incident polarization in Figure 4.5(d), with measured sensitivity of $S = 376\text{nm}/RIU$. The Q-factor of the LSP-like mode is measured as $Q = 26.2$, making a figure of merit of $FOM = 15.1$. As expected from the sensitivity mapping, the corresponding (S, λ_R) is located far from the $S \propto \lambda_R$ line, again affirming that the y -polarized mode is waveguide-like. The significant improvement in the figure of merit is therefore

attributed to two factors. The first factor is the increased light-analyte interaction caused by vertical oscillation of top and bottom plasmon modes that leads to improved sensitivity. Comparatively, although the spatial extent of the evanescent tail in x-polarized case is also large arising from height, the field oscillation is dominated transversally, therefore a smaller light-matter interaction. To illustrate this, calculated bulk sensitivity of $v_{60}S_{100}h_{500}$ in x-polarization, S_B is 401 nm/RIU ($\lambda \sim 700$ nm), yielding FOM of 25, while the y-polarization the values are higher with 700 nm/RIU and 35 respectively ($\lambda = 817$ nm). The second is the reduction in the radiative loss that leads to increased Q factor, which is caused by the far detuned spectral position of the waveguide-like mode from the background resonance. The differences in behaviour are evident in the radiation efficiency, calculated as the ratio of scattering cross-section with the extinction cross-section. Waveguide-like modes which exhibit low radiation efficiency and spectral detuning contribute to higher Q factor and therefore FOM (Figure 4.7). In fact, the largest numerically attainable Q for the v-SRRs is found in the intermediate regime of the y-polarization, at height of 175 nm. The experimental Q of ~ 41 for $v_{60}S_{100}$ is thus in good agreement with the numerical trends. In contrast, x-polarized resonances exhibit lower Q factor, attributed to the LSP-dominated characteristic of the mode.

Figure 4.7. Calculated radiation efficiency spectral height mapping for $v_{60}s_{100}h_{150}$ for the (a) x- and (b) y-polarization. The corresponding Q factors is shown in (c) for the fundamental modes of each polarization. Highest calculated Q is found with for $h = 175$ nm. The intermediate regime is denoted by the gray band.

The bulk performance of the tall vSRRs in comparison to those reported in the literature in terms of their sensitivities, resonance wavelengths, and figures of merit, is presented in Figure 4.8. We limit the scope of our comparison to reported LSPR sensing works with comprehensive characterization data in the bulk sensing performances, most of which are based on gold nanostructures fabricated by top-down and nanosphere lithography methods and measured at normal incidence. The sensing parameters (resonance wavelength, sensitivity, FOM, and resonance linewidth) of the reported works are summarized in the Appendix. The kinds of plasmonic nanostructures considered in the comparison include nanorods [120,127], crescents [122], nanorings [143,144], Fano-based structures [127], and rotationally symmetric gammadions and C_n star structures [130], which are represented by unique markers whose colors denote their respective sensitivities. It is important to note that the comparison is not comprehensive for all plasmonic sensing platforms, but applicable only to LSP-based resonance works which meet the inclusion criteria (top-down fabrication, data availability and excitation as mentioned earlier). Despite this, some trends of LSP-based sensing can be observed, and exceptional works which did not meet the inclusion criteria are highlighted.

Nanohole arrays, for example, were excluded due to the fact that it is an SPP-based resonance mechanism, governed by the wavevector matching conditions of the lattice and its period. Nevertheless, we note that high FOM (up to 162) and Q-factor (~ 200) was reported for nanohole arrays suspended on a silicon nitride (SiN) membrane [145]. Similarly, mushroom arrays on a gold film reported FOM of 108 when using an angled incidence of 34° to couple the mushroom LSP mode with a Wood's anomaly resonance. However, this is not included owing to the angled incidence and SPP nature of Wood's anomalies [146]. In another work, a dense array of tall nanorods (height = 380 nm) fabricated by anodic alumina templates on gold film were found to attain bulk sensitivity of 30,000 nm/RIU using an attenuated total internal reflection (ATR) geometry [147]. However, much like the previous two, the work was excluded owing to the SPP basis and angled excitation. In contrast, our work focuses on LSP-like and WG-like modes which excited at normal incidence for structures on glass.

As evidenced in Figure 4.8, the achievable FOM for planar nanostructures is roughly constant regardless of their geometrical shapes. This is attributed to the general properties of the LSP resonance, whose Q-factor is limited by the material properties of the given metal. The $S \propto \lambda_R$ relation is also observed in Figure 4.8, where higher reported sensitivities are typically observed for planar structures with resonance wavelengths in the near-infrared range. In the context of a practical and cost-effective sensing platform, where high FOM and high sensitivity are both desired in the visible range, we turn our attention to the sensing performance in region, denoted by the blue band in Fig. 5. Clearly, the tall ν SRR structures in this work exhibit much higher FOMs than those of the planar structures ($\text{FOM} < 5$), with ~ 24 as the highest achievable FOM. This corresponds to the $\nu_{60} s_{100} h_{150}$ ν SRR with the y-polarized waveguide-like mode at $\lambda_R = 679.8 \text{ nm}$, whose sensitivity and Q-factor are $S = 402 \text{ nm/RIU}$ and $Q = 41$,

respectively. Given that FOM is independent of resonator geometrical shape due to the properties of the LSP resonance as indicated in Figure 4.8, this affirms that the increase in the FOM for the tall vSRRs is attributed to the waveguide-like modes arising from the vertical oscillations of the top and bottom plasmon modes.

Figure 4.8 Sensing performance of plasmonic nanostructures in terms of their resonance wavelengths, sensitivities, and figure of merits. Different types of plasmonic nanostructures are indicated by unique makers, with their color denoting their reported sensitivities. The blue band denotes the targeted sensing region in the visible frequency range. For visualization purposes, sensitivity greater than 550 nm/RIU was set as the upper limit, all of which resonated beyond the area of interest.

We note that FOM of similar range is also achieved in high aspect ratio plasmonic nanostructures on metal film [138], whose resonance mechanism is purely governed by the longitudinal standing wave patterns due to the absence of LSP modes in electrically-connected plasmonic nanostructures. This is qualitatively different from the tall vSRR structures of the present work which are electrodeposited without a gold seed layer, and whose resonance mechanism is based on hybrid properties of LSP and waveguide modes. Despite this difference, an $FOM = 21.5$ (corresponding to $\lambda_R = 800nm$ and $Q = 32$) has been reported based on 1000 nm thick SRR structure on gold film [138], suggesting the same insight that waveguide modes exhibit higher sensing performance due to its increased interaction volume. The advantage of hybrid LSP-waveguide mode

lies in the fact that an FOM of ~ 24 can be achieved in ν SRR of 150 nm height ($\sim 6\times$ thinner). This is related to the onset height for the decoupling of top and bottom plasmon modes, which generates hybrid LSP-waveguide modes which progressively detunes from the background LSP resonance at increasing height. The position of the hybrid mode thus begins from that of the background transverse resonance, which can be pushed into the visible range by the ν -shaped SRR design. In addition, the Q-factor of the hybrid mode can be improved by further detuning it from the background LSP resonance at the expense of reduced spectral contrast. Thus, the moderate aspect ratio plasmonic nanostructures fabricated by seedless electrodeposition method paves a way for a practical and cost-effective sensing platform, not only in terms of high sensitivity and high FOM in the visible range, but also from the fabrication perspective.

4.3.4 Surface sensing characterization

While bulk sensing characteristics are important indicators, it does not provide a complete measure of suitability for applications given that plasmonic events occur near the surface of the metal. As such, surface sensitivity (S_s) is numerically studied by monitoring spectral shifts with respect to coating thickness. A constant refractive index, where $n = 1.602$ was chosen, representative of biologically relevant refractive indices [113][148]. When the refractive index is smaller (greater), the resonance shifts are expected to correspondingly be smaller (larger) and saturate more slowly (quickly) with increasing thickness. The transmission spectra for thickness from 0-80 nm layers in 10 nm increments under x -polarized and y -polarized cases are shown in Figure 4.9(a) and (b), respectively, for $\nu_{60} s_{100} h_{150}$. As discussed earlier, the LSP mode is characterized by a broad resonance linewidth, while the WG-like mode is characterized by a narrow linewidth of lower contrast. Saturation of the resonance wavelengths are shown in

Figure 4.9(c). We see that as the thickness of the layer increases the contrasts of the resonances correspondingly decrease. This can be ascribed to increased losses in the evanescent field, an increasing portion of which lies in the higher refractive index coating (experimentally, biomolecules).

Based on the linear region seen in Figure 4.9(c), the LSP-like mode in x -polarization shifts 3.6 nm per 1 nm layer for adsorbate thicknesses t up to 50 nm (dark blue line), while the WG-like layer shifts 4.78 nm per 1 nm layer up to $t = 40$ nm (light blue line). The y -polarized LSP mode exhibits comparatively lower dynamic range of wavelength shift per layer thickness and appears mostly linear up to 10 nm (red line). Interestingly, in the y -polarized case, the waveguide mode shows an extended dynamic range of more than 90 nm (pink line). The dynamic range is governed by the decay length of the exponential tail and can be found by curve fitting the points based on the relation [60]

$$\Delta\lambda = m\Delta n(1 - e^{-2t/l_d}), \quad (4-1)$$

where $m = S_B$ is the bulk refractive index sensitivity (also known as the sensitivity factor), Δn is the difference in refractive indices between coating and bulk, t is coating thickness, and l_d is the characteristic evanescent decay length for a given mode of a particular structure. Using previously determined bulk sensitivity values, the exponential decay lengths are found and summarized in Table 4.3.

Figure 4.9 Transmission spectra for surface coating of thickness 0 - 80 nm with refractive index of 1.602 in (a) x-polarization and (b) y-polarization. (c) The resonance wavelength with respect to coating thickness for the x-polarization (blue) and y-polarization (red). The dark shades indicate the LSP mode while the lighter shades indicate the waveguide mode.

Table 4.3 Decay length of modes in v60s100h150.

Polarization	Resonance Mode	Bulk Sensitivity m [nm/RIU]	Decay Length, l_d [nm]
x	LSP-like	318	26.08
	WG-like	363	61.54
y	WG-like	366	67.23

The LSP-like mode of the y-polarization was not characterized due to the modal overlap in increasing thickness, which makes the interpretation difficult, and was therefore excluded from further analysis. Nevertheless, the WG-like mode exhibits a decay length non-typical of LSP resonances at ~ 67 nm. Unlike other resonances, the WG-like mode exhibits a linear resonance behavior with respect to coating thickness. By contrast, the LSP-like resonance, which from this point forward refers to the x -polarized case exclusively, was found to have a decay length of 26 nm, within the

expected range (10-30 nm) for LSP resonances, and saturation with coating thickness ~ 50 nm. The WG mode brings about an atypical decay length (around 60 nm) in both x - and y -polarization as a result of longitudinal oscillations of the longitudinal oscillation of transversely confined surface plasmons. Despite the shorter starting resonance wavelength at 624 nm compared to the LSP mode (~ 711 nm), the WG-like mode demonstrates a higher bulk sensitivity, consistent with our earlier findings. Curiously, despite the longer decay length of WG-like x mode, the resonance saturates coating thickness greater than ~ 45 nm. This is attributed to modal mixing of the longitudinal and transversal mode, evidenced by the spectral proximity of the WG-like mode to the broad LSP mode. At saturation ($t = 50$ nm), the contrast of the WG-like mode recovers and increases. However, the resonance is no longer perturbed by the environment and behaves as with the bulk environment.

The difference in resonance mechanisms can further be illustrated in the planar structure with equivalent resonance wavelength where the resonance is LSP-dominated. Equivalent resonances to the tall case ($h = 150$ nm) for the planar regime were found by adjusting the s parameter, corresponding to arm length, while all other parameters remained fixed ($\theta_{60}, p_{3s}, w_{30}$). Wavelength normalization accounts for the proportionality relationship between LSP and bulk sensitivity to provide a more meaningful comparison of the resonance mechanisms. This is illustrated by the similarity of calculated S_B (x -polarized) of $v_{60}s_{66}h_{30}$ and $v_{60}s_{100}h_{150}$, with 316 and 318 nm/RIU, supporting the proportionality relation. $v_{60}s_{66}h_{30}$ resonates at 718 nm, 4 nm longer than the LSP mode of $v_{60}s_{100}h_{150}$. Although the resonances do not fall exactly in the same position, the trends are expected to be similar. Experimentally, bulk sensitivities are significantly lower for the planar (119 nm/RIU) and higher for the tall (327 nm/RIU).

Figure 4.10 Numerically simulated sensing characteristics of planar ($h = 30$ nm) and tall ($h = 150$ nm) vSRRs. The functionalization and capture layers are denoted by the yellow and green bands respectively, with model thickness of 10 nm as reported in the literature. The detection region for the analytes is denoted by the gray dashed arrow.

The differing resonance behaviors of such structures with equivalent resonance wavelengths indicate that height-induced mode can be utilized as a strategy for extending sensor dynamic range (Figure 4.10). This is evident for the y-polarized WG-like mode, for which the evanescent field is considerably larger than the planar LSP Figure 4.10(b). The extension comes at the expense of reduced surface sensitivity, but may be a necessary trade-off for practical applications where multiple surface functionalization is required for more specific sensing. The importance of plasmonic decay length lies in extending the dynamic range for the surface sensing applications. Having an evanescent field on the order of biomolecules is an advantage of pure LSP mode (in planar nanostructures), but also presents a dilemma in the sensing of specific targets where surface functionalization is needed to minimize nonspecific binding. Current strategies primarily implement polyethylene glycol (PEG) layers for suppressing molecule interactions with the substrate, of which generally thicker layers increase robustness [58,149]. The presence of functionalization layers effectively moves the target analytes further away from the metal surface, thereby reducing the effective

surface sensing range for analyte detection which follows. As layer thickness approaches the plasmonic decay length, molecular binding events with target analytes may become obscured, or more detrimentally (depending on the molecule dimensions), evade detection due to signal saturation. This is illustrated in Figure 4.10, where the thickness of functionalization [150] and capture layers are denoted by colored bands. The detection regions for analytes (denoted by the gray dashed arrow) are larger for the hybrid modes due to their larger plasmonic decay length, particularly for the y -polarized waveguide-like hybrid mode. Therefore, while such an extension of dynamic range comes at the expense of reduced surface sensitivity, this may be a necessary trade-off for practical applications that need multiple surface functionalization for more specific sensing. As such, we observe that the transverse-longitudinal modes found in the tall structures presents as a strategy to engineer the application-based optical response which can overcome the limitations of planar LSP resonances while maintaining high performance.

Appropriate characterization of surface-level sensing metrics is complex, and several metrics have been proposed such as the surface sensitivity $\eta_S = \Delta\lambda_{LSPR}/\Delta t$ [151] for a given analyte refractive index n_a and the second order surface sensitivity $\frac{\partial^2 \Delta\lambda_{LSPR}}{\partial n_a \partial t}$ [59], which, when applied to Equation (4-1), yields $(2m/l_d) \cdot \exp(-2t/l_d)$, in turn yielding $2m/l_d$ as $t \rightarrow 0$. Central to the discussion is the prefactor conditions for the surface figure of merit (FOM_s), which can be defined as $FOM_{PF} = \frac{2S_B}{l_d FWHM} = \frac{2FOM_B}{l_d}$. The effects of height on the prefactor for planar ($h = 30 \text{ nm}$) and tall ($h = 150 \text{ nm}$) vSRRs are determined using experimental characterization data and numerical decay length. The planar structures for the comparison are made of an array of e-beam evaporated nanostructures of 30 nm height on ITO ($150\Omega/\square$).

Electroplating is less suitable for structures of lower heights (which are easily achieved with physical deposition), as the resonance cannot overcome free-carrier loss originating from ITO conductivity ($20\Omega/\square$), which reduces the spectral contrast. Taller structures, owing to the larger presence of gold material, are able to overcome the contrast reduction from substrate-related damping (see Appendix). As seen in Table 4.4, the FOM_{PF} for tall structures are up to 9X higher than its planar counterparts.

Table 4.4. Surface sensing characteristics of planar and tall vSRRs.

Polarization	Dimension	Resonance Mode	$\lambda_R[nm]$	$S_B [nm/RIU]$	Linewidth [nm]	$l_{d,numerical} [nm]$	FOM_B	FOM_S prefactor
x	$s_{100}h_{150}$	LSP-like	755.7	327	43.32	26.08	7.55	0.29
	$s_{70}h_{30}$	LSP	753.5	118	123.5	24.75	0.96	0.04
y	$s_{100}h_{150}$	WG-like	679.8	402	16.59	67.23	24.23	0.36
	$s_{80}h_{30}$	LSP	637.8	118	82.02	34.33	1.44	0.04

Finally, to demonstrate the surface sensing capability of tall nanostructures, monolayer sensing of alkanethiols is conducted. Thiols are a family of molecules consisting of a sulfur headgroup, stabilizer hydrocarbon chain, and a terminal group which confers functionality. In the case of alkanethiols, the terminal group is $-CH_3$. Sulfur preferentially binds to gold owing to its high affinity, where a covalent bond is formed. Longer chain length thiols ($n > 14$) were used due to its improved packing density [152] compared to shorter chains which were observed to demonstrate the “short-chain effect” [153]. The presence of thiols on the surface induced red-shift in the spectra (Figure 4.11(a)). Using the approximation of Equation (4-1), thickness of the layer adsorbed onto the gold surface is deduced with mean values $1.89 \pm 0.18 nm$ and $2.54 \pm 0.0281 nm$ for tetradecanethiol ($C_n = 14$) and octadecanethiol ($C_n = 18$), respectively. Figure 4.11(a) – (b) presents the experimental transmittance of $v_{60}s_{80}h_{150}$ vSRRs functionalized by different alkanethiols, while the resonance shifts as a function

of carbon chain lengths are shown in Figure 4.11(c). In terms of nanometer per carbon chain (nm/cc), the surface sensitivity of $\nu_{60}S_{80}h_{150}$ vSRRs are found to be ~ 1.06 nm/cc (for x -polarized LSP-like hybrid mode) and ~ 0.6 nm/cc (for y -polarized waveguide-like hybrid mode). In addition, we functionalize $\nu_{60}S_{100}h_{150}$ vSRRs, from which surface sensitivities of ~ 1.49 nm/cc and ~ 0.73 nm/cc are obtained for x -polarized LSP-like and y -polarized waveguide-like hybrid modes, respectively, based on linear fitting results. Despite a surface sensitivity difference of over half, the deduced thicknesses for both polarizations are in good agreement, verifying the capability of either polarization to resolve carbon chain resolution. The obtained thickness is within published experimental and theoretical values for $C_n = 14, 18$ [154,155], where variations may be due to the chain orientation (tilting). We note that presence of carbon chain length on the nanostructure concurrently, caused contrast reduction, as longer chains are associated with higher absorption of the molecule in the visible region [156,157]. Experimentally, longer chain thiols are linearly associated with lower contrast. It should be noted that the extent of reduction depends on the molecule absorption rate in the spectral region. Biomolecule absorption bands are typically within the UV-vis region, of which depends on their chemical structure [158].

Figure 4.11 Surface sensitivity of tall vSRRs. (a)-(b) Experimental x-polarized (a) and y-polarized transmittances (b) of $v_{60}s_{80}h_{150}$ vSRRs functionalized with different alkanethiols. (c) The resonance shift with respect to carbon chain length of alkanethiols for $v_{60}s_{80}h_{150}$ vSRRs (circles) and $v_{60}s_{100}h_{150}$ vSRRs (squares) for the x-polarized LSP-like hybrid mode and y-polarized waveguide-like hybrid mode.

4.4 Conclusion

We have presented a detailed investigation of moderate to high aspect ratio v-shaped split ring resonators and experimentally characterized their performance as a plasmonic sensing platform. The resonance modes of tall plasmonic nanostructures can be understood as a hybrid between the transverse and longitudinal modes. The former is the localized surface plasmon resonance typically found in planar metal nanostructures, which blue shifts with the increasing height; while the latter is the resonance mode associated with longitudinal plasmonic oscillations, which red shifts with the increasing height. We focused our analysis on the intermediate regime in which the mode interference between the transverse and longitudinal modes give rise to split resonances associated with LSP-like and waveguide-like hybrid modes. The sensing performance of tall vSRR structure have been comprehensively characterized in terms of their figure of merit, sensitivity, and resonance wavelength in the bulk and surface cases. In

particular, we have shown that the significant improvements in the sensing performance are largely attributed to two factors, namely the increased interaction volume facilitated by the longitudinal plasmonic oscillations and higher Q-factor of the waveguide-like mode. We experimentally demonstrated a waveguide-like hybrid mode with $Q = 41$ from the 150-nm-thick ν SRR ($\theta = 60^\circ$, $s = 100\text{nm}$) which exhibits a bulk figure of merit as high as $FOM_B = 24$ at a 679.8 nm resonance wavelength. This is ~ 10 times higher than the typical FOM_B ranges of the planar plasmonic nanostructure, and to the best of our knowledge marks the highest achieved FOM in the visible frequency range. The tall structures were found to have up to 9X higher surface FOM prefactor ratio, and surface sensing is demonstrated experimentally for detecting the presence of monolayers of various chain length thiols. Despite different absolute carbon chain sensitivities for the x- and y-polarization, the obtained thickness estimates are in good agreement with each other and the literature, confirming the feasibility of the waveguide mode for surface-based sensing. We have also demonstrated a practical nanofabrication technique based on a combination of nanopatterning and seedless electrodeposition for the realization of a sensing platform with high sensitivity and high FOM in the visible range. In addition to better surface morphology of the electrodeposited gold which improves the Q-factor, the absence of the gold seed layer in the seedless electrodeposition process also expedites the excitation of the waveguide-like mode with $FOM = 24$ in the moderately high aspect ratio plasmonic nanostructures.

Chapter 5 SENSING PERFORMANCE OF TALL

NANOSTRUCTURES WITH NANOSCALE GAPS

In the previous two Chapters, we explored sensing using unconventional modes in split ring resonators (SRRs), specifically, v -shaped SRRs (v SRRs). In this Chapter, we focus on the modes and confinement in structures with nanoscale gaps, specifically planar and tall square dimers. The surface sensitivity of the v SRR structures was previously discussed in terms of the decay length l_d , which is the characteristic length of the evanescent tail or near-field enhancement surrounding the resonator, associated with a given mode. Metallic dimers have been a subject of theoretical and practical interest in nanophotonics due to their extremely high field localization and enhancement within the gaps [78,159–161]. In this chapter, the effects of height on the field enhancement in dimer structures and their variants are explored. As seen earlier, the optical properties of a nanoparticle largely depend on its material and physical properties, such as size and shape, with each absorbing and scattering light at different wavelengths. When nanoparticles are clustered together, the interactions of charge oscillations and near fields of particles and their neighbors yields more interesting results and presents another degree of freedom in terms of its tunability. When a pair of nanoparticles are placed adjacent to each other to form a dimer, plasmonic modes interact to form a unique optical response [162], which can result in interesting properties such as the Fano resonance for asymmetric squares [163]. The dimer structure was chosen in this study for its large local in-plane E-field across the dimer gap. Enhancement of light-matter interaction in dimers with sub-10 nm gaps have been widely studied, notably in the emission enhancement of quantum emitters [164,165].

Such large field enhancements can be useful in detecting the presence of adsorbed molecules on gold surfaces [166,167]. In this chapter, we theoretically and experimentally observe the mode evolution and associated coupling mechanisms in dimer arrays with modified geometry.

In Chapters 3 and 4, the use of alternative resonance mechanisms were investigated for the improvement of one or more sensing parameters in a low-symmetry (single mirror symmetry) geometry with v-shaped split ring resonators (vSRR). It was found that a height increase contributed to improved sensitivity. In this Chapter, we explore the role of height to other nanostructure geometries. More specifically, we use square dimers as the building block to study the waveguide hybridization dependencies in symmetric and asymmetric configurations which are based on capacitive and conductive coupling. The methods used here can be found in Chapter 4.2.

5.1 Results and Discussion

5.1.1 Capacitive Coupling

If a single metallic nanostructure can be thought of as a plasmonic “atom”, then dimers form the simplest configuration of plasmonic “molecules”. Two nanoparticles are placed adjacent to each other, separated by a dielectric spacer, and characterized by their gap separation g . In addition to the gap, the resonance is also determined by nanoparticle dimensions, by length and height. When the gap is increased beyond a certain threshold, there is no near-field coupling between structures, and its optical properties resembles those of isolated disks. At sufficiently short gap distances, electric fields from these constituent particles begin to interact and result in plasmon hybridization [160]. When the interparticle distance reaches zero, the structure resonates

as a nanorod. Notable to capacitively coupled dimers are the high field localizations within the dimer gap.

Figure 5.1. Numerical transmission height mapping of dimer modes for heights h between 10 - 500 nm for gold dimers with gap spacing $g = 16$ nm, and lateral dimensions $s = 100$ nm in the (a) x- and (b) y-polarization. Colored dashed curves indicate resonance modes while dashed vertical lines denote the planar, intermediate, and waveguide regimes.

Transmission mapping of height effects for square disk dimers with lateral dimensions of 100 nm and gap of 16 nm are shown in Figure 5.1. Numerical transmission height mapping of dimer modes for heights h between 10 - 500 nm for gold dimers with gap spacing $g = 16$ nm, and lateral dimensions $s = 100$ nm. Excitation parallel to the gap axis (x polarization) exhibits a strong field confined to the gaps. The planar regime, which supports purely LSP modes (m_1 , denoted by the blue dashed line), includes structures of height $h < 80$ nm. Planar resonances are characterized by a single broad resonance (Fig 5.2(a)). The transverse LSP-dominated mode (m_1) asymptotically blue-shifts with increasing height. Meanwhile, the intermediate regime ($80 \text{ nm} < h < 200 \text{ nm}$) is marked by emergence of a shorter mode (m_0) and longitudinal, waveguide-like mode (m_2). The latter mode is characterized by a narrow resonance in the longer wavelength region relative to the transversal LSP mode. It

should be noted that resonance mode labelling used in this chapter is a non-standard arbitrary assignment to simplify comparisons with the conductively-coupled dimer-based geometries seen later in the chapter. Dimer-associated longitudinal modes are found to linearly red-shift with respect to increasing height, i.e. $d\lambda_R/dh$ is a positive constant for a given guided mode. The resonance associated with constructive interference along this longitudinal oscillation is the longitudinal guided mode, whose resonance condition is expressed as:

$$2k_0 n_{eff} h + \phi_1 + \phi_2 = 2\pi m, \quad (5-1)$$

where $k_0 = 2\pi/\lambda_0$ is the free-space wavenumber of incident light, n_{eff} is the effective index of the propagating surface plasmon mode along the height, m is integer denoting resonance order, and $\phi_{1,2}$ are the wavelength dependent reflection phases at the top (air) and bottom (substrate) interfaces of the dimer. This guided mode is denoted by the dashed white lines in the transmission mapping. When $h > 200 \text{ nm}$, higher-order guided modes are observed and described as the waveguiding regime due to the dominance of the longitudinal mode oscillating along the nanostructure of taller heights. Higher order modes exhibit comparatively less spectral detuning, yielding greater spectral complexity. However, our analysis is limited to the intermediate region, at the onset of the first guided mode until the start of the next guided mode.

Consistent with previous observations for tall vSRRs, height increase in the planar regime results in blue-shifting of the LSP mode, due to decreased damping loss in taller structures. This is because taller nanostructures have a larger cross-sectional area for the plasmonic “wire”, which leads to smaller “ohmic loss”. The phase difference between the localized surface plasmons at the top and bottom interfaces of taller structures can no longer be ignored, which gives rise to resonance splitting around $h = 80 \text{ nm}$. The

plasmons decouple from each other and oscillate back and forth (m_2). This effect is observed in the electric field distributions along the XY and XZ midsection slices for 30 nm (Fig. 5.2(b,d)) and 140 nm (Fig. 5.2(c,e)). In particular, transversal plasmons are weaker in the intermediate owing to the plasmonic decoupling. By contrast, the planar case exhibits greater field confinement uniformity.

Figure 5.2.(a) Representative numerical transmission spectra for x-polarized dimer resonance modes with respect to height for planar to intermediate regime. In the planar regime ($h < 80$ nm), LSP modes exist which blue shift with increasing height ($h = 60$ -160 nm). In the intermediate regime, a guided mode marked with a narrow lineshape emerges, shown as m_2 . Contrast progressively increases and wavelength red-shifts for increased height. (b) E_x and (d) E_z field components for the planar case, and (c) E_x and (e) E_z field component cross sections for $h = 140$ nm. The XY cross-sections were sliced from the midsection.

The height-dependent spectral evolution is shown in Fig. 5.2(a). For $h = 70$ nm, m_1 resonates at 657.7 nm. At $h = 80$ nm, the mode splits to be m_0 at 549.7 nm while m_1 blue-shifts to 648.7 nm. Towards taller height, m_2 red-shifts with increasing contrast. m_0 and m_1 overlap, emerging as a spectrally indistinguishable broad resonance. For y polarization, a similar height-dependent behaviour is observed, with splitting in structures taller than 100 nm. The onset of a guided mode is first observed when $h = 100$ nm, albeit of low contrast. Between the first- and second-order guided mode, the

resonance of m_1 is broadened, due to its proximity with m_0 . Up to $h = 260$ nm, the higher order modes resonating within 500-700 nm are observed to undergo mixing, exhibiting a broadening resonance as a function of thickness, unlike guided modes in the longer region (700-800 nm).

Numerically simulated characteristics are observed experimentally for dimer disks of length and width $s = 100$ nm, $g = 16$ nm by methods described earlier. Measured transmission of electroplated structures at the planar to intermediate regions ($h = 60 - 140$ nm) are shown in Figure 5.3. Compared to electroplated v SRRs of the same pulse number, dimers are ~ 10 nm shorter for the tallest structures within a batch. The experimental variation is attributed to differences in the lateral dimensions between the two arrays. Although nominally the dimers in this study are of larger periodicity $p = 4s$ in both x and y directions (compared to $p = 3s$ for v SRRs), square dimers occupy a larger area than v SRRs of the same length. An LSP mode is observed experimentally for $h = 60$ nm, where blue-shifting trends in good agreement with numerical simulation. Experimentally, this mode resonates at the NIR region (~ 862 nm) for x -polarization (Figure 5.3(a)). We note that experimental results are red-shifted compared to the numerical due to non-idealities arising from sample fabrication, in addition to the use of an ITO substrate for the electroplating process which is known to impart an additional red-shift. With increasing height ($h = 80$ nm), mode splitting is observed, where m_0 is ~ 635 nm. m_1 is associated with localized plasmons at the substrate and the shorter mode m_0 is associated with localized plasmons at the top surface. A height of 100 nm is understood to lie at the transition region marking the onset of a guided mode (see Figure 5.2(a)). At $h = 140$ nm, the longer resonance is identified as a guided mode owing to the red-shifting behaviour with shorter modes attributed to m_0 and m_1 as seen in the numerical simulations. Experimental results in the y -polarization are

similarly consistent with the numerical trends. The optical spectrum consists of a mode contributed from the oscillations of the dimer short axis. Due to the lower damping loss, we observe blue-shifting of the mode and comparatively narrower linewidth for $h = 140$ nm as compared to $h = 60$ nm.

Figure 5.3. Experimental spectra of dimers with respect to height in the (a) x-polarization and (b) y-polarization. The colored arrows correspond to modes shown in the numerical transmission height map Figure 5.1. Representative SEM images (false color) are shown in (b) top view and oblique view (45°) for (c) planar and (d) tall cases.

5.1.2 Conductive Coupling

In addition to conventional non-electrically contacted dimers, the properties of conductively coupled dimers are explored. Structural symmetry is modified by geometric conditions such as junction width and position in the y-axis. In the first case, the junction is positioned at dimer center ($y = 0$), with two axes of symmetry in the x - and y - direction much like the capacitively coupled dimer. In the second case, the junction is positioned at the bottom of the dimer ($y = -s/2 + w_j/2$, where w_j is the junction width), referred to as the u -dimers in this section. These structures bear

resemblance to conventional u-shaped SRRs, although the dimer variants are composed of comparably wider vertical arms.

Recently, resonances arising from a conductive pathway between nanoparticles have been proposed for improved sensing applications, where high field localization is observed in bridge proximity [168,169]. Such plasmon resonances were later termed charge transfer plasmon (CTP) [170–172], which has been proposed for biosensing applications. The presence of a junction conductance results in charge transfer between the dimers that is dependent on the conductivity of the structure, altering the resonance properties. The conductivity is singularly affected by junction geometry. The dimensional effects are related to the conductance, with dielectric function expressed as $\varepsilon(\omega) = 1 + j\sigma_J/\varepsilon_0\omega$ [172], where ω is the angular frequency and σ_J is the conductivity of the junction. Its parameters can be related to its conductance by $G = \frac{\sigma_J A}{g}$, with A being the junction cross-section touching the dimer face and length g represents the gap length between the dimer disks. The aforementioned expression indicates G is proportional to conductivity and the cross-sectional contact area. Therefore, charge transfer can be mediated by two ways: increasing the junction area and/or decreasing the interparticle distance, both of which would facilitate larger current along the junction. Here, we attempt to increase the charge transfer via the former strategy, with respect to junction height. Simulated transmission height maps for dimers with center junction are shown in Figure 5.4 for both x - and y -polarized incident light.

Figure 5.4. Numerical transmission mapping for square dimers with a center junction of width $s/2$ for heights h between 10 - 500 nm for gold bridged dimers with gap spacing $g = 16$ nm, and lateral dimensions $s = 100$ nm in the (a) x- and (b) y-polarization. Colored dashed curves indicate resonance modes while dashed vertical lines denote the planar, intermediate, and waveguide regimes.

For simplicity, the center junction case is referred to as “dumbbell” structures. The addition of the junction to the dimer contributes to a resonance m_2 in the x polarization (denoted in Figure 5.4(a) with green dashed lines) associated with a substrate-dominated field. Characteristic of localized plasmon modes, m_2 blue-shifts with respect to height, asymptotically shifting faster compared to the dimer mode m_1 until $h = 80$ nm. In the planar regime, m_2 corresponds to the resonance of a charge transfer plasmon (CTP), attributed to a current oscillating across the junction. Unlike a nanorod which has a low current density distribution, charge localizations in such coupled dimers give rise to large field enhancements which can potentially be implemented for sensing [173]. m_1 is identified as the screened bonding plasmon mode (SBDP) [170] due to reduced capacitance from the conductive medium in the form of a junction. The characteristic resonances profiles for the SBDP and CTPs are shown in Fig. 5.5(b) and (c) respectively. Beyond the planar regime, transversal CTP resonances decouple as seen for $h = 140$ nm and 200 nm in Figure 5.5(a), where CTP resonances are indicated by

blue arrows. In order to understand the resonance characteristics, we turn to the XZ cross-sections for $h = 140$ nm, with two resonances attributed to the CTP at ~ 633 nm (m_1) and ~ 795 nm (m_2) in Fig. 5.6. From (c) and (f), it can be observed that the m_2 resonance is associated with bottom CTP resonances, where the field is larger towards substrate. In comparison, m_1 is observed to have a larger electric field, localized in the gaps and oscillating out of phase. Meanwhile, m_0 at 563 nm exhibits SBDP plasmons where fields are not confined within the gaps. Taller heights are followed by decoupling of CTP modes, where three CTP-associated transversal modes are observed in $h = 200$ nm. As a result of the decoupling, the contrast of resonances at 671 nm and 747 nm reduces to ~ 0.0140 intensity units at $h = 190$ nm. Relative to the capacitively coupled dimer case, the intermediate regime spans greater range up to $h = 300$ nm. It is not until $h = 320$ nm that an additional split resonance emerges around 583.5 nm near a merged mode with resonance of 696 nm. Similarly, the guided mode within this region is broadened compared to the dimer case owing to multiple low contrast resonances. Interestingly, at $h = 400$ nm, the guided mode appears to transition from dip to peak modes, at ~ 700 nm.

Figure 5.5. (a) Transmission spectra for dumbbell resonances with height annotated. The blue arrows indicate resonances which are attributed to the charge transfer plasmon. (b) normalized E_z (top-view) of an SDBP mode and (c) CTP.

Figure 5.6. XZ cross-sections for $|E|^2$ (top) and normalized E_z (bottom) for (a,d) m_0 , (b,e) m_1 and (c,f) m_2 .

Figure 5.7. Characterization of the (a) experimental and (b) numerical response in x-polarization for dumbbell-type dimers of corresponding heights as labelled in (a). Top-view (b) and (c) oblique (45 deg) SEM images (false color) are shown for the bridged dimers. The colored arrows indicate resonance modes as seen in the transmission height mapping in Figure 5.4.

Experimental results for x -polarization are presented in Figure 5.7. Due to spectral similarities of the dumbbell with the dimer case, the y -polarized is not shown. Figure 5.7(b)-(c) present SEM images of fabricated dumbbells, in which gaps along top and bottom are observed. A junction half the width of s was chosen, and the gap length g remains at ~ 16 nm, as with previous dimers. Experimentally for $h = 60$ nm, a single broad resonance is observed which is attributed to the CTP resonance $m_2 \cdot m_0$ resonating at ~ 580 nm numerically is not evident experimentally, presumably due to lower contrast for shorter nanostructures until a sufficiently tall height ($h = 140$ nm), where contrast is generally lower in part due to non-ideal excitation conditions from the condenser. The signs of an emergent dip associated with the SBDP (m_1) become stronger with $h = 100$ nm, at 556 nm. However, it is not until $h = 140$ nm that spectral contrast becomes approximately half of m_2 . The experimental trends are found to be in good agreement with numerical results. While we observe the CTP mode (m_2), for high FOM sensing, a narrow linewidth is preferred. As such the narrower m_1 is used to monitor refractometric changes which will be discussed later in the chapter.

For the second case, the junction is positioned off-center at a bottom edge, referred to as a u -dimer, where the structure of which can be seen in the schematic inset in Figure 5.8(b) and in the normal- and oblique-incidence SEMs of Figure 5.10(b-c). The junction function is akin to a u -SRR. The modification of lateral properties alters the optical response to a more complex profile for heights taller than 150 nm, as evidenced by the height map in Figure 5.8.

Figure 5.8. Numerical height transmission mapping for gold dimers with bottom junctions in the (a) x- and (b) y-polarization with height h between 10 - 500 nm with gap spacing $g = 16$ nm, and lateral dimensions $s = 100$ nm in the (a) x- and (b) y-polarization. Colored dashed curves indicate resonance modes while dashed vertical lines denote the planar, intermediate, and waveguide regimes.

Much like the first two cases, a shorter m_1 mode (LSP, denoted by the blue line) and a longer m_3 (green dashed line), which can be understood as LC resonances when light is coupled parallel to the gap. The rate of blue-shift for m_3 , whose field contributions arise from gap tips, is more gradual than that of the m_2 resonance in the dumbbell case. For $h > 40$ nm, a narrow resonance at ~ 790 nm between m_1 and m_3 emerges, denoted as m_2 (green dashed line). Heights up to ~ 200 nm do not influence the resonance position of m_2 significantly. Within the intermediate regime ($40 < h < 300$ nm) m_3 exhibits higher spectral contrast and broadening compared to other modes (Figure 5.10). m_1 which is the transversal mode, decouples in $h = 140$ nm, where the XZ cross-section shows the field out of phase propagating along the gap. The mode is associated with the largest field relative to other modes for the height and exhibits low spectral contrast. By contrast, m_2 and m_3 modes demonstrate oscillations which are in-phase along the gap. Evolution of the spectral contrast from the planar to intermediate regime is illustrated in Figure 5.10(a), where the experimental spectra is in agreement

with the calculated trends (Figure 5.10 (d)). Attributed to low contrast, m_0 cannot be clearly discerned from m_1 .

Figure 5.9. Field distribution for the u -dimer. The first row shows the normalized E_x XY cross-section from above the structure. The second row pertains to normalized $|E_z|$ XZ cross-sections in front of the gap, while the $|E|^2$ is the third row. Each column corresponds to a resonance mode outlined in the transmission map denoted as (a) m_0 , (b) m_1 , (c) m_2 , and (d) m_3 .

Figure 5.10. Characterization of (a) experimental and (d) numerical data for u -dimers for heights = 50, 70, 80, 100 and 140 nm. Top-view (b) and (c) oblique (45°) SEM images are shown. The colored arrows indicates modes seen in the transmission height map in Figure 5.8.

Observation of the narrow m_2 mode is not apparent until around 140 nm height is reached, as the oscillations do not provide enough contrast for the inherently weaker resonance in practical measurements conditions. The mode is attractive for sensing and owing to its narrow linewidth, a Q-factor of 32.9 ($FWHM = 18 \text{ nm}$) is obtained for $\lambda_{m_2} = 608.9 \text{ nm}$, which is $\sim 5.9X$ higher compared to the Q-factor of 5.5 for m_3 ($\lambda_{m_3} = 793.6 \text{ nm}$, $FWHM = 142 \text{ nm}$). In agreement with height mapping trends, the slower blue-shifting rate for the u -dimer case means that the m_3 resonance for u -dimers would be more red-shifted compared to the dumbbell case ($\lambda_{m_2} = 766.3 \text{ nm}$).

5.1.3 Bulk and Surface Sensing

The resonance modes are characterized for bulk refractive index sensitivity, both numerically and experimentally. Experimental bulk sensing results for the three dimer variants are summarized in Figure 5.11, where marker sizes indicate the logarithmically-scaled FOM values for each. Measurements were conducted using Cargille Refractive Index (RI) liquids of different indices ($n = 1.3 - 1.38$). Observation of the m_0 mode in the y -polarization suggest similar resonance mechanisms, where bulk sensitivity (S_B) was found to be 138, 133, and 134 nm/RIU for the dimer, dumbbell, and u -dimer respectively, with air resonances 507-509 nm (denoted by red markers in Figure 5.11). This is consistent with behavior under y -polarized excitation in the numerical transmission height maps seen earlier. The FOM was found to be ~ 3.5 . On the other hand, for m_1 no shift is observed with respect to liquid index.

Figure 5.11. Summary of bulk sensitivities for dimers in the intermediate regime ($h=140$ nm). The sensitivity of waveguide modes appear to be linear for the x-polarization while the y-polarization is unchanged. The marker sizes denote FOM, scaled logarithmically with an additive constant.

The x-polarized modes were explored for sensing for m_1, m_1', m_2 , and m_3 modes. The trends indicate that for the x polarized case, the highest performing structures in terms of both FOM and bulk sensing arise from m_1' modes of a guided nature. m_1' refers to index-dependent resonances, characterized by a narrow linewidth. In air, the combination of insufficient contrast and modal overlap (e.g. as a shoulder resonance) makes its experimental observation challenging. The m_1' mode was not observed experimentally for dimers due to insufficient conditions of the medium needed to excite the mode, the behaviour which is described further later. For u-dimer, the mode is observable when n is 1.3. Meanwhile, m_2 (m_3) corresponding to the dumbbell (u-dimer) exhibits a linear trend, although the FOM values remain low (~ 1), despite resonating at longer regions (~ 800 nm). Recalling from XZ cross-sections earlier, these modes are attributed to substrate-dominated fields, relative to the field distribution of

other modes for the same structure. For dimer cases which exhibit higher order resonances, sensitivity linearly increases with respect to the resonance wavelength, in line with the initial resonance wavelength. Bulk sensing measurements in taller structures illustrate interesting spectral features, namely waveguide modes, due to the surpassing of the minimum height required to satisfy the resonance condition of Equation (5-1). Emergence of waveguide modes due to dependence of the effective modal refractive index n_{eff} (modal index) on the surrounding bulk and local dielectric permittivity happen when the structures are surrounded by a material with refractive index larger than unity, i.e. not in air. When a larger background refractive index is introduced, modal index increases, thereby lowering the height required to satisfy Equation (5-1). However, the conditions for this emergence also depend on the coating thickness and follows with a saturation of the m_0 mode response. Such behavior can potentially be exploited to tailor the spectral response to achieve two distinct features: (1) the surface depth at which the characteristic narrow waveguiding resonances emerges can be tuned to the depth of the target analyte without expending the most sensitive region (closest to the metal) on the functionalization layers, and (2) the narrow linewidth characteristic for waveguide-like modes contributes to a high performing sensor by attaining high FOM which has not been demonstrated in planar structures.

We begin by examining the experimental and numerical spectra of capacitively coupled dimers, shown in Figure 5.12. The two modes examine red-shifting behavior with refractive index changes. S_B is found to be 262 nm/RIU (m_1) and 174 nm/RIU (m_2), yielding bulk figure of merit (FOM_B) values of 3.8 and 4.7. m_1 was numerically found to consist of two overlapping modes which were indistinguishable experimentally due to low contrast of the resonance. Simulations in Figure 5.12(b) indicate that when refractive index n is between 1 – 1.3, the modes experience larger spectral detuning from

each other, towards the NIR/IR region. However, at $n = 1.4$, an additional broad mode is found around 800 nm, which continues with higher refractive indices.

Figure 5.12 (a) Experimental spectra of dimers in air and immersed in refractive index liquids between 1.3 - 1.38. (b) Numerical values of nanostructures in background indexes between 1-1.6 in steps of 0.1. The higher refractive index increases the spectral detuning of the long resonance.

For dumbbells, the effect of refractive index is observed in resonance narrowing of m_1 towards an asymmetric lineshape depending on the index conditions (denoted as m_1' when $n > 1$, due to ambiguity of the air resonance). In the transition, m_0 overlaps with an emergent mode observed in $n = 1.2$, and a characteristic narrow resonance is seen in higher refractive index mediums, described as m_1' . Experimentally, m_0 is not observed in air but the apparent broadening of the resonance at around 580 nm is consistent with numerical simulations. The origins of m_1' are seen in the simulated spectra of Figure 5.13(b), as a function of refractive index in the bulk. An emerging mode is seen at $n = 1.1$, with a weak mode at ~ 700 nm, blue-shifting with higher index. By $n = 1.3$, the mode, with a higher contrast, asymmetrically splits to the right of m_1 . For comparison, the spectral response of the planar ($h = 30$ nm) dumbbells in Figure 5.13(c) exhibits a single broad mode. In the tall case, m_2 yielded bulk sensitivity values of 175 nm/RIU, which is near to the m_2 resonance of dimers. Based on these values, we deduce that the dumbbell m_2 performs comparatively worse for bulk sensing

considering its resonance is 66 nm more red-shifted than that of the dimer (700 nm) given the $S_B \propto \lambda_R$ relationship previously discussed. By contrast, $S_{B,m_1'}$ is experimentally found to be 318 nm/RIU, with a notably high FOM of 26. It should be noted that because of the absence of m_1' in air, the bulk sensitivity was determined with reference to the dips at $n = 1.3$.

Figure 5.13 (a) Experimental spectra of dumbbells immersed in refractive index liquids between 1.3 - 1.38. (b) Numerical values of nanostructures in background indexes between 1-1.6 in steps of 0.1. (c) For comparison, the planar ($h = 30$ nm) in the same environment is shown without the emergence of additional modes.

To better understand the mode emergence, the height transmission map for the dumbbell structure is shown for a background index $n = 1.3$ (Figure 5.14(a)). The emergence of m_1' is within the intermediate regime (for $h = 100$ -200 nm), between m_1 and m_2 . The m_1' resonance has a narrow linewidth in contrast to its counterpart nodes. Here, m_1' splits from a guided mode at $h = 200$ nm. This is qualitatively different from the case of air, where m_1 and m_2 converge with m_3 (Figure 5.4(a)). m_1 and m_2 modes are also more spectrally detuned from each other for $n = 1.3$. Our results suggest that the intermediate regime ($h \sim 150$ nm) is sufficient for practical implementation, where taller heights strengthen mode features. Although the study pertains to the intermediate regime, we briefly discuss the waveguiding regime. A blue-shifted waveguide resonance can also be found with $h = 300$ nm, however the mode features exhibit

weakened contrast. When approaching the waveguiding regime, higher order modes are less spectrally detuned, and result in a broad resonance. Interestingly, the transmission dip shifts to become a strong peak (Figure 5.14(b), for $h = 400$ and 500 nm). Having considered the effects of bulk refractive index on the resonance modes of dimers and their variants, we next look at surface sensitivity.

Figure 5.14. (a) Numerical height transmission map for the dumbbell structure in $n = 1.3$, where mode splitting occurs between $h = 100 - 200$ nm. The gray lines serve as a guide to the corresponding spectrum shown in (b).

First, we examine the conformally coated dumbbell structure. Figure 5.15(a) shows the spectral evolution for the coated dumbbell structure with increasing coating thickness t_{coat} and a coating index of $n_{coat}=1.602$. The shorter m_0 is noted to be a mode of two split resonances (compare with the numerical spectra in Figure 5.7(d)). For thicknesses $10 < t < 30$ nm, m_0 at 642 nm responds to variations in the coating thickness (Figure 5.15(b)). As the mode approaches saturation ($t \sim 20$ nm), a narrow resonance m_1' emerges at 788 nm. The linear region for m_1' corresponds to a shift of 1.56 nm/nm. Although this is lower than reported in the previous chapter, the onset thickness for the waveguide associated mode hybrid mode is 20 nm.

Figure 5.15. (a) Spectral evolution (numerical) with respect to coating thickness for $n = 1.602$ in a dumbbell structure. (b) A second mode emerges when the first waveguide mode is approaching saturation. (c) Experimental spectra of monolayer alkanethiols of different length, insufficient to excite the waveguide mode.

The dynamic feature of this resonance opens interesting applications within the context of biosensing. Namely, one of the challenges in practical application has been the inherently short evanescent decay field which saturates the optical response within 10-30 nm of the metal surface, discussed previously. The shallow field in LSP resonances are not conducive to multi-layers which is often standard for analyte detection, due to its limited surface sensing range. The surface chemistry addresses the ability to capture a target analyte specifically (e.g. to minimize parasitic effects from nonspecific binding of other molecules to the capture molecule or surface). These methods typically involve the addition of a polyethylene glycol (PEG) layer [11,149] of ~ 10 nm, though more layers can improve the performance [58]. While it is possible to implement strategies such as surface plasmon resonance with a thin film or nanohole array (as opposed to *localized* surface plasmon resonance) to extend the evanescent decay field to lengths on the order of 100 nm, the field is then no longer confined to the metal nanostructure vicinity. Essentially, the sensing volume is increased, making minute changes in the shift more difficult to detect and increasing susceptibility to bulk effects. On the other hand, waveguide resonances are mixed modes, modulated by a

background LSP resonance. By increasing height, we gain two additional degrees of freedom to tune the resonance: (effective) refractive index, and coating thickness, owing to the specific onset conditions of m_1' . Therefore, the effective range of operation of the sensor can be tuned more flexibly according to the capture molecule refractive index and dimensions. Furthermore, the response benefits from higher performance in two aspects. The higher Q factor arising from narrower linewidths support enhanced sensing resolution (higher FOM), where the hybrid mode exhibits narrow resonance in contrast to pure LSP modes. Second, the proposed approach facilitates the feasibility of conducting more accurate measurements by ensuring an inert surface to reduce false positives in analyte detection.

The feasibility of this method is demonstrated from experimental surface sensing results in Figure 5.15(c). Alkanethiols (represented in the darker blue lines) with carbon chain lengths of 14 and 18 functionalized on the metal surface induce a red shift in the resonance modes. For our analysis, we focus on the more sensitive m_0 . The refractive indices of tetradecanethiol (14 C atoms) and octadecanethiol (18 C atoms) is 1.461. According to our numerical results, this is a sufficient refractive index for the introduction of the m_1' mode. However, the monolayer thickness, between 1.8 – 2.5 nm thick [154,155,174] does not meet the thickness criteria. As such, only the original two air-resonance modes are observed (m_0, m_1) in the spectrum. Nevertheless, m_0 is shown to be capable of resolving monolayer thiols. Furthermore, the evidence of m_1' seen in the bulk measurements support the viability of the proposed m_1' mode for sensing.

Finally, the bulk properties of the *u*-dimer are presented in Figure 5.16. Numerically, the air resonance supports four modes. Like the dumbbell case, m_1 is indistinguishable in the air resonance. This mode was identified to be associated with

decoupled oscillations (Figure 5.9(b)), and when in medium of higher refractive index (such as $n = 1.3$). Experimentally, three modes can be found, where two weak modes between 550-700 nm are indistinguishable. m_1' emerges experimentally at 660 nm when background index is 1.3, with a sensitivity of 211 nm/RIU and FOM of 11. By contrast, m_2 has a bulk sensitivity of 144 nm/RIU and FOM 8. We note that m_3 for $n > 1.3$ shifts beyond the spectrometer limit at 900 nm, leading to the cutoff.

Figure 5.16. (a) Experimental spectra of *u*-dimers immersed in refractive index liquids between 1.3 - 1.38. (b) Numerical values of nanostructures in background indexes between 1-1.6 in steps of 0.1. (c) For comparison, the planar ($h = 30$ nm) in the same environment is shown without the emergence of additional modes.

The spectral evolution of surface thickness (Figure 5.17, $n = 1.602$) indicates that the functionalization region (before waveguide excitation) is 50 nm, longer than the 20 nm seen with the dumbbell case. However, this comes at the expense of lower surface sensitivity as the field distribution is spread amongst more modes (Figure 5.17(b)).

Figure 5.17. (a) Spectral evolution of u -dimers with respect to coating thickness for $n = 1.602$. (b) A second mode emerges when the first waveguide mode is approaching saturation. (c) Experimental spectra of monolayer alkanethiols of different length, insufficient to excite the waveguide mode.

As expected, alkanethiol functionalization red-shifts the air resonance, without exciting the waveguide mode Figure 5.17(c). For octadecanethiol, the contrast of the air-supported m_1' mode becomes difficult to distinguish, which could be due to the formation of new absorbance bands in the 600-800 nm region that would reduce transmission contrast, as has been observed for thiols [175]. While this may be true for thiols, protein absorption differs due to its chemical structure [158], which typically consist of peptides and aromatic chains, absorbing in the UV range (~ 180 -300 nm).

Although the spectral complexity seen with the u -dimers may not be ideal in practice stemming from the many (> 4) modes, other dimer geometries were explored which showed potential for surface functionalization applications. In particular, center-bridged dimer can provide an alternative resonance mechanism to overcome the challenges of practical biosensing.

5.2 Conclusion

In this chapter, we explored the effects of height on dimer-based nanostructures and their viability for sensing. Dimers are an interesting case study owing to its inherently radiative nature and ability to localize light within nanoscale gaps, where the extent of localization is dependent on the gap distance. Compared to its planar counterparts, taller structures provide an added dimension of design flexibility by way of effective refractive index and coating thickness for tuning sensing performance. The inclusion of a conductive junction between the dimers was found to induce a more complex spectral response, the degree to which is determined by the position of the junction. This is because the longitudinal position determines the symmetry of the structures. By vertical extrusion, the cross-sectional area of the junction can be increased, resulting in a higher conductance. In both cases, it was found that high Q resonances of waveguide-like modes can be excited when the effective index is modified by a surface coating of appropriate index and thickness. The onset of the resonance is dependent on the thickness of the surface coating and refractive index. From this work, we have demonstrated dimers as another platform in moderately tall nanostructures.

Chapter 6 CONCLUSIONS AND FUTURE WORK

Nanoscale light confinement in subwavelength metallic structures gives rise to plasmons which are sensitive to the dielectric environment. This property can be exploited for sensing refractometric changes from analyte layers. The overarching aim in this work is to investigate strategies to improve one or more sensing parameters for attaining high performing transducers in the visible wavelength range, where this spectral region is preferred in the interest of low-cost. The findings from the work go towards the long-term aim of biosensing for multiplexed detection. LSP-based sensing has several challenges impeding its applications. First, the visible range will inherently underperform in terms of sensitivity, compared to longer wavelength regions, as a result of the linear relationship between resonance wavelength and sensitivity. Furthermore, the short decay length from the surface limits the surface chemistries for reducing parasitic signals (nonspecific binding) in targeted analyte binding. In this work we have identified strategies to tailor the resonance properties, such as by the magnetic resonance or the waveguide mode, while addressing and improving the challenges as-stated.

6.1 Summary of work

In this work, we proposed and demonstrated strategies to enhance LSP-based sensing towards the realization of a practical low-cost biosensor. Various facets of nanoplasmonic sensing were studied to this end. In our investigation of fabrication methods (Chapter 2), we found top-down methods addressed the needs of the project in terms of design versatility of the nanostructures. Planar v-shaped split ring resonators were scaled down to resonate in shorter wavelengths and excite the fundamental

magnetic mode, which was presented in Chapter 3. As a result of removing the bottom arm of the conventional u-shaped split ring resonator, the resonance of higher order modes can be eliminated, facilitating the push of the magnetic resonance in shorter wavelength regions (~600-800 nm). By this method, it was found that analyte dynamic range and sensitivity are greater as compared to the electrical resonance normalized to the air resonance of the wavelength. These improvements are attributed to the circulating current and electric field enhancement, where the field strength can be tuned according to the opening angle of the v-shape. In the context of multiplexed sensing, several dimensions can be adjusted: opening angle, arm length, and arm width, parameters which will allow adjusting the air reference. For this, the modes are highly localized and confined within the sensing volume.

In Chapter 4, a height parameter is introduced to vary the resonance of the ν SRR. By increasing the height sufficiently to moderately tall nanostructures in the intermediate regime (heights between 80 nm – 200 nm), hybrid transversal-longitudinal modes are introduced. The taller structures improve visible range biosensing in two aspects. First, the height dimension can blue-shift the resonance for larger resonator geometries (simpler fabrication) to the target region. Second, when height is extended sufficiently, top and bottom surface plasmons decouple and oscillate along the length of the structure, where mode contributions arise due to LSP and waveguide-like modes. It was found that the larger spectral detuning from the background LSP mode, achieved by excitation in the waveguide propagation direction, can give rise to lower damping loss and narrower linewidths, higher Q-factor and figure-of-merit, which corresponds to higher surface sensing parameters. The Q-factor for LSP-based resonances are limited by the material permittivity, but are overcome with the longitudinal mode. FOM_B of up

to 24 was found, and the structures were demonstrated in resolving surface sensitivity of carbon chains.

In Chapter 5, the concept of a transversal-longitudinal mode is extended beyond the v-shape. Dimers were used owing to the high field-localization in nanoscale gaps, which is a well-studied phenomenon. Two cases were investigated: the capacitive and conductive coupling. For conductive coupling, a junction was added in between the dielectric spacer of the square disks. The effects of the junction lateral position (at the center and bottom) were found to significantly alter the response owing to the symmetry changes from its position. The modification of the effective refractive index gave rise to narrow linewidth spectral features, absent in the air resonance. The onset of some waveguide modes are found to depend on analyte thickness, which can overcome shallower localized evanescent fields, which may be necessary for specific binding in biosensing. The emergence of the longitudinal mode was verified experimentally by both bulk and surface sensing measurements. An FOM_B of 26 was observed in the x-polarization, resonating at 642 nm for the dumbbell case. In addition, a delayed onset of the longitudinal mode (e.g. initial thickness of 20 nm (for $n = 1.602$)) for height of 140 nm gives rise to a 40 nm dynamic range for surface sensing within a linear region unconsumed by functionalization layers. In the practical application, the first 20 nm of allowance can be designated as functionalization layers, and designed according to the functionalization needs, which is in contrast to conventional planar LSP modes saturating after ~20-30 nm.

Furthermore, we found that tall structures can introduce narrow-linewidth resonance modes in the intermediate regime. The delineations for these regions are modulated by transversal LSP mode characteristics according to its lateral geometry. The LSP-like longitudinal mode can be implemented as an alternative biosensing resonance

mechanism and engineered according to application requirements. The merits of our work include its simplicity in several aspects. In measurement, the modes are excited only by normal incidence as opposed to oblique incidences. Secondly, additional degrees of freedom are found when tailoring the resonance (lateral dimensions, onset thickness) while remaining resonances in the visible region (robustness, low-cost).

The subsequent investigation would be the selection rationale and appropriateness of geometry. It should be noted that there is no ‘one-size-fits-all’ which can be applied for all biomolecules owing to the variability in their optical properties. Shape-appropriateness is dependent on priorities of the application outcome. The characteristics of molecule (and its related interfacial chemistries) under investigation should be used as a guide. Parameters such as arm length, opening angle, coupling strategy, height introduces more design versatility and flexibility. We found that the intermediate wavelength regime facilitated by the moderately tall structures could introduce spectral features which can provide solutions for current LSP-based challenges in surface sensing.

Finally, it should be highlighted that although the fabrication aspect was not the focus of this thesis, the seedless electrodeposition method used to realize the nanostructures in this work is a cost-effective method that can improve metal quality owing to its growth process. This does not require expensive precious metal targets (low-cost), but instead hobbyist electroplating solution and simpler compared to milling or X-ray lithography methods (robust), which are slow and have a higher chance of sample contamination.

6.2 Recommendations and Future Work

Based on the outcome of this work, we recommend several follow-up studies outlined as follows:

1. The sensing characteristics of the ν SRRs and dimer structures have been studied in detail. However, the exponential decay length is numerically determined. Despite the good agreement between the simulations with experiments, it would be of interest to conduct experimental validation of exponential decay length in surface sensing using layer-by-layer deposition methods. LbL deposition can be accomplished by polyelectrolyte layers deposition such as by poly(sodium 4-styrenesulfonate) (PSS)/ poly(acrylic acid) (PAA) or the use of atomic layer deposition to deposit, for example, Al_2O_3 layers. These sets of experiments would contribute to the experimental characterization of the evanescent decay field of the plasmon modes.
2. We have demonstrated the biosensing capability for our planar ν -shaped split ring resonators and resolved carbon chains using tall structures. The next line of work is to conduct specific binding experiments of biological species of interest on tall structures. This would include developing the appropriate functionalization layers for attaining an inert surface. To improve measurement accuracy, multiple structures (multiplexed detection) on the sensing area (such as ν SRR resonators of various arm lengths, with fixed opening angle) could provide a more accurate quantification by narrowing the measurement error margin towards practical deployment.
3. The structures in this work exhibited symmetry conditions, which adds polarization-dependence in its measurements. Investigating rotationally-

invariant tall structures which do not have a polarization requirement can increase the robustness of the sensing platform. For example, simplified optical configuration (without polarizers) may be well-suited for measurements in point-of-care settings. The structures used in this thesis can act as the elementary particle by which rotational invariance is introduced. Conductive coupling of v-shapes sharing a vertex can give rise to star structures of rotational invariance where spokes present as another degree of freedom in the resonator design. Similarly, u -dimers can be conductively joined to form gammadion structures. The aims would then be towards the assessment of sensing performance, relative to those in this current work. It would also be interesting to investigate emergent resonances which can be exploited for biosensing.

4. Another parameter yet to be explored are the lattice resonance conditions on the high-aspect ratio structures. Lattice symmetries have been shown to introduce narrow linewidths, owing to the coupling of diffracted waves with localized surface plasmons. The effects of height can be explored for relevance for biosensing applications (surface sensitivity).

AUTHOR'S PUBLICATIONS

Journals

Thesis-Related

1. **Soehartono AM**, Tobing LYM, Mueller AD, Zhang DH, Yong K-T. Hybrid transverse-longitudinal modes for high figure-of-merit localized plasmonic refractometric sensing in the visible spectrum. *Advanced Optical Materials*. 2020. (**First Author**)
2. **Soehartono, AM**, Tobing LYM, Mueller AD, Yong K-T, Zhang DH. Resonance modes of tall plasmonic nanostructures and their applications for biosensing. *IEEE Journal of Quantum Electronics*. 2019; 56(2). (**First Author**)
3. **Soehartono AM**, Tobing LYM, Mueller AD, Zhang DH, Yong KT. Longitudinal modes of capacitively and conductively coupled dimers. (*In preparation*) (**First Author**)
4. **Soehartono AM***, Mueller AD*, Tobing LYM, Chan KK, Zhang DH, Yong K-T. Ultra-small v-shaped gold split ring resonators for biosensing using fundamental magnetic resonance in the visible spectrum. *Nanotechnology*. 2017;28:405305. (**Co-First Author**)

Collaborative Work

1. Tobing, LYM, **Soehartono AM**, Mueller AD, Yong K-T, Zhang DH. Interplay of near- and far-field coupling in 3-disk arrays for high figure-of-merit localized surface plasmon-based sensing. 2020. (*Submitted*)
2. Panwar N*, **Soehartono AM***, Chan KK, Zeng S, Xu G, Qu J, Coquet P, Yong K-T and Chen X. Nanocarbons for Biology and Medicine: Sensing, Imaging, and Drug Delivery. *Chemical Reviews*. 2019; 119 (16), 9559-9656.
(Co-First Author)
3. Han Z, **Soehartono AM**, Gu B, Wei X, Yong K-T, Shi Y. Tunable hybridization induced transparency for efficient terahertz sensing. *Optics Express*. 2019; 9032
4. Yang C, Chan KK, Lin WJ, **Soehartono AM**, Lin G, Toh H, Yoon HS, Chen C-K, Yong K-T. Biodegradable nanocarriers for small interfering ribonucleic acid (siRNA) co-delivery strategy increase the chemosensitivity of pancreatic cancer cells to gemcitabine. *Nano Research*. 2017;10:3049
5. Tng DJH, Song P, Lin G, **Soehartono AM**, Yang G, Yang C, Yin F, Tan CH, Yong K-T. Synthesis and characterization of multifunctional hybrid-polymeric nanoparticles for drug delivery and multimodal imaging of cancer. *International journal of nanomedicine*. 2015;10: 577

Book Chapters

1. **Soehartono AM**, Hong L, Yang G, Song P, Yap HKS, Chan KK, Chong PHJ, Yong K-T. Miniaturized Fluidic Devices and Their Biophotonic Applications. *Handbook of Photonics for Biomedical Engineering*. 2017;893-939 **(First Author)**

REFERENCES

- [1] Fu E, Yager P, Floriano PN, Christodoulides N, McDevitt JT. Perspective on diagnostics for global health. Vol. 2, IEEE Pulse. 2011. p. 40–50.
- [2] Aydin S. A short history, principles, and types of ELISA, and our laboratory experience with peptide/protein analyses using ELISA. Peptides [Internet]. 2015 Oct;72:4–15. Available from: <https://linkinghub.elsevier.com/retrieve/pii/S019697811500131X>
- [3] Choi S, Goryll M, Sin LYM, Wong PK, Chae J. Microfluidic-based biosensors toward point-of-care detection of nucleic acids and proteins. Vol. 10, Microfluidics and Nanofluidics. 2011. p. 231–47.
- [4] Lee S, Huang H, Zelen M. Early detection of disease and scheduling of screening examinations. Stat Methods Med Res. 2004;13(6):443–56.
- [5] Tokel O, Inci F, Demirci U. Advances in plasmonic technologies for point of care applications. Vol. 114, Chemical Reviews. 2014. p. 5728–52.
- [6] Li J, Macdonald J. Multiplexed lateral flow biosensors: Technological advances for radically improving point-of-care diagnoses. Vol. 83, Biosensors and Bioelectronics. 2016. p. 177–92.
- [7] Stockman MI. Nanoplasmonics: The physics behind the applications. Phys Today. 2011;64(2):39–44.
- [8] Sepúlveda B, Angelomé PC, Lechuga LM, Liz-Marzán LM. LSPR-based nanobiosensors. Nano Today. 2009;4(3):244–51.
- [9] Freestone I, Meeks N, Sax M, Higgitt C. The Lycurgus Cup - A Roman nanotechnology. Gold Bull. 2008;40(4):270–7.
- [10] Estevez MC, Otte MA, Sepulveda B, Lechuga LM. Trends and challenges of refractometric nanoplasmonic biosensors: A review. Vol. 806, Analytica Chimica Acta. 2014. p. 55–73.
- [11] Dahlin AB. Plasmonic biosensors: An integrated view of refractometric detection. Adv Biomed Spectrosc. 2011;4:1–293.
- [12] Anker JN, Hall WP, Lyandres O, Shah NC, Zhao J, Van Duyne RP. Biosensing with plasmonic nanosensors. Nat Mater [Internet]. 2008;7(6):442–53. Available from: <http://www.ncbi.nlm.nih.gov/pubmed/18497851>
- [13] Wood B, Pendry J, Tsai D. Directed subwavelength imaging using a layered metal-dielectric system. Phys Rev B. 2006 Sep;74(11):115116.
- [14] Silveirinha MG, Belov PA, Simovski CR. Ultimate limit of resolution of subwavelength imaging devices formed by metallic rods. Opt Lett. 2008;33(15):1726–8.
- [15] Wu X, Zhang J, Gong Q. Metal-insulator-metal nanorod arrays for subwavelength imaging. Opt Express. 2009;17(4):2818–25.

- [16] Liu Y, Cheng R, Liao L, Zhou H, Bai J, Liu G, et al. Plasmon resonance enhanced multicolour photodetection by graphene. *Nat Commun.* 2011 Sep;2(1):579.
- [17] Chang C-C, Sharma YD, Kim Y-S, Bur JA, Shenoi R V., Krishna S, et al. A Surface Plasmon Enhanced Infrared Photodetector Based on InAs Quantum Dots. *Nano Lett.* 2010 May;10(5):1704–9.
- [18] Berini P. Surface plasmon photodetectors and their applications. *Laser Photon Rev.* 2014 Mar;8(2):197–220.
- [19] Tong J, Suo F, Ma J, Y. M. Tobing L, Qian L, Hua Zhang D. Surface plasmon enhanced infrared photodetection. *Opto-Electronic Adv.* 2019;2(1):18002601–10.
- [20] Pillai S, Green MA. Plasmonics for photovoltaic applications. *Sol Energy Mater Sol Cells.* 2010 Sep;94(9):1481–6.
- [21] Kulkarni AP, Noone KM, Munechika K, Guyer SR, Ginger DS. Plasmon-Enhanced Charge Carrier Generation in Organic Photovoltaic Films Using Silver Nanoprisms. *Nano Lett.* 2010 Apr;10(4):1501–5.
- [22] Clavero C. Plasmon-induced hot-electron generation at nanoparticle/metal-oxide interfaces for photovoltaic and photocatalytic devices. *Nat Photonics.* 2014 Feb;8(2):95–103.
- [23] Liedberg B, Nylander C, Lunström I. Surface plasmon resonance for gas detection and biosensing. *Sensors and Actuators.* 1983;4(C):299–304.
- [24] L. Andrew Lyon, Michael D. Musick and, Natan* MJ. Colloidal Au-Enhanced Surface Plasmon Resonance Immunosensing. 1998;
- [25] Maier SA. PLASMONICS: FUNDAMENTALS AND APPLICATIONS. Springer Science+Business Media; 2007.
- [26] Ordal MA, Bell RJ, Alexander RW, Long LL, Querry MR. Optical properties of fourteen metals in the infrared and far infrared: Al, Co, Cu, Au, Fe, Pb, Mo, Ni, Pd, Pt, Ag, Ti, V, and W. *Appl Opt.* 1985 Dec;24(24):4493.
- [27] McPeak KM, Jayanti S V., Kress SJP, Meyer S, Iotti S, Rossinelli A, et al. Plasmonic Films Can Easily Be Better: Rules and Recipes. *ACS Photonics.* 2015 Mar;2(3):326–33.
- [28] Johnson PB, Christy RW. Optical Constants of the Noble Metals. *Phys Rev B.* 1972;6(12):4370–9.
- [29] Akowuah EK, Gorman T, Haxha S. Design and optimization of a novel surface plasmon resonance biosensor based on Otto configuration. *Opt Express.* 2009;17(26):23511.
- [30] Abdulhalim I, Zourob M, Lakhtakia A. Surface plasmon resonance for biosensing: A mini-review. *Electromagnetism.* 2008;28(3):214–42.
- [31] Homola J, Yee SS, Gauglitz G. Surface plasmon resonance sensors: review. *Sensors Actuators, B Chem.* 1999;
- [32] BioNavis. SPR Configurations. 2019.
- [33] Huang C, Bonroy K, Reekmans G, Laureyn W, Verhaegen K, De

Vlaminck I, et al. Localized surface plasmon resonance biosensor integrated with microfluidic chip. *Biomed Microdevices*. 2009;11(4):893–901.

[34] Aćimović SS, Ortega MA, Sanz V, Berthelot J, Garcia-Cordero JL, Renger J, et al. LSPR chip for parallel, rapid, and sensitive detection of cancer markers in serum. *Nano Lett*. 2014;14(5):2636–41.

[35] Toma M, Cho K, Wood JB, Corn RM. Gold Nanoring Arrays for Near Infrared Plasmonic Biosensing. *Plasmonics*. 2014;9(4):765–72.

[36] Lee SW, Lee KS, Ahn J, Lee JJ, Kim MG, Shin YB. Highly sensitive biosensing using arrays of plasmonic Au nanodisks realized by nanoimprint lithography. *ACS Nano*. 2011;5(2):897–904.

[37] nanoComposix. *The Science of Plasmonics*. 2019.

[38] Fan X, Zheng W, Singh DJ. Light scattering and surface plasmons on small spherical particles. *Light Sci Appl*. 2014;(March):1–14.

[39] Bohren CF, Huffman DR. *Absorption and Scattering of Light by Small Particles*. John Wiley & Sons, Inc.; 1998.

[40] Mie G. Contributions on the Optics of Turbid Media, Particularly Colloidal Metal Solutions. Vol. 25, *Annalen der Physik, Series IV*. 1908. p. 377–445.

[41] Stratton JA. *Electromagnetic Theory*. IEEE Press; 2007. 615 p.

[42] Svedendahl M, Chen S, Dmitriev A, Käll M. Refractometric sensing using propagating versus localized surface plasmons: A direct comparison. *Nano Lett*. 2009;9(12):4428–33.

[43] Bryant GW, García De Abajo FJ, Aizpurua J. Mapping the plasmon resonances of metallic nanoantennas. *Nano Lett*. 2008;8(2):631–6.

[44] Asano S. Light scattering properties of spheroidal particles. *Appl Opt*. 1979;18(5):712–23.

[45] Voshchinnikov N V, Farafonov VG. Optical properties of spheroidal particles. *Astrophys Space Sci*. 1993;204(1):19–86.

[46] Maier SA, Kik PG, Atwater HA, Meltzer S, Requicha AAG, Koel BE. Observation of coupled plasmon-polariton modes of plasmon waveguides for electromagnetic energy transport below the diffraction limit. In: *Proceedings of SPIE Vol 4810 INTERNATIONAL SYMPOSIUM ON OPTICAL SCIENCE AND TECHNOLOGY*. 2002.

[47] Rodrigo SG, García-Vidal FJ, Martín-Moreno L. Influence of material properties on extraordinary optical transmission through hole arrays. *Phys Rev B - Condens Matter Mater Phys*. 2008;77(7):1–8.

[48] Burrows C. *Plasmonic resonances of metallic nanoparticles in arrays and in isolation*. University of Exeter; 2010.

[49] Sain B, Kaner R, Bondy Y, Prior Y. Plasmonic flat surface Fabry-Perot interferometry. *Nanophotonics*. 2018;7(3):635–41.

[50] Saleh BEA, Teich MC. *Fundamentals of Photonics*. John Wiley & Sons, Inc.; 2001.

- [51] Jin J-M. The Finite Element Method in Electromagnetics. Wiley-IEEE Press; 2014. 876 p.
- [52] Draine BT, Flatau PJ. Discrete-Dipole Approximation For Scattering Calculations. *J Opt Soc Am A*. 1994;11(4):1491.
- [53] Taflove A, Hagness SC. Computational Electrodynamics: The Finite-Difference Time-Domain Method, Third Edition. 3rd ed. Artech House; 2005. 1038 p.
- [54] Parsons J, Burrows CP, Sambles JR, Barnes WL. A comparison of techniques used to simulate the scattering of electromagnetic radiation by metallic nanostructures. *J Mod Opt*. 2010;57(5):356–65.
- [55] Martinsson E, Aili D. Refractometric Sensing Using Plasmonic Nanoparticles. In: *Encyclopedia of Nanotechnology*. 2016. p. 3432–40.
- [56] Zalyubovskiy SJ, Bogdanova M, Deinega A, Lozovik Y, Pris AD, An KH, et al. Theoretical limit of localized surface plasmon resonance sensitivity to local refractive index change and its comparison to conventional surface plasmon resonance sensor. *J Opt Soc Am A* [Internet]. 2012;29(6):994–1002. Available from: <http://www.ncbi.nlm.nih.gov/pubmed/22673431>
- [57] Otte MA, Sepulveda B. Figures of merit for refractometric LSPR biosensing. In: *Nanoplasmonic Sensors*. 2012. p. 317–31.
- [58] Mazzotta F, Johnson TW, Dahlin AB, Shaver J, Oh SH, Höök F. Influence of the evanescent field decay length on the sensitivity of plasmonic nanodisks and nanoholes. *ACS Photonics*. 2015;2(2):256–62.
- [59] Li J, Ye J, Chen C, Li Y, Verellen N, Moshchalkov V V., et al. Revisiting the surface sensitivity of nanoplasmonic biosensors. *ACS Photonics*. 2015;2(3):425–31.
- [60] Jung LS, Campbell CT, Chinowsky TM, Mar MN, Yee SS. Quantitative Interpretation of the Response of Surface Plasmon Resonance Sensors to Adsorbed Films. *Langmuir* [Internet]. 1998;14(19):5636–48. Available from: <https://pubs.acs.org/doi/10.1021/la971228b>
- [61] Ameling R, Langguth L, Hentschel M, Mesch M, Braun P V., Giessen H. Cavity-enhanced localized plasmon resonance sensing. *Appl Phys Lett*. 2010;97(25).
- [62] Cao J, Sun T, Grattan KTV. Gold nanorod-based localized surface plasmon resonance biosensors: A review. *Sensors and Actuators, B: Chemical*. 2014.
- [63] Louis C, Pluchery O. Gold Nanoparticles for Physics, Chemistry and Biology. *Gold Nanoparticles for Physics, Chemistry and Biology*. 2017.
- [64] Nehl CL, Hafner JH. Shape-dependent plasmon resonances of gold nanoparticles. *Journal of Materials Chemistry*. 2008.
- [65] Pérez-Juste J, Pastoriza-Santos I, Liz-Marzán LM, Mulvaney P. Gold nanorods: Synthesis, characterization and applications. In: *Coordination Chemistry Reviews*. 2005.
- [66] Jana NR, Gearheart L, Murphy CJ. Wet chemical synthesis of

high aspect ratio cylindrical gold nanorods. *Journal of Physical Chemistry B*. 2001.

[67] Yu YY, Chang SS, Lee CL, Wang CRC. Gold nanorods: electrochemical synthesis and optical properties. *J Phys Chem B*. 1997;

[68] Kim F, Song JH, Yang P. Photochemical synthesis of gold nanorods. *J Am Chem Soc*. 2002;

[69] Skrabalak SE, Au L, Li X, Xia Y. Facile synthesis of Ag nanocubes and Au nanocages. *Nat Protoc*. 2007;

[70] Sun Y, Xia Y. Shape-controlled synthesis of gold and silver nanoparticles. *Science* (80-). 2002;

[71] Skrabalak SE, Chen J, Sun Y, Lu X, Au L, Cobley CM, et al. Gold nanocages: Synthesis, properties, and applications. *Acc Chem Res*. 2008;

[72] Wiley BJ, Chen Y, McLellan JM, Xiong Y, Li ZY, Ginger D, et al. Synthesis and optical properties of silver nanobars and nanorice. *Nano Lett*. 2007;

[73] Wang H, Brandl DW, Le F, Nordlander P, Halas NJ. Nanorice: A hybrid plasmonic nanostructure. *Nano Lett*. 2006;

[74] Song W, Chi M, Gao M, Zhao B, Wang C, Lu X. Self-assembly directed synthesis of Au nanorices induced by polyaniline and their enhanced peroxidase-like catalytic properties. *J Mater Chem C*. 2017;

[75] Trigari S, Rindi A, Margheri G, Sottini S, Dellepiane G, Giorgetti E. Synthesis and modelling of gold nanostars with tunable morphology and extinction spectrum. *J Mater Chem*. 2011;

[76] Senthil Kumar P, Pastoriza-Santos I, Rodríguez-González B, Javier García De Abajo F, Liz-Marzán LM. High-yield synthesis and optical response of gold nanostars. *Nanotechnology*. 2008;

[77] Hao F, Nehl CL, Hafner JH, Nordlander P. Plasmon resonances of a gold nanostar. *Nano Lett*. 2007;

[78] Rycenga M, Camargo PHC, Li W, Moran CH, Xia Y. Understanding the SERS Effects of Single Silver Nanoparticles and Their Dimers, One at a Time. *J Phys Chem Lett*. 2010;1:696–703.

[79] Sun Y, Xia Y. Increased Sensitivity of Surface Plasmon Resonance of Gold Nanoshells Compared to That of Gold Solid Colloids in Response to Environmental Changes. *Anal Chem*. 2002;74(20):5297–305.

[80] Principles and Mechanisms of Nanoparticle Stabilization by Polymers. In: *Metallopolymer Nanocomposites*. 2005. p. 65–113.

[81] Martinsson E, Otte MA, Shahjamali MM, Sepulveda B, Aili D. Substrate effect on the refractive index sensitivity of silver nanoparticles. *J Phys Chem C*. 2014;118(42):24680–7.

[82] Howes PD, Chandrawati R, Stevens MM. Colloidal nanoparticles as advanced biological sensors. Vol. 346, *Science*. 2014.

[83] Chegel V, Rachkov O, Lopatynskiy A, Ishihara S, Yanchuk I, Nemoto Y, et al. Gold nanoparticles aggregation: Drastic effect of cooperative

functionalities in a single molecular conjugate. Vol. 116, *Journal of Physical Chemistry C*. 2012. p. 2683–90.

[84] Otte MA, Sepúlveda B, Ni W, Juste JP, Liz-Marzán LM, Lechuga LM. Identification of the optimal spectral region for plasmonic and nanoplasmonic sensing. *ACS Nano*. 2010;4(1):349–57.

[85] Raphael MP, Christodoulides JA, Byers JM, Anderson GP, Liu JL, Turner KB, et al. Optimizing Nanoplasmonic Biosensor Sensitivity with Orientated Single Domain Antibodies. *Plasmonics*. 2015;10(6):1649–55.

[86] Ben Haddada M, Blanchard J, Casale S, Krafft JM, Vallée A, Méthivier C, et al. Optimizing the immobilization of gold nanoparticles on functionalized silicon surfaces: Amine- vs thiol-terminated silane. *Gold Bull*. 2013;46(4):335–41.

[87] Lichtenberg JY, Ling Y, Kim S. Non-specific adsorption reduction methods in biosensing. Vol. 19, *Sensors (Switzerland)*. 2019.

[88] Phan HTM, Bartelt-Hunt S, Rodenhausen KB, Schubert M, Bartz JC. Investigation of bovine serum albumin (BSA) attachment onto self-assembled monolayers (SAMs) using combinatorial quartz crystal microbalance with dissipation (QCM-D) and spectroscopic ellipsometry (SE). *PLoS One*. 2015;10(10).

[89] Chithrani DB. Polyethylene Glycol Density and Length Affects Nanoparticle Uptake by Cancer Cells. *J Nanomedicine Res*. 2014;1(1).

[90] Oliverio M, Perotto S, Messina GC, Lovato L, De Angelis F. Chemical Functionalization of Plasmonic Surface Biosensors: A Tutorial Review on Issues, Strategies, and Costs. *ACS Appl Mater Interfaces*. 2017;9(35):29394–411.

[91] Lumerical Inc.

[92] Palik ED. *Handbook of Optical Constants of Solids*. San Diego: Academic Press; 1998. 804 p.

[93] Welch NG, Scoble JA, Muir BW, Pigram PJ. Orientation and characterization of immobilized antibodies for improved immunoassays (Review). *Biointerphases*. 2017;12(2):02D301.

[94] Gwinner MC, Koroknay E, Liwei F, Patoka P, Kandulski W, Giersig M, et al. Periodic large-area metallic split-ring resonator metamaterial fabrication based on shadow nanosphere lithography. *Small*. 2009;5(3):400–6.

[95] Tobing LYM, Tjahjana L, Zhang DH, Zhang Q, Xiong Q. Deep subwavelength fourfold rotationally symmetric split-ring-resonator metamaterials for highly sensitive and robust biosensing platform. *Sci Rep*. 2013;3.

[96] Tobing LYM, Tjahjana L, Zhang DH. Sub-10-nm size and sub-40-nm pitch metal dot patterning for low-cost bit patterned media application. *IEEE Trans Nanotechnol*. 2014;

[97] Tobing LYM, Tjahjana L, Zhang DH. Direct patterning of high density sub-15 nm gold dot arrays using ultrahigh contrast electron beam lithography process on positive tone resist. *Nanotechnology*. 2013;24(7).

- [98] Franssila S. Introduction to Microfabrication. Introduction to Microfabrication. 2010.
- [99] Paunovic M, Schlesinger M. Fundamentals of Electrochemical Deposition. 2nd ed. Wiley-Interscience; 2006.
- [100] Zhang J, Cao C, Xu X, Liow C, Li S, Tan P, et al. Tailoring alphabetical metamaterials in optical frequency: Plasmonic coupling, dispersion, and sensing. ACS Nano. 2014;
- [101] Lee HJ, Lee JH, Moon HS, Jang IS, Choi JS, Yook JG, et al. A planar split-ring resonator-based microwave biosensor for label-free detection of biomolecules. Sensors Actuators B Chem. 2012;169:26–31.
- [102] Lee HJ, Lee HS, Yoo KH, Yook JG. DNA sensing using split-ring resonator alone at microwave regime. J Appl Phys. 2010;108:014908.
- [103] Xu X, Peng B, Li D, Zhang J, Wong LM, Zhang Q, et al. Flexible visible-infrared metamaterials and their applications in highly sensitive chemical and biological sensing. Nano Lett. 2011;11(8):3232–8.
- [104] Enkrich C, Wegener M, Linden S, Burger S, Zschiedrich L, Schmidt F, et al. Magnetic Metamaterials at Telecommunication and Visible Frequencies. Phys Rev Lett. 2005;95:203901.
- [105] Jeppesen C, Mortensen NA, Kristensen A. Capacitance tuning of nanoscale split-ring resonators. Appl Phys Lett. 2009;95(19).
- [106] Zhou J, Koschny T, Kafesaki M, Economou EN, Pendry JB, Soukoulis CM. Saturation of the magnetic response of split-ring resonators at optical frequencies. Phys Rev Lett. 2005;95(22).
- [107] Delgado V, Sydoruk O, Tatartschuk E, Marqués R, Freire MJ, Jelinek L. Analytical circuit model for split ring resonators in the far infrared and optical frequency range. Metamaterials. 2009;3(2):57–62.
- [108] Tobing LYM, Zhang DH. Preferential Excitation of the Hybrid Magnetic-Electric Mode as a Limiting Mechanism for Achievable Fundamental Magnetic Resonance in Planar Aluminum Nanostructures. Adv Mater. 2016;28(5):889–96.
- [109] Etchegoin PG, Le Ru EC, Meyer M. An analytic model for the optical properties of gold. J Chem Phys. 2006;125:164705.
- [110] Wu PC, Sun G, Chen WT, Yang KY, Huang YW, Chen YH, et al. Vertical split-ring resonator based nanoplasmonic sensor. Appl Phys Lett. 2014;105(3).
- [111] Tobing LYM, Luo Y, Low KS, Zhang D, Zhang DH. Observation of the Kinetic Inductance Limitation for the Fundamental Magnetic Resonance in Ultrasmall Gold v-Shape Split Ring Resonators. Adv Opt Mater. 2016;4(7):1047–52.
- [112] Wang F, Shen YR. General properties of local plasmons in metal nanostructures. Phys Rev Lett. 2006;97(20).
- [113] Sano Y. Optical anisotropy of bovine serum albumin. J Colloid Interface Sci. 1988;124(2):403–6.

- [114] Szucs A, Hitchens GD, O'M. BJ. ELLIPSOMETRY OF CYTOCHROME c ON GOLD SURFACES: EFFECT OF 4,4'-DIPYRIDYL DISULFIDE. *Electrochim Acta*. 1991;37(3):403–12.
- [115] Cetin AE, Etezadi D, Galarreta BC, Busson MP, Eksioglu Y, Altug H. Plasmonic Nanohole Arrays on a Robust Hybrid Substrate for Highly Sensitive Label-Free Biosensing. *ACS Photonics*. 2015;
- [116] Guo X. Surface plasmon resonance based biosensor technique: A review. Vol. 5, *Journal of Biophotonics*. 2012. p. 483–501.
- [117] Grobnc AG. Challenges in the optical alignment of optoelectronic components. In 2017. p. 178.
- [118] Miller MM, Lazarides AA. Sensitivity of metal nanoparticle surface plasmon resonance to the dielectric environment. *J Phys Chem B*. 2005;109(46):21556–65.
- [119] Soehartono AM, Mueller AD, Tobing LYM, Chan KK, Zhang DH, Yong KT. Ultra-small v-shaped gold split ring resonators for biosensing using fundamental magnetic resonance in the visible spectrum. *Nanotechnology*. 2017;28(40).
- [120] Ueno K, Juodkazis S, Mino M, Mizeikis V, Misawa H. Spectral sensitivity of uniform arrays of gold nanorods to dielectric environment. *J Phys Chem C*. 2007;111(11):4180–4.
- [121] Dodson SL, Cao C, Zaribafzadeh H, Li S, Xiong Q. Engineering plasmonic nanorod arrays for colon cancer marker detection. *Biosens Bioelectron*. 2015;63:472–7.
- [122] Bukasov R, Shumaker-Parry JS. Highly tunable infrared extinction properties of gold nanocrescents. *Nano Lett*. 2007;7(5):1113–8.
- [123] Lee J, Hasan W, Odom TW. Tuning the thickness and orientation of single au pyramids for improved refractive index sensitivities. *J Phys Chem C*. 2009;113(6):2205–7.
- [124] Noguez C. Optical properties of isolated and supported metal nanoparticles. In: *Optical Materials*. 2005. p. 1204–11.
- [125] Hao F, Sonnefraud Y, Van Dorpe P, Maier SA, Halas NJ, Nordlander P. Symmetry breaking in plasmonic nanocavities: Subradiant LSPR sensing and a tunable Fano resonance. *Nano Lett*. 2008;8(11):3983–8.
- [126] Lodewijks K, Van Roy W, Borghs G, Lagae L, Van Dorpe P. Boosting the figure-of-merit of LSPR-based refractive index sensing by phase-sensitive measurements. *Nano Lett*. 2012;12(3):1655–9.
- [127] Verellen N, Van Dorpe P, Huang C, Lodewijks K, Vandenbosch GAE, Lagae L, et al. Plasmon line shaping using nanocrosses for high sensitivity localized surface plasmon resonance sensing. *Nano Lett*. 2011;11(2):391–7.
- [128] Wu C, Khanikaev AB, Adato R, Arju N, Yanik AA, Altug H, et al. Fano-resonant asymmetric metamaterials for ultrasensitive spectroscopy and identification of molecular monolayers. *Nat Mater*. 2012;11(1):69–75.
- [129] Lassiter JB, Sobhani H, Fan JA, Kundu J, Capasso F, Nordlander

P, et al. Fano resonances in plasmonic nanoclusters: Geometrical and chemical tunability. *Nano Lett.* 2010;10(8):3184–9.

[130] Tobing LYM, Goh GY, Mueller AD, Ke L, Luo Y, Zhang DH. Polarization invariant plasmonic nanostructures for sensing applications. *Sci Rep.* 2017;7(1):1–14.

[131] Mueller AD, Tobing LYM, Zhang DH. Combining sonicated cold development and pulsed electrodeposition for high aspect ratio sub-10 nm gap gold dimers for sensing applications in the visible spectrum. *Nanoscale.* 2018;5221–8.

[132] Tobing LYM, Tjahjana L, Zhang DH. Large contrast enhancement by sonication assisted cold development process for low dose and ultrahigh resolution patterning on ZEP520A positive tone resist. *J Vac Sci Technol B, Nanotechnol Microelectron Mater Process Meas Phenom.* 2012;30(5):051601.

[133] Mueller AD, Tobing LYM, Zhang DH. Reliable Fabrication of High Aspect Ratio Plasmonic Nanostructures Based on Seedless Pulsed Electrodeposition. *Adv Mater Technol.* 2019;4(1).

[134] Snyder AW, Love JD. Optical Waveguide Theory [Internet]. Vol. 2, Chapman & Hall, London, 1983, Chap. Boston, MA: Springer US; 1984. 29 p. Available from: <http://link.springer.com/10.1007/978-1-4613-2813-1>

[135] Xiao ZY, Wang ZH. Dispersion characteristics of asymmetric double-negative material slab waveguides. *J Opt Soc Am B.* 2006;23(9):1757.

[136] Henson J, Dimaria J, Paiella R. Influence of nanoparticle height on plasmonic resonance wavelength and electromagnetic field enhancement in two-dimensional arrays. *J Appl Phys.* 2009;106(9).

[137] Zhu D, Bosman M, Yang JKW. A circuit model for plasmonic resonators. *Opt Express.* 2014;22(8):9809.

[138] Päivänranta B, Merbold H, Giannini R, Büchi L, Gorelick S, David C, et al. High aspect ratio plasmonic nanostructures for sensing applications. *ACS Nano.* 2011;5(8):6374–82.

[139] Giorgis V, Zilio P, Ruffato G, Massari M, Zacco G, Romanato F. Resonance properties of thick plasmonic split ring resonators for sensing applications. *Opt Express [Internet].* 2014;22(22):26476. Available from: <https://www.osapublishing.org/oe/abstract.cfm?uri=oe-22-22-26476>

[140] Chiam SY, Singh R, Gu J, Han J, Zhang W, Bettiol AA. Increased frequency shifts in high aspect ratio terahertz split ring resonators. *Appl Phys Lett.* 2009;94(6):92–5.

[141] Ross MB, Mirkin CA, Schatz GC. Optical Properties of One-, Two-, and Three-Dimensional Arrays of Plasmonic Nanostructures. *J Phys Chem C.* 2016;120(2):816–30.

[142] Ragheb I, Braik M, Mezeghrane A, Boubekur-Lecaque L, Belkhir A, Felidj N. Lattice plasmon modes in an asymmetric environment: from far-field to near-field optical properties. *J Opt Soc Am B.* 2019;36(7):E36.

[143] Larsson EM, Alegret J, Käll M, Sutherland DS. Sensing

characteristics of NIR localized surface plasmon resonances in gold nanorings for application as ultrasensitive biosensors. *Nano Lett.* 2007;7(5):1256–63.

[144] Tsai CY, Lu SP, Lin JW, Lee PT. High sensitivity plasmonic index sensor using slablike gold nanoring arrays. *Appl Phys Lett.* 2011;98(15).

[145] Yanik AA, Cetin AE, Huang M, Artar A, Mousavi SH, Khanikaev A, et al. Seeing protein monolayers with naked eye. *IEEE Photonic Soc 24th Annu Meet PHO 2011.* 2011;108(29):425–6.

[146] Shen Y, Zhou J, Liu T, Tao Y, Jiang R, Liu M, et al. Plasmonic gold mushroom arrays with refractive index sensing figures of merit approaching the theoretical limit. *Nat Commun.* 2013;4.

[147] Kabashin A V., Evans P, Pastkovsky S, Hendren W, Wurtz GA, Atkinson R, et al. Plasmonic nanorod metamaterials for biosensing. *Nat Mater.* 2009;8(11):867–71.

[148] McMEEKIN TL, GROVES ML, HIPPI NJ. Refractive Indices of Amino Acids, Proteins, and Related Substances. In 2009. p. 54–66.

[149] Hucknall A, Rangarajan S, Chilkoti A. In pursuit of zero: Polymer brushes that resist the adsorption of proteins. *Adv Mater.* 2009;21(23):2441–6.

[150] Mazzotta F, Johnson TW, Dahlin AB, Shaver J, Oh S-H, Höök F. Influence of the Evanescent Field Decay Length on the Sensitivity of Plasmonic Nanodisks and Nanoholes. *ACS Photonics.* 2015 Feb;2(2):256–62.

[151] Estevez MC, Otte MA, Sepulveda B, Lechuga LM. Trends and challenges of refractometric nanoplasmonic biosensors: A review. *Anal Chim Acta.* 2014;806(January):55–73.

[152] Bhadra P, Shajahan MS, Bhattacharya E, Chadha A. Studies on varying n-alkanethiol chain lengths on a gold coated surface and their effect on antibody-antigen binding efficiency. *RSC Adv.* 2015;5(98):80480–7.

[153] Porter MD, Bright TB, Allara DL, Chidsey CED. Spontaneously organized molecular assemblies. 4. Structural characterization of n-alkyl thiol monolayers on gold by optical ellipsometry, infrared spectroscopy, and electrochemistry. *J Am Chem Soc.* 1987 Jun;109(12):3559–68.

[154] Hill RT, Mock JJ, Hucknall A, Wolter SD, Jokerst NM, Smith DR, et al. Plasmon ruler with angstrom length resolution. *ACS Nano.* 2012;6(10):9237–46.

[155] Tarn-Chang SW, Biebuyck HA, Whitesides GM, Jeon N, Nuzzo RG. Self-Assembled Monolayers on Gold Generated from Alkanethiols with the Structure RNHCOCH₂SH. *Langmuir.* 1995;11(11):4371–82.

[156] Soliwoda K, Tomaszewska E, Tkacz-Szczesna B, Rosowski M, Celichowski G, Grobelny J. The influence of the chain length and the functional group steric accessibility of thiols on the phase transfer efficiency of gold nanoparticles from water to toluene. *Polish J Chem Technol.* 2014;16(1):86–91.

[157] Marshall GM, Bensebaa F, Dubowski JJ. Observation of surface enhanced IR absorption coefficient in alkanethiol based self-assembled monolayers on GaAs(001). *J Appl Phys.* 2009;105(9).

- [158] Schmid F-X. Biological Macromolecules: UV-visible Spectrophotometry. In: Encyclopedia of Life Sciences [Internet]. Chichester, UK: John Wiley & Sons, Ltd; 2001. Available from: <http://doi.wiley.com/10.1038/npg.els.0003142>
- [159] Hao E, Schatz GC. Electromagnetic fields around silver nanoparticles and dimers. *J Chem Phys*. 2004;120(1):357–66.
- [160] Nordlander P, Oubre C, Prodan E, Li K, Stockman MI. Plasmon Hybridization in Nanoparticle Dimers. *Nano Lett*. 2004;4(5):899–903.
- [161] Chirumamilla M, Toma A, Gopalakrishnan A, Das G, Zaccaria RP, Krahne R, et al. 3D nanostar dimers with a sub-10-nm gap for single-/few-molecule surface-enhanced raman scattering. *Adv Mater*. 2014;26(15):2353–8.
- [162] Aćimović SS, Kreuzer MP, González MU, Quidant R. Plasmon near-field coupling in metal dimers as a step toward single-molecule sensing. *ACS Nano*. 2009;3(5):1231–7.
- [163] Slaughter LS, Wu Y, Willingham BA, Nordlander P, Link S. Effects of symmetry breaking and conductive contact on the plasmon coupling in gold nanorod dimers. *ACS Nano*. 2010;4(8):4657–66.
- [164] Ureña EB, Kreuzer MP, Itzhakov S, Rigneault H, Quidant R, Oron D, et al. Excitation enhancement of a quantum dot coupled to a plasmonic antenna. *Adv Mater*. 2012;
- [165] Kinkhabwala A, Yu Z, Fan S, Avlasevich Y, Müllen K, Moerner WE. Large single-molecule fluorescence enhancements produced by a bowtie nanoantenna. *Nat Photonics*. 2009;
- [166] Wang H. Plasmonic refractive index sensing using strongly coupled metal nanoantennas: Nonlocal limitations. *Sci Rep*. 2018;
- [167] Chen JIL, Chen Y, Ginger DS. Plasmonic nanoparticle dimers for optical sensing of DNA in complex media. *J Am Chem Soc*. 2010;
- [168] Atay T, Song JH, Nurmikko A V. Strongly interacting plasmon nanoparticle pairs: From dipole-dipole interaction to conductively coupled regime. *Nano Lett*. 2004;4(9):1627–31.
- [169] Romero I, Aizpurua J, Bryant GW, García De Abajo FJ. Plasmons in nearly touching metallic nanoparticles: singular response in the limit of touching dimers. *Opt Express*. 2006;14(21):9988.
- [170] Pérez-González O, Zabala N, Borisov AG, Halas NJ, Nordlander P, Aizpurua J. Optical Spectroscopy of Conductive Junctions in Plasmonic Cavities. *Nano Lett*. 2010 Aug;10(8):3090–5.
- [171] Fontana J, Charipar N, Flom SR, Naciri J, Piqué A, Ratna BR. Rise of the Charge Transfer Plasmon: Programmable Concatenation of Conductively Linked Gold Nanorod Dimers. *ACS Photonics*. 2016;3(5):904–11.
- [172] Koya AN, Lin J. Charge transfer plasmons: Recent theoretical and experimental developments. *Appl Phys Rev [Internet]*. 2017;4(2). Available from: <https://doi.org/10.1063/1.4982890>
- [173] Halas NJ, Wen F, Zhang Y, Gottheim S, S.King N, Zhang Y, et

al. Charge Transfer Plasmons : Optical Frequency Conductances and Tunable. ACS Nano. 2015;0–7.

[174] König M, Rahmani M, Zhang L, Lei DY, Roschuk TR, Giannini V, et al. Unveiling the correlation between nanometer-thick molecular monolayer sensitivity and near-field enhancement and localization in coupled plasmonic oligomers. ACS Nano. 2014;8(9):9188–98.

[175] Bellino MG, Calvo EJ, Gordillo G. Adsorption kinetics of charged thiols on gold nanoparticles. Phys Chem Chem Phys. 2004;6(2):424–8.

[176] Barnes WL, Dereux A, Ebbesen TW. Surface plasmon subwavelength optics. Nature. 2003.

[177] Ebbesen TW, Lezec HJ, Ghaemi HF, Thio T, Wolff PA. Extraordinary optical transmission through sub-wavelength hole arrays. Nature. 1998;391(6668):667–9.

[178] Prasad A, Choi J, Jia Z, Park S, Gartia MR. Nanohole array plasmonic biosensors: Emerging point-of-care applications. Vol. 130, Biosensors and Bioelectronics. 2019. p. 185–203.

[179] Christ A, Zentgraf T, Tikhodeev SG, Gippius NA, Kuhl J, Giessen H. Controlling the interaction between localized and delocalized surface plasmon modes: Experiment and numerical calculations. Phys Rev B - Condens Matter Mater Phys. 2006;74(15).

[180] Ekşioğlu Y, Cetin AE, Petráček J. Optical Response of Plasmonic Nanohole Arrays: Comparison of Square and Hexagonal Lattices. Plasmonics. 2016;11(3):851–6.

[181] Jackman JA, Rahim Ferhan A, Cho NJ. Nanoplasmonic sensors for biointerfacial science. Vol. 46, Chemical Society Reviews. 2017. p. 3615–60.

[182] Escobedo C, Brolo AG, Gordon R, Sinton D. Flow-through vs flow-over: Analysis of transport and binding in nanohole array plasmonic biosensors. Anal Chem. 2010;82(24):10015–20.

[183] Murray-Methot MP, Menegazzo N, Masson JF. Analytical and physical optimization of nanohole-array sensors prepared by modified nanosphere lithography. Analyst. 2008;

[184] Zheng P, Cushing SK, Suri S, Wu N. Tailoring plasmonic properties of gold nanohole arrays for surface-enhanced Raman scattering. Phys Chem Chem Phys. 2015;

[185] Juremi NRM, Mustafa U, Agam MA, Nur H. Nanosphere lithography: Fabrication of periodic arrays of nanoholes. In: AIP Conference Proceedings. 2011.

[186] Lotito V, Zambelli T. Self-assembly and nanosphere lithography for large-area plasmonic patterns on graphene. J Colloid Interface Sci. 2015;447:202–10.

[187] Ormonde AD, Hicks ECM, Castillo J, Van Duyne RP. Nanosphere lithography: Fabrication of large-area Ag nanoparticle arrays by convective self-assembly and their characterization by scanning UV - Visible extinction spectroscopy. Langmuir. 2004;20(16):6927–31.

- [188] Laurvick T V., Coutu RA, Sattler JM, Lake RA. Surface feature engineering through nanosphere lithography. *J Micro/Nanolithography, MEMS, MOEMS*. 2016;15(3):031602.
- [189] Colson P, Henrist C, Cloots R. Nanosphere Lithography: A Powerful Method for the Controlled Manufacturing of Nanomaterials. *J Nanomater*. 2013;2013:1–19.
- [190] Haynes CL, Van Duyne RP. Nanosphere lithography: A versatile nanofabrication tool for studies of size-dependent nanoparticle optics. *J Phys Chem B*. 2001;105(24):5599–611.
- [191] Kosiorek A, Kandulski W, Glaczynska H, Giersig M. Fabrication of nanoscale rings, dots, and rods by combining shadow nanosphere lithography and annealed polystyrene nanosphere masks. *Small*. 2005;1(4):439–44.
- [192] Couture M, Ray KK, Poirier-Richard HP, Crofton A, Masson JF. 96-Well Plasmonic Sensing with Nanohole Arrays. *ACS Sensors*. 2016;
- [193] Zhu S, Li H, Yang M, Pang SW. High sensitivity plasmonic biosensor based on nanoimprinted quasi 3D nanosquares for cell detection. *Nanotechnology*. 2016;27(29).
- [194] Vazquez-Mena O, Sannomiya T, Villanueva LG, Voros J, Brugger J. Metallic nanodot arrays by stencil lithography for plasmonic biosensing applications. *ACS Nano*. 2011;5(2):844–53.
- [195] Mueller AD, Tobing LYM, Zhang DH. Combining sonicated cold development and pulsed electrodeposition for high aspect ratio sub-10 nm gap gold dimers for sensing applications in the visible spectrum. *Nanoscale*. 2018;10(11):5221–8.
- [196] Tobing LYM, Goh GY, Mueller AD, Ke L, Luo Y, Zhang DH. Polarization invariant plasmonic nanostructures for sensing applications. *Sci Rep*. 2017;7(1).
- [197] Rippa M, Castagna R, Tkachenko V, Zhou J, Petti L. Engineered nanopatterned substrates for high-sensitive localized surface plasmon resonance: An assay on biomacromolecules. *J Mater Chem B*. 2017;5(27):5473–8.
- [198] Jiang S, Saito M, Murahashi M, Tamiya E. Pressure free nanoimprinting lithography using ladder-type HSQ material for LSPR biosensor chip. *Sensors Actuators, B Chem*. 2017;242:47–55.

Appendix A

A.1 Quasi Bottom-Up Approach Based on Nanosphere

Lithography

We describe a quasi bottom-up approach based on nanosphere lithography (NSL), particularly in the context of realizing subwavelength metal nanohole array which was explored. The optical property of subwavelength hole structure has been intensely studied due to its potential applications in sensing, in particular the so-called extraordinary optical transmission (EOT) phenomenon [176].

When subwavelength periodic arrays of holes on metallic film interact with light, extraordinary optical transmission (EOT) occurs, enabling transmission efficiency of appreciably higher magnitude along with large electric field intensities [177] compared to classical aperture theory. It was found that interaction of light with metallic voids give rise of both SPPs and LSPs whose interactions contribute to the spectral response, where the former is associated with grating orders, and the latter with localized modes of individual holes. The resonance condition of nanoholes¹ is strongly dependent on the elementary lattice vectors for the lattice (e.g. hexagonal or square) of the surface plasmon wavevector, and the dielectric properties of the film and environment [178][179]. For example, the resonance condition for hexagonal lattice can be expressed

¹ The dispersion relation for the surface plasmon is expressed as $k_{SP} = k_0 \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}}$. The resonance condition can be found when lattice vectors (hexagonal: $\frac{2\pi}{P}$, square: $\frac{4\pi}{\sqrt{3}P}$) are used [180].

as $\lambda_R = \frac{a}{\sqrt{\frac{4}{3}(m^2+mn+n^2)}} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}}$ [180]. The void-like nature also facilitates additional functionality, namely physical confinement of adsorbate materials within the high field intensity regions [181] and flow-through capability to increase the analyte flux [182].

Nanosphere lithography (NSL) is a hybrid bottom-up/top-down lithography method which can be used to realize nanohole arrays [183–185], consisting of self-assembled template molecules combined conventional top-down processes (e.g. etching, metal deposition). Instead of nanoparticles, a hexagonally close-packed lattice of monolayer spherical colloids (polystyrene spheres) is self-assembled onto a substrate, and its diameter is reduced by oxygen plasma to define the hole diameter, following which the undercut of the sphere facilitates lift-off (sonication or mechanical removal by adhesive materials). NSL is attractive considering its low-cost wafer-scale fabrication and optical functionality. Furthermore, the default hexagonal lattice has been shown to support narrower nanohole resonances, hence higher FOM [180]. We conducted preliminary investigations on the feasibility of this technique for our studies.

Figure A.1. Schematic depicting the nanosphere lithography process [186]. The steps consist of (1) monolayer formation of microsphere mask (2) etching to reduce sphere size (3) metal deposition.

The monolayer formation is the most crucial aspect in NSL, where the interfacial assembly have been reported by spin coating, convective coating, and dip coating. The formation of monolayers by spincoating is attributed to the centrifugal forces acting on the spheres driven by high rotation speeds and rapid solvent evaporation. Meanwhile for convective self-assembly, an angled spreader translates solution across the substrate, for which a wet and dry zone is created. The wet zone carries the bulk solution, and the dry zone is the area of monolayer formation. This occurs when the meniscus edge of the liquid becomes less than the particle diameter, and is dependent on the with solvent evaporation rate [187]. A Dip coating transfers monolayers to a substrate upon dipping in a solution with polystyrene spheres at the liquid-air interface. Despite its simplicity, lacks control and precision in terms of particle distribution. For our investigations, we used spin-coating and convective coating methods.

Figure A.2. Methods of monolayer formation by (a) spin-coating, (b) convective coating, and (c) dip coating [188].

We conducted an investigation into spin coating and convective coating for creating nanohole arrays. Briefly, $1 \times 1 \text{ cm}^2$ glass substrates were ultrasonically rinsed successively in acetone, isopropanol alcohol (IPA), and water for 15 minutes each. The surface was subsequently treated with a mixture of sulfuric acid and hydrogen peroxide in 3:1 ratio was used to improve the hydrophilicity of the surface. The substrates were washed with water and dried under nitrogen before use, or stored in water in a sealed container prior to polystyrene deposition. The polystyrene sphere solution was mixed with 1.5% w/v sodium dodecyl sulfate (SDS), a surfactant to assist the sphere adhesion onto the surface. Polystyrene microspheres with a concentration of 2.5% w/v (Polysciences, Inc., Taiwan) and diameters of 350 nm and 500 nm were used to create the polystyrene mask.

For spin coating, a droplet of solution was placed on the substrate and spun between 3000-5000RPM, depending on the diameter of the spheres used. The rotation speed use is dependent on diameter and concentration of the colloidal suspension, surface wettability, parameters which determine the monolayer quality. In convective coating, the lateral movement speed of the spreader was programmatically controlled to form improved monolayers with greater large-scale uniformity. A small volume ($\sim 10 \mu\text{L}$) of solution was drop cast underneath the spreader to form a meniscus at the edge. Speed

was adjusted for monolayer formation. An interesting feature of this is the serial speed adjustment which can give rise to barcode stripe patterns when programmed as in intervals of fast-slow speeds. For all processes, oxygen plasma treatment followed to reduce the diameter of the spheres. The etching process should ensure sufficient distance between the close-packed spheres, thereby ensuring the realization of nanoholes. In the case of a suboptimal etching rate where spheres appear to touch and leave only edge gaps, star-type structures will be achieved upon metal deposition. A titanium adhesion layer followed by gold layer deposited by e-beam evaporation, of which the thickness should be less than $1/3$ of the reduced diameter. For 500 nm spheres reduced to 350 nm, a 70 nm gold layer was deposited. Lift-off was conducted under gentle sonication in acetone.

A segment of the polystyrene template by spincoating is shown in Figure A.3(a). The layer exhibits variability in coverage, with non-uniform regions indicating monolayers (light gray) and multilayers (dark gray) as denoted by the colored insets. The opacity provides a qualitative characterization which can be used to determine the layer deposition quality. Upon closer inspection, the most prevalent defects are grain boundaries appearing as cracks in the array, missing spheres as holes are found within the monolayer region, and spontaneous multilayer formation. Effectively, the footprint of a monolayer region varies, but is on the order of hundreds of microns. The challenges associated with spin-coating is optimizing inter-particle forces, and interaction forces between the spheres and substrates [188,189]. As such, convective methods are explored as well.

Figure A.3. (a) Scanning electron micrograph of spin-coated polystyrene spheres prior to etching with actual sample (b) shown with a ten Singapore cent coin for scale. The lighter areas indicate a monolayer, while multilayers are represented by darker shades. Monolayers were achieved, but some boundary defects (c) and multilayers (d) seen in the insets.

When prepared by convective self-assembly, the large-area coverage is on the order of 0.1 cm. The area of the monolayer is improved with multilayer regions confined to the edges, which is seen as opaque white lines Figure A.4(b). The inhomogeneity is associated with surface roughness of the spreader edge.

Figure A.4. (a) Scanning electron micrograph of large-scale coverage using convective self-assembly. (b) The layer type can be ascertained qualitatively based on the opacity of the color on the substrate.

Reduction of spheres to 350 nm is sufficient to obtain a nanohole array periodicity of 500 nm, as seen in Figure A.3. Despite the defects highlighted with red arrows, the lattice appears to demonstrate reasonably good periodicity. This is evidenced by the circular symmetry seen in the fast Fourier transform of the SEM image. The etched holes measure approximately 350 nm with the diameter distribution shown in Figure A.3(c).

Figure A.5. SEM micrograph of a completed nanohole array, where the monolayer was formed by spincoating polystyrene spheres. The red rectangle denotes grain boundary defects and the red circle highlights missing holes.

As seen in Figure A.6(b), the lineshape of the experimental spectra appears to be in good agreement with the simulations in Appendix. The spectra shown is averaged with a 30x30 window, and generally exhibit similar features. However, a variance with is seen with the green line located on the right side of the sample. The differences are

attributed to sample non-idealities, which would also result in the spectral broadening, where the resonance measures 186 nm.

Figure A.6. Microscope image of a nanohole array region. (b) Transmission spectra of the corresponding microscope image, with spectra corresponding to colored boxes in (a).

The merits of nanosphere lithography warranted an investigation into its suitability, with geometries including dots, stars [190], rings [191], and crescent [94], having been

demonstrated using NSL-based lithography². The periodic lattice arrangement is constrained to either a hexagonally close-packed (HCP) lattice, with periodicity fixed to the starting polystyrene sphere diameter. The hexagonal lattice has the advantage that (1,1) modes seen in square lattice configurations are inherently eliminated which simplifies the spectrum. Nevertheless, despite the hexagonal lattice, SPP nature makes it so that a substrate associated mode will always be present. Others have demonstrated that fabricating on a silicon nitride layer can red-shift this resonance away from the visible range, although at the cost of reduced transmission contrast due to the opacity of high refractive index materials [115].

For NSL, the period can be tuned based on the starting nanosphere diameter. However, there is a limit to the resonances which can be achieved, owing to the physical limitation in the fabrication process itself. For nanoholes, periodicity is a determinant of the resonance wavelength. The inter-particle distance in the HCP (determined by the etched diameter size) is constrained by lift-off conditions related to the metal height deposited. However, as shown in numerical analysis in Appendix, thinner metal layers contribute to spectral broadening. Therefore, a metal layer thicker than the skin depth of the plasmonic field (~50 nm) is desirable for achieving the narrowest linewidth reasonably possible. The presented nanoholes with period of 500 nm resonate in the 800 nm region. Because of the smaller sphere diameters ($d < 500 \text{ nm}$) needed for visible wavelength resonances, there is a compromise between sufficient metal deposition, lift-

² For more complicated structures such as crescents, shadow nanosphere lithography is used. The process presents a process variation of NSL in which a rotating tilted sample holder is used in the metal evaporation chamber [94].

off capability and performance. Furthermore, spheres which were etched to ~ 150 nm diameters could not be removed by our sonication processes leading to the conclusion that the metal height should not be more than $1/3$ of the nanosphere for successful lift-off. This would then limit thickness of the metal to be deposited, where a thicker film layer improves the EOT transmission signal contrast.

In the context of multiplexing and low-cost, which is of the general interest in the biosensing, large scale patterning may be a drawback considering that multiplexing may call for dimensions small enough for a single pass measurement. The rearrangement of a large-scale footprint to micrometer scale may warrant considerable efforts to ensure correct placement and alignment of the structures. It is interesting to note that the highest performing nanoholes used in sensing, atop a silicon nitride layer, use lithographic methods such as focused ion beam milling and interference lithography, indicative of the reproducibility issue [192] in the use of NSL for reliable nanohole array fabrication [115,145]. Our analysis and results suggest that NSL does not possess sufficient robustness for the purposes of the work, of which the drawbacks are interconnected between practicality and structural versatility. For the above reason, we turn to top-down fabrication approach for realizing sensing platform based on low symmetry metal nanostructures. Top-down approaches allow tuning of parameters such as shapes, orientation, size, and periodicity, characteristics of which are better suited for our intended work.

A.2 Numerical Analysis of Hexagonally Close-Packed

Nanohole Arrays

Nanohole arrays in a hexagonal lattice were simulated using finite-difference time domain (FDTD, Lumerical, Inc) for periodicities p of 350 nm and 500 nm, varying diameter and thickness parameters. The periodicities that were studied were chosen according to sizes of commercially available spheres. Gold thickness of 40 nm to 320 nm was studied, in increments of 30 nm, with diameters from 25 nm – 250 nm in 25 nm increments.

Unlike a square hole array, the spectral response shows two modes excited in a hexagonal lattice. For a fixed diameter and period, the transmission peak linewidth of the initially more prominent mode become narrower with increasing thickness. The spectral narrowing additionally corresponds to a reduced contrast of the air mode and a blue-shift this mode. In contrast, the resonance position of the initially weaker mode remains fairly constant. The linewidth narrowing can result in a reduced FOM but the evanescent tail of the plasmonic field from increasing thickness must be factored in to its applications. In particular, for thicker films, the evanescent decay length will increase. While higher bulk sensitivity can be afforded, the longer decay length comes at the expense of reduced surface sensitivity due to the decreasing fraction of surface sensing volume compared to the background. With hexagonal lattices, the effects of an additional two modes can be eliminated (as opposed to a square lattice) with a polarization-invariant response.

Figure A.7. Transmission spectra for hexagonally-close packed nanohole array of varying thickness.

For a fixed thickness at $t = 160$ nm, the effects of reducing the hole diameter is corresponds to a weaker signal contrast with a smaller hole size. Experimentally, the limiting factors that will determine the selected thickness of the gold film used is the diameter of the sphere mask after etching. When the deposited gold film is too thick, the sphere mask cannot be lifted off and will affect the measurements of the sensing substrate

A.3 Resonance Properties of a U-Shaped Split Ring Resonator

For completeness, the characteristics of a u-shaped SRR is presented where the magnetic resonance for width $w = 30$ nm, arm length $s = 60$ nm, and gap distance $g = 10, 20$, or 30 nm. The width remains fixed to emulate the practical fabrication limitations. The spectral response in the x - polarization (parallel to the gap axis) consists of a fundamental magnetic mode m_0 and a higher order magnetic mode m_1 . For g at 30 nm, the resonance of m_0 is 908 nm. When the gap is reduced to 10 nm, the

shifts to is 866 nm in the NIR region. A higher order mode m_1 is also observed at ~ 600 nm, whose response is minimally affected by the gap distance reduction.

Figure A.8. The numerically calculated transmission response of u-shaped split ring resonators with width of 30 nm, arm length of 60 nm, and gap distance between 10-30 nm for a period of 2s. (a) The gap is reduced to blue-shift the spectral response towards the visible range. (b) The y-polarized response remains unchanged.

A.4 Substrate Effects on Patterned Samples

Commercially-available ITO-coated glass with resistances per area Ω/area of 20Ω , 50Ω , and 150Ω were used in this work. Such substrates are often used as electron beam lithography (EBL) substrates as they provide a conductive path to ground for electrons that bombard the substrate, in order to avoid charging of the sample. Additionally, the ITO on the same type of substrates provides the surface conductivity

needed to form a current pathway for the electrodeposited structures. The high aspect ratio plasmonic structures were realized by electron-beam lithography (EBL) patterning on 120-nm thick ZEP resist on ITO-coated glass. Apart from preventing charging during EBL patterning, the same ITO coating was also used for electrodeposition. Therefore, the ITO conductivity needs be carefully chosen so as to ensure electrodeposition takes place without imparting too much damping loss into the plasmonic resonance. In this work, the resistivity of the ITO was chosen to be 20Ω (across $1 \times 1 \text{ cm}^2$ glass). The plasmonic resonance for $h = 30 \text{ nm}$ is significantly dampened by the free-carrier loss originating from ITO conductivity (20Ω resistance). For this reason, planar structures of $h = 30 \text{ nm}$ structures on ITO with lower conductivity (150Ω resistance). However, the electroplating could not be achieved using the lower conductivity ITO, prompting the use of electron-beam evaporated structures. The effect of free-carrier loss of the 20Ω ITO substrate is less prominent for structure with larger thickness, and its effects on the spectral contrast are not dominant. We illustrate the effect of surface resistance on the resonance in the figure below, which shows the transmission spectra of e-beam evaporated planar ($h=30 \text{ nm}$) and electroplated tall ($h=80 \text{ nm}$) $\theta_{60}s_{60}$ v-shaped split ring resonators. We note from the figure that higher resistivity leads to higher contrast, due to lower damping, in the physically deposited (electron-beam evaporated) structures, but that a low resistivity does not decrease the contrast in the taller electroplated structure.

Figure A.9. Comparison of the contrast in the transmission spectra of arrays of v-shaped split ring resonator fabricated on glass substrates coated with ITO of varying resistivity and by either physical deposition (e-beam evaporation) or electroplating.

A.5 Spectral characteristics and their relation with the sensitivity mapping

Figure A.10(a) shows the (S, λ_R) mapping for the planar and tall vSRR structures, represented by $h = 50$ nm (blue) and $h = 150$ nm (red). When dominated by the LSP-like mode, sensitivity (S , [nm/RIU]) of the structure lies closer to the slope (dashed line), which denotes the $S \propto \lambda_R$ relation of LSP-based sensing in planar plasmonic nanostructures. When the dominant mode is waveguide-like (WG-like), S correspondingly moves further away from the dashed line. To illustrate the spectral difference of the waveguide-like and LSP-like mode characteristics in relation to the (S, λ_R) mapping, we present in Figure A.10(b) the experimental transmission spectra corresponding to different locations denoted in Figure A.10 (a). For similar resonance positions at 687 nm (“1”) and 687.7 nm (“2”), we see the spectral features of the hybrid

modes in that the y -polarized mode is the weak transmission dip detuned from the background LSP resonance and the x -polarized mode is the strong transmission dip located at the background LSP resonance. Both of these modes are located far from the $S \propto \lambda_R$ line, with corresponding sensitivities of 402 nm/RIU (for the y -polarized mode) and 355 nm/RIU (for the x -polarized mode). Note that the x -polarized mode in “1” is the waveguide-like mode whose radiative damping follows that of the LSP mode. This is clearly indicated by its high sensitivity and broad resonance linewidth, as evident from its experimental transmission spectra for $n = 1.00$ and $n = 1.30$ in Figure A.10 where the refractive index change introduces an asymmetric lineshape, attributed to the WG-like, LSP-overlapped characteristic. For the x -polarized (“3”) and y -polarized (“4”) modes of the $\theta_{45}s_{80}h_{150}$ vSRR, their experimental transmissions appear as those of LSP resonance with their broad and strong resonances (Figure A.10(b)). This is again consistent with the relative positions of these modes from the $S \propto \lambda_R$ line, from which an LSP-like sensing properties can be inferred of these modes.

Figure A.10. (a) The (S, λ_R) mapping of $vSRR(\theta, s, h)$ with $h = 50$ nm (blue) and $h = 150$ nm (red). The resonance modes are denoted by the square (for x polarization) and triangle (for the y polarization) markers. The variation of the SRR size (s) and opening angle (θ) are: $s = 60$ nm, 80 nm, and 100 nm; and $\theta = 40^\circ$, 60° , and 90° . The $S \propto \lambda_R$ relation of the planar nanostructure is denoted by the dashed line. (b)-(c) Experimental transmission spectra of $\theta_{70}s_{100}h_{150}$ vSRR and $\theta_{45}s_{80}h_{150}$ vSRR structures under x and y incident polarizations.

The square or triangle markers adjacent to the spectra correspond to the sensitivity characterization mapped in (a).

A.6 List of reported works of LSP-based sensing

The following table includes data from the literature pertaining to LSP-based sensors employing top-down fabrication methods (substrate supported) and characterized at normal incidence. Only works which reported full characterization data (resonance wavelength, linewidth, bulk sensitivity, Q-factor) were included for this comparison. For works where bulk sensitivity reference was $n = 1.3$, a fitting was used to infer the air resonance. Plasmonic sensors employing other resonance mechanisms such as SPP (as with nanohole arrays) or employing angled excitation were excluded, as it is beyond the scope of our comparison. Due to limited data availability for surface sensing, this aspect could not be evaluated.

Table A.1 Full table summarizing related literature based on LSPR, Fano-, and WG-like resonance mechanisms. Representative data was used in Fig. 5, while others omitted for visualization purposes. For publications reporting λ_R in aqueous environment only, λ_R in air was extrapolated (shaded in gray). For Others corresponding to Crescent, 'long'/'trans' pertains to the excitation orientation. The following abbreviations are used in the table: **PS** – polystyrene; **NS** – nanosphere; **PD** – physical deposition; **PMMA** – polymethyl methacrylate; **E-beam evap** – electron beam evaporation; **NIL** – nanoimprint lithography; **EBL** – electron beam lithography; **Si** – silicon; **lith** – lithography; **dep** – deposition; **PDMS** – polydimethylsiloxane; **AAO** – anodic aluminum oxide; **HSQ** – hydrogen silsesquioxane; **evap** – evaporation; **Au** – gold; **SiO2** – silicon dioxide; **LSPR** – localized surface plasmon resonance; **WG-like** – waveguide-like; **pol** – polarization; **p** – periodicity; **s** – arm length (as in this paper); **g** – gap; **n** – number of spokes; **lw** – linewidth; **d** – diameter; **id** – inner diameter; **trans** – transverse

Structure Properties						Optical Properties								
Shape	Length [nm]	Width [nm]	Height [nm]	θ [°]	Other	$\{\lambda_{R,aq}$ λ_R [nm]	S [nm/RIU]	Q-factor	FOM	Linewidth [nm]	Fabrication method(s)	Mechanism	Year	Ref.
Crescent	d=125		40-45	20	long	1083	368	3.48	1.18	311.46	NS template lith, PD (with ion beam milling)		2007	[122]
				40	long	1305	416	4.47	1.42	292.10				
	d=194			20	long	1586	485	7.04	2.15	225.31				
				40	long	1795	596	8.59	2.85	209.06				
	d=356			20	long	2184	682	5.68	1.77	384.62				
				40	long	2470	793	7.08	2.27	348.91				
	d=410				long	2650	879	6.71	2.22	395.13				
				20	trans	978	242	10.58	2.62	92.46				
	d=194			40	trans	1150	418	5.36	1.95	214.46				
				20	trans	1208	459	3.91	1.49	308.81				
	d=356			40	trans	1463	416	6.52	1.85	224.43				
					trans	1570	440	6.04	1.69	260.05				
Ring	d=75					970.1	561.8	5.97	3.46	162.40	PS NS, E-beam evap, ion beam etching, ozone treatment	LSPR		[143]
	d=90					1067.2	632.9	4.89	2.90	218.20				
	d=120					1151.7	724.4	4.30	2.70	267.90				
	d=150					1308.5	874.4	4.12	2.75	317.90				
	od=500	id=390	50		p=1000	1244.5	537.1	7.11	3.07	175.10	EBL, thermal evaporation		2011	[144]
		338				1274.3	584.8	8.21	3.77	155.20				
		266				1294.5	610.7	7.95	3.75	162.90				
		202				1317.3	650.8	7.12	3.52	184.90				
		102				1334.2	691.37	4.63	2.40	288.40				
Disk	d=120		30			$\{685\}$ 626.26	178	6.92	1.97	90.50	PMMA, PS NS, PD, tape stripping, PD	2009	[42]	
Raised square (peak 1)	280	280	20		p=535	1078	496	4.07	1.87	264.90	Nano-imprint SU8, PD	2016	[193]	
			35			1068	272	4.31	1.10	247.60				
			40			1064	162	4.62	0.70	230.20				
Raised square (peak 2)			20			787	167	8.36	1.77	94.10				
			35			751	76	9.02	0.91	83.30				
			40			751	104	7.62	1.06	98.50				
Square dots	100	100	45		p=400	641.1	179	8.42	2.35	76.10	Nano-stencil lith, E-beam evap	2011	[194]	
					p=300	689.7	93	5.33	0.72	129.50				

				p=200	lw>205.4	704.6	30	3.43	0.15	205.40				
Square dimer	80		30		g=30	658.1	116.6	4.87	0.86	135.13	EBL, E-beam evap		[195]	
			75.3			639.8	169.6	6.34	1.68	100.91	EBL, electro-deposition			
			30		g=40	654	115.6	5.03	0.89	130.02	EBL, E-beam evap			
			81.1			625	167.2	6.05	1.62	103.31	EBL, electro-deposition			
Uf	60				p=180	944.09	172.1	4.45	0.81	212.47	EBL, E-beam evap	2017	[196]	
					210	964.16	263.21	5.60	1.53	172.03				
					240	998.57	325.23	5.80	1.89	172.08				
	80				240	1311.06	493	3.67	1.38	357.25				
					280	1343.32	527.44	4.29	1.68	313.95				
					320	1380.18	507.06	4.34	1.60	316.91				
Cn	100	300			n=3	1071.43	335.16	4.99	1.56	214.85			[197]	
					n=4	1025.35	371.56	4.78	1.73	214.77				
					n=5	1002.3	333.19	4.68	1.56	213.58				
					n=6	960.83	319.76	4.56	1.52	210.37				
					n=8	864.06	295.73	4.30	1.47	201.18				
		400			n=3	1080.65	338.57	5.84	1.83	185.01				
					n=4	1039.17	299.67	5.43	1.57	190.87				
					n=5	1016.13	285.47	5.35	1.50	190.31				
					n=6	974.65	246.96	5.84	1.48	166.86				
					n=8	900.92	197.15	5.29	1.16	169.96				
C3 ("Y")	100	60	50		p=500	873.9	256	4.21	1.23	207.50				
Elliptical disks (T)	162	105	20		p=340	638.7*	167	11.97	3.13	53.38	NIL, tilted evap, plasma etch, evap, liftoff	2011	[36]	
Elliptical disks (L)	162	105	20			817*	327	7.89	3.16	103.50				
Pyramid (tip up)	310	310	80			{572.9} 534.81	130	5.63	1.37	95.00	PEEL (Si pits, Au deposition, etch, disperse)	2009	[123]	
	300	300	45			{575.9} 534.001 (pk 1)	143	6.36	1.70	84.00				
	300	300	45			{681.3} 616.547 (pk 2)	221	5.41	1.94	114.00				
	273	273	25			{643.1} 592.118	174	4.74	1.39	125.00				
Pyramid (tip down)	310	310	80			{600} 541.693	199	3.87	1.42	140.00		2017	[198]	
	300	300	45			{656.5} 600.537	191	3.78	1.20	159.00				
	273	273	25			{665.7} 616.183	169	4.25	1.17	145.00				
Pillar (mushroom w/ Au tip)	60(HSQ)+22Au	82	60HSQ+(40-50)Au			533.2	75.81	10.45	1.49	51.00	NIL (AAO, PDMS,			

	70nm Au instead of 50nm		60HSQ+(60-70)Au			556	48.7	5.60	0.49	99.30	HSQ), sputtering			
Rod	200	50	30		p=300, 500	922	309.6	7.09	2.40	130.00	EBL, thermal evap	2015	[121]	
	225	45	40		lw>225.2	1115.5	274.2	4.95	1.22	225.20	EBL, sputtering	2007	[120]	
	280	76	Au 50, SiO2 170			{1250} 1045	675	4.80	2.40	280.00	EBL, ion milling, etching	Fano	2011	[127]
	430	76				{1765} 1454.5	1035	4.30	3.10	335.00				
X	380	76				{1685} 1388	990	11.30	2.90	345.00				
XI, BDD	Lc=380 ,Lb=280	Wc=76 Wb=76			g=20	{1800} 1500	1000	8.00	4.60	215.00				
					g=30	{1760} 1466	980	6.20	3.90	250.00				
					g=40	{1725} 1319	1020	5.50	3.70	275.00				
XI, BQD	Lc=380 Lb=280	Wc=76 Wb=76			g=20	{1305} 1092	710	7.00	4.10	175.00				
					g=30	{1320} 1108.5	705	6.60	3.60	195.00				
					g=40	{1305} 1099	685	8.60	4.70	145.00				
vSRR (x-pol)	50	30	30	60		611.9	72	6.00	0.70	102.30	EBL, E-beam evap	LSPR	2017	[119]
	60					645.6	106.3	6.20	1.03	103.70				
	70					690.1	131.2	5.90	1.12	117.50				
	50			70		565.6	50.8	6.90	0.62	81.60				
	60					565.7	77.3	7.60	1.03	74.70				
	70					579.5	83.4	7.10	1.02	81.60				
	80					593.7	96.4	7.20	1.16	82.90				
	50			75	d=12	588.1	47.8	6.90	0.56	85.70				
	60					595.3	54.9	6.40	0.59	92.60				
	70					595.6	57.1	5.90	0.57	100.90				
	80					626.5	61.3	4.20	0.41	147.90				
	60				d=14	597	59.2	7.00	0.69	85.70				
	70					599.4	65.2	6.10	0.66	98.20				
	80					617.9	80.6	4.80	0.62	130.00				
	80		150	60	p=3s	658.1	227	7.32	2.53	89.86	EBL, Seedless electro-deposition	LSPR-like	2019	This work
	100					755.7	327	16.56	7.17	45.62		LSPR-like		
	80			70		661.4	352	43.49	23.15	15.21		WG-like		
	100					687	355	7.65	3.95	89.86		LSPR-like		
	80		80	60		763.2	222	7.08	2.06	107.83		LSPR		
	100					876.2	213	8.68	2.11	100.92		LSPR		
	80			70		668.6	129	8.34	1.61	80.18		LSPR		
	100					787.4	246	7.30	2.28	107.83		LSPR		
vSRR (y-pol)	80		150	60		650.9	376	26.16	15.11	24.88		WG-like		
	100					679.8	402	40.98	24.23	16.59		WG-like		
	80					654.8	369	31.58	17.79	20.74		WG-like		

	100				687.7	402	33.16	19.39	20.74		WG-like		
	80			60	624.3	65.7	8.52	0.90	73.27		LSPR		
	100				669.9	115	9.32	1.60	71.89		LSPR		
	80		80		629.5	51.9	8.59	0.71	73.27		LSPR		
	100			70	663.3	117	9.41	1.66	70.51		LSPR		