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Plasmonic Nanoantennas for Photochemistry and Photocatalysis

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Kamonpan CHUMPOL, M.Sc.

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Under the supervision of Richard HOBBS, Ph.D.

School of Chemistry and AMBER

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Kamonpan Chumpol, M.Sc.

Summary

When metals are engineered on nanoscale dimensions, they can serve as nanoantennas that convert light into localised surface plasmon resonances (LSPRs). The LSPRs give rise to enhanced optical near-fields over the surface of the metal within subwavelength volumes, beyond the optical diffraction limit. The near-field enhancement of metallic nanoantennas leads to greatly improved light-matter interactions and holds great promise for numerous applications ranging from plasmonic photocatalysis to biosensing applications. Although these applications are made possible through the LSPR-related energy transfer, understanding physical and chemical mechanisms of the LSPR-related energy transfer from metallic nanostructures at the single nanoantenna level remains elusive and often relies on complex experimental setups. Insight into mechanisms of energy transfer from metallic nanoantennas could not only provide fundamental guidelines for optimising existing plasmonic systems, but could also pave the way for producing next-generation plasmonic devices. Therefore, special attention has been paid to energy conversion processes that are low-cost, sustainable, and high-performance.

This thesis investigates LSPR-related energy transfer from Al and Au nanoantennas whose LSPRs were in resonance with laser excitation wavelengths. LSPR-related energy transfer from Al was observed by studying the volume of a photosensitive probe – polymethylmethacrylate (PMMA) – decomposed in the near-field of the metal. By applying the Beer-Lambert law, it is understood that the energy transfer mechanism arose from two-photon absorption. Such energy conversion could also drive chemical changes in PMMA that were identified by Raman fingerprints. Chemical structures of PMMA were observed to transform from polymeric properties to graphitic properties. In the case of Au nanoantennas, the growth of Ge nanocrystals driven by the LSPRs of Au nanoantennas was studied. The formation of Ge nanocrystals from diphenylgermane was evident on Au nanoantennas where plasmonic hotspots were present. The energy conversion mechanism for this case was understood to arise from the contribution of both localised surface plasmon resonances and a non-resonant lightning rod effect. The resonant and non-resonant effects could subsequently drive the nucleation and formation of Ge nanocrystals at the local plasmonic hotspots. These two findings relating to energy

conversion mechanisms highlight the possibility to generate metal-semiconductor hybrid materials, which can potentially be useful for photocatalysis, biosensing, plasmon-enhanced spectroscopy, and solar cells.

The optical near-field enhancement at the single nanoantenna level was further investigated theoretically and experimentally using Al bowtie nanoantennas as a model. An analyte was selectively fabricated at specific locations associated with different electric near-field intensities around the nanoantenna, with respect to the polarization directions of the incident light. Surface-enhanced Raman scattering (SERS) obtained from the analyte at different positions around the Al nanoantenna provides evidence to probe the locations of plasmonic hotspots at the single nanoantenna level. The enhancement factor was confirmed to arise from the gap-antenna with the value of $(0.55 \pm 0.11) \times 10^3$. Aluminium was previously known as an inferior plasmonic metal compared to Au and Ag. However, engineering shape, size, and periodic arrangement of Al can mitigate radiative loss in the Al platform with the contribution of surface lattice resonances. The present work demonstrated that an ultra-narrow resonance linewidth as low as 3 nm, associated with the high-quality factor ~ 150 which is about ten times greater than the typical quality factors of LSPRs, in addition to multi-plasmon resonances in the visible region of the spectrum can be achieved for rigid substrate-bound Al bowtie nanoantennas. These findings suggested that Al bowtie nanoantennas with stringent engineering conditions can potentially be exploited for SERS and sensing applications and towards cost-effective, sustainable, and large-scale production.

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List of Abbreviations

a-C	Amorphous Carbon
AMBER	Advanced Materials and BioEngineering Research Centre
AML	Advanced Microscopy Laboratory
BSE	Backscattered Electron
CCD	Charge-Coupled Device
CDA	Coupled Dipole Approximation
CLS	Cathodoluminescence Spectroscopy
CMOS	Complementary Metal-Oxide Semiconductor
CRANN	Centre for Research on Adaptive Nanostructures and Nanodevices
CVD	Plasmon-Induced Chemical Vapour Deposition
CW	Continuous-Wave
DDA	Discrete-Dipole Approximation
DPG	Diphenylgermane
EBL	Electron Beam Lithography
EDX, EDS	Energy-Dispersive X-Ray Spectroscopy
EF	Enhancement Factor
EM	Electromagnetic
FDTD	Finite-Difference Time-Domain
FEM	Finite-Element Method
FWHM	Full Width at Half Maximum
HRTEM	High-Resolution Transmission Electron Microscopy
IPA	Isopropanol
ITO	Indium Tin Oxide
LSPR	Localised Surface Plasmon Resonance
MIBK	Methyl Isobutyl Ketone
NA	Numerical Aperture
NIR	Near-Infrared
PDMS	Polydimethylsiloxane
PEEM	Photoemission Electron Microscopy

PL	Photoluminescence
PML	Perfectly Matched Layer
PMMA	Polymethylmethacrylate
PSF	Point Spread Function
PTT	Photothermal Therapy
QD	Quantum Dot
RI	Refractive Index
SE	Secondary Electron
SEBL	Scanning-Electron Beam Lithography
SEF	Surface-Enhanced Fluorescence
SEM	Scanning Electron Microscopy
SERS	Surface-Enhanced Raman Spectroscopy, Surface-Enhanced Raman Scattering
SFLS	Supercritical Fluid-Liquid-Solid
SLR	Surface Lattice Resonance
SLS	Solution-Liquid-Solid
SNOM	Scanning Near-Field Optical Microscopy
SPIE	Society of Photo-optical Instrumentation Engineers
SPP	Surface Plasmon Polaritons
TCD	Trinity College Dublin
TERS	Tip-Enhanced Raman Spectroscopy
TFSF	Total-Field Scattered Field
UCD	University College Dublin
UV	Ultraviolet
VLS	Vapour-Liquid-Solid
VSS	Vapour-Solid-Solid

CHAPTER 1

Background

1.1 Plasmonics

Noble metals such as Au, Ag, and Cu were used in arts and architecture in the ancient world. An example is the Lycurgus cup, which is a chalice. The cup exhibits remarkable optical properties when illuminated by light. Under normal (reflective) lighting, the cup appears jade green, but ruby red when illuminated from behind or through the glass. This outstanding phenomenon is the result of colloidal gold and silver nanoparticles and other metal nanocomposites incorporated in the glass.¹



Figure 1.1 Lycurgus cup illustrated in different colours.

The cup appears jade green when viewed (a) in reflection while it appears ruby red (b) in transmission.¹

Since scientists discovered that the colour changes of the Lycurgus cup are mainly due to the special optical properties of metal nanocomposites in the glass, the study in relation to light interaction with metal nanostructures – known as “*plasmonics*” – has been expanded for use in other applications.

Metallic nanostructures having dimensions smaller than the free-space wavelength of light exhibit special optical properties different from the bulk.² The light that interacts with sub-wavelength metallic nanostructures can cause free surface electrons in the conduction band of the metal to oscillate. Under the correct illumination conditions, the oscillation of the free electrons is at resonance with the incident light, resulting in an enhanced optical near-field that is either localised or propagates along the metal surface.³ These modes of enhanced optical near-field can be exploited for various applications. For instance, metal nanostructures can act as nanoantennas that direct light to desired locations making them suitable for photothermal therapy⁴ or focus light to subwavelength volumes beyond the diffraction limit, allowing high-resolution imaging.^{5,6}

1.1.1 Brief summary of surface plasmons

The field of plasmonics involves the study of localisation, guiding, and manipulation of electromagnetic waves beyond the diffraction limit to the nanometre scale.⁶ The free electrons present in metals are key to supporting the existence of surface plasmons. Plasmonic metals can generate an enhanced optical field at the nanometre-length scale, widely known as “*near-field enhancement*”.⁷ The phenomenon arises from the collective oscillations of surface free electrons, typically known as “*surface plasmons*” in the metal that are in resonance with the incident light. The surface plasmons can mainly be classified into two main types, localised surface plasmon resonances (LSPRs) and surface plasmon polaritons (SPPs).⁴

In LSPRs, an external oscillating electric field $\vec{E}$ can induce a dipole (*i.e.* positively and negatively charged centres) to form on each end of a subwavelength metallic nanoparticle. Under optimal conditions, the dipole will oscillate in phase with the external lightwave, resulting in an intense electromagnetic near-field localised on the surface of the metal with intensity from tens to thousands of times of the incident light.^{8,9} A schematic illustration of the phenomenon is displayed in Figure 1.2(a).

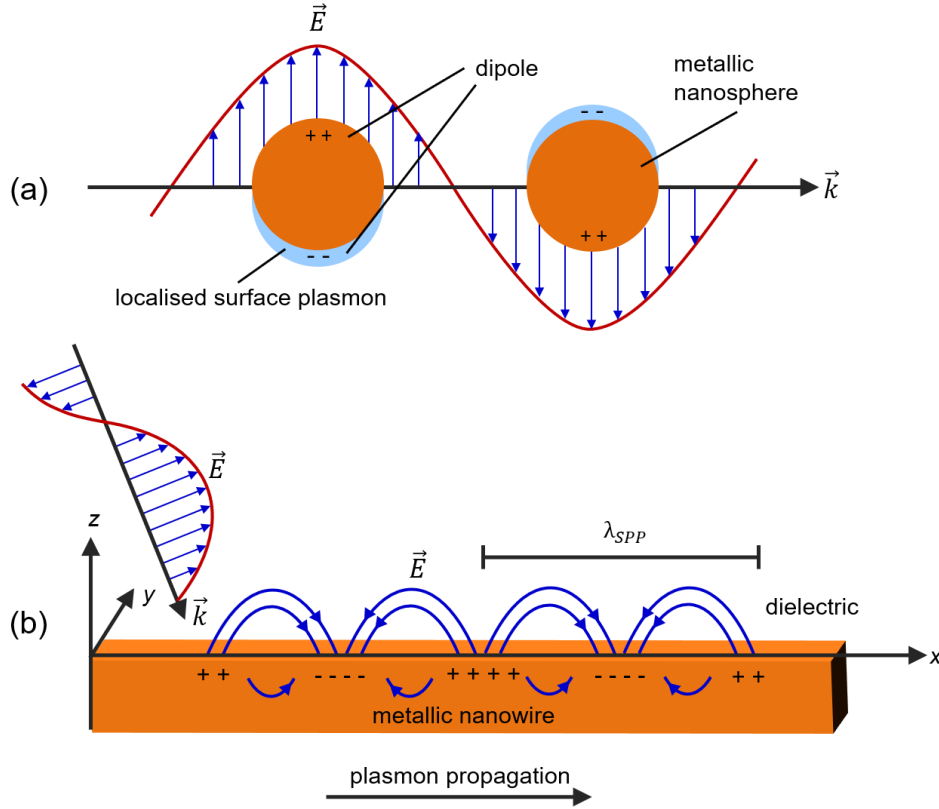


Figure 1.2 Common types of surface plasmons.

(a) localised surface plasmon resonances (LSPRs), and (b) propagating surface plasmons or surface-plasmon polaritons (SPPs). $\vec{E}$ is the electric field of an incoming lightwave with wavevector $\vec{k}$. λ_{SPP} indicates the wavelength of SPP.

Surface-plasmon polaritons (SPPs) usually occur at the interface between a metal and a dielectric (a non-conductive material such as air or glass).¹⁰ By properly engineering geometries of the metal structure into gratings¹¹ or nanowires¹², the oscillations of the surface plasmons can be matched with the frequency of the electromagnetic field outside the metal. This phenomenon results in surface plasmons that propagate along the surface of the metal. In the case of the nanowire (illustrated in Figure 1.2(b)), surface plasmons travel along the wire back and forth between its ends while the propagation length can be as large as tens of micrometres.¹³ Applications of SPPs include ultra-fast signal processing systems¹⁴ and photovoltaic devices that allow maximum absorption of light in the device for high solar efficiency.¹⁵

1.1.2 Localised surface plasmon resonance

The LSPR of metallic nanostructures is sensitive to the nanostructure shape and size, and the dielectric properties of the medium surrounding the metal. By modifying these parameters, one can tune the LSPR across the spectrum from ultraviolet (UV) to near-infrared (NIR).^{8,16} Spherical metallic nanoparticles in a non-magnetic homogeneous environment such as colloidal Au nanoparticles support a single LSPR mode, which correlates to a dipolar resonance,¹⁷ while complex structures such as nanorods,^{18,19} nanocubes,²⁰ and triangular plates²¹ can support multipolar plasmon resonances.

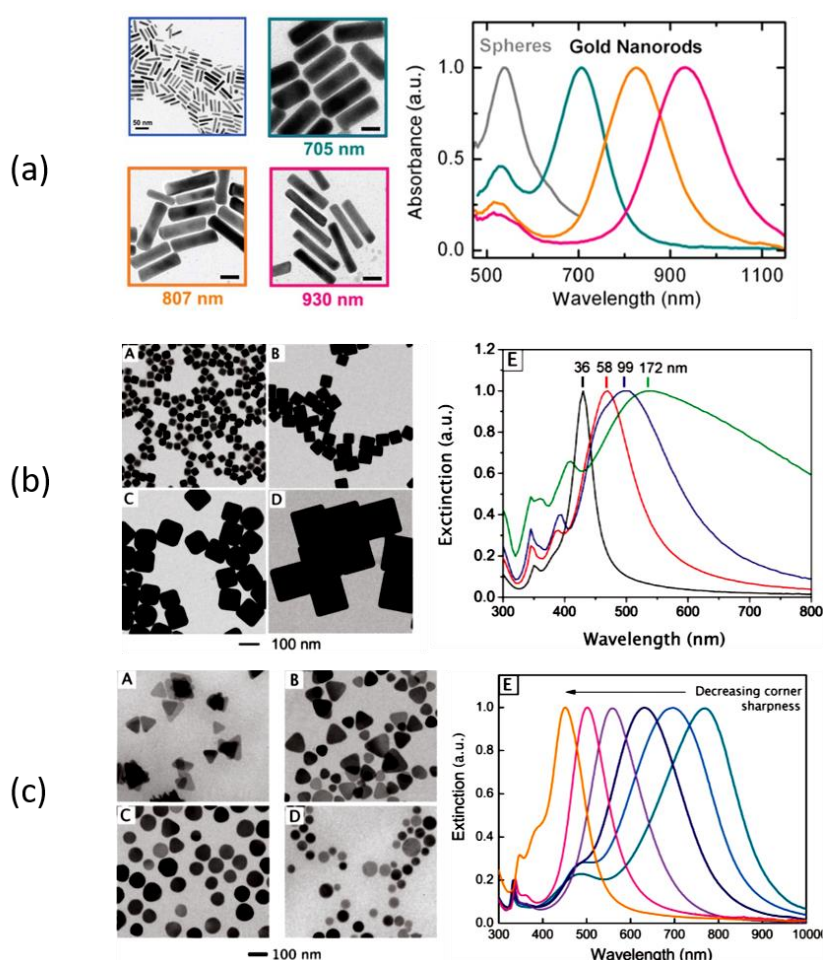


Figure 1.3 LSPRs of distinct shaped nanostructures.

(a) LSPRs of gold nanorods are red-shifted with increasing aspect ratio (length/width).¹⁸ (b) Ag nanocubes exhibit multipolar plasmon resonances when the edge length is increased.²⁰ (c) By increasing the radius of curvature at the corners of triangular Ag nanoplates, LSPRs are blue-shifted and the multipolar plasmon resonances are altered.²¹

The excitation of multipolar plasmon resonances in complex structures depends on the direction of the wave vector and the polarization vector of the excitation field.⁸ In contrast, a nanosphere whose entire surface is exposed to a homogeneous environment exhibits a dipolar plasmon resonance regardless of the polarization direction of an excitation wavelength. For the sake of simplicity, in this section, a metallic nanosphere will be used as a model to help explain the concept of LSPRs through Mie theory.

Mie theory, also known as “*Mie scattering*” employs Maxwell’s equations to calculate optical scattering properties of the electromagnetic radiation by spherical nanoparticles. For the “*quasi-static approximation*” in which a spherical nanoparticle has dimensions much smaller than the excitation wavelength, the change in phase of the external electromagnetic field is trivial and can be excluded in the calculations. The condition is valid only for the particles with the size up to 100 nm.²²

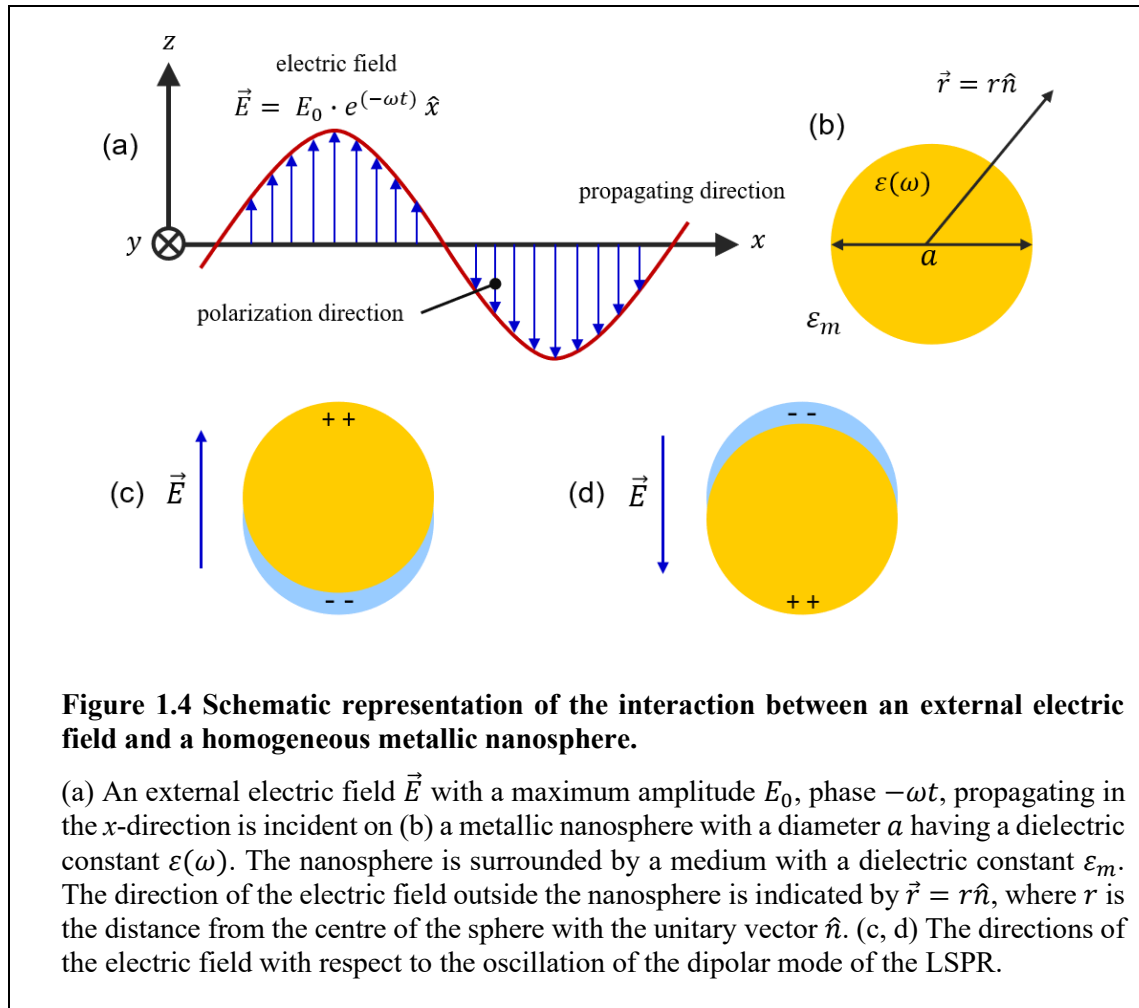


Figure 1.4 illustrates the interaction of a plane-wave of light propagating in the x -direction and a homogeneous nanosphere with a diameter $a \ll \lambda$ and a wavelength-dependent complex dielectric constant $\varepsilon(\omega)$. The nanosphere is surrounded by a homogeneous, non-absorbing and nonmagnetic medium with a dielectric constant ε_m .

The electric field of the incident wave can be expressed as:

$$\vec{E} = E_0 \cdot e^{(-\omega t)} \hat{x} \quad 1.1$$

Here, the electric field of light is represented by $\vec{E}$, E_0 is a constant value representing the amplitude of the wave, and ω refers to the angular frequency. Once an external electric field is applied to the nanosphere, the conduction electrons in the nanosphere are displaced to create a negatively charged centre on one end and a positively charged centre on the other end, thus forming a dipole. For the condition when ω is not very large, the dipole can oscillate fast enough to follow the phase of $\vec{E}$. The relationship between the dipole moment $\vec{\mu}$ and $\vec{E}$ can be expressed as;

$$\vec{\mu} = \varepsilon_m \alpha \vec{E} \quad 1.2$$

Here α is the static polarizability of the sphere. Outside of the sphere, the dipole creates an electric field, which superimposes on the incoming $\vec{E}$. The static polarizability, α , is correlated to other parameters as expressed in equation 1.3.²³

$$\alpha = 4\pi\varepsilon_0 a^3 \frac{\varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m} \quad 1.3$$

In equation 1.3, ε_0 is the permittivity of a vacuum. It is also interesting to consider the distance far away from the sphere. This direction is represented by $\vec{r} = r\hat{n}$, where r refers to the distance to the centre of the sphere and $\hat{n}$ is the unitary direction vector. The relationship of the electric field outside the sphere, $\vec{E}_{out}$ and distance, r far from the sphere can be expressed by equation 1.3.

$$\vec{E}_{out} = \vec{E} + \frac{1}{4\pi\epsilon_0\epsilon_m} \frac{1}{r^3} [3\hat{n}(\hat{n} \cdot \vec{\mu}) - \vec{\mu}] \quad 1.4$$

On the right side of equation 1.4, the first term represents incident light, whereas the second term refers to the radiation of the point dipole $\vec{\mu}$. The term $\frac{1}{r^3}$ explains that the dipole distribution reduces quickly with distance away from the surface of the nanosphere. As a consequence, the enhancement of the electric field is restricted to the nearby vicinity.

To examine the effect of surrounding medium on the metal nanosphere, the Drude model with the association of plasma frequency, ω_p and relaxation time, τ can be applied. Although the Drude model typically describes bulk metals and not the particular conditions required by the quasi-static approximation, this model is quantitatively correct when used to determine the resonant plasmon frequency, ω_{LSPR} of a metal situated in different environments. According to the Drude model, ω_{LSPR} can be determined using equation 1.5.

$$\omega_{LSPR} = \omega_p \sqrt{\frac{1}{1+2\epsilon_m} - \frac{1}{\omega_p^2 \tau^2}} \approx \frac{\omega_p}{\sqrt{1+2\epsilon_m}} \quad 1.5$$

Here, ω_p refers to the plasma frequency given by equation 1.6.

$$\omega_p = \sqrt{\frac{n_e e^2}{\epsilon_0 m^*}} \quad 1.6$$

Herein, n_e represents the number density of electrons, e is the electric charge, and m^* refers to the effective mass of the electrons.

In metals such as gold and silver, the term, $\omega_p^2 \tau^2$ in equation 1.5 is five orders of magnitude (e.g. (1.1×10^5) for gold and (5.2×10^5) for silver) larger than the term, $1 + 2\epsilon_m$. Therefore, the term $\frac{1}{\omega_p^2 \tau^2}$ approaches zero and is negligible, thus giving rise to

the reduced form which depends largely on the dielectric function of the surrounding medium as the bulk frequency is intrinsic to the metal and is fixed.

From the reduced form of equation 1.5, it is apparent that the dielectric constant of the medium around the metal plays a vital role in altering ω_{LSPR} . A higher dielectric constant results in a smaller ω_{LSPR} and thus a longer resonance wavelength, λ_{LSPR} . The relationship between the aforementioned parameters can be expressed in equation 1.7 where c is the speed of light in a vacuum.

$$\lambda_{LSPR} = \frac{2\pi c}{\omega_{LSPR}} \quad 1.7$$

From Mie theory and the Drude model with consideration of the quasi-static approximation, it can explicitly be concluded that shape, size, and medium surrounding the metal nanostructures play a crucial role in modifying LSPRs. In the next section, other parameters including types of metal and geometry (*e.g.* particle-particle separation) that influence the LSPRs will be discussed.

1.1.3 Plasmonic materials

In addition to shape, size, and the dielectric of the medium surrounding the metal, the type of metals also plays a key role in controlling LSPRs.

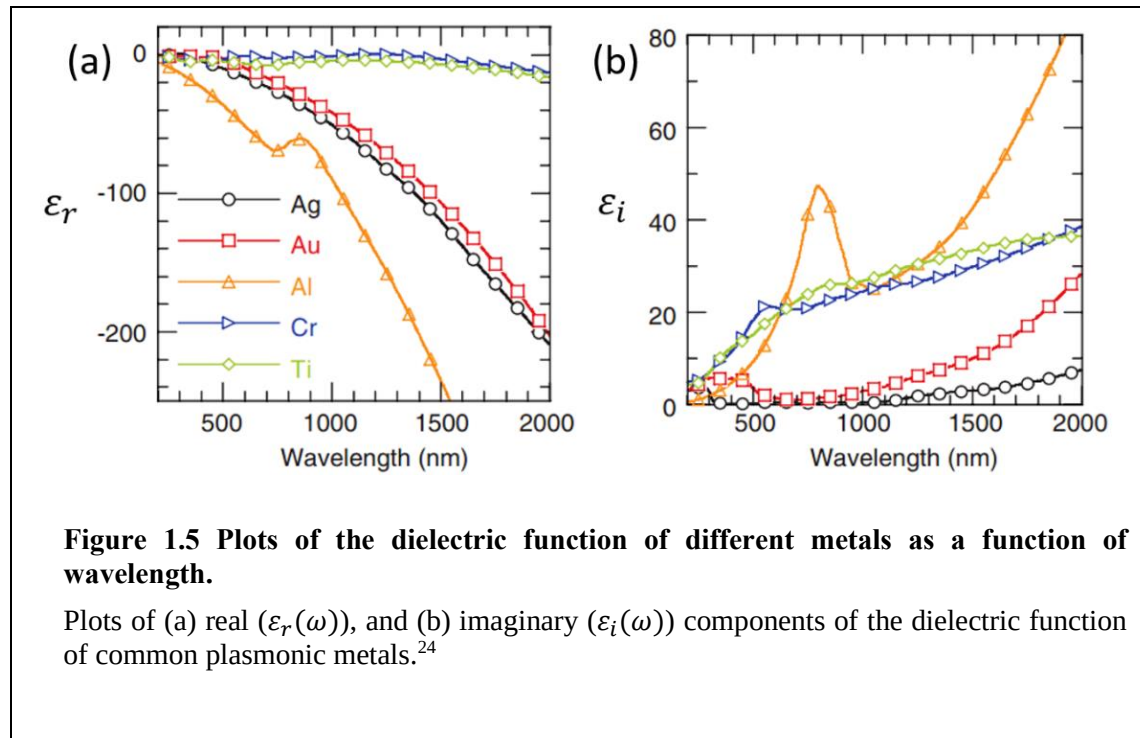
To identify materials that are suitable for plasmonic applications, Mie theory with the consideration of optical extinction cross-section, C_{ext} , (*i.e.* sum of absorption and scattering)²³ will be used.

$$C_{ext} = \frac{24\pi^2 r^3 \epsilon_m^{3/2}}{\lambda} \left[\frac{\epsilon_i(\omega)}{(\epsilon_r(\omega) + 2\epsilon_m)^2 + \epsilon_i(\omega)^2} \right] \quad 1.8$$

For simplicity in this context, a nanosphere model is used to explain the extinction cross-section. In equation 1.8, it can be seen that extinction cross-section of a

nanosphere with a radius, r is dependent on the relative dielectric constant of the medium surrounding the sphere, ϵ_m the excitation wavelength, λ and the real, $\epsilon_r(\omega)$ and imaginary, $\epsilon_i(\omega)$ components of the dielectric function of the metal.

In practice, the parameters including the excitation wavelength and the surrounding medium are often fixed by the experiment. The geometry of metals is also reserved for engineering design and can be modified to meet research purposes. In contrast, the optical response (*i.e.* dielectric function) of metals is an intrinsic property. Therefore, the choice of metals can be considered the foremost quality to determine the suitability for certain applications.



To optimise the extinction cross-section (which also indicates the surface plasmon strength⁴ or a large signal-to-noise ratio of absorption and scattering), it is important to consider the real and imaginary parts of the dielectric function. From equation 1.8, the denominator of the term in the brackets should approach zero. For the wavelength range of interest (*e.g.* in the visible spectral range), this condition can be achieved for metals that have small $\epsilon_r(\omega)$, ideally close to $-2\epsilon_m$, which is impossible for non-metals as their $\epsilon_r(\omega)$ is typically positive.^{25,26} This is the reason why materials such as glass or insulators

do not support surface plasmon resonances. In addition to the negative real part of the dielectric function, surface plasmons exhibit pronounced resonances when losses are low and this is indicated by a small value of $\epsilon_i(\omega)$.

Figure 1.5 shows plots of the real ($\epsilon_r(\omega)$) and imaginary ($\epsilon_i(\omega)$) parts of the dielectric function of metals that support surface plasmons. Au and Ag exhibit excellent optical properties that support LSPRs in a wide range of the spectrum. Large negative values of $\epsilon_r(\omega)$ and small values of $\epsilon_i(\omega)$ in the visible region of the spectrum for Au and Ag result in these materials having large optical extinction cross-sections, compared to Al, Cr, and Ti. Therefore, Au and Ag are favourable plasmonic materials.

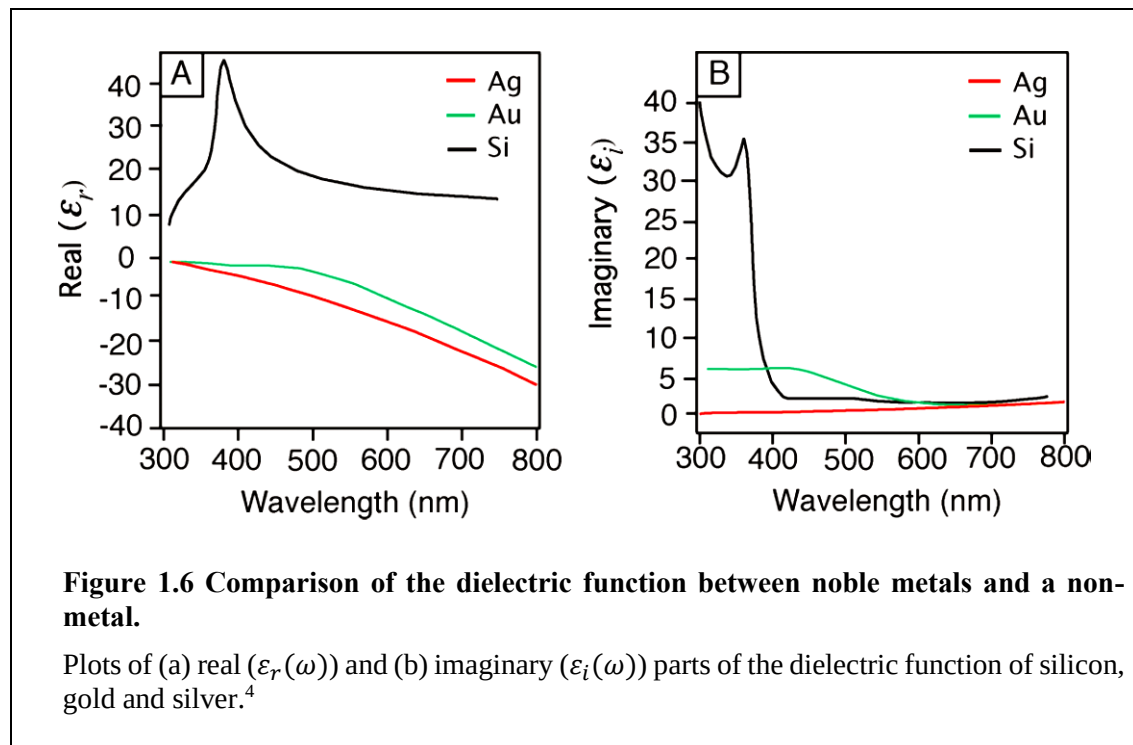


Figure 1.6 compares the real and imaginary parts of the dielectric functions of Si (black line) and common plasmonic metals *i.e.* Au (green line) and Ag (red line) as a function of wavelength from 300 to 800 nm. Si has large positive values of $\epsilon_r(\omega)$ and $\epsilon_i(\omega)$ in the range of 300-400 nm, making it a less favourable plasmonic material compared to Au and Ag. Although Si exhibits small values of $\epsilon_i(\omega)$ in the range of 400-800 nm, its $\epsilon_r(\omega)$ is positive, resulting in small C_{ext} and is unlikely to support surface plasmon resonances.

Quality factors, also known as figures of merit are widely demonstrated as metrics to characterise the performance of materials for plasmonic applications.²⁷ Various forms of the quality factors have been demonstrated depending on the nature of applications. However, in general, the quality factors indicate how many times the local electric field E at the surface of a plasmonic material exceeds the incoming field E_0 . The general form of the quality factors Q_f , also known as the field enhancement factor can be defined as follows:

$$Q_f = \frac{E}{E_0} \quad 1.9$$

The field distribution significantly depends on the $\varepsilon_r(\omega)$ and $\varepsilon_i(\omega)$ of a material. The $\varepsilon_r(\omega)$ indicates the ability a material can store the electric energy or the ability to permit the electric field through it, whereas the $\varepsilon_i(\omega)$ represents the loss in the material. Therefore, the quality factors can also be defined in terms of $\varepsilon_r(\omega)$ and $\varepsilon_i(\omega)$ for a plasmonic material at a specific wavelength or frequency. The quality factor for the LSPR depends on the shape of the material. For a nanosphere in a homogeneous environment, the quality factor Q_{LSPR} can be written as follows:

$$Q_{LSPR} = \frac{-\varepsilon_r(\omega)}{\varepsilon_i(\omega)} \quad 1.10$$

Equation 1.10 conveys that the Q_{LSPR} becomes large if a material has a large negative $\varepsilon_r(\omega)$ and a small $\varepsilon_i(\omega)$ at a frequency of interest. When considering these parameters, noble metals such as Au and Ag which possess a large negative $\varepsilon_r(\omega)$ and a low $\varepsilon_i(\omega)$ over a wide range in the spectrum *e.g.* the visible to NIR, have been considered plasmonic materials of choice for most applications.²⁷

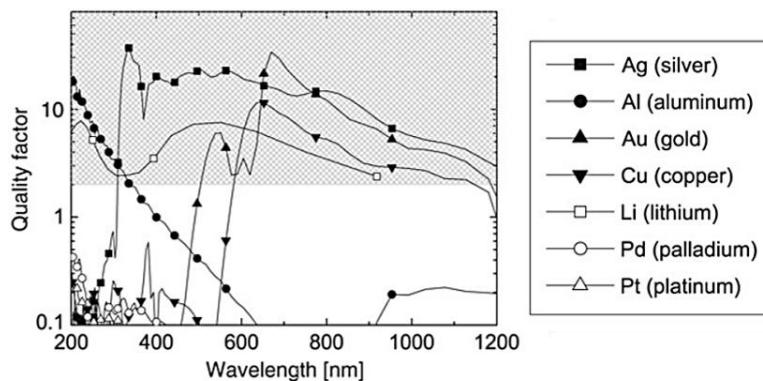


Figure 1.7 Quality factors (Q) of the LSPRs of different metals at the metal-dielectric interface.

The shaded region depicts the ideal Q factors for various applications.²⁸

It should be noted that different applications may have different definitions for the Q factors. However, equations 1.9-1.10 give an idea of how the type of materials plays a vital role in indicating performance metrics.

Figure 1.7 illustrates the Q factors of the LSPRs of different metals as a function of wavelength. The shaded region indicates the ideal Q factors which are favourable for many applications.²⁸ Al has Q factors above 10 in the UV region, whereas Au and Ag exhibit the Q factors above 10 over a broad range of the spectrum *i.e.* UV to NIR for Ag and visible to NIR for Au.

By considering the dielectric function as well as the Q factor of those metals, Ag offers remarkable properties that can support strong surface plasmon resonances across the spectrum (*i.e.* from UV to NIR) while Au is a perfect metal to support surface plasmon resonances from the visible region to NIR. Au and Ag have then become the main choices when it comes to selecting metals for plasmonic applications that require light harvesting in the visible to NIR.

Over the past decades, plasmonic Au nanoparticles have received significant attention for applications in life science such as biosensing, drug delivery, and photothermal therapy (PTT).^{29,30} These applications make use of special plasmonic optical properties that result from physicochemical features of nanostructured Au. Many studies have shown that Au nanoparticles in various shapes and sizes are compatible with

biological cells, have low toxicity, high stability in all kinds of environments, and are multi-functional towards biomedical activities.

In biosensing, a non-invasive imaging technique such as fluorescence-based imaging offers precise and real-time diagnostics. However, the use of organic fluorophores suffers from rapid photobleaching, high-toxicity, and lack of penetration into cell tissues. Therefore, Au nanoparticles with supportive LSPRs are considered a promising approach for biosensing.²⁹ Extensive research³¹ has revealed that light scattered by Au nanoparticles can be a million times more intense than light emitted by fluorophores. Furthermore, LSPRs in Au nanoparticles support strong absorption in the NIR. This region of light is compatible with deep penetration of light into cell tissues, hence offering deep-tissue imaging. In addition, Au nanoparticles can also be used to kill cancerous tissues either by transporting drugs to targeted cells^{32,33} or heating the target cells.^{34,35}

Although nanostructured Au has shown great promise in many applications, the material itself is scarce, hence costly. Table 1.1 demonstrates the cost per ounce of selected metals. Au is approximately three orders of magnitude more expensive than Al. This limitation is a hindrance for scalable production of plasmonic Au materials.

Table 1.1 Comparison of cost per ounce with respect to associated metals. Data tabulated from reference 4.

Metal	Cost (per ounce)
Aluminium (Al)	\$0.049
Silver (Ag)	\$13.4
Palladium (Pd)	\$265
Platinum (Pt)	\$1,207
Gold (Au)	\$950

Unlike nanostructured Au whose LSPRs are tunable across the visible region and NIR, especially for biological applications, Ag extends the range of LSPRs to the UV. This remarkable feature allows Ag to be used in a wide variety of applications. For instance, Ag nanoparticles were used for photocatalytic degradation of textile dyes under

exposure to sunlight. Upon optical irradiation, the excited surface electrons act as donors to the dissolved oxygen molecules in the reacting medium to form oxygen anion radicals. These radicals are capable of driving dissociation of the organic dye into simpler organic molecules, resulting in rapid photodegradation of the dye.³⁶

In addition to photocatalytic activities, Ag nanoparticles have shown great promise in increasing the efficiency of perovskite photovoltaic devices.³⁷ This achievement is due to the enhanced light-trapping performance supported by the presence of nanostructured Ag and the increased charge transfer from the perovskite active layer to the Ag nanoparticles. Although Ag has attracted much attention from researchers for its wide-ranging applications, when exposed to air it forms a silver sulfide film which grows rapidly with time and presents visually as a black material. This intrinsic sulfidation of Ag tarnishes its outstanding plasmonic properties.

1.1.4 Aluminium for plasmonics

Although Au and Ag have offered superior plasmonic properties over other metals, especially in the visible and NIR spectral regions, they are rare-earth metals, thus making them more expensive than other metals. This condition limits their use in applications requiring mass commercial production. Therefore, research into alternative sustainable plasmonic metals has become an intriguing topic in the field of plasmonics.

Cu exhibits high thermal and electrical conductivity, which makes it suitable for electronic applications.³⁸ However, the fabrication of Cu nanostructures is challenging, because it tends to oxidize easily in air.³⁹ Furthermore, Cu suffers from instability and toxicity, which limit its use for biological applications.^{4,40}

Aside from the noble metals, Al has recently been introduced as an alternative plasmonic metal that can serve applications in the UV and visible regions in the optical spectrum. Al has appealing advantages over the noble metals (*e.g.* Au and Ag) due to its earth-abundance, low-cost, and compatibility with complementary metal-oxide semiconductor (CMOS) technology.^{41,42} To date, Al nanoparticles have been applied to many photovoltaic applications. For instance, Al nanoparticles integrated with thin-film silicon,⁴² bulk silicon,⁴³ and titanium dioxide⁴⁴ have been reported to increase light trapping performance in solar cells, hence increasing solar-cell efficiency. This achievement is possible due to the contribution of LSPRs in nanostructured Al.

Al has interesting optical and electrical properties among the plasmonic metals. It possesses a high density of free electrons compared to the noble metals (*i.e.* Au, Ag and Cu). That is, an atom of Al contains 3 electrons in its conduction band, whereas Au, Ag, and Cu have one. The density of free electrons is a key component that determines the breadth of the surface plasmon frequency range (ω_{LSPR}) of the metal.⁴⁵

As was demonstrated in equation 1.6, a larger number density (n_e), which arises from the density of free electrons (*e.g.* 3 electrons for Al versus 1 for Au) can lead to a larger plasma frequency (ω_p) which subsequently results in higher plasmon energy ($\hbar\omega_p$). The values of number density and related bulk plasma properties of aluminium versus the noble metals are tabulated in Table 1.2 below.

Table 1.2 Free electron density characteristics and bulk plasma properties of Au, Ag, Cu and Al at room temperature.

Metal	No. of conduction electrons/atom	n_e (10^{28} m^{-3})	$\omega_p/2\pi$ (10^{15} Hz)	λ_p (nm)	$\hbar\omega_p$ (eV)
Au	1	5.90	2.18	138	9.01
Ag	1	5.85	2.17	138	8.97
Cu	1	8.96	2.54	115	10.81
Al	3	18.1	3.81	79	15.76

From Table 1.2, it appears that the higher valency of Al leads to a larger plasmon energy, $\hbar\omega_p$ (15.8 eV compared with $\approx 8\text{-}9$ eV for Au and Ag). By using the Drude model with the consideration of the quasi-static approximation (denoted in equation 1.5), the localised surface plasmon resonance frequency (ω_{LSPR}) of the metal is predicted to occur in the range from zero to $\frac{\omega_p}{\sqrt{1+2\varepsilon_m}}$. As a consequence, the larger ω_p , the broader the possible frequency range of the surface plasmon resonance. Although Al supports LSPRs over a broad range of the spectrum, its quality factors become low, especially in the NIR as illustrated in Figure 1.7.

To further gain insight into the optical response of Al to an external field, the electronic band structure of Al will be considered (shown in Figure 1.8). In the band structure of Al, there are interband transitions (indicated in the black arrows in Figure 1.8) that are responsible for the absorption of a photon. These interband transitions allow direct transitions of electrons from the bottom to the top of the band.

For Al, because the band below the Fermi level, E_F and the one above are positioned the same in the first Brillouin zone or have the same wave-vector, $\vec{k}$ (see Figure 1.8), a high population of electrons can make the same energy transition, thus increasing the density of states and the transition rate is higher. The difference between the bands observed is approximately 1.5 eV which corresponds to a vacuum wavelength of about 800 nm. It is worth noting that the spectrally localised interband transition absorption energy of Al is responsible for the peak in the plot of the imaginary part ($\epsilon_i(\omega)$) of the dielectric function (illustrated in Figure 1.5(b)). This explains why Al has a high loss (absorption) and low LSPR quality factor at a wavelength of around 800 nm.

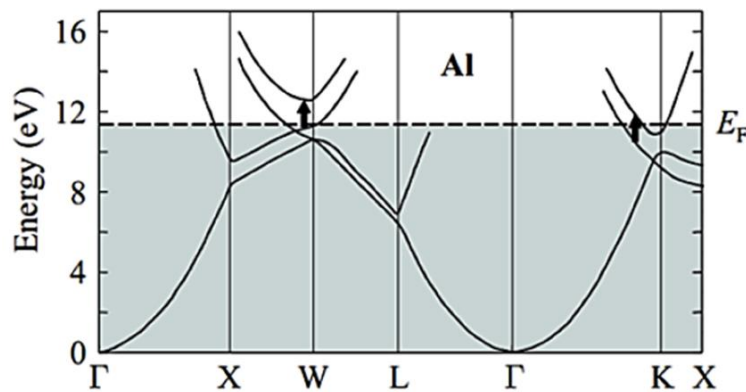
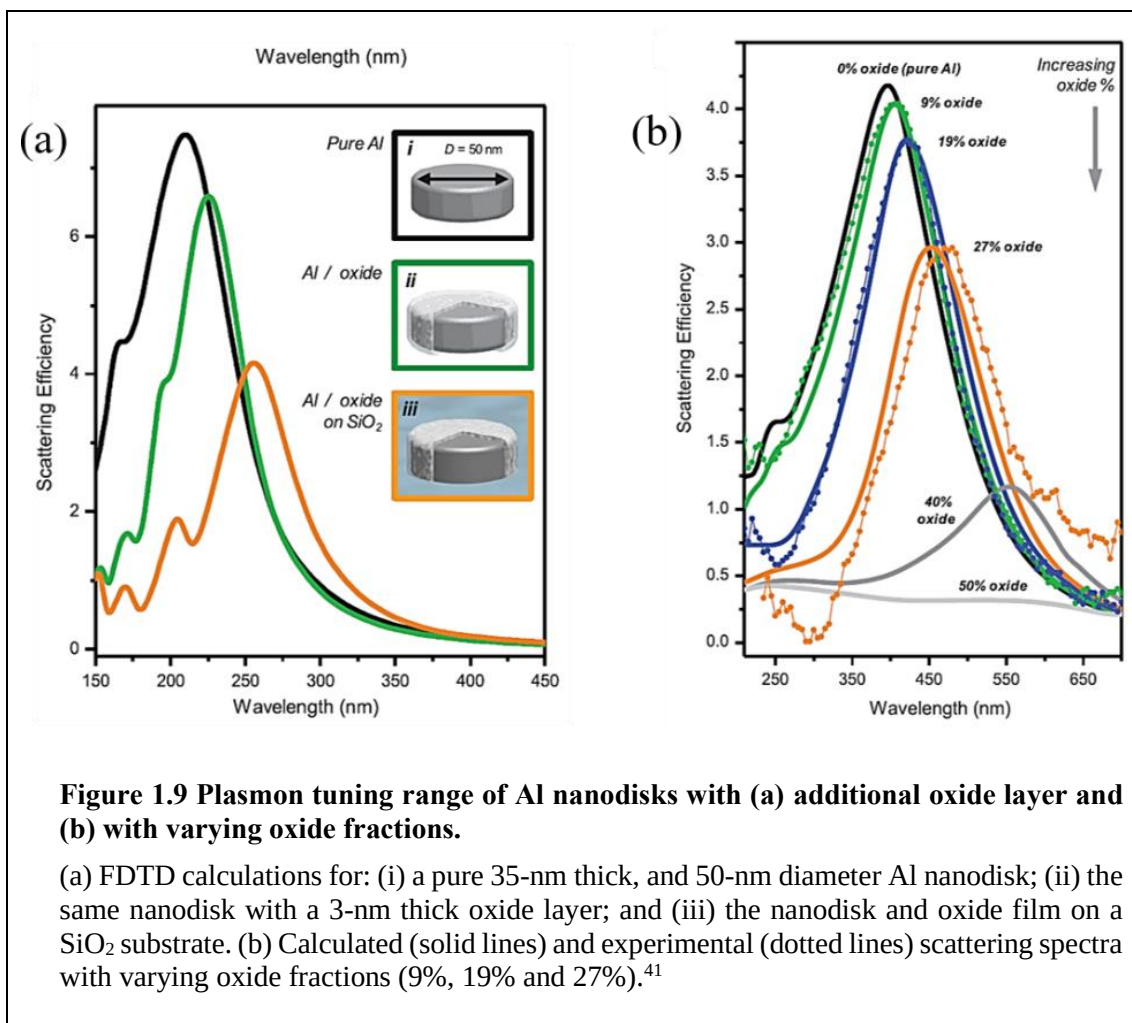


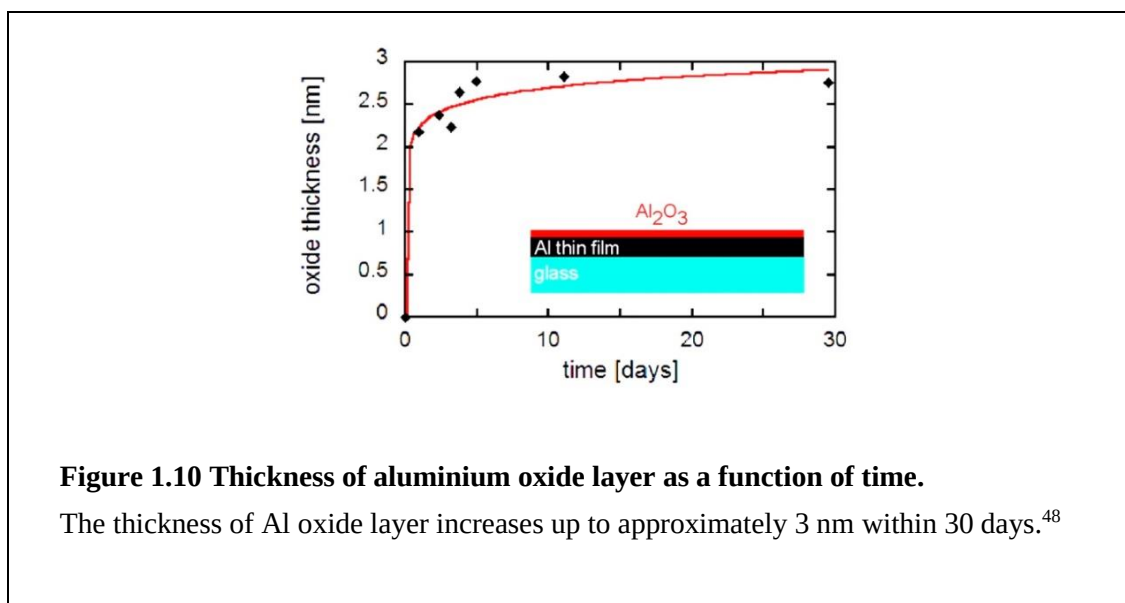
Figure 1.8 Band structure of aluminium.

Fermi level energy E_F is indicated horizontally with the dashed line. The vertical black arrows depict the interband transitions of Al corresponding to the energy around 1.5 eV.⁴⁶ The x-axis indicates the wave-vector, $\vec{k}$ in the first Brillouin zone.

Although Al has a high loss in the NIR region (high value of ϵ_i at 800 nm), it has a relatively low loss in the UV region. This is the reason why Al is a favourable metal for UV plasmonic applications compared to Au and Ag. Due to the presence of interband

transitions at around 550 nm for Au and at around 350 nm for Ag, these metals are limited to surface plasmon resonances with longer wavelengths above the aforementioned wavelengths. That is, Au is an ideal candidate for applications that require surface plasmon resonance wavelengths above 550 nm, while Ag can support surface plasmon resonance wavelengths down to 350 nm.⁴⁷ In contrast, with the consideration of both real and imaginary parts of the dielectric function, Al has a broader range of surface plasmon resonance from the deep-UV to the visible spectral region (*e.g.* 800 nm) before the interband transitions play a role in absorption activity.





Al is known as an active metal. When exposed to air, it rapidly forms an aluminium oxide or alumina (Al_2O_3) layer on its surface.⁴⁸ The alumina film grows naturally over time with an increasing thickness, which causes a red-shift in surface plasmon resonance (shown in Figure 1.9(a)).⁴⁷ Despite the spontaneous growth of the alumina film, the thickness of the film remains stable at approximately 3 nm for at least 30 days as illustrated in Figure 1.10.^{45,48} The stability of the film thickness is advantageous in terms of preventing Al from further oxidation.

In addition, the study also demonstrated that increasing trace levels of oxide result in the same trend as for increasing the thickness of an oxide film (see Figure 1.9(b)). The variable oxide features of Al could be useful to modify the desired LSPRs for *in-situ* applications.

1.1.5 Surface lattice resonance

In section 1.1.2, an external electric field (*i.e.* light) interacting with an isolated metallic nanoparticle resulting in LSPRs was described. In this section, the effect of geometry (*e.g.* periodicity of nanostructure array and size of the nanostructures) of metallic nanostructures and type of metal on the optical responses will be addressed.

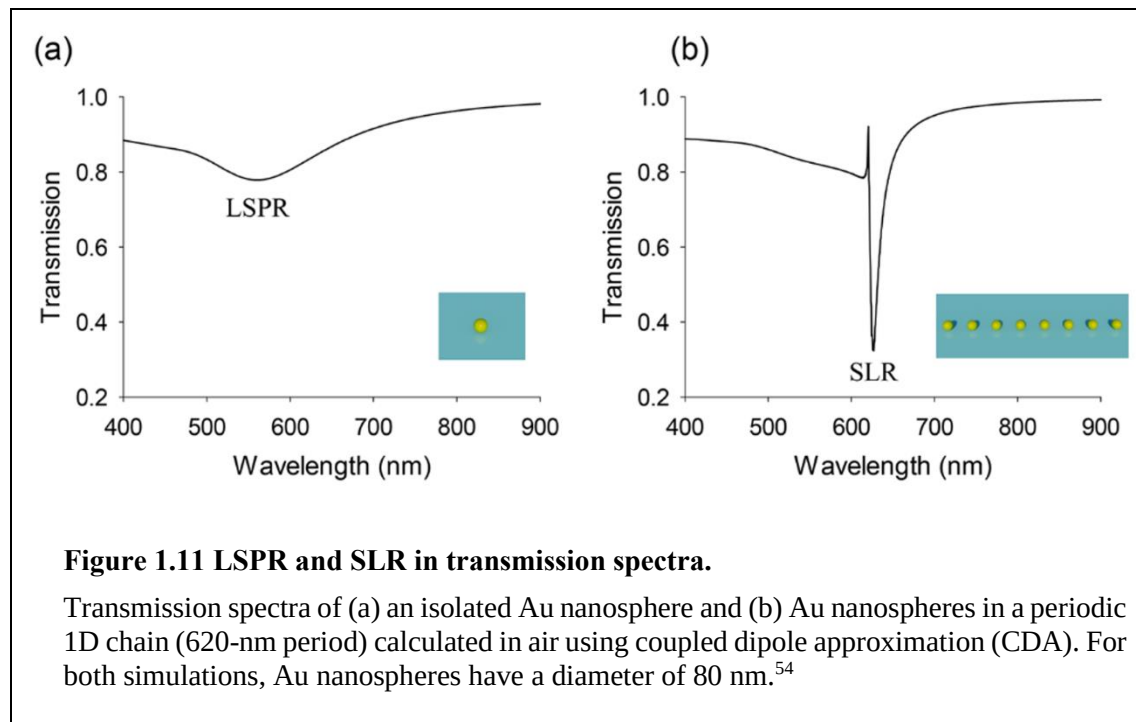
Single, isolated metallic nanostructures often exhibit a broad LSPR linewidth, consistent with high radiative losses. However, many studies^{49–53} have shown that metallic nanostructures that are arranged in a periodic array with appropriate separations

may scatter light to produce diffracted light waves. If one of the diffracted waves propagates in the plane of the array, it may couple with the LSPRs associated with individual nanostructures, giving rise to ultra-narrow resonance linewidths (<5 nm is achievable) compared to >80 nm resonance linewidths for isolated nanostructures. Such an intriguing phenomenon resulting from the hybridization of the diffracted light and the LSPRs is often referred to as plasmonic surface lattice resonances (SLRs).

A resonance linewidth – full width at half maximum, FWHM – is a factor that can also be used to determine the Q factor of a resonator. To calculate the Q factor based on the resonance linewidth, one can use the following formula:

$$Q = \frac{\omega}{\Delta\omega} \quad 1.11$$

Where ω is the resonance frequency and $\Delta\omega$ is the resonance linewidth associated with FWHM. Equation 1.11 also indicates how many optical periods of surface plasmon oscillations encounter before the field decays. Large Q factors are associated with narrow resonance linewidths.



Although, as illustrated in equation 1.10, the Q factor depends on the dielectric function associated with the metal and typically ranges from 10-20,^{49,54} which limits use in some applications, studies have shown that engineering metallic nanostructures in periodic arrays can lead to the generation of a dramatically narrow resonance linewidth. This property of the array can potentially result in an improved Q factor up to ~ 1000 for Au⁴⁹ and Ag⁵⁰.

An example displaying the effect of array geometry on the resonance frequency is shown in Figure 1.11. This figure shows a comparison of LSPR and SLR in transmission spectra calculated for a single Au nanosphere (Figure 1.11(a)) and Au nanospheres arranged in a 1D chain with a 620-nm period (Figure 1.11(b)), while the nanospheres have a diameter of 80 nm. It is clear that for an isolated Au nanosphere, the resonance linewidth is broad. On the other hand, when a number of nanospheres are arranged with appropriate conditions, the interparticle interactions play a role causing an extremely narrow resonance linewidth.

1.1.6 Theoretical studies of SLRs

To better understand the diffractively coupled LSPRs and SLRs, one can use the coupled dipole approximation (CDA). This method provides a basic principle that allows one to predict the diffraction coupled resonances.⁵⁴

In CDA, an array of N nanoparticles are considered as an array $\vec{A}_{ij}$ of electric dipoles where each dipole $\vec{\mu}_i$ has polarizability α_i at position $\vec{r}_i$. A dipole is induced in each particle, given by

$$\vec{\mu}_i = \alpha_i \vec{E}_{loc} \quad 1.12$$

Where $\vec{E}_{loc,i}$ is the local field of the nanoparticle at position $\vec{r}_i$ and is the sum of the incident $\vec{E}_{inc,i}$ and the retarded fields produced by the neighbouring nanoparticles ($N - 1$) with dipoles $\vec{E}_{dip,i}$. For a given wavelength λ , $\vec{E}_{loc}$ can be expressed as

$$\vec{E}_{loc,i} = \vec{E}_{inc,i} + \vec{E}_{dip,i} = E_0 e^{(i\vec{k} \cdot \vec{r}_i)} - \sum_{\substack{j=1 \\ i \neq j}}^N \vec{A}_{ij} \cdot \vec{\mu}_j \quad 1.13$$

Where E_0 and $\vec{k} = 2\pi/\lambda$ are the amplitude and the momentum of the incident field, respectively.

For an infinite array of identical nanoparticles with polarizability α_{NP} , each nanoparticle has the same induced polarization (IP) which depends on the real parts of the inverse of polarizability and the dipole sum S , given by

$$IP = \frac{E_0}{Re\left(\frac{1}{\alpha_{NP}}\right) - Re(S)} \quad 1.14$$

In the case when the wavevector of the incident plane wave is perpendicular to the plane of the array, the dipole sum S can be calculated as follows:

$$S = \sum_{j=1} \frac{(1 - ik \cdot r_{ij})(3 \cos^2 \theta_{ij} - 1) \cdot e^{(ik \cdot r_{ij})}}{r_{ij}^3} + \frac{k^2 \sin^2 \theta_{ij} \cdot e^{(ik \cdot r_{ij})}}{r_{ij}} \quad 1.15$$

Where the angle θ_{ij} is between r_{ij} and the direction of the polarization induced by the incident electric field.

The extinction cross-section per dipole can be calculated as:

$$C_{ext} = \frac{-4\pi k \left[Im\left(\frac{1}{\alpha_{NP}}\right) - Im(S) \right]}{\left[Re\left(\frac{1}{\alpha_{NP}}\right) - Re(S) \right]^2 + \left[Im\left(\frac{1}{\alpha_{NP}}\right) - Im(S) \right]^2} \quad 1.16$$

In equation 1.16, it is found that when the real parts of $\left(\frac{1}{\alpha_{NP}}\right)$ and the dipole sum S are equal, the extinction cross-section per dipole becomes large, leading to a narrow resonance linewidth. This condition can be satisfied in the presence of array parameters (e.g. particle size and geometry of array).

Figure 1.12(a) compares the calculated extinction cross-section per particle of an isolated Ag nanoparticle (green curve) and Ag nanoparticles arranged in a square array (blue curve). It is clear that for an isolated nanoparticle, a resonance linewidth at 727 nm is broad. In contrast, for the Ag nanoparticle array, the resonance linewidth with the maximum intensity at 770 nm, becomes narrower. This phenomenon can be explained using equation 1.16 as shown in Figure 1.12(b).

Figure 1.12(b) shows plots of the real parts and imaginary parts of the inverse of the α_{NP} and the dipole sum S for the array corresponding to the calculated results presented in Figure 1.12(a). As demonstrated in equation 1.16, when the real parts of $\left(\frac{1}{\alpha_{NP}}\right)$ and S vanish, *i.e.* $\frac{1}{\alpha_{NP}} = S$, as denoted by the red dots in Figure 1.12(b). If this condition is reached in the vicinity of diffracted waves, radiative losses can be compensated and that could lead to a small value of $\left[Im\left(\frac{1}{\alpha_{NP}}\right) - Im(S)\right]$, *i.e.* the difference in the vertical gap between the green and the turquoise data points at a wavelength of interest.

For the intersection at 727-nm wavelength, the value of $\left[Im\left(\frac{1}{\alpha_{NP}}\right) - Im(S)\right]$ is large, thus resulting in a broad LSPR linewidth, denoted as an intensity peak of the green curve in Figure 1.12(a). In contrast, for the intersection at 770-nm wavelength, the difference between the imaginary parts of $\frac{1}{\alpha_{NP}}$ and S becomes small, leading to a narrow resonance linewidth as shown in the blue curve in Figure 1.12(a).

In conclusion, the enhanced quality of SLR notably depends on the dipole sum S , which is determined by the geometric parameters of the array (lattice period, array shape, nanoparticle size, *etc.*) as denoted in equation 1.13. As illustrated in equation 1.16, the resonance linewidth of SLR is governed by $\left[Im\left(\frac{1}{\alpha_{NP}}\right) - Im(S)\right]$ and can be made smaller by compensating $Re\left(\frac{1}{\alpha_{NP}}\right)$ with $Re(S)$. Studies have shown that only at proper conditions where the metallic nanoparticles are arranged in a periodic array, the probability that the diffracted waves can propagate along the surface of the array is increased and potentially results in $\left[Im\left(\frac{1}{\alpha_{NP}}\right) - Im(S)\right]$ to be small.

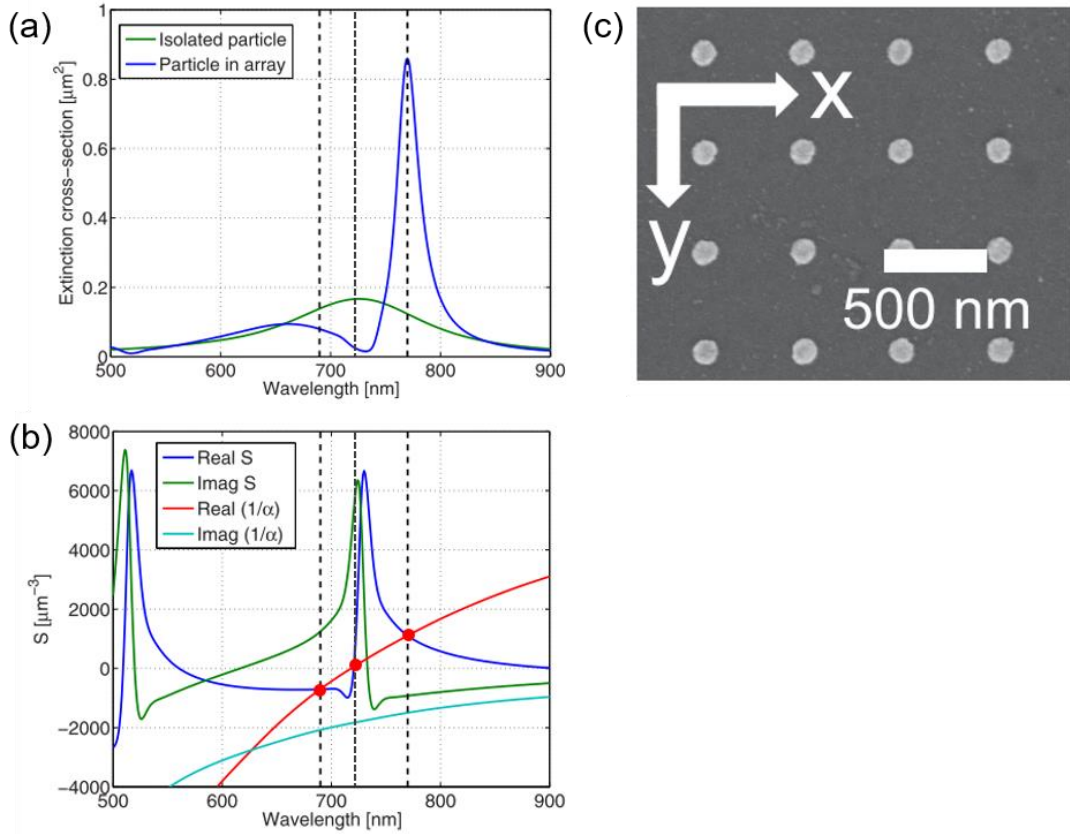


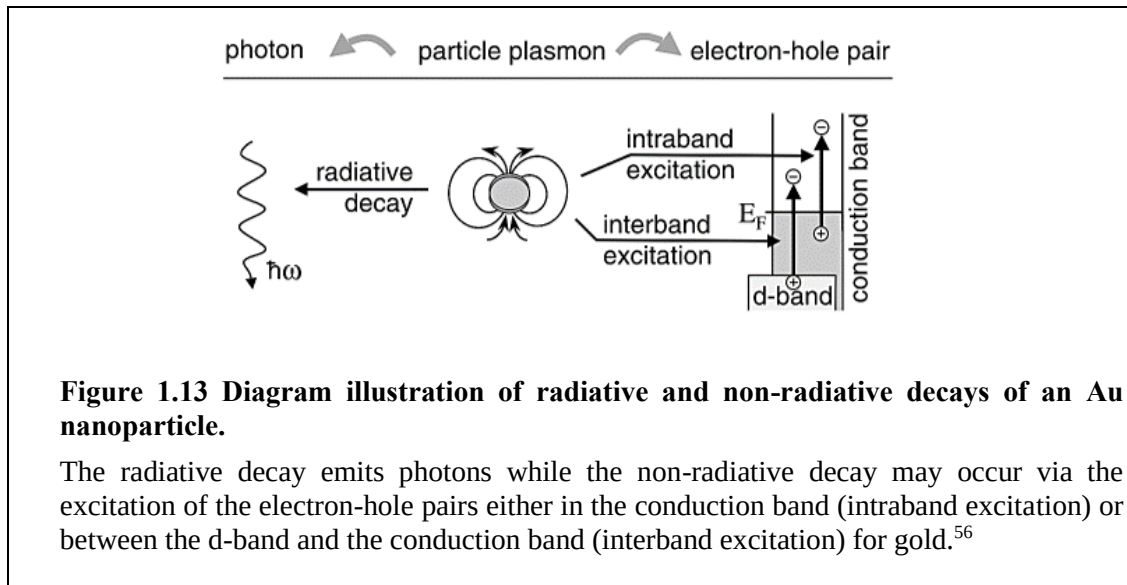
Figure 1.12 Calculated extinction cross-section per Ag nanoparticle and real and imaginary parts of the inverse of α_{NP} and the dipole sum S .

(a) Calculated extinction cross-section per Ag nanoparticle when isolated (green curve) and arranged in a square array (blue curve). (b) The inverse of α_{NP} and the dipole sum S of the associated configurations in (a). The square array has a period of 480 nm, a diameter of 120 nm and a thickness of 30. The particles were illuminated by a normal incident electric field with a polarization direction along the y -axis, and were surrounded by index matching material (*i.e.* a homogeneous environment with refractive index 1.515). The red dots indicate intersections of the real parts of $1/\alpha_{NP}$ and S .⁵⁵

1.2 Energy transfer in plasmonic materials

Upon optical illumination, the oscillating electric field in light can induce a collective oscillation of conduction electrons in a metal. If the incident electric field has a frequency matching that of an LSPR, an intense electric field whose intensity is much greater than that of the incident electric field will be generated near the surface of the metal. This is

the so-called near-field enhancement, which relates to the dipole distribution of the LSPR.



As was described in equation 1.4, such near-field enhancement decays with distance away from the surface of the metal and is restricted to the vicinity of the metal surface. Two competitive forms of dephasing of the resonant oscillation are radiative and non-radiative decays. For radiative decay, photons are emitted from the nanostructured metal. In non-radiative relaxation, electron-hole pairs may be generated via either intraband or interband excitation of the conduction electrons.^{7,56} These processes are displayed in Figure 1.13.

In addition, during the generation of electron-hole pairs, heat dissipation may also occur due to electron-electron and electron-phonon collisions. Such collisions may cause a temperature increase and can be transferred to the surrounding medium.⁵⁷

These forms of plasmon relaxation are key parameters for insight into energy transfer from a plasmonic material to the surrounding medium. The following sections will discuss relaxation processes that can be exploited in various applications. The processes include hot electron injection, thermal distribution, radiative relaxation, and near-field enhancement.

1.2.1 Hot carrier injection

Hot carrier injection processes are essential in photocatalysis where electrons and holes can be used to drive oxidation-reduction reactions. In conventional photocatalysis that makes use of a metal-oxide semiconductor photocatalyst, electron-hole pairs can be generated by capturing energy from incident photons that have energies greater than the bandgap energy of the semiconductor. Most common semiconductor photocatalysts such as TiO_2 , ZnO , and WO_3 possess bandgap energy of around 3 eV,^{22,58} which means photons in the UV range of the spectrum are required to generate electron-hole pairs, hence limiting the use of light in other spectral regions. Moreover, electrons and holes generated from semiconductor photocatalysts have a low mean-free path meaning they tend to recombine before initiating chemical reactions.

Plasmonic photocatalysis has become a promising approach to enhance the performance of traditional semiconductor photocatalysts. Plasmonic photocatalysis employs metallic nanostructures often in combination with common semiconductor photocatalysts. This synergy allows light in the visible regions to be harvested through the modification of LSPRs of the metallic nanostructures.^{7,59,60}

Figure 1.14 demonstrates the process of hot carrier injection from an Au nanostructure to TiO_2 . Herein, the term “*hot electrons*” refers to electrons that are not in thermodynamic equilibrium with the atoms in the metal. Such electrons are excited by an external electric field. When the metallic nanostructure is in direct contact with the semiconductor material, an internal electric field forces electrons and holes to move in opposite directions forming a depletion zone (indicated by the two-sided arrow in Figure 1.14). The depletion zone causes an energy barrier – the so-called Schottky energy barrier (ϕ_{SB}). Hot electrons that are generated in the metal have a broad range of energies and some with sufficient energies may be able to overcome the Schottky barrier and inject into the conduction band of the semiconductor before driving chemical reduction activity, while positively charged holes may initiate chemical oxidation process.

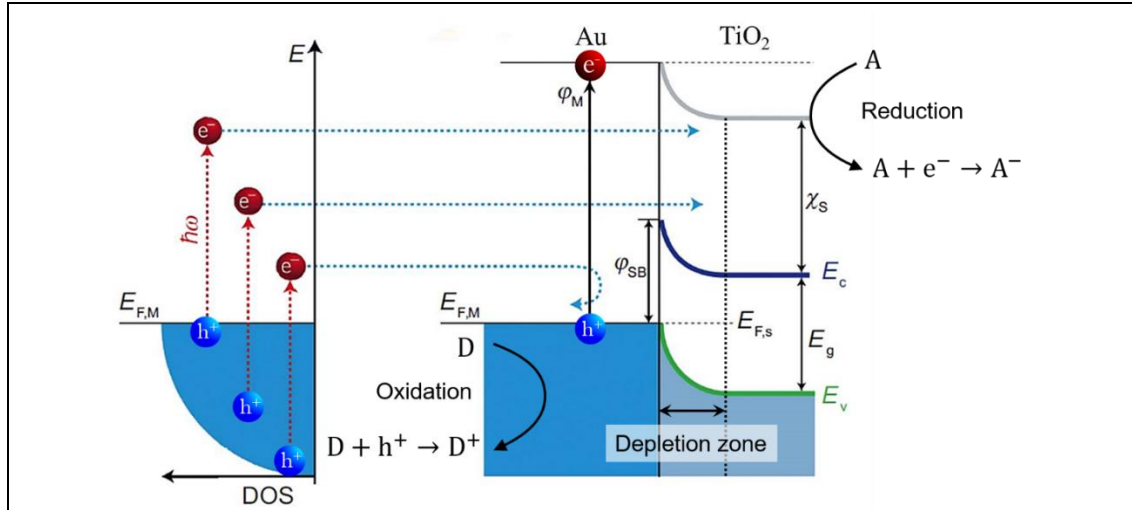


Figure 1.14 Scheme showing hot electron injection process.

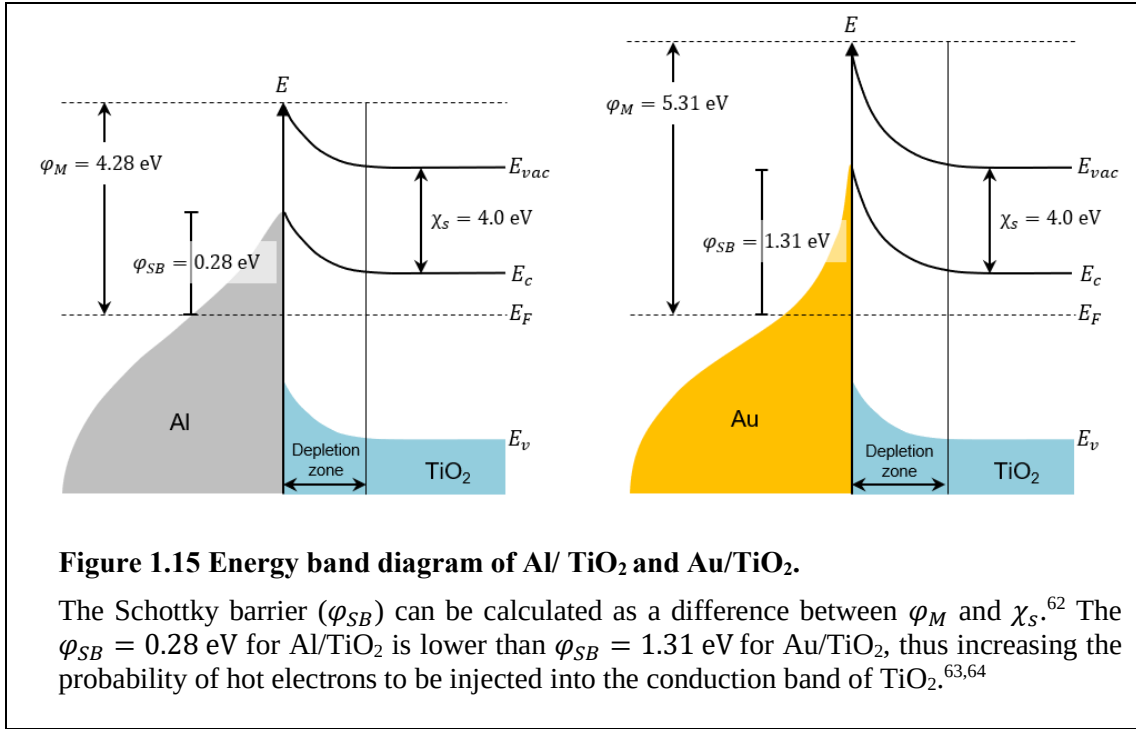
Energies of hot electrons generated in a metallic nanostructure have a wide distribution range. Electrons with large energies can surmount the Schottky energy barrier (ϕ_{SB}), which can subsequently process redox reactions *i.e.* $A + e^- \rightarrow A^-$ for reduction and $D + h^+ \rightarrow D^+$ for oxidation. E_c is the conduction band energy, E_v is the valence band energy, E_g is the energy bandgap, E_F is Fermi level energy, χ_s indicates the electron affinity of the semiconductor and ϕ_M refers to the work function of the metal. Figure adapted and reproduced with permission.²²

The Schottky barrier is advantageous in terms of preventing the recombination of electrons and holes, thus increasing photocatalytic efficiency. Hot carriers can be generated by tuning the shape, size, and composition of the metal to harvest energy from light and direct it towards the semiconductor material.

According to White and Catchpole,⁶¹ it is possible to estimate the metal-to-semiconductor hot-electron photo-current j_{sc} using the following equation.

$$j_{sc} = e \int S(\lambda) \cdot \sigma_{abs}(\lambda) \cdot \eta(\lambda, \phi_{SB}) d\lambda \quad 1.17$$

Here, e refers to electron charge, $S(\lambda)$ [number of photons/(s nm μm^2)] is the incident photon flux, $\sigma_{abs}(\lambda)$ [μm^2] is the absorption cross-section of the metallic nanostructure and $\eta(\lambda, \phi_{SB})$ is the probability of hot electron injection from the metallic nanostructure into the semiconductor material.



As per equation 1.17, the absorption cross-section of the metallic nanostructure $\sigma_{abs}(\lambda)$ can be modified by shape, size, and geometric arrangements while the fraction $\eta(\lambda, \phi_{SB})$ which depends significantly on ϕ_{SB} , can be optimised through the choice of metal. For instance, the Schottky energy barrier between Au and TiO₂ has been shown to be 1.31 eV, which is larger than the Schottky energy barrier between Al and TiO₂ (0.28 eV), which implies that the population of hot electrons that can overcome the Schottky barrier is larger for Al/TiO₂ than for Au/TiO₂.⁶⁵ A schematic illustration comparing the Schottky energy barrier between Al/TiO₂ and Au/TiO₂ is displayed in Figure 1.15.

1.2.2 Near-field enhancement

Although many studies relating to plasmonic photocatalysis for solar-to-chemical energy conversion applications have demonstrated that a plasmonic material conjugated with an oxide semiconductor enables enhanced photocatalytic efficiency due to the contribution of hot carriers from the plasmonic material, other underlying mechanisms have also been investigated. Understanding energy-transfer processes between the two materials not only aids the design of plasmonic nanostructures for the best photocatalytic conversion efficiency, but also allows tunable optical properties in plasmonic nanostructures.

Studies^{66,67} have demonstrated two promising competitive mechanisms – near-field enhancement and hot-carrier generation – in promoting photocatalytic activity in metal-semiconductor nanocomposites. The near-field enhancement arises from the LSPR in the metal, thus enabling direct participation of interfacial species from the surroundings. In contrast, hot carrier generation involves electromagnetic field strength inside the metal to promote hot carriers. These hot carriers must migrate to surfaces before they can initiate chemical reactions in the surrounding environment, meaning an indirect energy transfer mechanism. The two mechanisms have distinct electron pathways, thus requiring different optimization of plasmonic properties.

To evaluate the surface electric field enhancement E_f , one can use equation 1.18.

$$E_f = \frac{1}{A} \int \frac{|E(r)|^2}{|E_0|^2} dr \quad 1.18$$

Where r is the distance from the metal surface with respect to the electric field $E(r)$, E_0 is the incoming field and A is the area over which the field is integrated.

The calculation of hot carrier density N_c can be performed using equation 1.19.

$$N_c = \frac{1}{V_{MFP}} \int_S^{MFP} \frac{|E(r)|^2}{|E_0|^2} dr \quad 1.19$$

Here, V_{MFP} refers to the volume of the integrated field enhancement from the surface (S) of the metal to the mean free path of an electron inside the metal. For example, for a metallic nanosphere, V_{MFP} is the entire volume of the nanosphere while the mean free path of an electron is the radius of the nanosphere.⁶⁷

1.2.3 Thermal distribution

LSPRs in plasmonic nanostructures are responsible for both enhanced optical absorption (σ_{abs}) and scattering (σ_{scat}). The enhanced optical absorption in plasmonic nanostructures can subsequently result in a temperature increase. The heat generated can

be useful in various applications such as plasmonic photothermal therapy, nano-surgery, drug delivery, and photothermal imaging.^{19,54,68}

As described by Joule heating effects, heat generation can be estimated from the heat power density $q(r)$ inside the plasmonic nanostructure. This can be expressed as:

$$q(r) = \frac{\omega}{2} \cdot \varepsilon_i(\omega) \cdot \varepsilon_0 \cdot |E(r)|^2 \quad 1.20$$

Where ω is the angular frequency, $\varepsilon_i(\omega)$ is the imaginary part of complex relative permittivity, ε_0 is the permittivity of a vacuum, and $E(r)$ is the amplitude of the internal electric field.⁶⁸

According to equation 1.20, it is suggested that heat generation is directly proportional to the square of the electric field inside the metal. This concept is crucial when it comes to designing plasmonic nano-sources for heat production.

Equation 1.20 can also be written in the form of heat power $Q(r)$ absorbed by the metal as follows:

$$Q(r) = \int_V q(r) d^3r \quad 1.21$$

In which the integral runs over the volume V of the plasmonic nanostructure. Figure 1.16 shows an example of the heat generation in a single Au nanorod (50 nm × 12 nm). The Au nanorod has an LSPR frequency at 760 nm when illuminated by a plane wave linearly polarized along its long axis. The maximum heat generation occurs in the centre of the nanorod (coloured in yellow), which correlates with the Joule effect. That is, the electronic current judiciously flows in the centre of the nanorod rather than the tip apexes, which are responsible for accumulating charges.⁶⁹

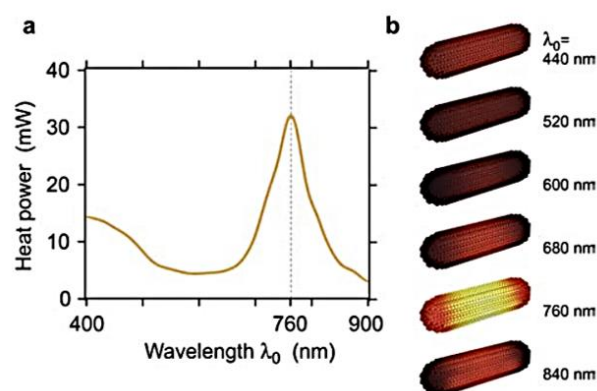


Figure 1.16 Wavelength-dependent heat generation of a single Au nanorod.

(a) Heat power generation as a function of incident wavelength. The heat power is maximum at the wavelength of 760 nm which corresponds to the maximum heat generated in the centre (represented in yellow colour) of the nanorod shown in (b). Colour bar: yellow > red > black represents the level of maximum-to-minimum heat power generation⁶⁹

Another example makes use of heat generation in plasmonic nanostructures to locally synthesize ZnO. ZnO was synthesized using a hydrothermal synthesis system where plasmonic nanostructures were fully covered with the precursor solution and sealed in a closed system.⁷⁰ The study suggests that ZnO formation on nanostructures directly depends on the polarization direction of the light illumination corresponding to heat generation.

1.2.4 Radiative relaxation

Aside from non-radiative relaxation that emits hot carriers or phonons, upon dephasing of the LSPR, photons may be re-emitted from metallic nanostructures, known as radiative relaxation. In biosensing applications, emission of photons from plasmon decay can be exploited to amplify or enhance fluorescence signals of nearby emitters (*e.g.* organic dyes or quantum dots) for improved clinical analysis and shortened diagnostic times.^{71–75}

Photons that are generated during radiative plasmon relaxation from a plasmonic material can directly be absorbed by a fluorophore at a wavelength λ_{ab} . The fluorophore is then excited from its ground state to an excited state. After excitation, the fluorophore returns to its ground state by emitting a photon at a longer wavelength λ_{em} with radiative

decay rate, γ_{rad} or without emitting photons with non-radiative decay rate, $\gamma_{non-rad}$. Assuming the fluorophore has absorption and emission dipole moments μ_{ab} and μ_{em} , respectively. By placing a fluorophore in regions where the LSPR exists and produces light with a wavelength that favours absorption by the fluorophore, the excitation rate of the fluorophore γ_{exc} that is irradiated by the incident electric field $\mathbf{E}$ can be expressed as⁷¹:

$$\gamma_{exc} \propto |\mu_{ab} \cdot \mathbf{E}|^2 \quad 1.22$$

When the fluorophore is in the vicinity of metallic nanostructures, the fluorescence rate γ_{em} can be altered. For optical pumping below saturation, the fluorescence rate can be determined using equation 1.23.⁵

$$\gamma_{em} = \gamma_{exc} \left(\frac{\gamma_{rad}}{\gamma_{rad} + \gamma_{non-rad}} \right) \quad 1.23$$

This quantity is associated with the plasmon-enhanced field intensity $|\mathbf{E}|^2$ that can be optimised by shape, size, and geometric arrangement of metallic nanostructures. Plasmon tunability range based on the type of metals also plays a crucial role in fluorophore selection. For instance, Au nanostructures have a plasmon tunability range in the visible spectral region to longer wavelengths which supports the use of fluorophores whose absorption or emission falls in these regions, hence restricting the selection of fluorophores. However, many fluorescence-based sensing applications make use of fluorophores that absorb or emit UV wavelengths. Therefore, Al-based plasmonic materials LSPRs across the UV to the NIR region of the spectrum provide more options for extended research investigations.^{74,75}

1.3 Thesis aims and objectives

This thesis aims to investigate physical and chemical mechanisms of plasmon-mediated energy transfer from nanostructured metals, particularly focusing on aluminium and gold.

Aluminium is known as an inferior plasmonic metal compared to noble metals, yet, holds great promise for sustainable, low-cost, and plasmon-tunable applications. Gold is an ideal plasmonic metal due to its outstanding optical and electrical properties and has been widely studied for numerous applications. However, in order to optimise device functionalities as well as to improve performance in plasmon-mediated applications, it is necessary to gain insight into underlying physical and chemical mechanisms of energy transfer from these plasmonic metals down to the single nanoantenna level.

The following sections serve as the aims and objectives of research studies whose detailed studies are outlined in Chapters 4-6 in this thesis.

1.3.1 Plasmon-induced graphitization in PMMA-coated aluminium nanoantennas

Chapter 4 aims to investigate LSPR-related energy transfer from Al nanoantennas using polymethylmethacrylate (PMMA) as a photosensitive probe. Raman spectroscopy with a continuous-wave (CW) laser is employed to excite LSPRs of Al nanostructures and to observe chemical changes of PMMA coated around Al nanoantennas.

Upon laser irradiation, the volume of decomposed PMMA around Al nanoantennas is expected to be consistent with the near-field enhancement obtained from theoretical studies using the finite-difference time-domain (FDTD) simulation method. In addition, chemical transformations of PMMA from polymeric properties to graphitic properties are expected to appear in Raman spectra while a potential mechanism that can drive the graphitization in PMMA is also investigated.

1.3.2 Aluminium Nanoantennas for SERS and sensing applications

Chapter 5.1 aims to propose a novel method to probe locations of plasmonic hotspots at the single nanoantenna level using a technique combining electron beam irradiation and surface-enhanced Raman spectroscopy.

An Al bowtie nanoantenna is used as a model in this study. Electron beam lithography (EBL) is employed to fabricate a negative-tone PMMA dot as a nanoprobe at different locations associating with different levels of electric field enhancement calculated using the FDTD method.

Upon laser illumination in Raman spectroscopy together with the polarization-dependent study, Raman signals (the signal-to-noise ratio) associating with characteristics of negative-tone PMMA should be identified to correlate well with the simulation results where the near-field maxima occur.

The method can not only be used to probe the locations of plasmonic hotspots, but also to quantify an enhancement factor originating from specific locations around a single nanoantenna.

Although the gap modes of plasmonic bowtie nanoantennas have been reported to contribute to the maximum enhancement factor, the calculations were particularly based on theoretical approximations. Therefore, Chapter 5.1 additionally aims to provide a reliable method to verify that the maximum enhancement factor originates from the gap mode of a plasmonic bowtie nanoantenna.

Chapter 5.2 aims to study surface lattice resonances (SLRs) of substrate-bound Al bowtie nanoantenna arrays in two different periodic arrangement conditions *i.e.* equal periods and equal edge-to-edge spacings. SLRs of Al bowtie nanoantenna arrays are experimentally observed in air and the environment with refractive index matching that of the substrate using micro-spectrophotometry. SLRs of Al bowtie nanoantenna arrays that result in highly shape resonance linewidths, associating with high-quality factors hold great promise for sustainable and low-cost SERS and sensing applications. Environmental conditions that can give rise to high-quality factors are also investigated in this study.

1.3.3 Germanium growth induced by localised surface plasmon resonance

Chapter 6 aims to investigate plasmon-mediated catalytic Ge growth using laser irradiation and selective absorption of Au catalysts.

Au catalysts are designed with the shapes of rod dimer and bowtie having a 15-nm gap. In theoretical studies using the FDTD method, these structures possess a plasmonic hotspot at the central gap when illuminated by an excitation wavelength polarized along the connecting axis of the dimers.

The near-field enhancement is expected to mediate the chemical conversion of diphenylgermane into germanium nanocrystals. Raman and energy-dispersive X-ray spectroscopy are exploited to indicate the growth of Ge nanocrystals while scanning electron microscopy is used to identify locations where Ge nanocrystals are formed.

CHAPTER 2

Nanofabrication

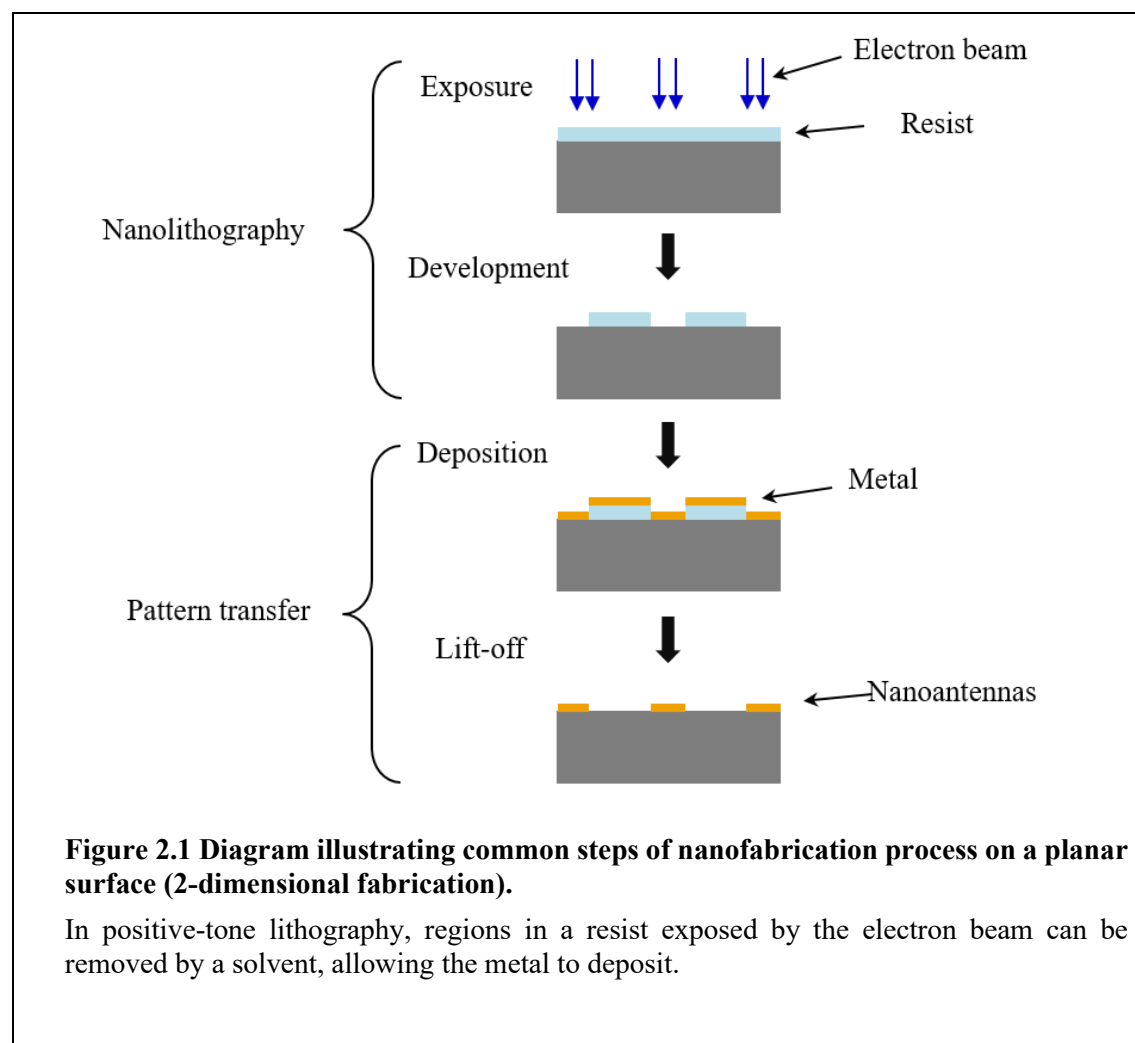
2.1 Introduction

To date, metal nanostructures can be generated by either bottom-up synthesis or top-down nanofabrication. Chemical synthesis has long been used for growing metal nanoparticles of various shapes such as rods, stars, cubes, and triangular plates. This method also offers 2D and 3D growth of complex structures by selectively controlling temperature, surfactants, and precursors. The resultant metal nanoparticles in a solution phase have been widely exploited for biomedical applications.⁷⁶ Although this solution-based approach allows large-scale production of metal nanoparticles, it offers little control over the placement of nanoparticles. Owing to these restrictions, producing metal nanostructure arrays (*i.e.* with a desired particle-particle separation) by chemical synthesis is not direct and simple, thus limiting their use in electronic applications.

Top-down nanofabrication is an alternative approach used to fabricate metal nanostructures. One example of a top-down nanofabrication technique is nanolithography. Fabrication of arrays of metal nanostructures by nanolithography typically consists of four main steps including exposure, development, deposition, and lift-off as illustrated in Figure 2.1. This method is practically performed on a planar surface (*i.e.* the construction can be achieved in a 2D manner).

In order to simplify the explanation in this context, the fabrication process can be separated into two steps the first being “*nanolithography*” to define the mask containing a pattern and the second being “*pattern transfer*” where the mask is removed and the nanostructure is formed. As shown in Figure 2.1, in a first step the substrate is coated with a resist. For positive-tone electron-beam lithography, the electron-sensitive resist is

exposed by an electron beam in order to generate corresponding pattern. Once the exposure is carried out, changes in the chemical structure of the exposed regions of the resist make it more soluble in the developer. During the development, the exposed area of the resist is subsequently removed while the unexposed region remains and is used as a mask. In pattern transfer, the specimen with the mask is coated with metal by electron beam evaporation. The metallic film is deposited anisotropically as shown in Figure 2.1. To remove overlying metal (*i.e.* metallic film on top of the resist), a solvent is used to dissolve the resist and lift off the unwanted metal. This step is known as a “*lift-off*”. To achieve this process it is necessary that the resist thickness be greater than that of the metal film evaporated.



The quality of the nanofabrication depends significantly on the image formed in the resist (*i.e.* the pattern), which depends on the optical setup and materials used as a resist (*e.g.* photoresist or electron-sensitive resist). The lithographic resolution will depend on the wavelength of the radiation used for exposure as well as resist properties. Lithography can be carried out with photons in the visible spectrum, UV, deep UV, extreme UV, x-rays, electrons, and ions. Due to the long wavelengths of photons in the visible region, the pattern generated using this source will result in larger structures compared to those generated by shorter wavelength sources. In contrast, electrons have much smaller wavelengths and are capable of generating nanoscale features in a resist with a higher resolution than visible or UV photons. Such a technique using a focused electron beam to create a pattern in a substrate material is called “*electron beam lithography – EBL*”.

In this research, EBL is the main approach used to fabricate metallic nanostructures. Although this technique is time-consuming and not suitable for large-scale production of metal nanostructures, it offers precise control of metal nanostructure shape, size, and spacing. As a consequence, desired two-dimensional structures with tunable features (*e.g.* controllable shapes and particle-particle distance) can be achieved. Such structures can subsequently produce a high Q factor that can be used for optoelectronic devices and biosensing applications.

The principles and key components of EBL, as well as the steps to achieve high-resolution patterning, will be discussed in the following sections.

2.2 Electron-beam lithography

One of the most common methods of nanolithography in the research world and in industry is electron beam lithography (EBL). EBL is widely and commercially used for fabricating nanostructured materials, photomasks and nanoscale devices.⁷⁷

The basic concept of EBL can be explained in terms of writing a pattern in a raster scan manner on an electron sensitive resist using an electron beam. The writing process is a pixel-by-pixel exposure that requires the assistance of a beam blanker. The beam blanker is usually composed of a pair of electrode plates. By applying a voltage to the plates, the beam will be deflected off the optical axis or “*blanked*”. In order to obtain fine

features, the diameter of the electron beam should be small. For advanced EBL systems, the beam diameter can approach 1 nm. Such a small beam spot supports patterning features down to 5 nanometres and below.⁷⁸ Nevertheless, the small size of the beam will subsequently result in a slow scan. As a consequence, more time is required to write a large pattern.

In addition to the size of the beam, other parameters such as the thickness of the resist, current density, and quality of the microscopy (the quality of the image obtained through the microscope) also play a crucial role in achieving fine patterns.

2.2.1 Electron-beam systems

For a typical electron beam lithography system, there are three major components including the electron source, the stage, and the control electronics. Figure 2.2 illustrates the main components of electron beam lithography tools. The electron source is typically a conducting material that can emit electrons by either heating it up to a certain point where electrons have sufficient energy to overcome the work function barrier of the conductor or by applying an electric field that is sufficiently strong for electrons to tunnel through the barrier.

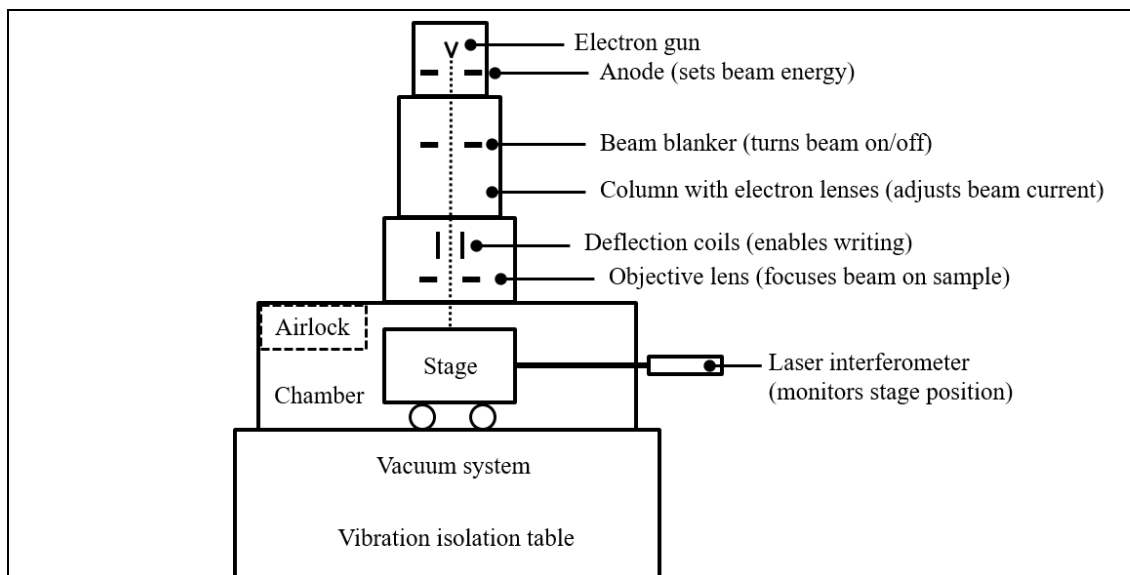


Figure 2.2 Block diagram illustrating the major components of a typical electron beam lithography system.

In Figure 2.2, once the electron beam is generated from the electron source, it will pass through an aperture before it is formed and controlled by either electrostatic or magnetic lenses within the column. To obtain fine features, the beam should be well aligned throughout the column. The optimal beam alignment, as well as the choice of aperture, are the key parameters to determine the quality of the pattern. For example, by choosing a small beam aperture (7- μm aperture) rather than a standard aperture (30- μm aperture), fine features down to sub-10-nm resolution can be achieved.

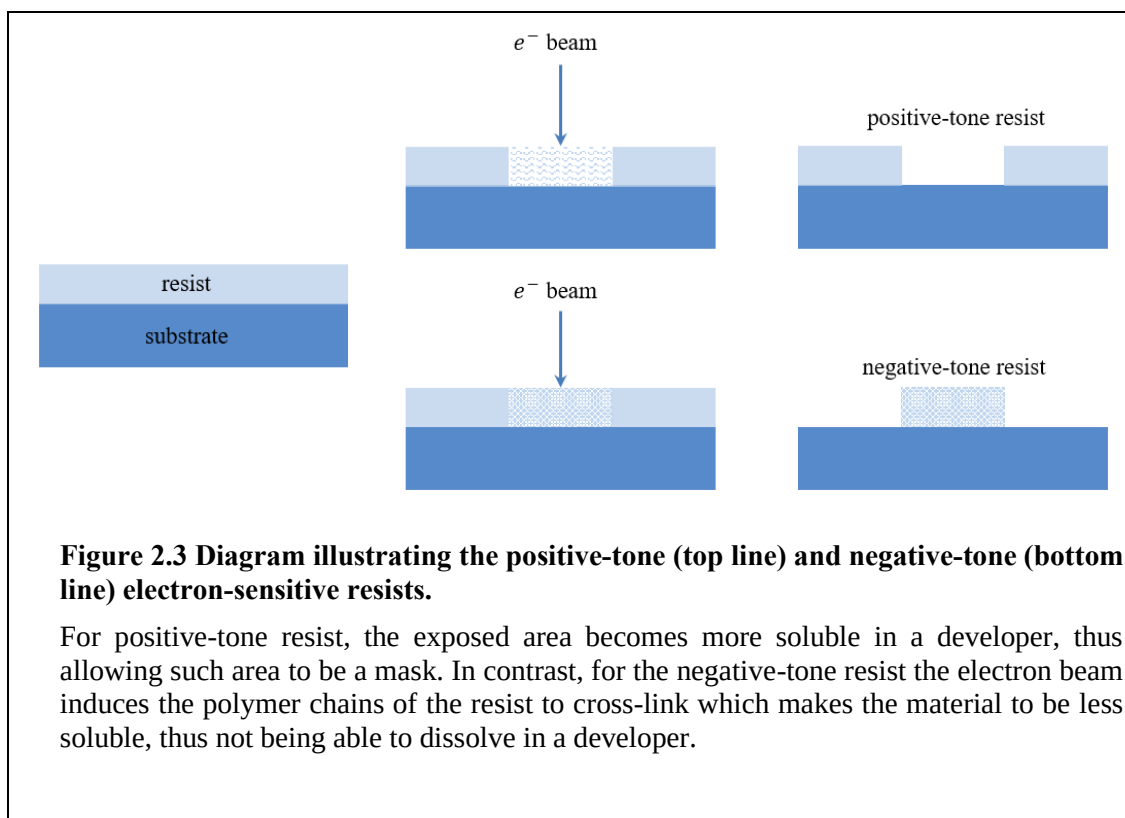
Underneath the column is the sample chamber connected to a vacuum system that maintains an appropriate vacuum level throughout the system. The chamber consists of a stage for moving the sample associated with the patterning positions. A set of control electronics is used for supplying power and signals to the system.

A computer is another important component that is responsible for various functions such as loading and unloading the sample, aligning and focusing the electron beam, setting up exposure parameters, sending pattern data to pattern generator, and controlling the beam blanker on and off associated with the pattern data.

2.2.2 Beam exposure mechanisms

In EBL, a resist that is sensitive to an electron beam is required to record the image of the pattern before being transferred to form the final structures. Commonly used electron-sensitive resists are high molecular-weight polymers that can be dissolved in a liquid solvent. When exposed to an electron beam, the polymer changes its structure which can be either more soluble or less soluble in a developing solution, known as “*positive-tone* and *negative-tone resists*”, respectively.

In positive-tone resists, the polymer is broken into smaller molecular fragments due to scission of the main- and side-chains, thus resulting in the material being more soluble in a developer solution. The solvent developer selectively removes the exposed polymer which is low in molecular-weight, thus the positive-tone pattern is formed (see Figure 2.3 (top line)). In contrast, negative-tone resists tend to be associated with increases in molecular weight when exposed to the electron beam. The polymer is cross-linked becoming less soluble in a solvent developer, thus remaining on a substrate after development (see Figure 2.3 (bottom line)).



Polymethylmethacrylate (PMMA) is one of the first resists that was developed for EBL and still remains the most commonly used as a positive-tone resist today. PMMA was used as a resist throughout this thesis. It comes in a powder form and is dissolved in a solvent, such as anisole or chlorobenzene to produce a desired concentration. The film of PMMA resist can be deposited on a substrate by spin-coating the resist solution onto a substrate, followed by soft baking at a suitable temperature (above glass transition temperature, $T_g = 105^\circ\text{C}$ but lower than decomposition temperature, $T_d = 200^\circ\text{C}$ of PMMA) on a hot plate or an oven. The softbake process facilitates the removal of the casting solvent, thus preventing mixing of exposure products and to improve the resolution of exposed zones during development. Additionally, During the softbake process, the temporary adhesion of the resist on the substrate is also established.⁷⁹

The final thickness of the resist is determined by the spin speed while depositing the resist and the concentration of PMMA. For example, a thickness of approximately 80 nm can be achieved by spinning 950 K PMMA (2% in anisole) resist on a silicon substrate at 3,000 rpm. The typical developers consisting of a mixture of solvent and non-solvent (*e.g.* methyl isobutyl ketone: isopropanol (MIBK:IPA)) with different ratio can be used

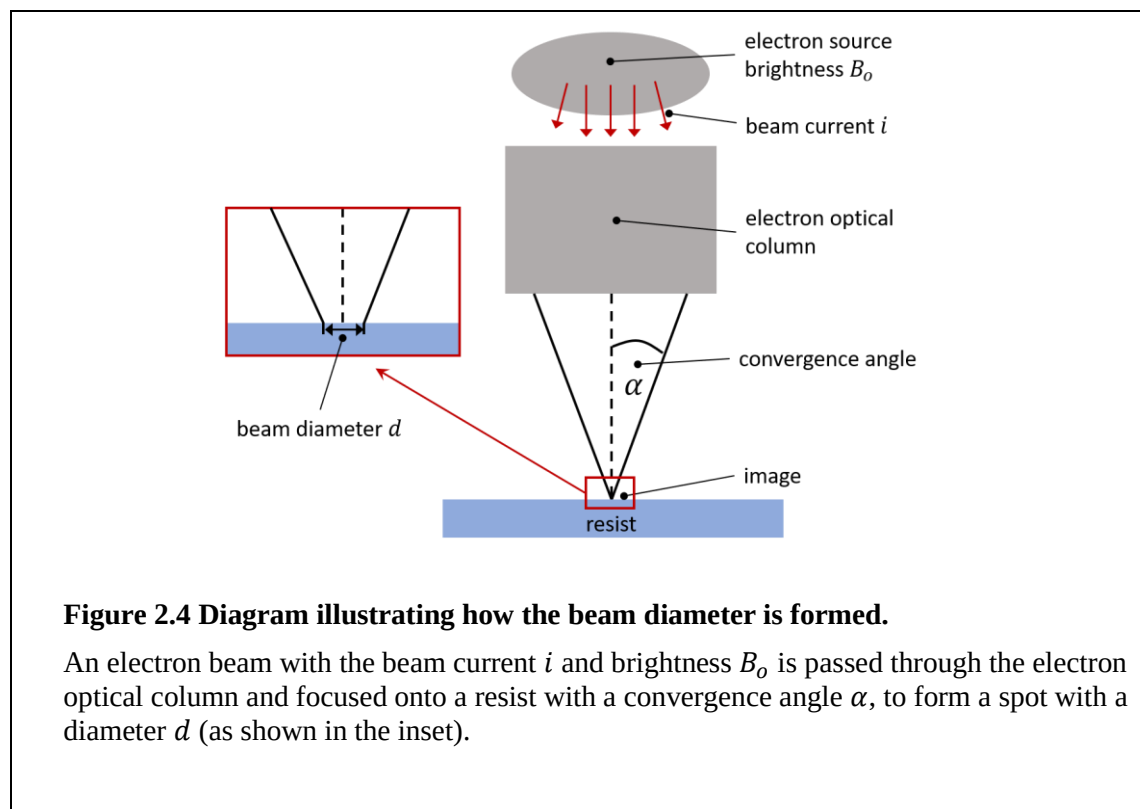
for the highest contrast (high resolution) or the highest sensitivity (high-speed pattern writing).⁸⁰

2.2.3 Resolution limitation

In scanning electron beam lithography (SEBL), resolution of the features that can be achieved depends on the quality of the electron optics and the resist used for patterning. In terms of the electron microscope, the resolution is determined by the beam diameter d which is determined by the beam current i [A], source brightness B_o [A/cm² sr], and the convergence angle α [sr]. The relationship of the parameters can be expressed in equation 2.1^{81,82} with a diagram illustration displayed in Figure 2.4.

$$d = \sqrt{\frac{4i}{\pi^2 B_o}} \frac{1}{\alpha} \quad 2.1$$

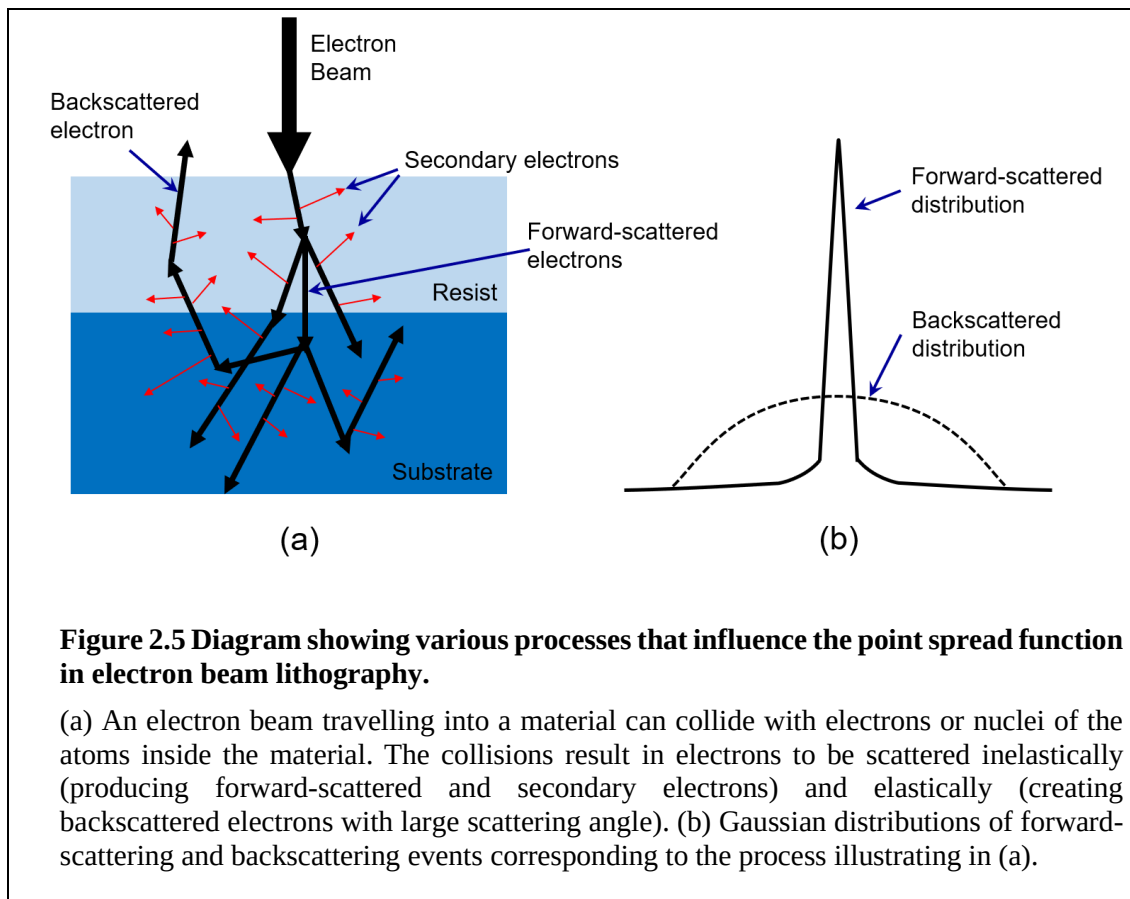
According to equation 2.1, high resolution can be achieved by either using an electron source with greater brightness or by increasing the convergence angle.



Although modification of parameters in equation 2.1 can improve patterning resolution, in practice, other parameters resulting from interactions between electrons in a resist also play an important role in determining the resolution.

2.2.3.1 Proximity effect

To date, typical electron-beam lithography machines employ electron beams with energy ranging from 1-200 keV. Primary electrons with energy in this energy range can interact with nuclei or electrons in the resist and undergo various scattering events and may penetrate into a substrate below the resist. Types of scattering events that may occur including forward scattering, backscattering, and generation of secondary electrons as displayed below in Figure 2.5(a).



As is illustrated in Figure 2.5(a), an incident primary electron can collide with an electron in an atom within the resist or substrate. The primary electron changes its direction, then becomes a forward-scattered electron. It also transfers part of its energy to the atom. Due to the extra energy received from the incident electron, the atom can become excited (*i.e.* excitation of an electron to a higher energy state) or ionised (*i.e.* an electron leaves the atom as a secondary electron). If the atom is part of a resist molecule, the molecular chain of the resist can be cut due to the excitation and ionisation processes. For inelastic scattering events (where an electron changes its energy), scattering angles are small.

On the other hand, if a primary electron is deflected by a nucleus, it can scatter elastically with a large scattering angle which may result in the electron being backscattered. Figure 2.5(b) shows two Gaussian distributions of forward-scattering (sharp peak with a narrow linewidth) and backscattering (broad peak with a wide linewidth). Both forward-scattering and backscattering events contribute to a condition known as “*proximity effect*”.

When primary electrons transit through the resist, their energy is dissipated in the form of secondary electrons having energy typically ranging from 2-50 eV. For such an energy range, electrons have short mean free paths, thus they can only travel a few nanometres in the resist. This consequence is that secondary electrons can contribute less to the proximity effect (illustrated as a narrow peak in Figure 2.5(b)) but are the major contributor to resist exposure. However, such a phenomenon together with backscattering (scattering of electrons with a larger angle) effectively causes a broadening exposure region in the resist which is one of the limiting factors of resolution in EBL systems.

The fraction of the backscattered electrons significantly depends on the type of substrate materials (located underneath the resist). Substrates with high atomic number produce more backscattered electrons than those with low atomic number.⁸¹

To prevent unnecessary damage in a substrate underneath the resist, the energy dissipated by incident electrons E_m should not exceed the displacement energy E_d , which depends upon the atomic weight, bond strength and crystal lattice of a material. The transfer of energy E_m of an incident electron to a nucleus is given by:⁸³

$$E_m = \frac{E_i}{465.7 \cdot A_t} \left(1.02 + \frac{E_i}{10^6} \right) \quad 2.2$$

From equation 2.2, the dissipated energy is dependent on the incident energy of electrons E_i and atomic number A_t . For solids including glass or silicon that are typically used as substrates, E_d ranges from 10-50 eV.^{84,85} This generally means that incident electrons with a typical E_i ranging from less than 1 keV to 30 keV in standard SEM⁸¹ are unlikely to cause damage in the substrate materials.

2.2.3.2 Point spread function

The sum of two Gaussian distributions relating to elastic and inelastic scatterings (see Figure 2.5(b)) that gives rise to proximity effect, is basically the energy deposited in a resist layer as a point or pixel exposure, can be explained in terms of the energy density profile, also known as *point spread function* (PSF). A simple model of PSF⁸⁶ can be expressed as:

$$f(r) = \frac{1}{1+\eta} \left\{ \frac{1}{\pi\alpha^2} e^{\left(-\frac{r^2}{\alpha^2}\right)} + \frac{\eta}{\pi\beta^2} e^{\left(-\frac{r^2}{\beta^2}\right)} \right\} \quad 2.3$$

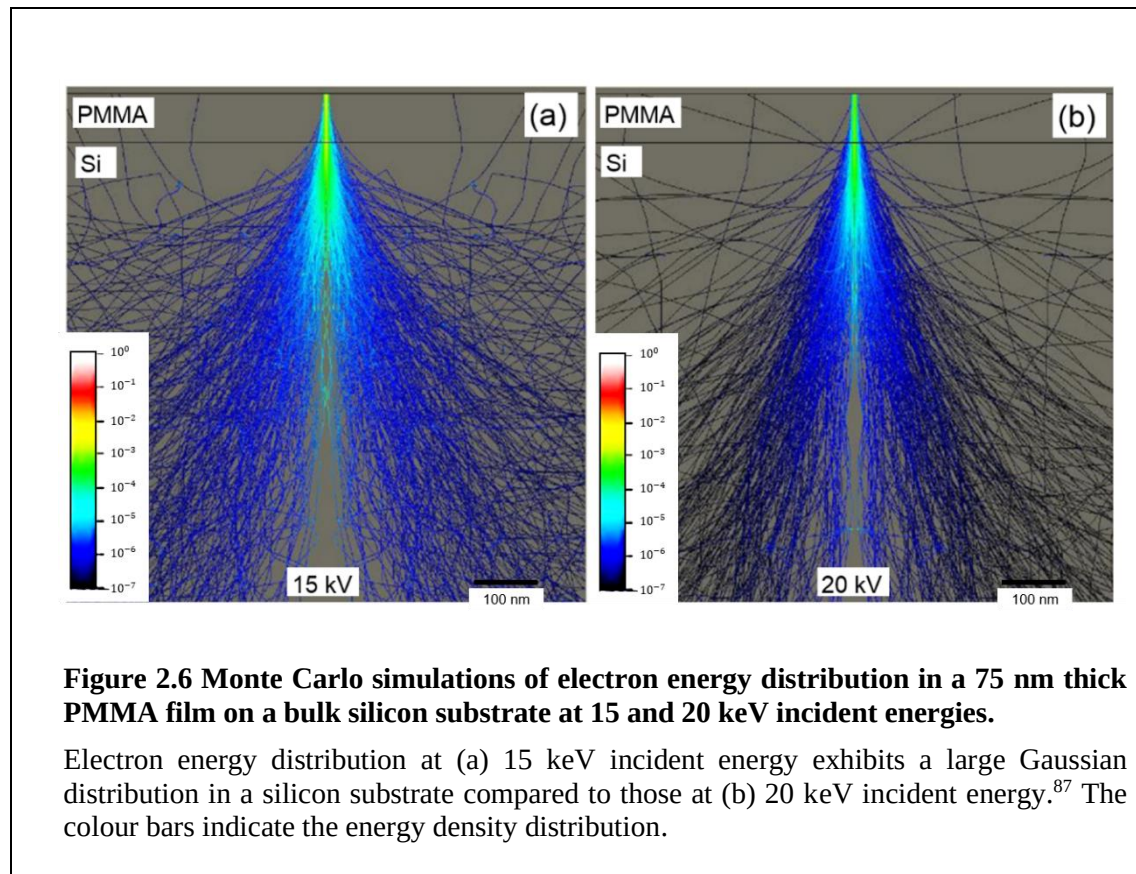
Where r is the distance from the point of electron incidence, η is the ratio of the backscattered energy to the forward-scattered energy, α is the forward scattering range parameter and β is the backscattering range parameter.

In general, equation 2.3 is normalized so that the maximum intensity profile is unity as written in equation 2.4.⁸⁶

$$\int_0^\infty f(r) 2\pi r dr = 1 \quad 2.4$$

Figure 2.6 shows electron scattering trajectories in PMMA as a resist on a silicon substrate at 15 keV and 20 keV incident energies calculated using Monte Carlo simulations.⁸⁷ In the simulations, a thin membrane of 75 nm PMMA was deposited on a bulk silicon substrate. As the incident energy increases, the forward scattering decreases,

while the backscattered electrons are able to travel through the substrate from deeper and wider positions. Although for 20 keV incident energy, the backscattered electrons are widely spread in the resist when they travel back from the substrate (as indicated by black lines in Figure 2.6(b)), they are usually considered as a small and constant dose effect, thus less effective to the exposure.^{88,89} The exposure is mainly caused by the primary electrons which produce a narrower width. Therefore, one way to improve the resolution of the exposure is to use thin resist and/or high incident beam energies.^{88,89}



As demonstrated in Figure 2.6(a) and (b), it should be noted that with the incident beam energies of 15 keV and 20 keV, there is no obvious difference of the exposure width at the point of electron incidence (*i.e.* the diameter of the beam exposure at the surface of the resist). This basically means that for the positive resist, after the development, both samples result in similarly sized openings in PMMA for metal deposition. As a consequence, the lower incident beam energy of 15 keV was employed for all fabrications throughout the work proposed in this thesis.

2.2.3.3 Process parameters in EBL

In relation to the resolution of EBL, parameters including resist thickness R_t [nm] and the beam voltage V_e [keV] can also be used to calculate an approximate beam diameter d [nm]. The relation is given by the following formula:⁹⁰

$$d = 0.9 \left(\frac{R_t}{V_e} \right)^{1.5} \quad 2.5$$

From equation 2.5, by using a 75 nm thick positive-tone resist and 15 keV incident beam energy, small features down to 10 nm can be achieved.

Additional parameters including electron dose, current density, exposure time, development time also affect the resolution of EBL. These parameters will be addressed in the following sections.

2.3 Fabrication of metallic nanoantennas

2.3.1 Fabrication procedure

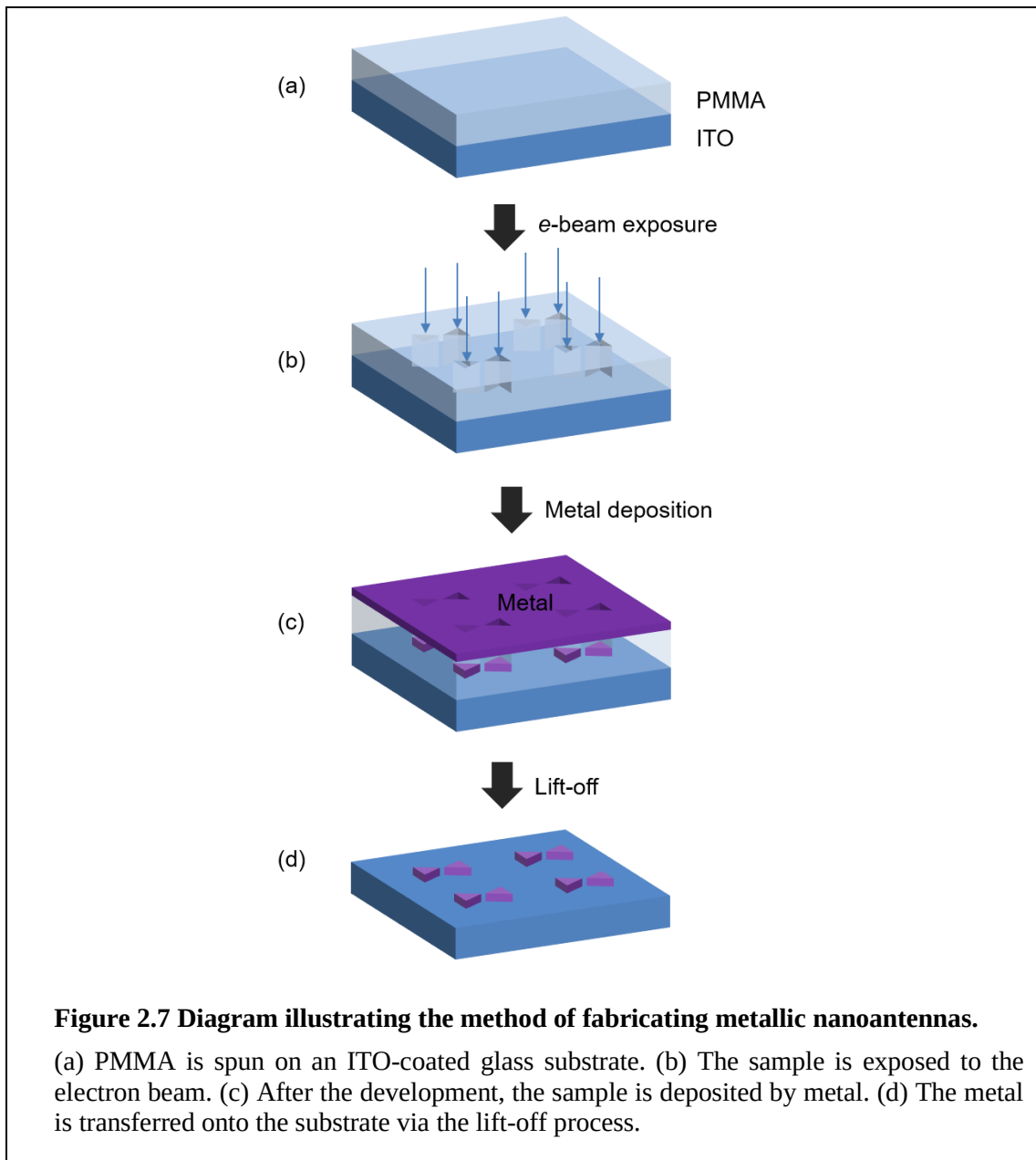
Metallic nanoantennas were fabricated using EBL. A 100-nm-thick indium-tin-oxide (ITO) layer on a glass substrate (purchased from Ossila Ltd.) was immersed in 1% Hellmanex surfactant solution for 5 min in an ultrasonicator and was rinsed by deionised water and isopropyl alcohol (IPA), respectively. The substrate was then plasma-cleaned with an oxygen plasma using a Diener PICO Barrel Asher for 3 min at 0.3 mbar at a plasma power of 100 W.

In Figure 2.7(a), a 70 nm-thick layer of PMMA (2% 950k PMMA in anisole, purchased from EM Resist Ltd.) was spun on the substrate at 3 krpm for 60 s and was then baked at 180°C for 2 min on a hotplate.

In Figure 2.7(b), EBL was performed using a Zeiss SUPRA 40 scanning electron microscope with a commercial pattern generator – Raith Elphy Quantum. The resist was exposed by the electron beam using an acceleration voltage of 15 kV and an area dose of 1300 $\mu\text{C}/\text{cm}^2$ (see section 2.3.2 for more details) to generate a two-dimensional pattern

of desired nanoantennas. To achieve high-resolution patterning, a small objective aperture of 7 μm and a short working distance of about 3.5 mm were used.

To improve pattern resolution, the sample was developed in a 1:3 MIBK:IPA solution at a homogeneous low temperature of 0°C for 30 s using a thermoelectric cold plate with a stirring bar before being dried by a nitrogen spray gun.



In Figure 2.7(c), the developed sample was thereafter coated with metal(s) using a Temescal FC-2000 deposition system. For Al deposition, the deposition recipe is as follows: Al is evaporated at 1 Å/s deposition rate at a pressure of 3.0×10^{-6} Torr, with the thickness measured by a quartz crystal monitor. For Au deposition, a 1 nm thick Ti adhesion layer is required. The deposition rates for Ti and Au are 1 Å/s and 0.5 Å/s, respectively.

In Figure 2.7(d), the pattern was subsequently transferred to the substrate via a lift-off process by immersing the sample in n-methylpyrrolidone (NMP) at 55°C for 45 min. The sample was then rinsed in acetone and IPA, respectively before drying with a nitrogen spray gun.

2.3.2 Dose-dependent nanolithography

As previously mentioned in section 2.2.2, the current density or exposure dose is one of the key parameters that determines the resolution of EBL. To examine a suitable exposure dose for fabricating structures (*e.g.* bowties or rod dimers) with a narrow gap down to 10-15 nm using EBL, various doses were implemented.

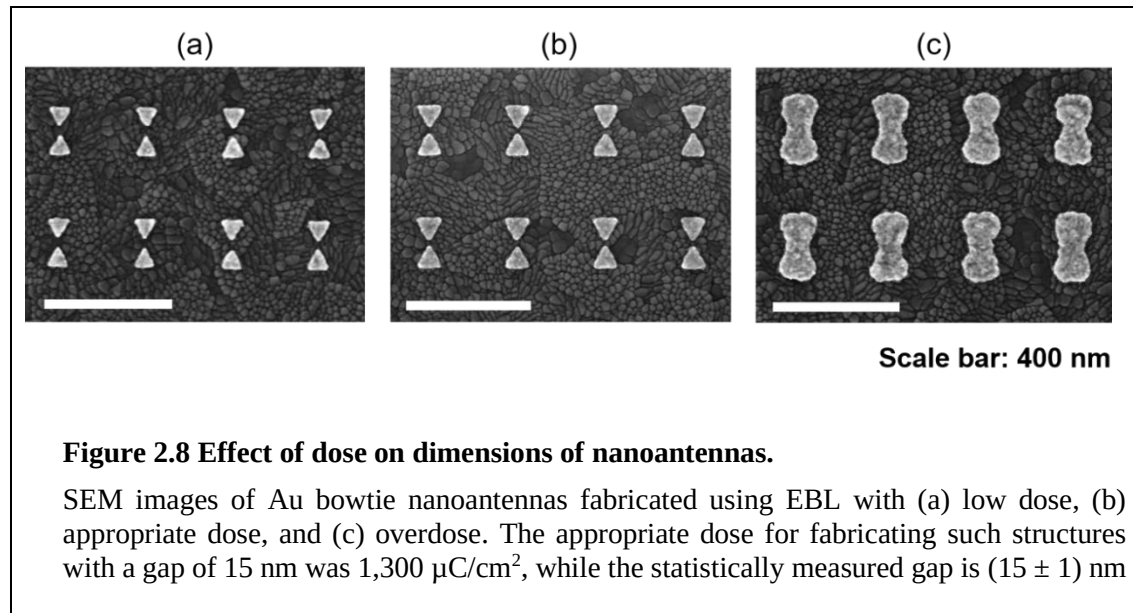


Figure 2.8 shows as-prepared Au bowtie nanoantennas on top of an ITO-coated glass substrate fabricated by EBL using three different exposure doses: (a) $700 \mu\text{C}/\text{cm}^2$; (b) $1,300 \mu\text{C}/\text{cm}^2$; and (c) $2,000 \mu\text{C}/\text{cm}^2$. It is clear that the dimensions of the nanoantennas depend significantly on the exposure dose. A low dose ($700 \mu\text{C}/\text{cm}^2$) results in smaller dimensions than the desired structures while an overdose ($2,000 \mu\text{C}/\text{cm}^2$) results in the structures to be larger than expected. In this case, a dose of $1,300 \mu\text{C}/\text{cm}^2$ allows the fabrication of Au nanoantennas with desired dimensions (*i.e.* an 85 nm side length and a 15 nm gap).

2.3.3 Single-beam spot technique

Prior to EBL, it is important to ensure that the beam is focused on the surface of a resist as the point at beam incidence is used to determine the effective beam diameter which improves the exposure resolution.

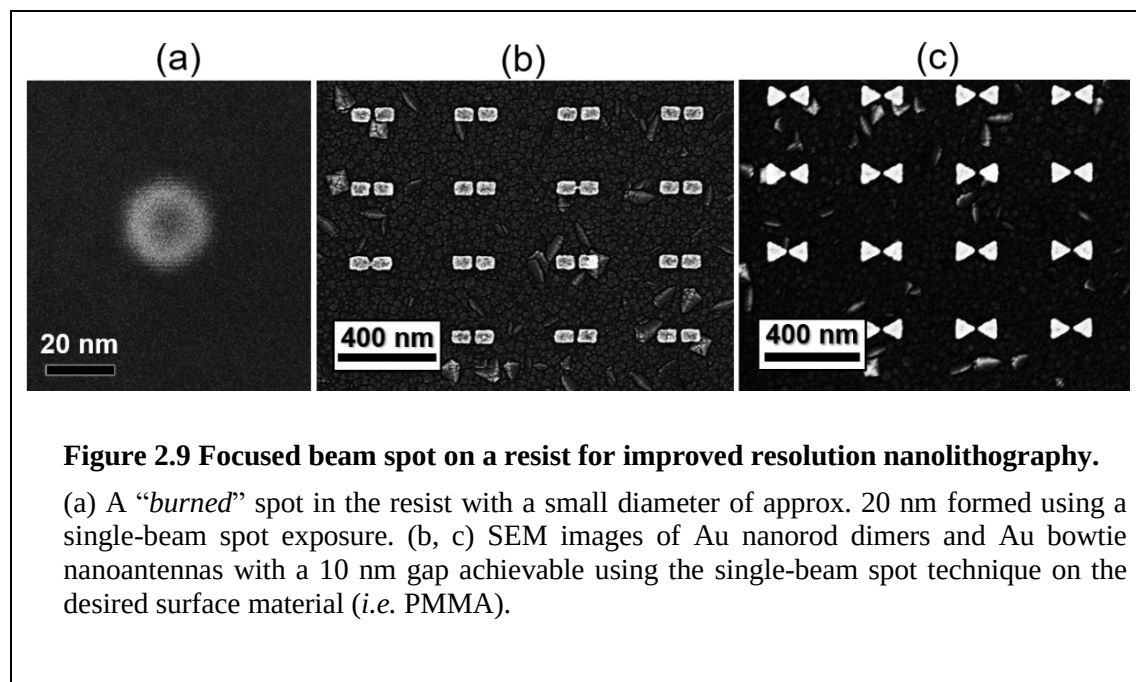


Figure 2.9(a) illustrates a focused burned spot formed in a 75-nm-thick PMMA resist layer coated on a 100-nm-thick ITO film on a glass substrate. Any astigmatism in the beam was corrected and the aperture alignment and sample height were adjusted so that a circular beam spot can be achieved. The burned spot measures approximately 25

nm in diameter indicating a well-focused beam. Such a well-focused beam enables fabrication of metallic antennas with dimensions on the order of tens of nanometres. As demonstrated in Figure 2.9(a, b), the rod dimers have a width of 50 nm and a length of 80 nm, while bowtie nanoantennas possess a side length of 85 nm. Sub-10-nm nanoantenna gaps can be achieved using this exposure method.

CHAPTER 3

Characterisation Techniques

3.1 Numerical methods

The simulation of the optical response of plasmonic nanostructures is based on the mathematical calculation of electromagnetic fields given by Maxwell's equations. Several numerical methods that make use of such an approach are Mie theory, finite-difference time-domain (FDTD), discrete-dipole approximation (DDA) and finite-element method (FEM) simulations. These simulation techniques help us understand light-matter interactions for plasmonic nanoantennas.

Mie theory is applicable for simulating optical responses of metallic nanospheres. The Mie method is also advantageous in terms of being less time-consuming. It can rapidly compute the scattered-field and the computational time is proportional to $\frac{r}{\lambda}$, where r is the radius of the sphere and λ is the wavelength of the incident light.⁹¹ Mie theory is independent of resolution-limited parameters such as the inter-dipole spacing or element length as the scattered-field can be represented as a sum of vector spherical harmonics. However, this method is not suitable for simulating non-spherical particles such as a two-dimensional periodic array of metallic particles, which are not axially symmetric.

Such limitations of Mie theory lead to alternative approaches such as DDA, FEM or FDTD methods. DDA can be used to simulate optical responses of isotropic non-spherical particles, which are axially symmetric. However, it is impractical for simulating optical responses of a two-dimensional periodic array of metallic particles, which are not rotationally or axially symmetric. Another limitation of DDA is that this method is time-consuming in computing optical responses because the simulation time is heavily dependent on inter-dipole spacing and the number of dipoles in a cubic lattice, which has

a period much smaller than the wavelength of the incident radiation. Unlike DDA, in FEM modelling and FDTD method, the electromagnetic field distribution is computed within an individual unit cell of the array for FEM or cubic mesh for FDTD method, and periodic boundary conditions are applied along the edges and faces of the unit cell. Since the periodic boundary conditions are equal in both magnitude and direction for electric and magnetic fields associated with a unit cell, *e.g.* tetrahedral for FEM, they are computed within a unit cell instead of every lattice, thus shortening simulation time when compared to DDA.

3.1.1 Finite-difference time-domain method

When using FEM or the FDTD method to compute the optical response of a single particle, perfectly matched layers (PMLs) are employed to absorb the scattered field by the structure. The refractive index of the PML is optimised depending on the radiation incident on the PML. For such radiation, the transmission coefficient is equal to unity. Beyond the interface, the imaginary part of the complex refractive index is gradually enlarged as a function of depth into the PML as the scattered radiation propagates into the medium. The parameters including a range of frequencies or wavelengths and incident angles for which the PML absorbs radiation is set by the user.⁹²

In this work, the FDTD method was selected as a method for simulating the interaction of electromagnetic fields with plasmonic nanoantennas having various shapes, geometries, and nanocomposites. Incident light in the visible region of the spectrum was applied to excite the surface plasmons of plasmonic nanoantennas.

3.1.1.1 Fundamentals

Finite-difference time-domain (FDTD) approach or Yee's method is a numerical analysis technique that is used for modelling computational electrodynamics. FDTD method involves solutions of Maxwell's equations in complex geometries. The important steps of FDTD approach include the insertion of a plane wave at an initial time and calculation of new field components from differences determined using the field components which are applied during the previous time interval. Owing to the ability of free space solution and instant calculation, this method allows users to study a variety of problems related to

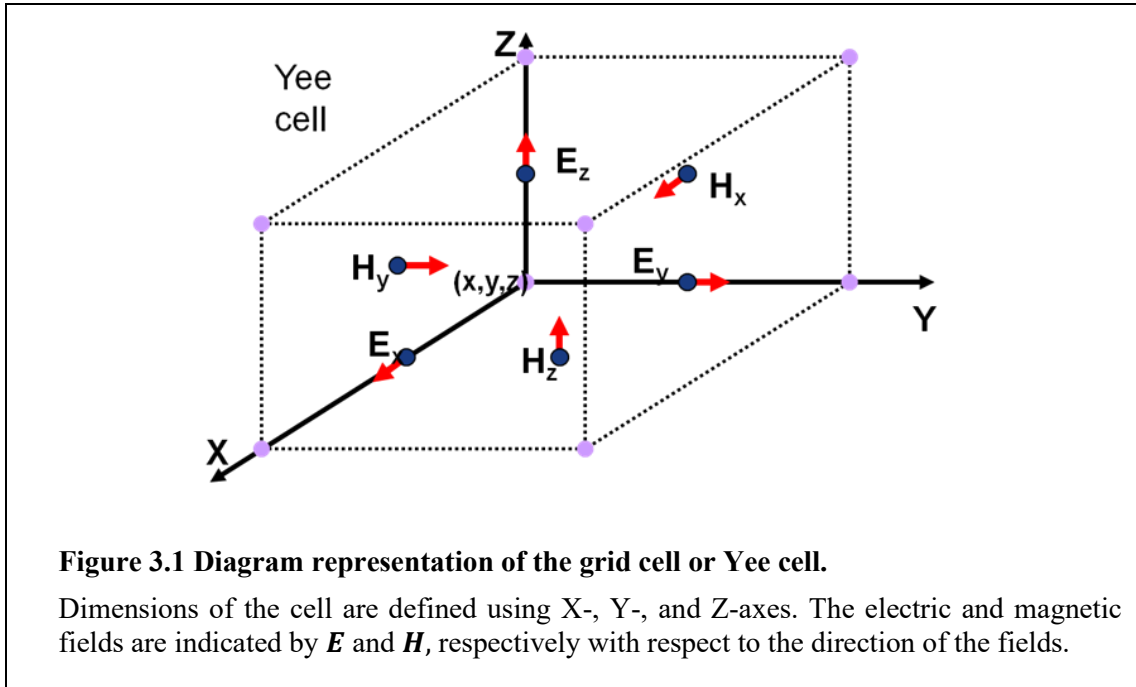
photonics and electromagnetic properties of a preferred structure such as the complex Poynting vector and the transmission and reflection of light.⁹³

The FDTD method solves Maxwell's curl equations in non-magnetic materials surrounded by an isotropic medium in which the dielectric permittivity, ϵ and magnetic permeability, μ of the medium are uniform in all directions. For the simplest free-space model, Maxwell's equations are expressed as follows:

$$\nabla \times \vec{E} = -\frac{\partial \vec{H}}{\partial t} \quad 3.1$$

$$\nabla \times \vec{H} = \epsilon \frac{\partial \vec{E}}{\partial t} \quad 3.2$$

Where $\vec{E}$ and $\vec{H}$ are the electric and magnetic fields, respectively. The dielectric permittivity, $\epsilon = \epsilon_0 \epsilon_r$ where ϵ_0 and ϵ_r are the free space permittivity and complex relative dielectric constant, respectively. In general, ϵ_r is frequency-dependent, which is represented by $\epsilon_r(\omega) = n^2$, where n is the refractive index.



The FDTD method utilises the grid cell or Yee cell to solve Maxwell's equations. In the grid cell, six electromagnetic field components (*i.e.* $\vec{E}_x, \vec{E}_y, \vec{E}_z, \vec{H}_x, \vec{H}_y$, and $\vec{H}_z$) are shown in Figure 3.1.

For the structure that is infinite in the z -direction, the electromagnetic components are independent of z , thus, $\frac{\partial \vec{H}}{\partial z} = \frac{\partial \vec{E}}{\partial z} = 0$. Owing to this condition, Maxwell's equations split into two independent sets of equations which are defined by transverse electric (TE) mode and transverse magnetic (TM) mode. Each mode is composed of three vector quantities as only the x - y plane can be solved. That is, for the TE mode, the components $\vec{E}_x, \vec{E}_y$ and $\vec{H}_z$ can be solved, whereas the TM mode has the components of $\vec{H}_x, \vec{H}_y$ and $\vec{E}_z$. The ultimate Maxwell's equations are expressed below.⁹⁴

For the TE mode,

$$\varepsilon \frac{\partial \vec{E}_x}{\partial t} = \frac{\partial \vec{H}_z}{\partial y} \quad 3.3$$

$$\varepsilon \frac{\partial \vec{E}_y}{\partial t} = -\frac{\partial \vec{H}_z}{\partial x} \quad 3.4$$

$$\mu \frac{\partial \vec{H}_z}{\partial t} = -\frac{\partial \vec{E}_y}{\partial x} + \frac{\partial \vec{E}_x}{\partial y} \quad 3.5$$

For the TM mode,

$$\mu \frac{\partial \vec{H}_x}{\partial t} = -\frac{\partial \vec{E}_z}{\partial y} \quad 3.6$$

$$\mu \frac{\partial \vec{H}_y}{\partial t} = \frac{\partial \vec{E}_z}{\partial x} \quad 3.7$$

$$\varepsilon \frac{\partial \vec{E}_z}{\partial t} = \frac{\partial \vec{H}_y}{\partial x} - \frac{\partial \vec{H}_x}{\partial y} \quad 3.8$$

In addition to Yee cell, the FDTD method also employs a Cartesian mesh. Using a very fine mesh results in more accurate results. Nevertheless, it is time- and cost-consuming because the finer mesh results in increasing simulation time and memory requirements.

3.1.1.2 Simulations

Simulations of the near-field distributions and extinction spectra (scattering and absorption) of Al and Au nanoantennas were carried out using available commercial software from *Lumerical Solutions Inc.* (FDTD Solutions, versions 8.23.2271 and 8.20.1661).

In the simulations performed throughout this thesis, Al or Au nanoantennas were placed on a 100-nm-thick ITO coated on a bulk glass substrate. To simulate an isolated metal nanoantenna, a total-field scattered-field (TFSF) source was launched from the air above the nanoantenna at normal incidence following the experimental configuration. A unit cell with a fine mesh size of $2.5 \times 2.5 \times 2.5 \text{ nm}^3$ was applied for high-resolution while perfectly matched layers (PML) were employed for all sides of the unit cell.

To simulate Al or Au nanoantenna arrays, a plane-wave light source was launched from the air above a unit cell of the nanoantennas at normal incidence. This is to ensure that all metal elements were simulated with a uniform incident wave for the entire area at the initial time of the calculation. PML was used as boundary conditions along the z-axis to represent the bulk substrate while periodic boundary conditions were performed in the x- and y-directions to include coupling to neighbouring antennas. A mesh unit of $2.5 \times 2.5 \times 2.5 \text{ nm}^3$ was used to perform the electric field distribution maps for high-resolution images while a mesh unit of $5 \times 5 \times 5 \text{ nm}^3$ was sufficient to calculate extinction spectra.

In practical experiments, Al rapidly reacts with oxygen in the air to form a self-limiting alumina film of approximately 3 nm.⁴⁸ Therefore, a 3-nm-thick alumina film (Al_2O_3) was also employed in addition to Al nanostructures. In the simulations using Au, a 1-nm-thick layer of Ti was applied, this Ti layer is used to improve the adhesion of the Au nanostructures to the ITO-coated glass substrate in the experiment.

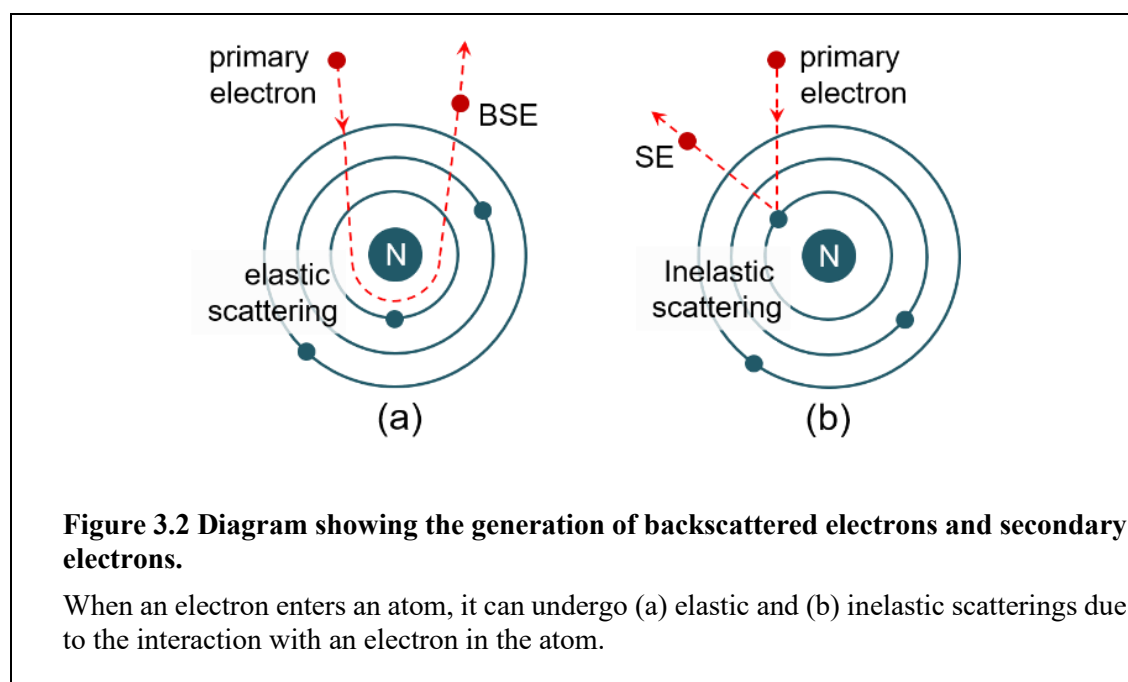
The optical properties of Al and Al_2O_3 were taken from Palik.⁹⁵ The dielectric functions of Au and Ti were taken from CRC.⁹⁶ The optical properties of glass (SiO_2) were taken from Palik.⁹⁵ The optical responses of ITO were taken from König⁹⁷ and Sopra Material Database.⁹⁸ The use of different sources of optical properties of ITO is aimed to provide the best match of optical responses of the nanoantennas at the time of conducting experiments.

3.2 Scanning electron microscopy

Scanning electron microscopy is the technique that is used to observe the morphology of metallic nanostructures in this research. A scanning electron microscope (SEM) generates an image of micro/nanostructures using the focused beam of electrons to scan on the sample surface in a rectangular raster manner. The position of the sample combined with the intensity of the detected signals are used to generate an image. The constitution and operational system of an SEM are addressed in section 2.2.1.

3.2.1 Principles

In most common SEM systems, secondary electrons (SEs) and backscattered electrons (BSEs) are the major signals that are used to generate an image. SEs give information related to surface topography while BSEs carry information about the sample's composition.⁸¹



As primary electrons reach the surface of the sample, they can undergo two types of scattering effects – elastic and inelastic scatterings (as illustrated in Figure 3.2). In the elastic scattering event, the primary electrons are reflected due to their interaction with the nuclei of atoms within the sample. The majority of BSEs retain at least 50% of the

incident beam energy, thus having high energies. The BSEs emerge from deeper locations of the specimen, thus producing lower resolution images than those generated from secondary electrons. The number of backscattered electrons is sensitive to the materials being studied. Materials with a high atomic number (Z) yield larger backscattered electrons than those with a low atomic number. By using a BSE detector in an SEM, one can characterise the elemental properties of the investigated materials.

In the inelastic scattering event, the primary electrons have transferred energy to electrons in the atoms of the sample before being scattered in the form of secondary electrons. SEs typically have low energies and can easily be absorbed in the sample material. As a consequence, the detector can only collect secondary electrons from the top thin layer of the sample, thus suitable for surface topology analysis.

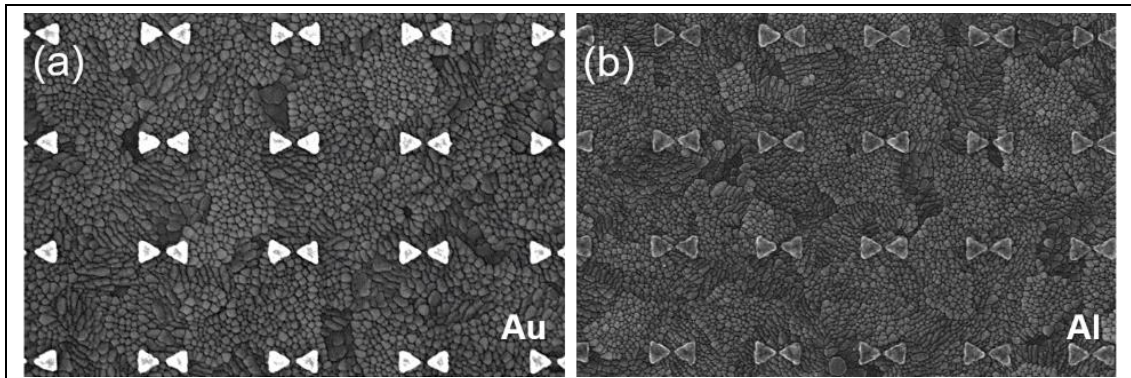


Figure 3.3 SEM images of Au and Al bowties fabricated on ITO-coated glass substrate. The images were obtained using a secondary electron (in-lens) detector.

(a) Au structures appear brighter compared to (b) Al structures because the secondary electron emission coefficient (δ) of Au is almost twice that of Al.⁹⁹

In general, the secondary electron coefficient (δ) which is the ratio of the number of SEs to the number of beam electrons incident on the sample is relatively constant regardless of atomic number. However, with an exception for Au, δ is about twice that of Al (0.2 versus 0.1) with the incident beam energy of 20 keV.⁹⁹ The higher δ for Au compared to that of Al implies that the SE emission signal generated from Au is much greater than the SE emission signal generated from Al. Therefore, Au appears brighter in an SEM image compared to Al. This phenomenon is demonstrated in Figure 3.3(a, b).

Au bowties produce higher contrast to the background substrate compared to that of Al bowties.

3.2.2 Sample preparation

All samples were fabricated on an ITO-coated glass substrate where only one side is conductive. The samples were mounted on top of an SEM holder while the conductive surface was oriented toward the electron column. A metal clip was used to bridge between the conductive surface of the sample and the SEM holder. This is to prevent the accumulation of electrostatic charge on the sample as the sample is electrically grounded.

In this thesis, an in-lens mode in an SEM (Zeiss SUPRA 40) was used to image metallic nanoantennas and characterise the formation of materials on metallic nanoantennas. In-lens detectors in the SEM instrument allows collection of secondary electrons which can be generated by direct interaction with the primary electron beam, thus carrying the highest spatial resolution information of the specimen.

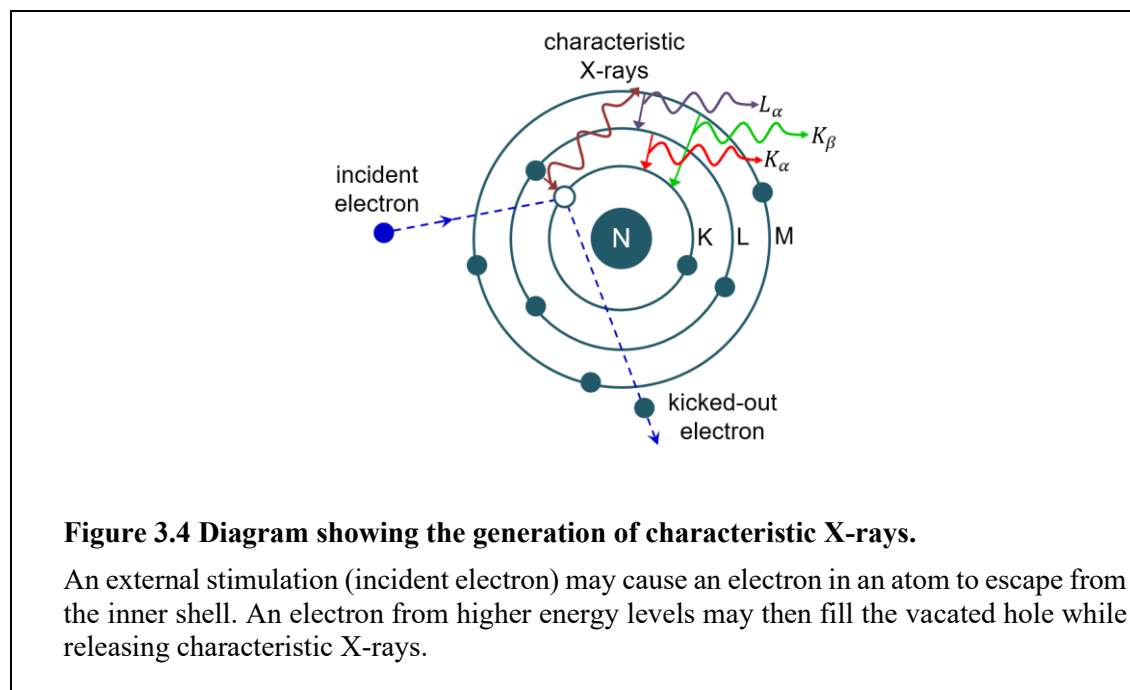
To enhance the effect of secondary electrons, the low-energy primary electron beam is applied. Typical energies of the electron beam are ranging from 5-10 keV passing through an objective aperture of 30 μm . To achieve optimal resolution, a short working distance of approximately 4 mm was applied.

3.3 Energy-dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDX or EDS) is an analytical technique that is used to identify the elemental characteristics of specimens. The technique involves the interaction between an external excitation and the energy an atom may release due to the change of energy level of an electron. Each element has a unique atomic structure, thus giving rise to a unique set of an electromagnetic emission spectrum.

To stimulate emission of characteristic X-rays from a sample, an incident beam, such as an electron beam in an SEM, is focused on a sample being analysed. In the ground state, electrons in an atom of the specimen bound to the nucleus and have discrete energy levels – so-called electron shells (see Figure 3.4). The incident electron beam may have sufficient energy to ionise an electron in an inner shell, leaving a hole. An electron from an outer shell with a higher-energy level may fill the hole while the difference between the higher-energy level and the lower-energy level is released in the form of an X-ray.

By collecting the number and the energy of the characteristic X-ray emission using an energy-dispersive spectrometer, one can analyse the elemental composition of the specimen.



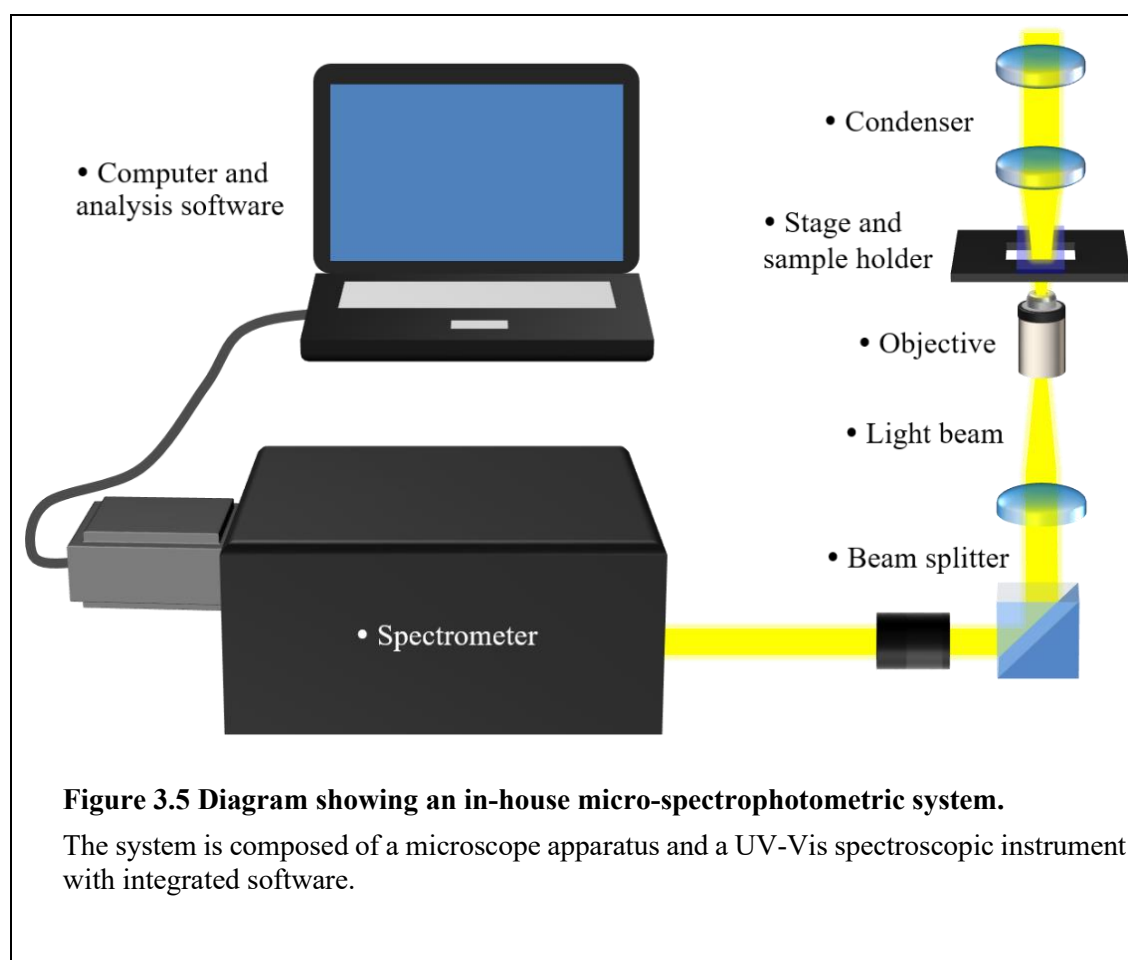
In this thesis, a scanning electron microscope (Zeiss ULTRA plus) with an integrated 20 mm² Oxford Inca EDX detector was employed to investigate characteristic X-rays of an as-prepared specimen. The microscope was operated using the in-lens secondary electron detector, an acceleration voltage of 5 keV and an objective aperture of 30 μm. A working distance of approximately 6.5 mm was used. A spot analysis was selected with an acquisition time of 15 s and an average of 5 spectra were collected using the Oxford INCA software.

3.4 Micro-spectrophotometry

To experimentally study the optical properties of metallic nanoantennas, micro-spectrophotometry was employed. Due to the microscopic level of structures, it is important to ensure that the structures of interest are resolved in the optical path. The technique that combines an optical microscope with a spectrophotometer enables the spectral measurements of the nanostructures.

3.4.1 Components

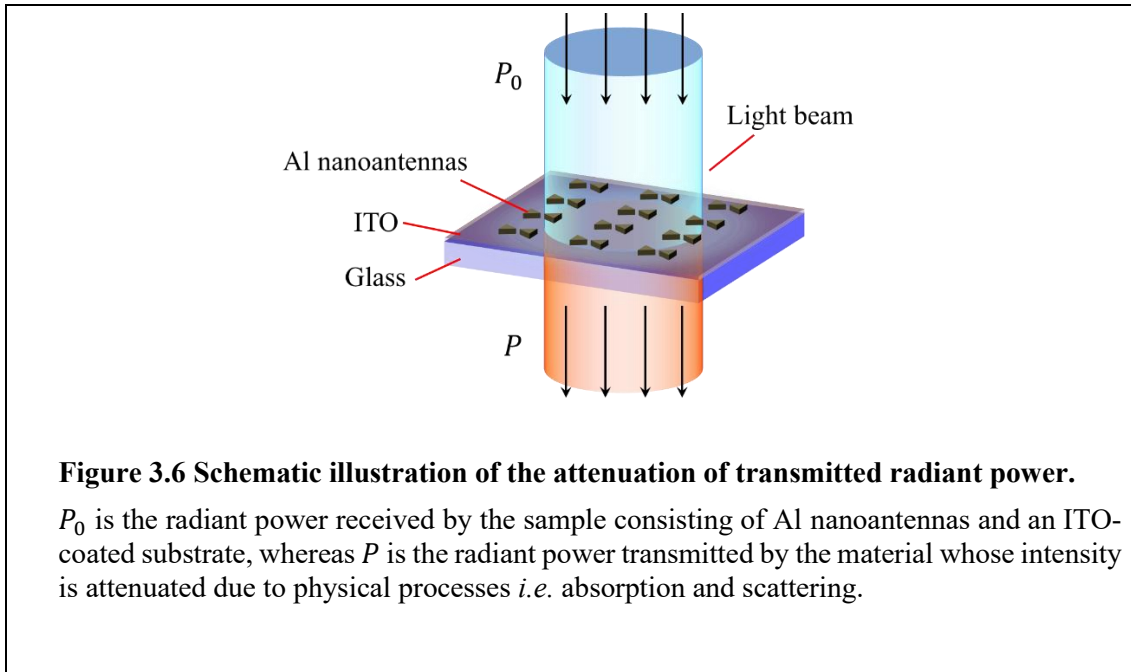
Optical measurements were carried out using an in-house optical system. The system consists of two main sections including an inverted microscope (Zeiss Axiovert 100M Microscope System) and a UV-Vis spectrometer (Andor Kymera 328i) integrated with an electron-multiplying charge-coupled device (CCD) camera (Newton 970, Andor). Figure 3.5 shows a diagram of the micro-spectrophotometer system used to measure optical responses of metallic nanoantennas in this work.



Light generated from the lamp housing is collimated and passed through the condenser lens. An objective lens is set prior to adjusting the stage to bring the sample into the focus. To increase the magnification of the image appeared on the image plane, a 40 $\times$ objective (NA = 0.65) was normally selected. With the assistance of the beam splitter, light from the microscope is reflected by 90 degrees. This light beam containing

information of the generated image is then set to pass through a slit of the UV-Vis spectrometer with integrated software (Andor SOLIS) with a 500 nm blazed grating at 150 l/mm. The resulting wavelengths passing through the spectrometer can be collected as a transmittance.

3.4.2 Optical measurements



In general, the transmittance, T can be written in a percentage form, as demonstrated in equation 3.9.

$$\%T = 100T \quad 3.9$$

From the Beer-Lambert law, the transmittance is correlated with the absorbance. The diagram in Figure 3.6 shows the direction of the light beam (represented in the blue cylinder), directed at the sample surface, given a reference radiant power, P_0 . After passing through the sample, the power of the transmitted light (indicated by the orange cylinder) has changed to P . In most cases, P is less than P_0 which generally means that some of the wavelengths are absorbed in the sample material. The relationship between the absorbance, A and the change in the radiant power can be expressed as:

$$A = \log_{10} \frac{P_0}{P} \quad 3.10$$

From equation 3.10, the absorbance can be explained as attenuation of transmitted radiant power which can be caused by various physical processes including absorption and scattering.

The transmittance can also be written as a change of radiant power.

$$T = \frac{P}{P_0} \quad 3.11$$

Substitute 3.10 with 3.11 to obtain equation 3.12

$$A = \log_{10} \frac{1}{T} \quad 3.12$$

Put 3.9 in 3.12

$$A = \log_{10} \frac{100}{\%T} \quad 3.13$$

$$A = \log_{10} 100 - \log_{10} \%T \quad 3.14$$

$$A = 2 - \log_{10} \%T \quad 3.15$$

The final equation 3.15 describes the correlation between the absorbance and the transmittance. This equation is used to calculate the extinction (absorption and scattering) of the metallic nanoantennas used in this research.

3.5 Raman spectroscopy

3.5.1 Fundamentals

When light is incident on a sample, some of the light will be absorbed in the molecules of the sample and some will be scattered. Scattered light can be classified into two main

types – elastic and inelastic scattering. These types of scattering are based on the difference in frequencies of the scattered light. The majority of light will be scattered with the same frequency as that of the incident radiation – known as “*elastic scattering*”. However, there will also be a small fraction of light that is scattered with a different frequency from that of the incident light. The difference in frequency arises from the interaction between the incident radiation and the molecular vibrations of the sample which result in “*inelastic scattering*”.

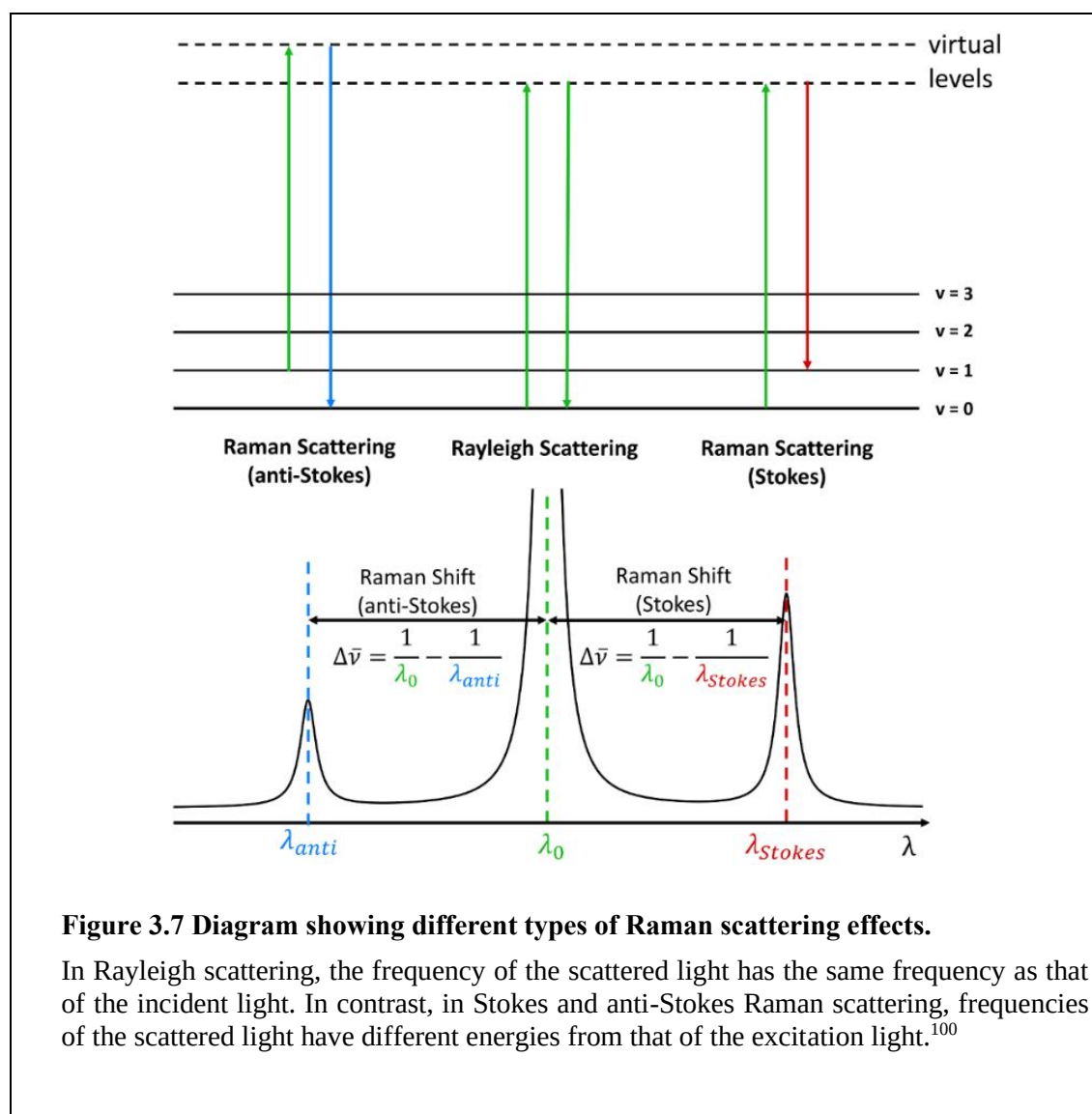


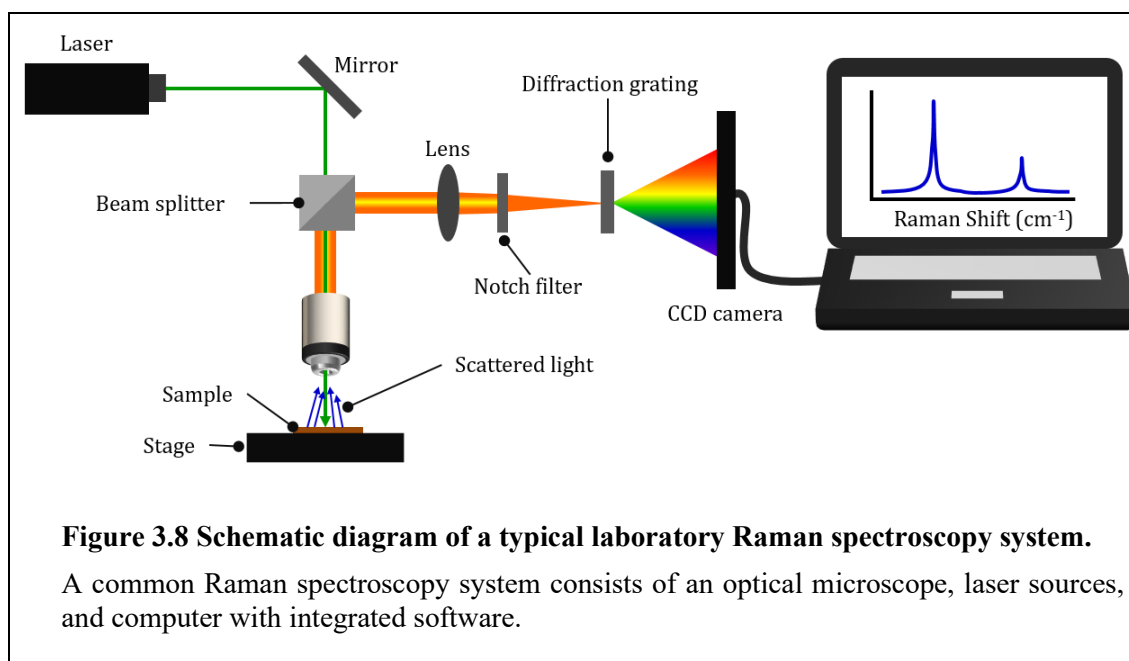
Figure 3.7 shows a diagram illustrating elastic and inelastic scatterings. If we assume that monochromatic light having a wavelength λ_0 is incident on a sample, after interacting with the molecules of the sample, the light will be scattered. Much of the light will be scattered with the same wavelength as that of the incident light which is termed “*Rayleigh scattering*”. If the scattered light has a larger wavelength (smaller frequency) than that of the incident light, Stokes lines will appear in the Raman spectrum. On the other hand, if the scattered light has a smaller wavelength (larger frequency) than that of the illuminated light, anti-Stokes lines will occur in the Raman spectrum.

Typically, Stokes lines occur when molecules are excited from a ground state to excited state (from lower to higher vibrational energy levels), whereas anti-Stokes lines appear due to transition of the molecules from higher to lower vibrational levels.

The intensity of Stokes and anti-Stokes bands can be determined based on the number of molecules present within the initial energy state. The larger the number of molecules in the initial state, the more intense the Raman bands. From the Boltzmann distribution, it is known that states with lower energy levels will have a higher probability of being occupied. As a consequence, molecules that are excited from ground state to higher energy state in Stokes scattering will give more intense peaks than those in anti-Stokes scattering.

3.5.2 Raman set-up

Figure 3.8 illustrates a typical laboratory Raman spectroscopy system. The system consists of a selection of laser sources that provide a stable and intense beam of radiation. A laser travels to a mirror and is reflected onto a beam splitter. A portion of the laser is focused on a sample using an objective lens. Once the laser interacts with the sample, interactions between the laser photons and molecules in the sample will cause inelastic scattering of light. The scattered light will be reflected and passed through the beam splitter. The beam will then be confined to pass through a notch filter which is used to eliminate Rayleigh scattering. Finally, the beam will pass through a diffraction grating before detection at a CCD camera while the information of the scattered light is collected and generated on a computer in the form of Raman fingerprints.



Two different Raman systems were used in this thesis. To study plasmon-induced chemical changes in PMMA, a Raman microscope (WITec alpha300 R with an integrating software Project FIVE) with a 532 nm CW laser source was employed. The beam was focused on the sample using a 100× objective (NA = 0.95) to produce a spot with a nominal diameter of ~300 nm and a power of 4.75 mW, measured at the focal point. A Raman map (ranging from 2 μm $\times$ 2 μm to 5 μm $\times$ 5 μm) was achieved with a point integration time of 1 s, and step size of 500 nm.

For the study of multiphoton absorption, Horiba Raman system (LabRAM ARAMIS HORIBA Jobin Yvon) with integrated software – LabSpec 5 was used with a 100× objective (NA = 0.90) and varying laser power. The remaining parameters were set similar to those in the aforementioned system, while an integration time varied ranging from 1-5 s. Additionally, for the studies of SERS and laser-driven catalytic Ge growth, Horiba Raman system was employed with 532 nm CW laser and 785 nm CW laser, respectively. Because this system provides a polarized light output, thus suitable for the polarization-dependent studies.

3.6 Ellipsometry

Ellipsometry is an optical technique involving measurements of the amplitude and phase change of reflected light upon the interaction of the material being studied. Such data is useful for determining dielectric properties, composition, roughness, and thickness of a thin film.¹⁰¹ In this research, ellipsometry was used to determine the thickness of PMMA films spin-coated on a Si substrate to determine appropriate spin speeds and resist concentrations for use in coating the ITO-glass substrates.

3.6.1 Basic principles

Linearly polarized light incident on a sample at an angle of 45° consists of p-polarized and s-polarized components. P-polarized light has an electric field vector oscillating in the plane of incidence while s-polarized light has its electric field vector oscillating perpendicular to the plane of incidence (see Figure 3.9). Some of the light may be absorbed, transmitted, and reflected at a certain angle which can be collected by a detector. Because the material has unique optical properties, therefore the reflected light contains a polarization distinct from the incident light providing useful information regarding the material properties. The reflected light collected at the detector due to the change in light's phase and amplitude has elliptical polarization, hence the name.

3.6.2 Measurements

Figure 3.9 illustrates a diagram of light reflection from a thin film coated on a substrate. The film and the substrate have a complex refractive index of N_f and N_s with a refractive index n_f and n_s and an extinction coefficient k_f and k_s , respectively. The sample is exposed to air with a refractive index of 1 ($N_0 = 1$).

Light is incident on the sample with an angle of incidence θ_i consisting of p and s polarization directions. Some part of the light is transmitted into the film with a thickness t with an angle of refraction θ_f . Another component of light is reflected into the air and can be collected at a detector. At the interface between the air and the film, the reflection coefficient is defined as γ_{of} and γ_{fs} for the interface between the film and the substrate.

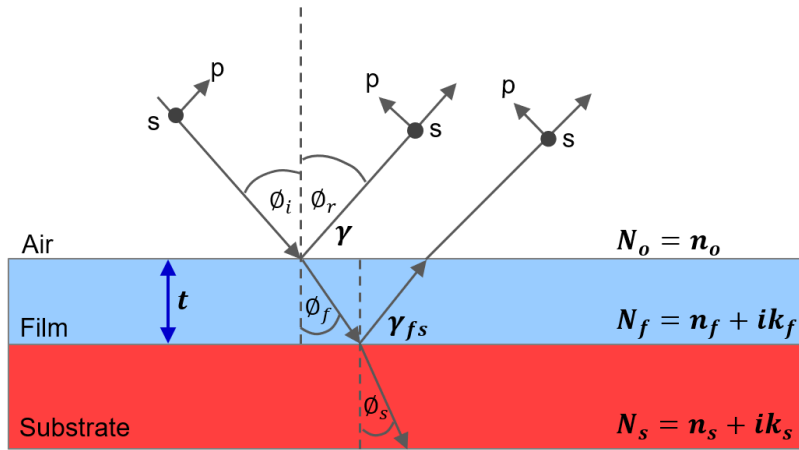


Figure 3.9 Diagram illustration of major parameters used to determine the thickness of a thin film.

The s and p vectors indicate the direction of s and p polarized light following the plane of incidence. ϕ_i , ϕ_f , and ϕ_s represent the angle of incidence and the angles of refraction of the film and the substrate, respectively. N_o , N_f , and N_s are the complex refractive indices of air, film and substrate, respectively where n is the refractive index and k is the extinction coefficient of the material. The γ is the reflection coefficient.

To calculate the film thickness, the film phase factor δ must be identified. The phase factor indicates that the light reflected from the film undergoes a phase shift. It can be determined by the reflection ratios R_p and R_s as expressed in equation 3.16^{102,103} below.

$$\frac{R_p}{R_s} = \frac{\frac{\gamma_{p,of} + \gamma_{p,fs} \cdot e^{-i2\delta}}{1 + \gamma_{p,of} \cdot \gamma_{p,fs} \cdot e^{-i2\delta}}}{\frac{\gamma_{s,of} + \gamma_{s,fs} \cdot e^{-i2\delta}}{1 + \gamma_{s,of} \cdot \gamma_{s,fs} \cdot e^{-i2\delta}}} \quad 3.16$$

$$\delta = \frac{2\pi t \cdot N_f \cdot \cos(\phi_f)}{\lambda} \quad 3.17$$

Where $\gamma_{p,of}$, $\gamma_{p,fs}$, $\gamma_{s,of}$, and $\gamma_{s,fs}$ can be determined as follows:

$$\gamma_{p,of} = \frac{N_f \cos(\phi_i) - N_o \cos(\phi_f)}{N_f \cos(\phi_i) + N_o \cos(\phi_f)} \quad 3.18$$

$$\gamma_{p,fs} = \frac{N_s \cos(\theta_f) - N_f \cos(\theta_s)}{N_s \cos(\theta_f) + N_f \cos(\theta_s)} \quad 3.19$$

$$\gamma_{s,of} = \frac{N_o \cos(\theta_i) - N_f \cos(\theta_f)}{N_o \cos(\theta_i) + N_f \cos(\theta_f)} \quad 3.20$$

$$\gamma_{s,fs} = \frac{N_f \cos(\theta_f) - N_s \cos(\theta_s)}{N_f \cos(\theta_f) + N_s \cos(\theta_s)} \quad 3.21$$

In this thesis, alpha-SE Ellipsometer – J.A. Woollam with integrated software – CompleteEASE was used to analyse the thickness of PMMA film deposited on a Si substrate. In measurements, a Si substrate coated with a PMMA film with an unknown thickness was simply mounted on the ellipsometer. An incident angle of 65° was employed while material data (*i.e.* optical properties) of Si was defined. By collecting reflected light carrying phase-changing properties at the detector, the software could determine the thickness of the film.

CHAPTER 4

Plasmon-Induced Graphitization in PMMA-Coated Aluminium Nanoantennas

This chapter is written based on the article entitled “*Multiphoton Absorption and Graphitization in Poly(methyl methacrylate)-Coated Aluminum Nanoantenna Arrays*” published in *The Journal of Physical Chemistry C*. with the reference J. Phys. Chem. C 2020, 124, 8930–8937.¹⁰⁴

4.1 Introduction

Subwavelength metallic nanostructures can serve as nanoantennas to efficiently convert freely propagating electromagnetic radiation to localised energy, and vice versa.¹⁰⁵ The confinement of light into subwavelength volumes holds great promise for high-resolution nanoimaging applications while the relaxation of the localised energy could enhance light-matter interaction in applications such as photochemistry, photocatalysis, and sensing.^{7,60,66,67,106,107} These applications are made possible due to the localised surface plasmon resonances (LSPRs) – the collective coherent electron oscillations excited by resonant incident light – resulting in enhanced optical intensities at metal surfaces.¹⁰⁸

LSPRs can give rise to an intense optical near-field at the surface of metal nanostructures. However, this enhanced near-field decays with distance away from the metal surface. The decay occurs through plasmon relaxation which results in energy distribution in various forms including phonons, hot carriers, and photons. These forms of energy can be exploited in a variety of applications such as plasmonic photothermal

therapy,¹⁰⁹ photocatalysis and energy conversion,^{7,59} and biosensing applications.^{71,72} In order to optimize the performance of these plasmon-assisted applications, it is essential to understand how plasmonic materials transfer energy to the surrounding medium at the single-nanoantenna level.

In this chapter, we show that the energy distribution from LSPRs in Al nanoantennas can be probed through the volume of decomposed PMMA around Al nanoantennas using Raman spectroscopy. A continuous-wave (CW) laser in a Raman microscope was used to excite the LSPRs of the nanoantennas while Raman fingerprints reveal chemical changes in PMMA with the contribution of Al nanoantennas. Evidence of a potential mechanism that drives chemical changes in PMMA is also discussed in this chapter.

4.1.1 Polymethylmethacrylate (PMMA)

Polymethylmethacrylate (PMMA), also known as acrylic, was first introduced as a transparent material alternative to glass due to its excellent durability and lightweight composition. PMMA has also been widely used in micro and nanolithography as a high-resolution resist.

4.1.1.1 PMMA in nanolithography

PMMA has been used extensively in electron-beam lithography, X-ray lithography and deep ultraviolet lithography. It has desirable properties for high-resolution lithography as it is easily processed, low-cost, widely available, non-toxic, and optically transparent. Its exceptional optical transparency allows light in a broad range of wavelengths from the near-ultraviolet to mid-infrared to transmit which is useful for aligning lithographic patterns with respect to existing features already patterned on the chips or wafers.^{110,111}

As a polymer, PMMA is composed of many monomers that are connecting together to form a long chain of the polymer. It can be synthesized using suitable radical polymerisation initiators. It can be found in nearly monodisperse forms with molecular weights available from less than 10 kg/mol to more than 1,000 kg/mol.

In electron-beam lithography, PMMA can be used as a positive-tone and negative-tone resist. For the positive-tone resist, the molecular weight of the polymer chains is reduced by an electron beam. In general, a beam of energetic electrons having

kinetic energies from ~1 to ~100 keV is capable of initialising polymer chain scission processes in PMMA. The PMMA fragments become highly soluble in an organic solvent.

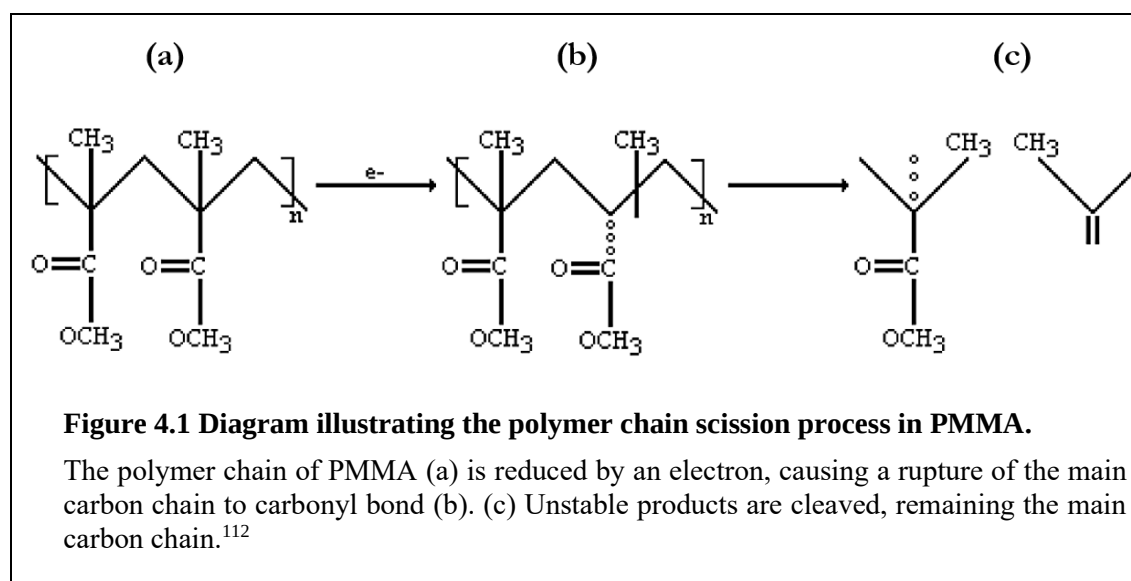


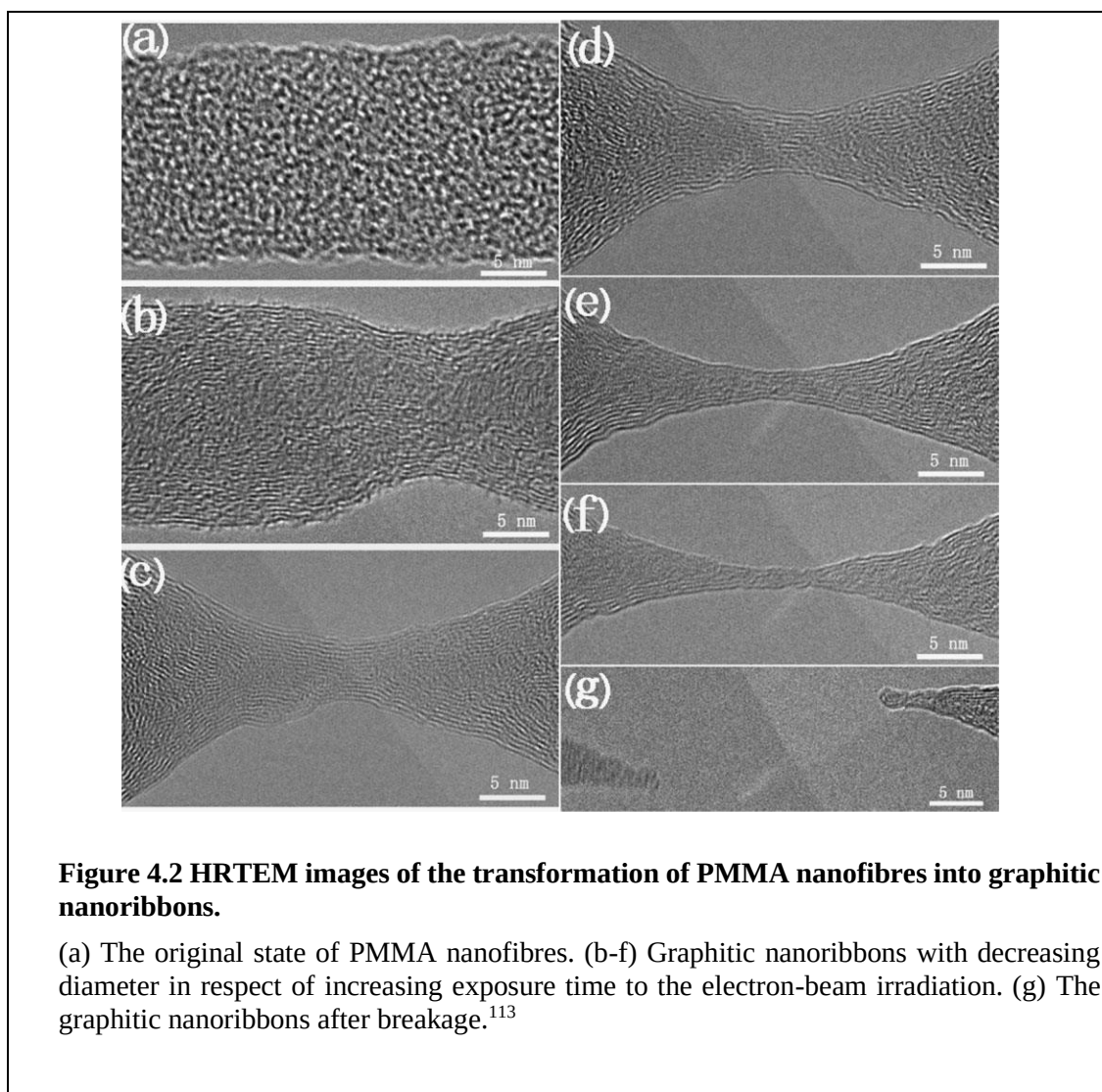
Figure 4.1 above illustrates the chain scission process in PMMA upon irradiation with an electron beam. The process occurs when an energetic electron initiates radiolysis (ionisation damage) in the main chain. The chain is then cleaved, yielding unstable products that can be dissolved in a developer.

PMMA can also act as a negative-tone resist when exposed to a very high dose of electrons. To achieve this, a thin membrane of PMMA is normally used. Upon exposure, the electron beam above certain threshold electron dose can cause the production of an abundance of free radicals which eventually cross-link to form an insoluble material. Because the remaining material is not soluble in the developer or solvents like acetone,¹¹³ this leads to interesting questions about the composition of the negative-tone PMMA material. What is the new form of cross-linked products produced by an electron beam irradiation? Do they have special characteristics? Can cross-linked PMMA be initiated by other types of irradiation treatment?

The following subsection (4.1.1.2) will discuss the special characteristics of cross-linked PMMA under various circumstances. The structural transformation of PMMA, as well as its theoretical study, will also be considered in this section.

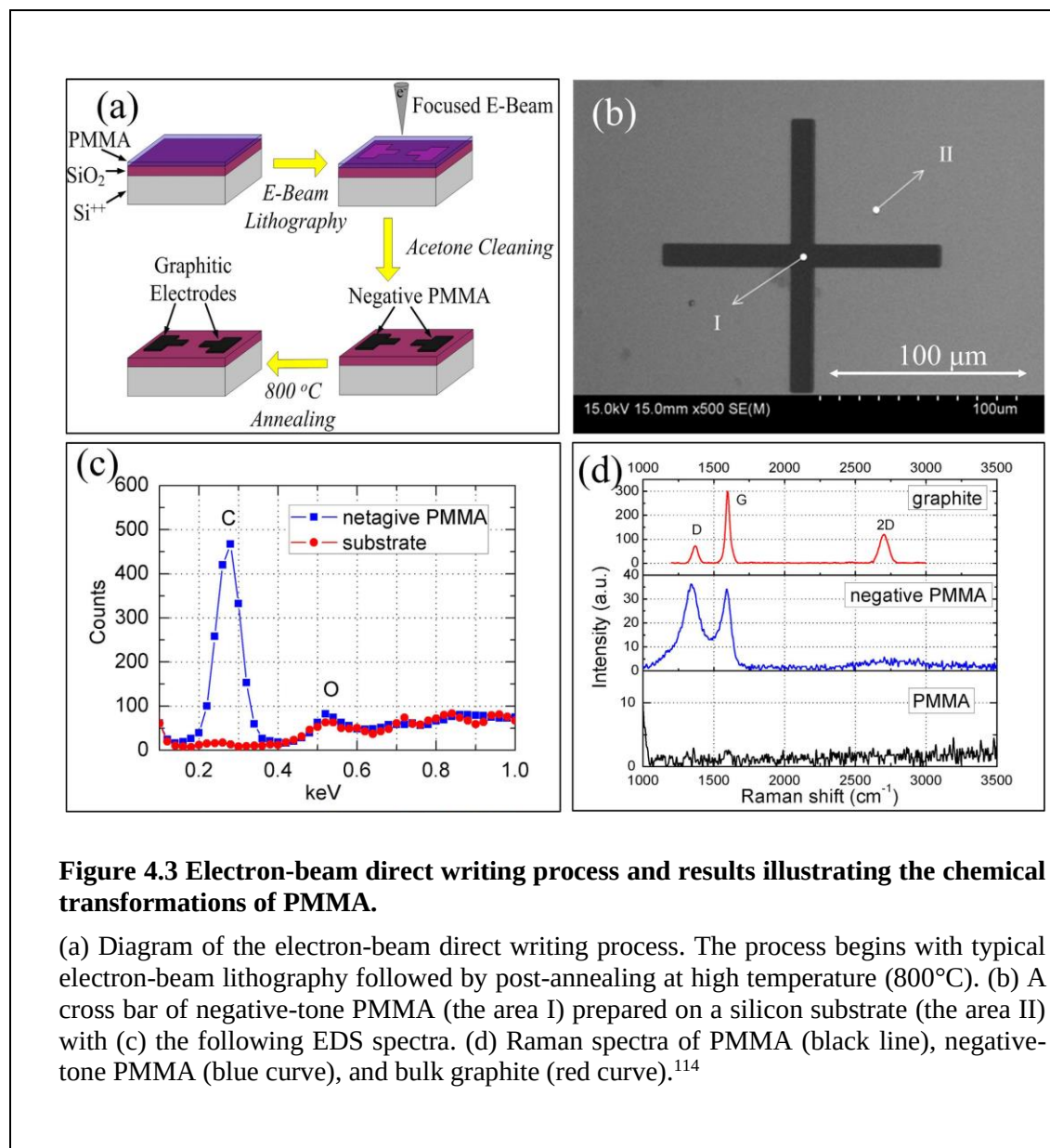
4.1.1.2 Recent studies of graphitization of PMMA

Duan *et al.*¹¹³ showed that PMMA nanofibres prepared by electrospinning can be converted into graphitic nanoribbons upon irradiation with an electron beam at an accelerating voltage of 200 kV (with the corresponding dose of about 1,000 C/cm²). The diameter of PMMA nanoribbons decreased with increasing exposure time and eventually carbonised and graphitized completely. The graphitized nanofibres were observed to be a single-crystalline feature and the graphitic sheets were attributed to form due to the high energy of the electron beam.



High-resolution transmission electron microscopy (HRTEM) images shown in Figure 4.2(a-g) provide information regarding the structural transformation of PMMA

nanofibres into graphitic nanoribbons. It is intuitively seen that with increasing irradiation time the diameter of PMMA nanofibres decreased. The fibres subsequently became graphitic nanoribbons.



Another study demonstrated that direct electron-beam writing on PMMA with a low energy electron beam (10 keV) and post-exposure thermal annealing (800°C) can produce graphitic electrodes.¹¹⁴ Figure 4.3(a) shows the process of direct electron-beam writing on PMMA and the chemical transformation of PMMA into negative-tone

PMMA. In Figure 4.3(b, c), it is evident that after the electron-beam treatment, a carbon-rich deposit remains. In Figure 4.3(d), the Raman spectrum of the negative-tone PMMA exhibits similar characteristics to that of graphite. That is, the D- and G-peaks that are assigned to mono- or poly-crystalline graphite and the defects of graphite, respectively can clearly be seen in the Raman spectrum of the negative-tone PMMA.¹¹⁵ The second order of the D-peak, known as 2D peak, related to the layer thickness of graphene¹¹⁶ also appears in the Raman spectrum of the negative-tone PMMA.

4.1.1.3 The structural transformation of graphene-like PMMA

To understand how PMMA can form graphene-like structures, it is worth considering the structural geometry of PMMA. As was already mentioned in section 4.1.1.1, PMMA is a long-chain polymer that consists of many monomers that are arranged in different forms including atactic, syndiotactic and isotactic. For atactic form, the free radical polymerization has no special stereochemistry between pendant groups (*i.e.* atoms attached to a carbon backbone chain), in contrast to syndiotactic and isotactic forms whose pendant groups are arranged in a specific sequence manner.

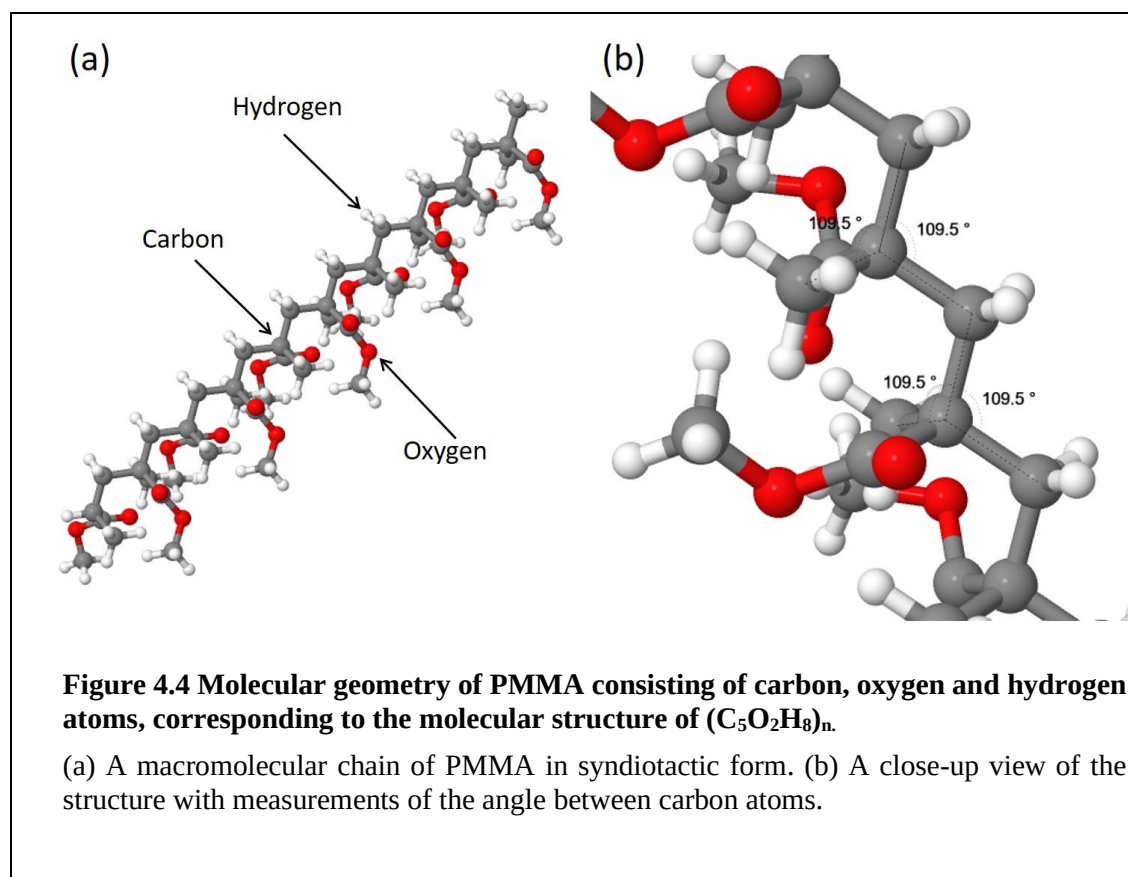
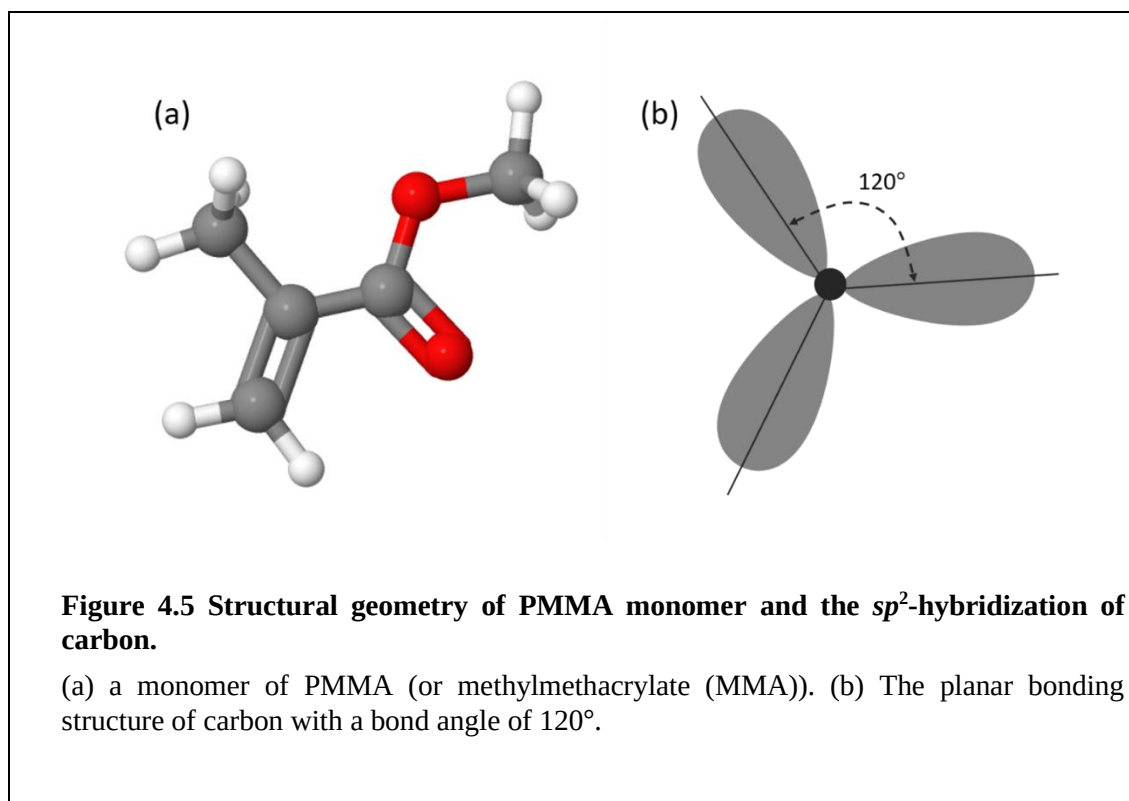


Figure 4.4 shows the structural geometry of PMMA in syndiotactic form. The structure has a very regular sequence of pendant groups in which the two pendant groups are aligned on one side of the carbon backbone. Owing to the repeated pattern of the structure, it is feasible for such a structure to pack into crystals.



Upon irradiation with an energetic beam of electrons, the macromolecular chains of PMMA can be cut. The long chains of polymer are cut into small fragments (see Figure 4.5 above). Such irradiation is also capable of producing volatile groups such as CO_2 , H_2 and CH_3O which can be removed within the high-vacuum chamber, hence leaving a carbon-rich material on the substrate. The remaining carbon atoms with the support of *knock-on displacement* (*i.e.* the displacement of atoms as a result of knock-on collisions of highly energetic electrons)¹¹⁷ can potentially drive the formation of an sp^2 -hybridized carbon network as shown in Figure 4.5(b).^{113,114}

4.1.2 Hybridization of carbon in PMMA

Carbon intrinsically has 6 electrons that are arranged in different orbitals. The electron configuration of carbon is arranged in the form of $1s^2 2s^2 2p^2$ where electrons are filled from the inner to the outer orbitals as shown in Figure 4.6(a). The electron configuration can result in three distinct hybridizations including sp -, sp^2 - and sp^3 -hybridization (see Figure 4.6 (c-e)).

As illustrated in Figure 4.6(b), each $2p$ orbital ($2p_x$, $2p_y$ and $2p_z$) is filled with an electron. These orbitals combine with the $2s$ orbital to form hybrid orbitals. To form an sp -hybridization, $2s$ orbital is shared with $2p_x$ orbital, resulting in a triple bond where the forming structure appears linear (see Figure 4.6(c)).

In sp^2 -hybridization, $2s$, $2p_x$ and $2p_y$ orbitals share the same energy level to form sigma bonds of a bond angle of 120° , while leaving unhybridized $2p_z$ to form pi-bonds which exist above and below $2s$ orbital (Figure 4.6(d)).

For sp^3 -hybridization, it is a similar idea to sp - and sp^2 -hybridizations. When $2s$ orbital is shared with $2p_x$, $2p_y$ and $2p_z$ orbitals, the overlapping of the orbitals results in sigma bonds which form tetrahedral molecular geometry of a bond angle of 109.5° (see Figure 4.6(e)). The sp^3 -hybridization is an intrinsic molecular geometry of PMMA as seen in Figure 4.4.

As shown in Figure 4.4, section 4.1.1.3, a macromolecular chain of PMMA consists of sp^3 hybrids of carbon. Carbon is sensitive to a variety of radiation effects. The effects such as electronic excitation, radiolysis, and knock-on displacement are capable of breaking chemical bonds, enabling it to rearrange to a more stable form, *i.e.* to form sp^2 carbon networks.

Sp^2 -hybridization of carbon is known as the key feature of graphene and graphene-based materials. Section 4.1.3 and 4.1.4 will discuss the main characteristics of graphene-based materials and the means to probe sp^2 -hybridization of carbon, respectively.

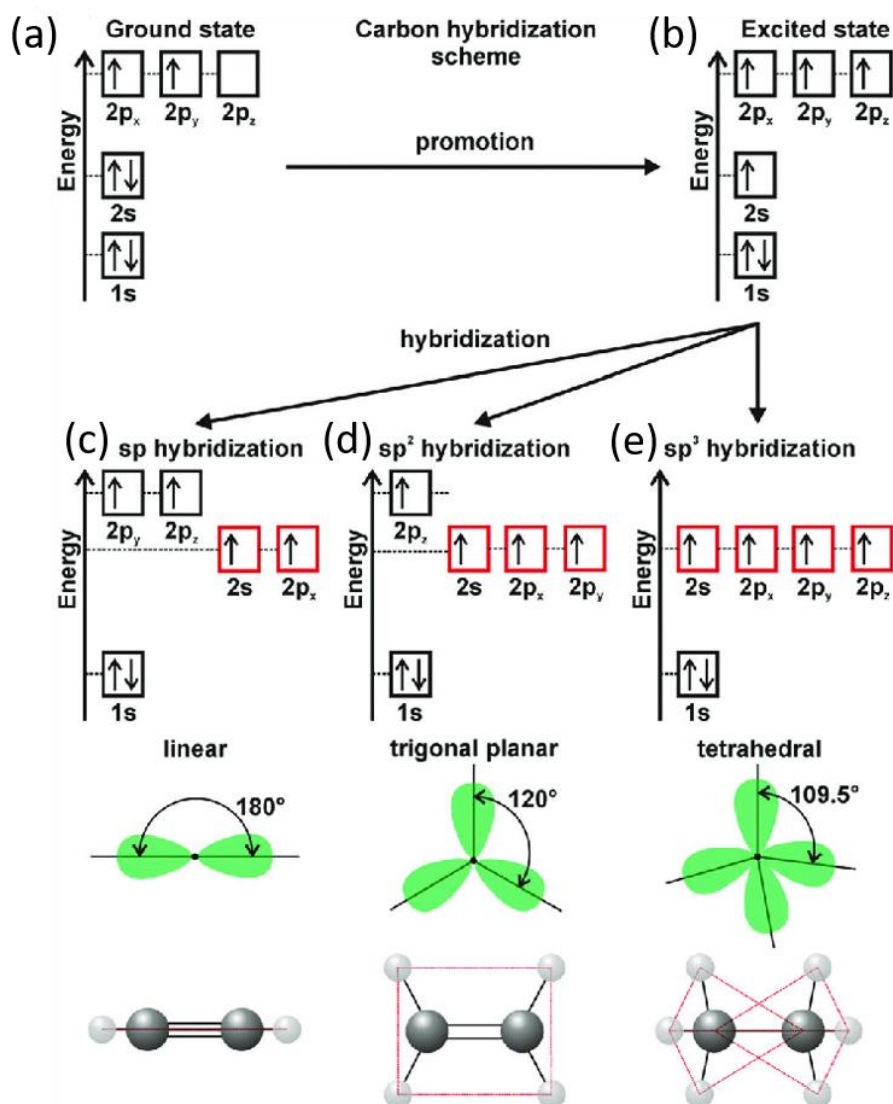
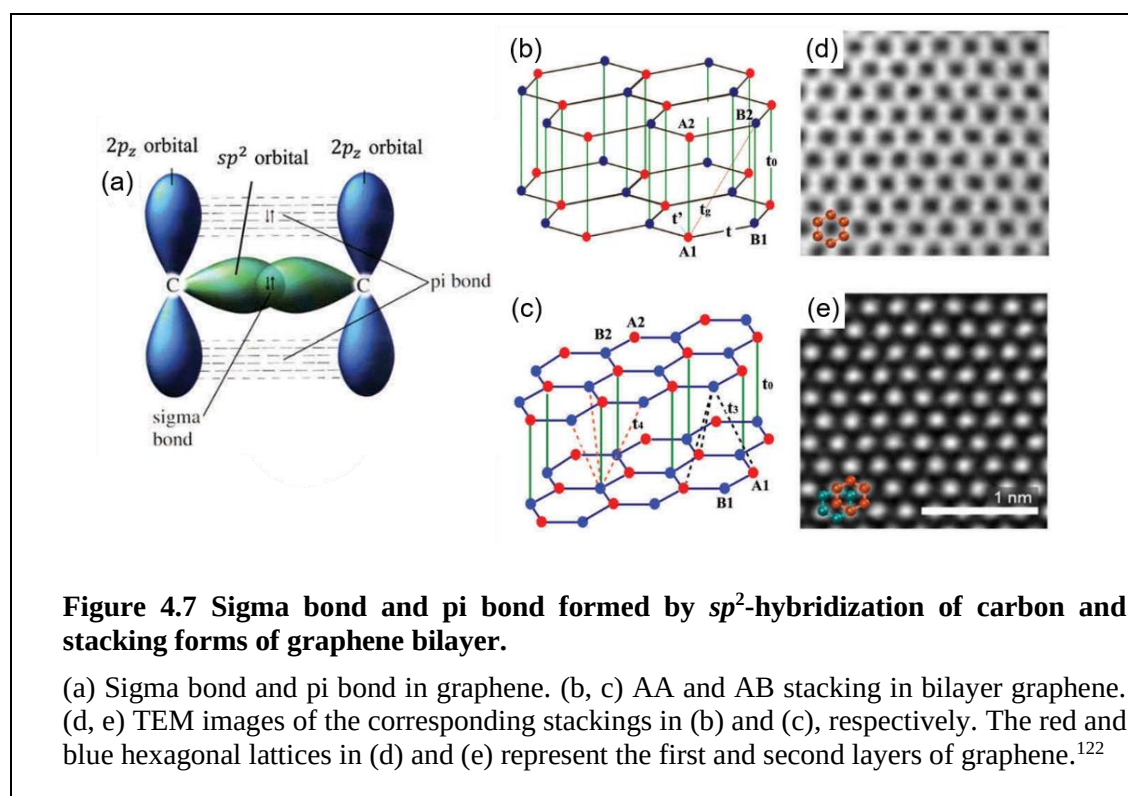


Figure 4.6 Diagram illustrating sp , sp^2 and sp^3 -hybridizations of carbon with relative electron configurations.

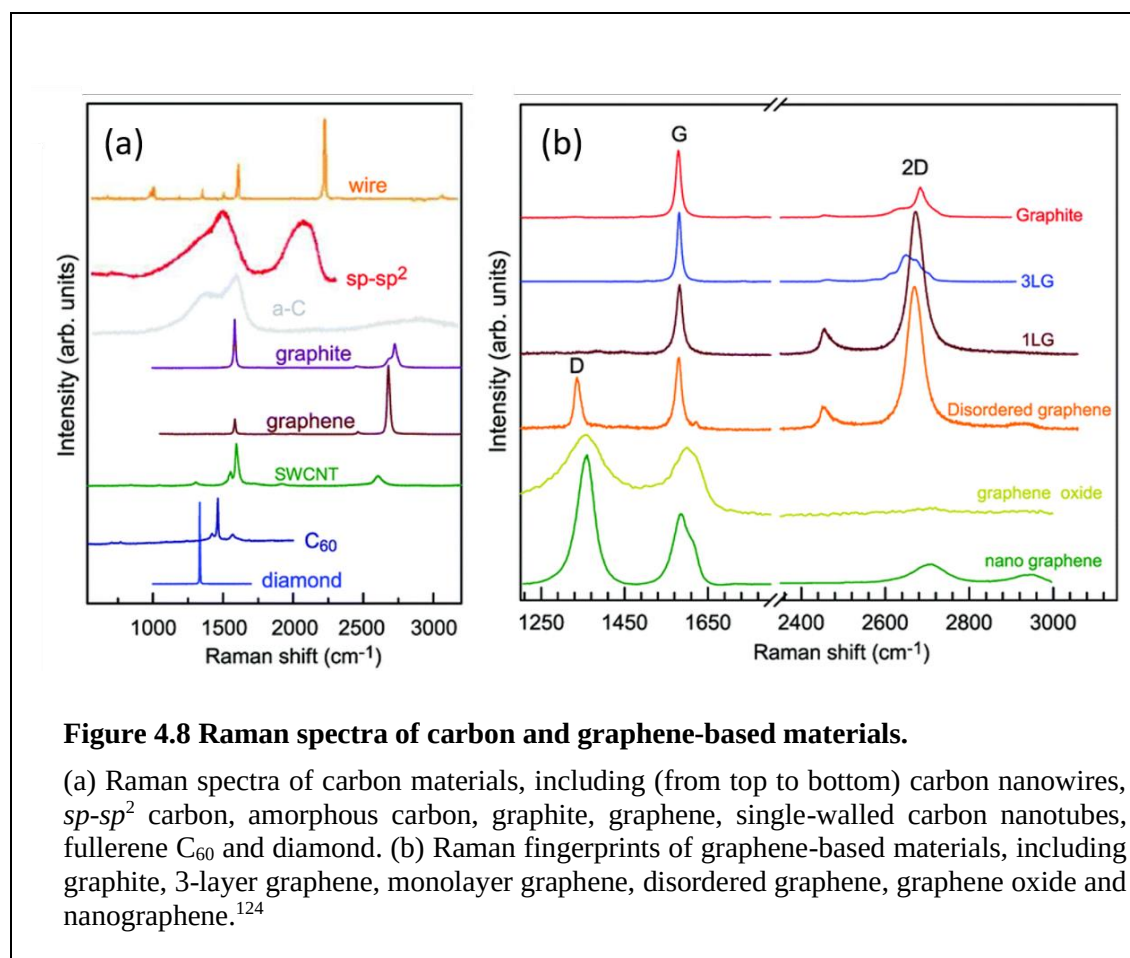
The electron configuration of (a) ground state and (b) excited state for carbon. (c-e) Planar view of sp -, sp^2 - and sp^3 -hybridizations of carbon, respectively.¹¹⁸

4.1.3 Characteristics of graphene-based materials

Graphene is intrinsically a two-dimensional (2D) material, consisting of an atom-thick layer of sp^2 -bonded carbon in a hexagonal network with strong covalent bonds. The graphene layer can be stacked either in an AA or AB manner to form multilayer graphene through weak van der Waals coupling, as shown in Figure 4.7(b, c). For AA stacking, each carbon atom in the second layer is directly aligned on top of another carbon atom in the first layer. On the other hand, for AB stacking, a set of carbon atoms in the second layer sits over the empty centres of the hexagonal lattice in the first layer. The stacking configurations of bilayer graphene are illustrated in Figure 4.7(b-e). The stacked layer of graphene is known as graphite. 1D and 0D forms of graphene can also be found such as graphene nanoribbons^{119,120} and nanographene.¹²¹ All these materials that are derived from monolayer graphene exhibit remarkable properties as those of graphene, and hence can be termed *graphene-based materials*.



Regardless of shape and size (*i.e.* 3D for graphite, 2D for graphene, 1D for nanoribbon or 0D for nanographene), graphene-based materials possess prominent features which can be seen in Raman spectra. As illustrated in Figure 4.8, pristine graphene and graphene-based materials exhibit a prominent G-peak which indicates the presence of sp^2 -bonded hexagonal carbon networks. The 2D-peak is used to determine the layer thickness of graphene, while the D-peak is assigned for defect, disorder and impurity of graphene.^{113,123,124}



The similar characteristics can also be seen in the Raman spectrum of amorphous carbon (a-C), see Figure 4.8(a). These peaks derive from different vibrational modes. The G-peak corresponds to the movement of neighbouring atoms in opposite directions perpendicular to the plane of the graphene sheet. The peak ranges from 1500-1600 cm^{-1} . The D-peak ranging from 1320-1360 cm^{-1} associates with atoms moving in radial directions in the plane of graphene sheet as a result of dislocations in the lattice, also

known as disorder-induced mode, hence the name. The ratio of the intensity peak between the D- and G-peaks can be used to determine the degree of disorder in the materials.¹²⁵

4.1.4 Raman spectroscopy for graphene-based materials

Raman spectroscopy is a rapid, sensitive, and non-destructive method that is widely used for characterisation of graphitic materials.^{116,124,126} Various information including chemical functionalities, presence and type of defects, edge and grain boundaries, crystal size, thickness, and electrical and thermal conductivity of graphene or graphitic materials can be obtained from the Raman spectrum.^{120,123,124,127–129}

Since Raman spectroscopy is sensitive to chemical vibrations of the materials, the characteristic of sp^2 -hybridized carbon can be probed by this technique. In this study, Raman spectroscopy was used to investigate chemical changes in PMMA deposited on Al nanoantennas fabricated on an ITO-coated substrate. Upon excitation using a 532 nm CW laser, chemical changes in PMMA were detected in Raman fingerprints. More importantly, two prominent peaks in the Raman spectra correlating with D- and G-bands expected for graphitic carbon that are common in systems containing sp^2 -hybridized carbon were observed with the presence of Al nanoantennas.

To investigate whether the LSPRs of Al nanoantennas play a role in supporting chemical changes in PMMA, we also collected Raman spectra from pure PMMA on the same substrate. In this case, the D- and G-peaks were not found, suggesting that the LSPRs of Al nanoantennas play a key role in supporting polymer chain scission in PMMA, which subsequently results in the production of graphitic materials. Raman spectroscopy can not only reveal plasmon-induced chemical transformations of PMMA but also allow us to investigate the energy distributed by Al nanoantennas towards PMMA.

4.2 Optical responses of Al bowtie nanoantennas

The LSPR of a subwavelength metallic nanostructure is sensitive to shape, size, type of metal and its surrounding medium. Although Au and Ag have demonstrated great promise for various applications in the visible and near-infrared spectral regions, they are scarce and costly, making them unsuitable for large-scale use. Therefore, searching for sustainable plasmonic materials is urgently required. In this work, we chose Al as the

plasmonic material. Although Al is known as good plasmonic material in the UV region, LSPRs of Al can be tuned to fall into the visible region of the spectrum.^{47,48}

Subwavelength metallic nanostructures with sharp corners have been reported to exhibit strong optical near-field intensities tens to thousands of times greater than that of the incident light.⁷ In this work, Al bowtie nanoantennas consisting of two opposing equilateral triangles with a narrow gap were studied. FDTD method was used to calculate the optical near-field enhancement of an isolated Al bowtie nanoantenna along the x - and y -polarization directions. The idea was to investigate dimensions of such nanoantennas that produce the LSPR that matches the 532 nm laser excitation wavelength in Raman spectroscopy.

In FDTD simulations, a total-field scattered-field (TFSF) source was launched from the air above the nanoantenna at normal incidence following the experimental configuration. An isolated Al bowtie nanoantenna with a 3-nm thick alumina film was placed on top of an ITO-coated glass substrate. The structure was simulated using perfectly matched layers (PML) as boundary conditions for all sides of the simulation region with a fine mesh size of $2.5 \times 2.5 \times 2.5 \text{ nm}^3$.

Figure 4.9 (a) and (b) illustrate the calculated electric field distribution maps of a single Al bowtie with a 20 nm height, an 85 nm side length, a 10 nm curvature radius, and a 15 nm gap when illuminated by light polarized along the x - and y -directions (the polarization directions are indicated by the white arrows). The nanoantenna was found to produce a resonance wavelength matching the excitation wavelength (532 nm) used in Raman spectroscopy. Additional simulation results for various dimensions of Al bowtie nanoantennas are provided in Figure A-1, Appendix A.

In Figure 4.9(a, b), with the x -polarization, the near-field enhancement occurs in the gap of the bowtie with a maximum field intensity $|\mathbf{E}|^2 \approx 102$, typically known as “hotspots”, whereas with the y -polarization, the near-field enhancement is localised at the outer corners of the bowtie with a lower field intensity less than 20. Regarding the extinction spectra, when illuminated by x -polarized light, the Al bowtie had an LSPR close to 532 nm while exhibiting a blue-shifted LSPR when illuminated by the y -polarized light (Figure 4.9(c, d)). The results of the shift in wavelength correlate with longitudinal and transverse plasmon resonance modes which were previously studied.¹³⁰

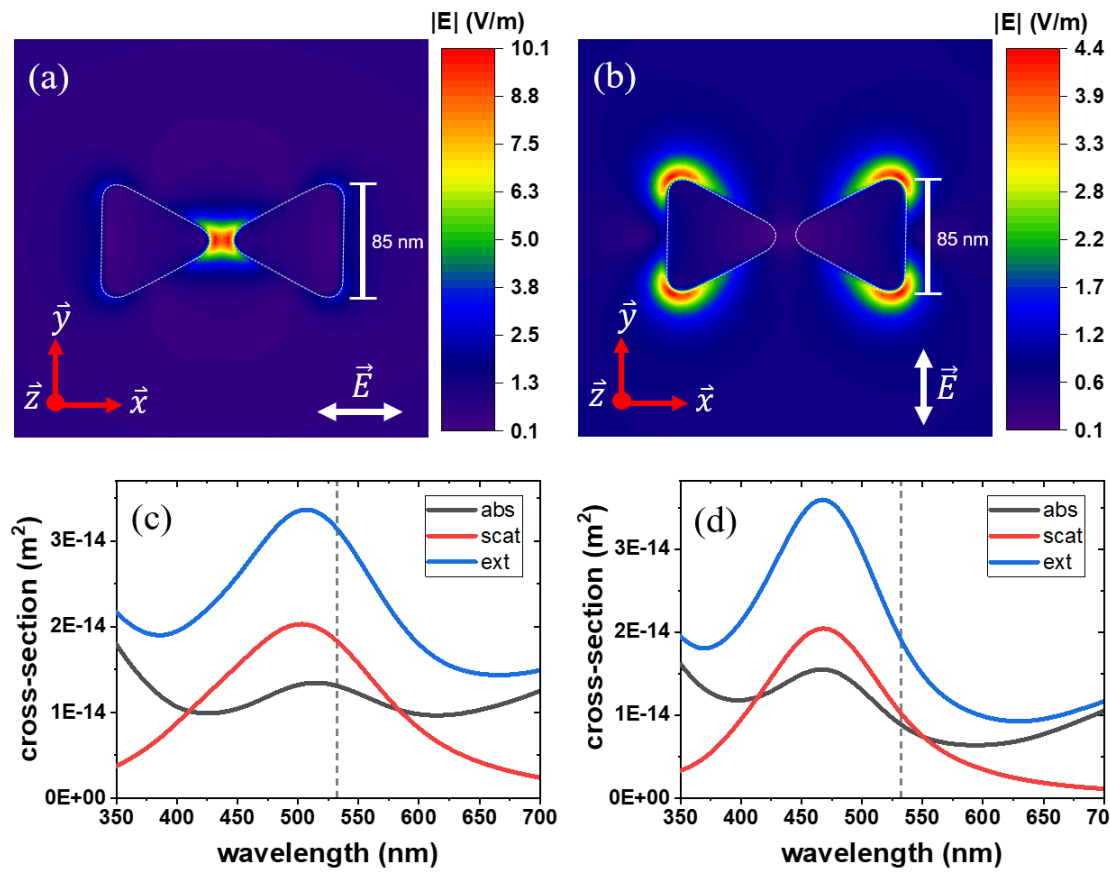


Figure 4.9 Electric field distribution maps in the x - y plane of an isolated Al bowtie nanoantenna and cross-section spectra of the related nanoantenna with x - and y -polarizations calculated using FDTD method.

(a, b) The near-field enhancement ($|E|$ in units V/m) of Al bowtie nanoantenna occurred in the gap when excited by x -polarized light and at the outer corners when excited by y -polarized light. (c, d) Absorption (grey curve), scattering (red curve) and extinction (blue curve) cross-section spectra of the related nanoantenna with x - and y -polarizations, respectively. The vertical dashed grey lines at 532 nm indicate the excitation wavelength used in Raman spectroscopy.

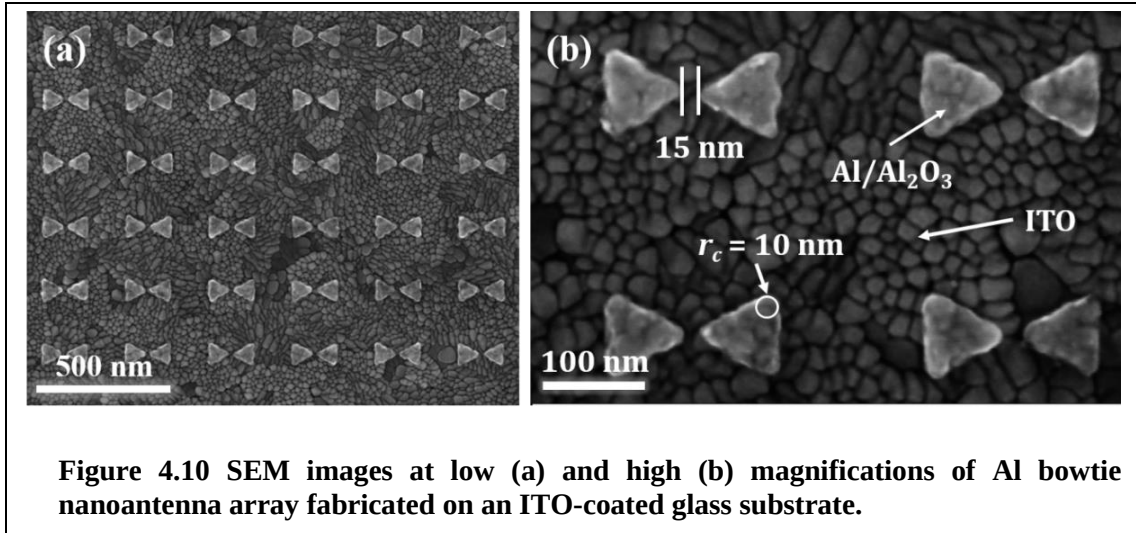
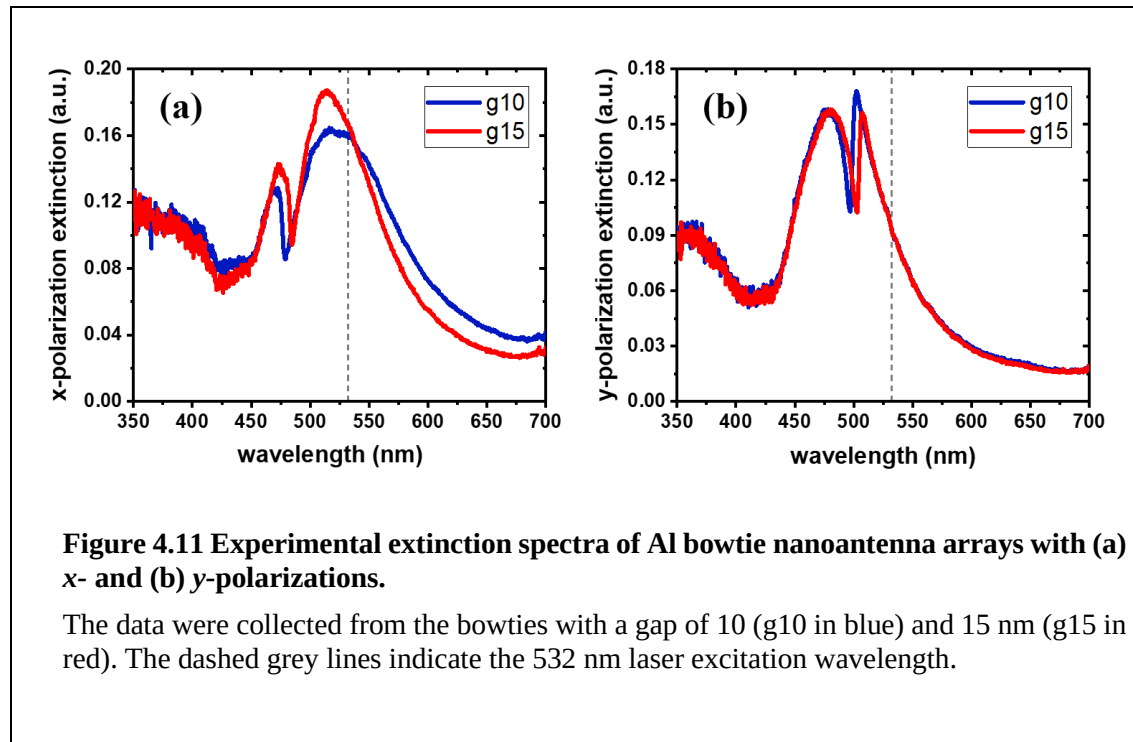


Figure 4.10 illustrates Al bowtie nanoantennas fabricated using the EBL technique, as described in section 2.3.1. The nanoantennas were fabricated with an array of 150 nm spacing in the x - and y -directions on an ITO-coated soda-lime glass substrate. The nanoantennas including Al and aluminium oxide (Al_2O_3) have an average physical edge-length of (85 ± 1) nm, a gap of (15 ± 1) and a curvature radius of (10 ± 1) nm, statistically measured from scanning electron micrographs. To investigate the effect of the gap antenna in Al bowties, we fabricated Al bowtie nanoantenna arrays with a central gap of 10 and 15 nm. For simplicity in explanation, we define Al bowtie nanoantennas with a gap of 10 and 15 nm as g10 and g15, respectively.

Figure 4.11(a) and (b) show experimentally measured extinction spectra of Al bowtie nanoantenna arrays with distinct gaps (*i.e.* g10 and g15) when excited by light in the x - and y -directions, respectively. For both polarization directions, the extinction spectra exhibit two peaks. The intriguing peak splitting is attributed to the coupling between the LSPR and surface lattice resonances (SLRs), which may occur when the incident light is diffracted and scattered by periodic arrays of metallic nanostructures.⁵⁴ It should be noted that in fabrication, Al bowtie nanoantennas were arranged in a periodic array with a 150 nm spacing which differs from the configuration in FDTD simulations where only an isolated nanoantenna was calculated, *i.e.* no periodic boundary conditions were applied. Therefore, the SLRs were not observed in FDTD simulations. Although the peak splitting occurred for bowties g10 and g15, the peaks of the LSPR remain close to

the 532 nm laser excitation wavelength, especially for the case of x-polarized light. Further studies in relation to the SLRs are presented in Chapter 5, section 5.2.



4.3 Near-field distribution of Al plasmonics

PMMA A1 (1% 950k PMMA in anisole, purchased from EM Resist Ltd.) was spin-coated on Al nanoantenna arrays at 1,000 rpm to achieve a 42 nm thick PMMA film. The PMMA film acts as a photosensitive molecular probe that can be used to investigate the near-field distribution around the bowtie nanoantennas when excited by a resonant laser. The illumination was provided by a 532 nm CW laser in a Raman system (WITec alpha300 R).

In the first test, an incident power of 4.75 mW was used per exposure for 1 s in a raster scan manner with an area of $5\ \mu\text{m} \times 5\ \mu\text{m}$ and a step size of 500 nm. The sample was then immersed in a standard developer (MIBK:IPA 1:3) for 40 s at room temperature to remove the exposed areas revealing the near-field distribution of energy transfer from the Al bowtie nanoantennas.

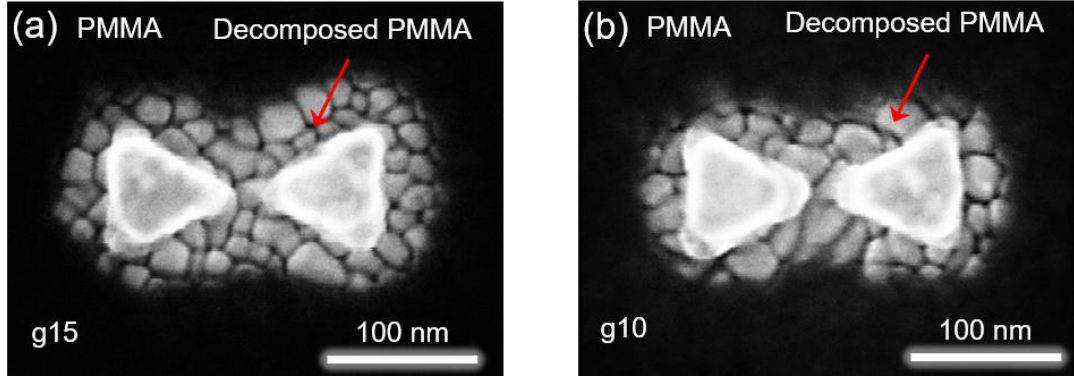


Figure 4.12 Scanning electron micrographs of Al bowties with a gap of 15 nm (a) and 10 nm (b) after laser exposure and development.

The regions of decomposed PMMA reveal the near-field distribution around Al bowties.

Figure 4.12(a) and (b) demonstrate the areas of decomposed PMMA (bright regions indicated by the red arrows) around a bowtie after laser exposure and development, respectively. The images were observed using an SEM with an acceleration voltage of 10 kV. Additional SEM images illustrating the clear contrast between PMMA and decomposed PMMA can be found in Figure A-2 in Appendix A.

4.4 Polarization-dependent study

As was illustrated in Figure 4.9(a, b), the near-field enhancement is sensitive to the polarization direction of the incident light. In the case of bowtie structure, with the x-polarized light, the maximum field intensity occurring in the gap is 6 times greater than that at the outer corners when excited by the y-polarized light. To experimentally demonstrate this effect, we used the same method as in section 4.3 while a polarizer was implemented to ensure the polarization of the incident light.

A 532 nm CW laser was used to excite the surface plasmons of Al bowtie nanoantennas with an 85 nm side length and a 15 nm gap. A polarizer was placed in front of the laser output at a well-aligned optical axis to allow control of the polarization direction. The laser exposure was conducted on a PMMA-coated Al bowtie nanoantenna array. The laser power was set at 60%, corresponding to an output measured at the sample

of 10.7 mW. A total area of exposure was $2\ \mu\text{m} \times 2\ \mu\text{m}$, while each integration time was 5 s and the step size was 500 nm.

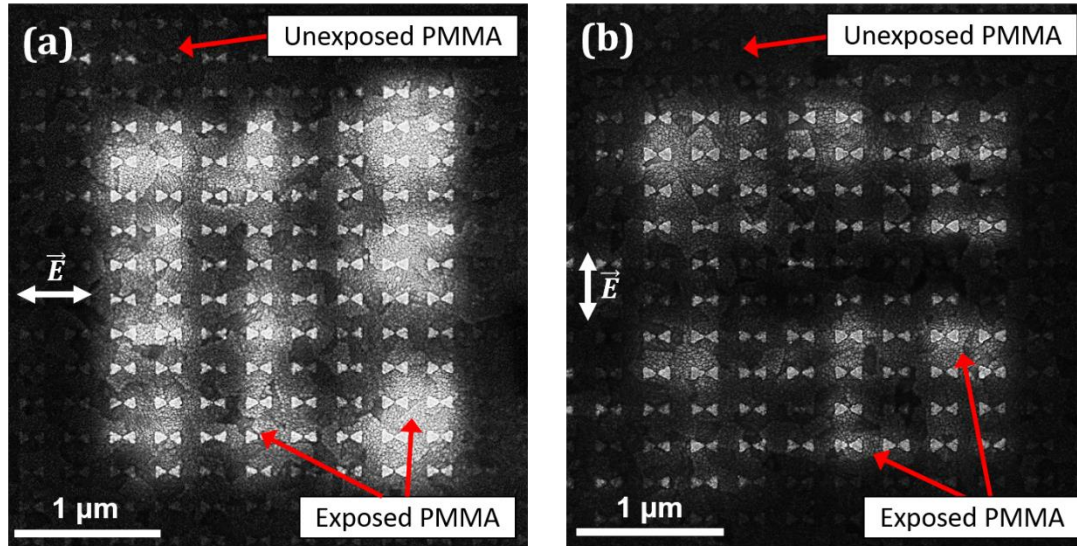


Figure 4.13 The exposed PMMA volume around Al bowties (bright regions) as a function of polarization direction along the (a) x - and (b) y -axes (indicated by two-sided arrows), respectively.

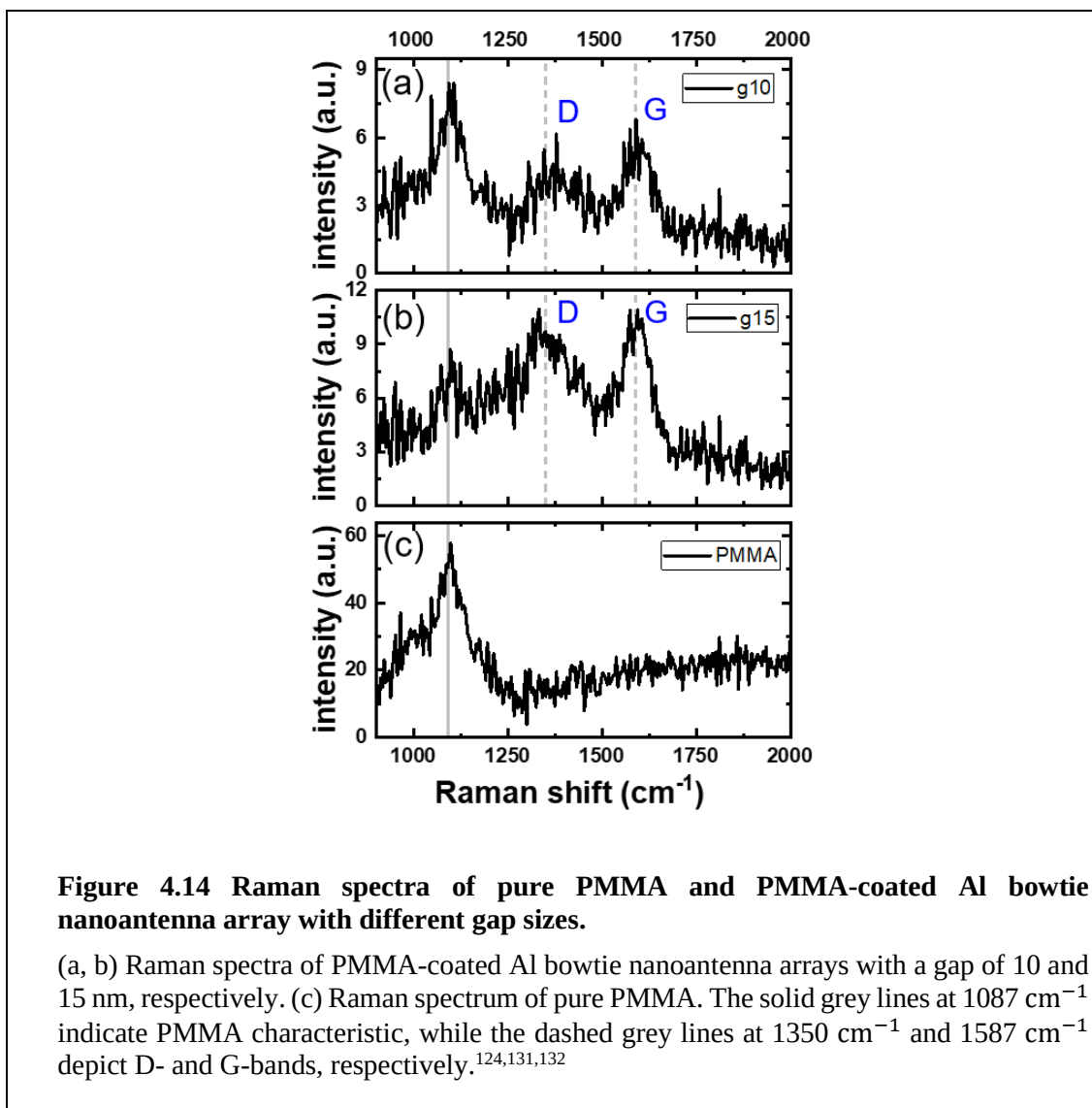
The magnitude of regions of exposed PMMA corresponds to the electric near-field strength and is sensitive to the polarization directions of the incident light.

SEM images in Figure 4.13 show the polarization dependence of the decomposed PMMA regions around Al bowties. It is evident that when the sample was excited by the x -polarized light, a greater amount of PMMA was decomposed compared with that when excited by the y -polarized light.

The experimental results correlate well with the simulation results demonstrated in Figure 4.9(a, b). For the bowtie structure, when excited by the x -polarized light, the maximum field intensity occurring in the gap is 6 times greater than that at the outer corners of the bowtie when excited by the y -polarized light. Therefore, it can be concluded that the field distribution of energy transfer of Al bowties is sensitive to the polarization direction of the incident light.

4.5 Graphitization of PMMA

In addition to probing energy transfer in the near-field of Al nanoantennas, we also observed chemical changes in PMMA through Raman fingerprints. Figure 4.14(a) and (b) show the Raman spectra of PMMA coated on Al bowtie nanoantenna arrays with a gap of 10 and 15 nm, respectively. Two peaks at 1350 cm^{-1} and 1587 cm^{-1} correspond to the D- and G-bands expected for graphitic carbon and represent sp^2 -hybridized carbon.

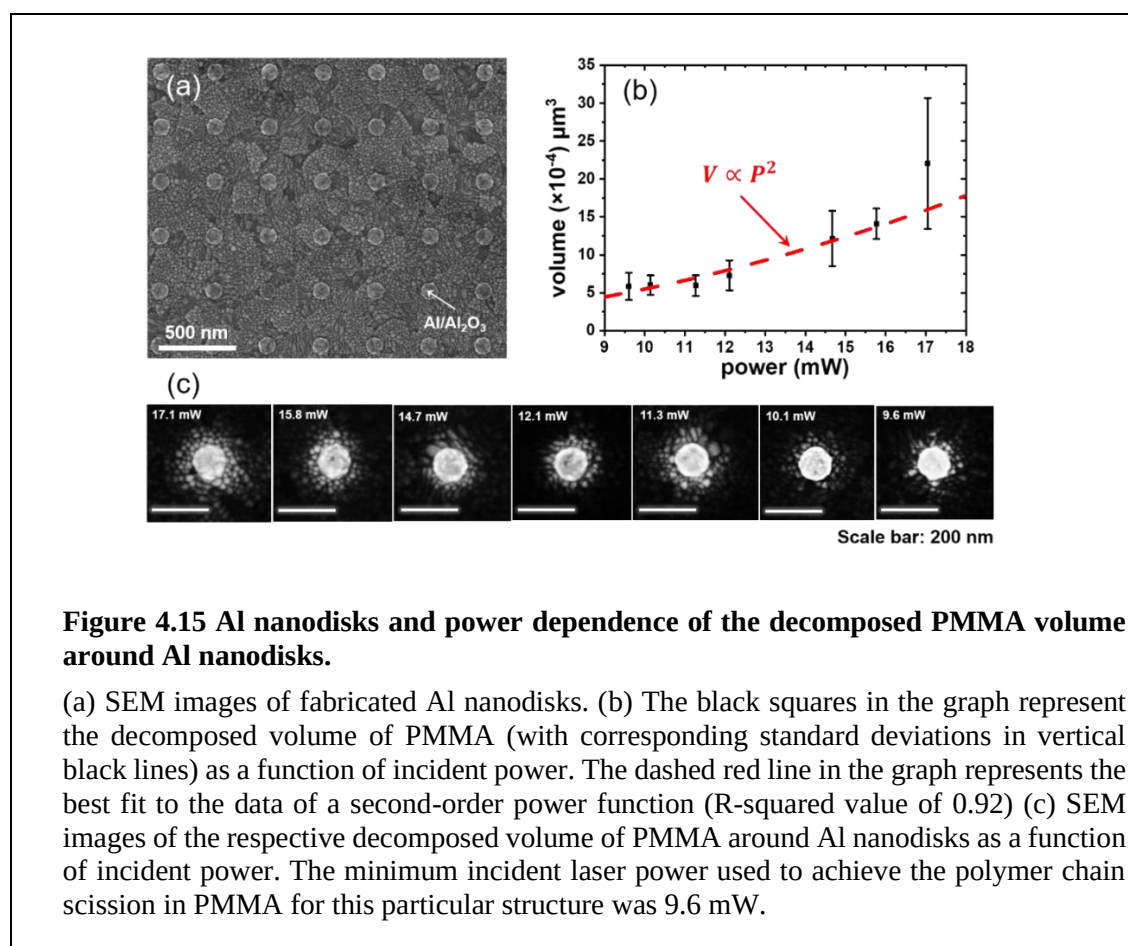


To investigate whether Al nanoantennas play an important role in contributing to the chemical changes in PMMA, we also collected Raman spectra of pure PMMA from regions on the substrate where Al nanoantennas were not present. Figure 4.14(c) shows an average result of Raman spectra obtained from pure PMMA. The Raman peak at

1087 cm^{-1} is intrinsic to PMMA^{131,132} and also appeared on both spectra where Al bowties were present. The same results occurred on both PMMA-coated Al bowtie nanoantennas with gaps of 10 and 15 nm suggesting that PMMA conversion into graphitic materials is driven by surface plasmons in Al nanoantennas.

4.6 Multiphoton absorption

To better understand the mechanism of energy transfer from Al nanoantennas to the surrounding medium (*i.e.* PMMA), we fabricated another sample comprising Al nanodisks which were arranged periodically in the x- and y-directions. The Al nanodisks were fabricated on an ITO-coated soda-lime glass substrate. The nanodisks had diameters of 100 nm and were separated by 350 nm in a square array. FDTD simulations of the structures in response to the 532 nm excitation wavelength are provided in Figure A-3 in Appendix A.



The sample was inspected using an SEM as shown in Figure 4.15(a). The symmetry of the nanodisks simplifies the calculations of the decomposed volume of PMMA in the near-field of the nanodisks after laser exposure (see Figure A-4 in Appendix A). Calculating data for the volume of decomposed PMMA is presented in Table A-3, Appendix A. The standard deviation of at least 10 measurements for each volume is provided.

In Figure 4.15(c), the volume of decomposed PMMA was observed to vary with the laser power in the power range from 9.6 to 17.1 mW. Additional SEM images demonstrating decomposed PMMA can be found in Figure A-5, Appendix A. The volume of decomposed PMMA surrounding Al nanodisks increased with increasing laser power as shown in Figure 4.15(b). The volume of exposed PMMA was observed to scale with laser power according to a second-order power function (red dashed curve). To further analyse our experimental data, we used the Beer-Lambert law as a model to explain the energy transfer mechanism in PMMA. From the Beer-Lambert law of multiphoton absorption, $\frac{dI}{dx} = -\alpha_n I^n$, the decay in the intensity of light, I at a depth, x in a material is proportional to a coefficient, α_n where n is the number of photons absorbed in the material. In the case of this experiment, we have studied the volume of exposed PMMA, V as a function of the laser power, P which is directly proportional to the laser intensity at the sample. From the Beer-Lambert law, we can then relate the exposed volume to the laser power by, $V \propto P^n$. A second-order power function was found to best fit the data in the graph in Figure 4.15(b), which suggested that a two-photon absorption process was involved in the polymer-chain scission and possibly led to chemical transformations of PMMA into graphitic materials.

4.6.1 Electron-beam irradiation and graphitization of PMMA

Studies have shown that electron-beam exposure of PMMA causes graphitization of the polymer at high electron-beam energy (200 kV)¹¹³ and low energy (10 kV) with post-exposure thermal annealing (800°C).¹¹⁴ PMMA cross-links under these exposure conditions and such cross-linking may be initiated by knock-on damage *i.e.* hydrogen and oxygen atoms displaced by energetic electrons and expelled as gases, leaving carbon atoms that can assemble to form sp^2 -hybridized networks.

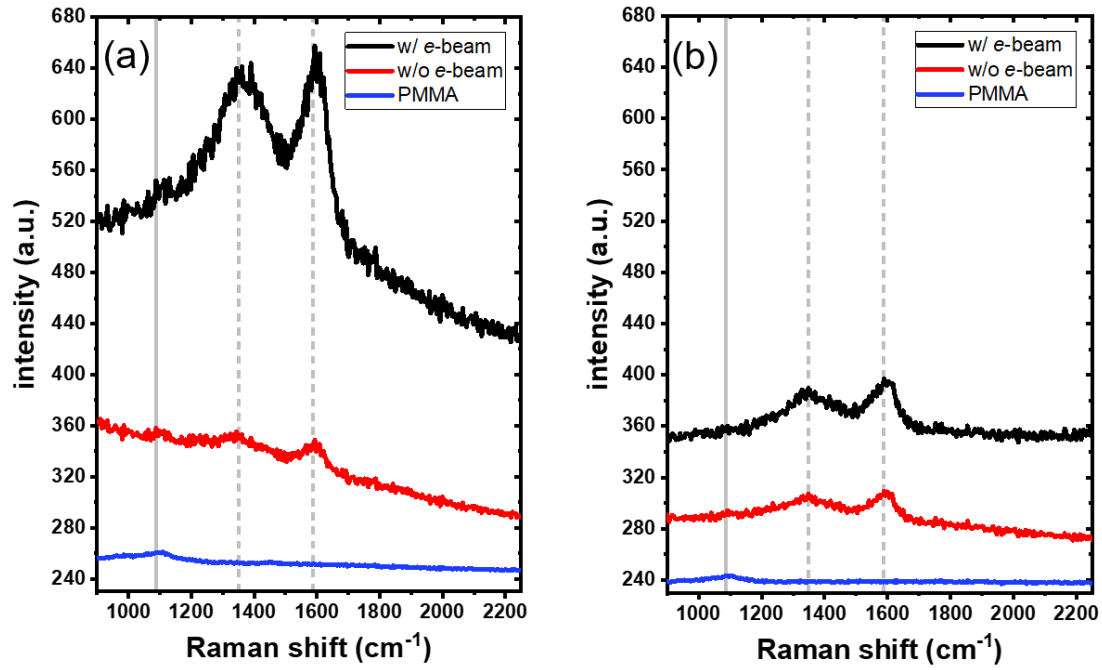


Figure 4.16 Raman spectra of Al nanoantenna-embedded PMMA when treated with and without electron-beam irradiation.

Raman spectra of PMMA coated on (a) Al bowtie nanoantenna arrays and (b) Al nanodisk arrays with (black curves) and without (red curves) the treatment of electron-beam irradiation prior to the Raman experiment. The blue curves represent the Raman spectra of isolated PMMA deposited on the same substrate. The vertical solid grey lines at 1087 cm^{-1} indicate a characteristic of PMMA while the vertical dashed grey lines at 1350 cm^{-1} and 1587 cm^{-1} are correlated to the D- and G-bands, respectively.

To gain insight into how electron-beam irradiation affects the graphitization of PMMA with the existence of Al nanoantennas, we used a commercial scanning electron microscope (Zeiss SUPRA 40) with software (Raith Elphy Quantum) to study electron-beam irradiation of PMMA-coated Al bowtie and nanodisk nanoantennas with a relatively low operating voltage of 15 kV. By opting for a beam spot exposure (a $30\text{-}\mu\text{m}$ objective aperture) instead of the usual raster scan, we can selectively expose small regions of interest.

For the bowties, we allowed the central gaps to be exposed to the electron beam, while for the nanodisks, the exposure was performed at the edges of the nanodisks. These areas of interest correspond to the regions of maximum field enhancement when excited

by the 532 nm laser. To be consistent, each electron beam exposure was performed for 15 s. This electron-beam irradiation was carried out prior to immersion of the sample into a chemical developer. The sample was then characterised by Raman spectroscopy.

Raman spectra of PMMA coated on Al bowties and Al nanodisks are displayed in Figure 4.16(a) and (b), respectively. It is evident that with the treatment of electron-beam irradiation prior to the Raman characterisation, the Raman signals (black curves) of PMMA coated on both bowties and nanodisks are greater than those (red curves) without the electron-beam treatment. However, the increasing relative intensity of the spectra from samples treated by the electron beam is different for the bowties and nanodisks. That is, for the bowties there is a greater enhancement of the Raman signal than that for the nanodisks, suggesting that shape, size, and geometry of metallic nanoantennas can potentially determine the degree of graphitization as well as providing single-particle-level analysis by Raman spectroscopy. The spectra in Figure 4.16 show that plasmonic Al nanoantennas can generate local graphitization of PMMA in plasmonic hotspots and can also enhance Raman signals from carbon nanodots graphitized by electron-beam exposure.

4.7 Conclusion

In conclusion, we have proposed and tested a method to map the near-field distribution of energy transfer around Al nanoantennas using a CW laser in a Raman spectroscopic system. The same method also allowed us to observe plasmon-driven chemical transformations in PMMA. Aluminium – a cheap, abundant and air-stable material – is shown to be a viable alternative plasmonic material that can serve applications not only in the UV range, but also in the visible region (*i.e.* at 532 nm).

Tunable localised surface plasmon resonances in Al nanostructures are capable of generating a strong optical near-field at the nanostructure surface when excited by resonant incident illumination. The strong optical enhancement can be absorbed in a material surrounding the metal *i.e.* PMMA. We have shown that the absorbed energy was consistent with a two-photon absorption mechanism and resulted in local graphitization of PMMA.

The graphitization can not only be generated by a CW laser, but also by electron-beam irradiation. The evidence in Raman spectra reveals that the synergy between electron-beam irradiation and Al plasmonic nanoantennas could contribute to a higher degree of graphitization of the polymer, even at low-energy electron-beam irradiation doses and may provide a route to generate plasmon-enhanced carbon nanodot structures which can serve as nanosensors and photocatalysts.

CHAPTER 5

Aluminium Nanoantennas for SERS and Sensing Applications

5.1 Probing plasmonic hotspots at single nanoantenna levels

5.1.1 Introduction

Roughened metallic surfaces or sub-wavelength metallic nanostructures with various shapes and sizes such as nanospheres, nanostars, nanotriangles, nanorods, nanodimers, *etc.* have been reported to enhance Raman scattering signals of probe molecules, even at low concentration.^{133–136} The phenomenon arises from the excitation of localised surface plasmon resonances, which result in enhanced local electric fields in the vicinity of the metal. If a probe molecule is within regions of the enhanced electric field, Raman scattering can be amplified. Such a sensitive and label-free technique that employs nanostructured metals to amplify the inherently low Raman scattering is typically known as *surface-enhanced Raman spectroscopy (SERS)*.

Metallic nanodimers such as two spheres,¹³⁶ two nanodisks,¹³⁴ and bowtie nanoantennas consisting of two opposing triangles,¹³⁷ with a small gap distance on the order of a few Angstroms to tens of nanometres have been widely studied for SERS applications. Among these structures, metallic bowtie nanoantennas are the most interesting structure due to the presence of multiple *plasmonic hotspots* arising from charge accumulation at the gap and sharp terminations with a small radius of curvature, which can produce larger electric field enhancement compared to the structures with a large radius of curvature.

Choice of metals also plays an important role in determining electric field strengths due to their optical properties (see section 1.1.3). Al supports tunable LSPRs from the UV to the visible region of the spectrum, thus making it a suitable SERS substrate for various excitation sources (wavelengths). A previous study¹³⁷ has reported that Al bowtie nanoantennas made of two equilateral triangles of 100 nm side length and a 20 nm apex-to-apex gap distance could greatly enhance resonance Raman peaks of liquid benzene in the near-field of a single bowtie. The enhanced resonance Raman peaks were theoretically assumed to originate from the local electric near-field in the gap of an Al bowtie when excited by a pulsed UV laser at a wavelength of 258.8 nm which resulted in a high SERS enhancement factor of $\sim 10^5$. However, it is likely that the enhanced Raman signals were not only contributed by the gap mode, but also by the outer corners of the bowtie structure, thus adding extra Raman signals which further resulted in a very high enhancement factor.

In addition to aluminium, noble metals such as gold and silver have been a great choice for SERS applications. SERS substrates made of free-standing Au¹³⁸ and Ag¹³⁹ bowtie nanoantennas have been reported to produce SERS EFs as high as 10^{11} and 10^9 , respectively. Yet these calculations were based on overall performance and not for particular spots of interest.

Although many studies have shown that Raman scattering can be enhanced by metallic SERS substrates or metallic colloidal nanoparticles, experimentally identifying the locations of hotspots at the single nanoantenna level remains challenging. Conventional optical microscopy techniques, such as dark-field microscopy together with UV-Vis spectroscopy, whose resolution is limited by diffraction, can only be used to acquire LSPR-induced far-field optical responses, which are insufficient to reflect the near-field distribution without the assistance of theoretical calculations. Advanced techniques including scanning near-field optical microscopy (SNOM), electron energy loss spectroscopy (EELS), photoemission electron microscopy (PEEM), and cathodoluminescence spectroscopy (CLS) can provide optical information at a spatial resolution breaking the diffraction limit. Nevertheless, these techniques operate under complex setups and their crucial apparatus can complicate experimental results. Especially in the case of SNOM, the presence of the conductive tip may interfere with the intrinsic near-field of the nanoantennas being studied.^{136,140,141} Additionally,

obtaining the 3D-information of the near-field distribution around the nanoantennas remains a challenge. Therefore, there is a demand for new methods that can probe the near-field distribution of a single nanoantenna.

Here, a novel method that exploits the SERS effect, originating from the near-field distribution of an Al bowtie nanoantenna is presented. To probe the locations of plasmonic hotspots, negative-tone PMMA was selectively deposited at different locations with respect to distinct electric near-field strengths around the nanoantenna, when excited by a 532 nm CW laser. Negative-tone PMMA possesses graphitic properties, which can be identified in the Raman spectra *i.e.* D- and G-peaks. The difference in Raman intensities obtained from negative-tone PMMA at different locations around an Al bowtie antenna correlates with the electric near-field intensities calculated from FDTD simulations. The dependence of Raman intensities on polarization is also demonstrated.

5.1.2 Fabrication of Al nanoantennas

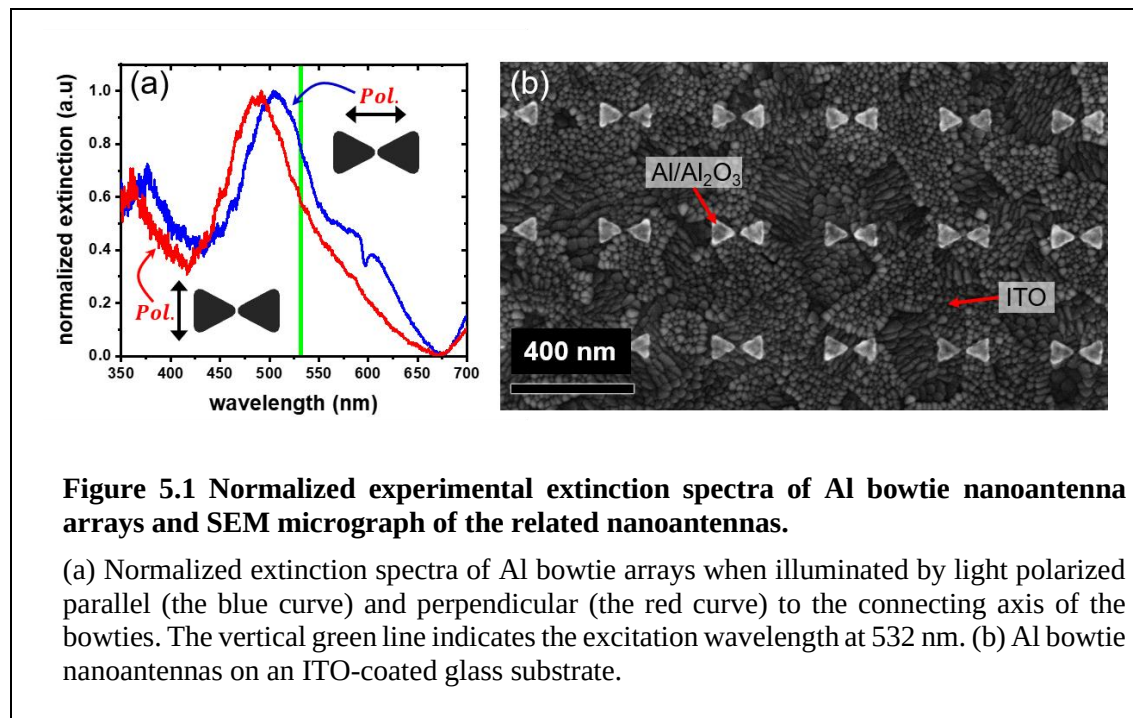
Al nanoantennas were fabricated using EBL as described in Chapter 2 section 2.3. Al bowtie nanoantennas consisting of two equilateral triangles of 85 nm side length and 20 nm thickness separated by 15 nm apex-to-apex gap were fabricated on an ITO-coated glass substrate. The nanoantennas were arranged in a square array of 380 nm period. The calculation of the wavelength-dependent near-field distribution of the nanoantennas was performed using FDTD using the simulation parameters as described in Chapter 3, section 3.1.1.2.

5.1.3 Extinction spectra of Al nanoantennas

Extinction spectra of Al bowtie nanoantenna arrays were obtained using an in-house micro-spectrophotometry setup described in section 3.4. The polarization dependence was also studied in the x - and y -directions. Optical measurements were performed shortly after the fabrication and before SEM imaging. This is to avoid interferences in spectra due to the degradation of materials and carbon contaminants deposited during SEM imaging.

Figure 5.1 illustrates the experimentally normalized polarization-dependent extinction spectra of Al bowtie arrays with 100 repeated measurements. When illuminating the sample with the polarization parallel to the connecting axis of the

bowties, the peak maxima in the spectrum (blue curve) appears close to 532 nm with the grating effect occurring around 600 nm. Detailed explanations regarding the grating effect or the surface lattice resonance will be discussed in section 5.2. On the other hand, when the sample was illuminated by light perpendicular to the plane of the sample with the polarization orthogonal to the connecting axis of the bowties, the peak maxima (red curve) were blue-shifted. In this work, an excitation wavelength at 532 nm was employed and is indicated by the vertical green line in Figure 5.1(a). An array of Al bowtie nanoantennas after fabrication is shown in Figure 5.1(b). Al rapidly reacts with oxygen in the air resulting in a self-grown film of alumina around Al bowtie nanoantennas which is included in the topology of the Al structures, illustrated in Figure 5.1(b).



5.1.4 Fabrication of negative-tone PMMA

The sample of Al bowties on an ITO-coated glass substrate was treated under oxygen plasma etching to eliminate organic contaminants. A 42-nm-thick PMMA film was then deposited on the sample using the method described in the first paragraph of section 4.3.

A dot of negative-tone PMMA was selectively fabricated at the central gap, the corner, and the edge of individual Al bowties using electron-beam irradiation. A square area of $2\ \mu\text{m} \times 2\ \mu\text{m}$, consisting of Al bowtie nanoantennas arranged in an array, was

used for fabrication of negative-tone PMMA dots. For example, in square A, negative-tone PMMA dots were fabricated only at the central gaps of the bowties while in squares B and C negative-tone PMMA dots were generated at the corners and edges, respectively.

An electron beam with an energy of 15 keV and a 30 μm aperture was focused on the sample at a working distance of 3.5-4 mm. A beam spot exposure was selected, allowing the electron beam to precisely interact with PMMA at a single specific location at a time. For consistency, each exposure was performed for 5 s. After electron-beam irradiation, the sample was developed in acetone at room temperature for 5 min to remove unexposed and positive-tone PMMA.

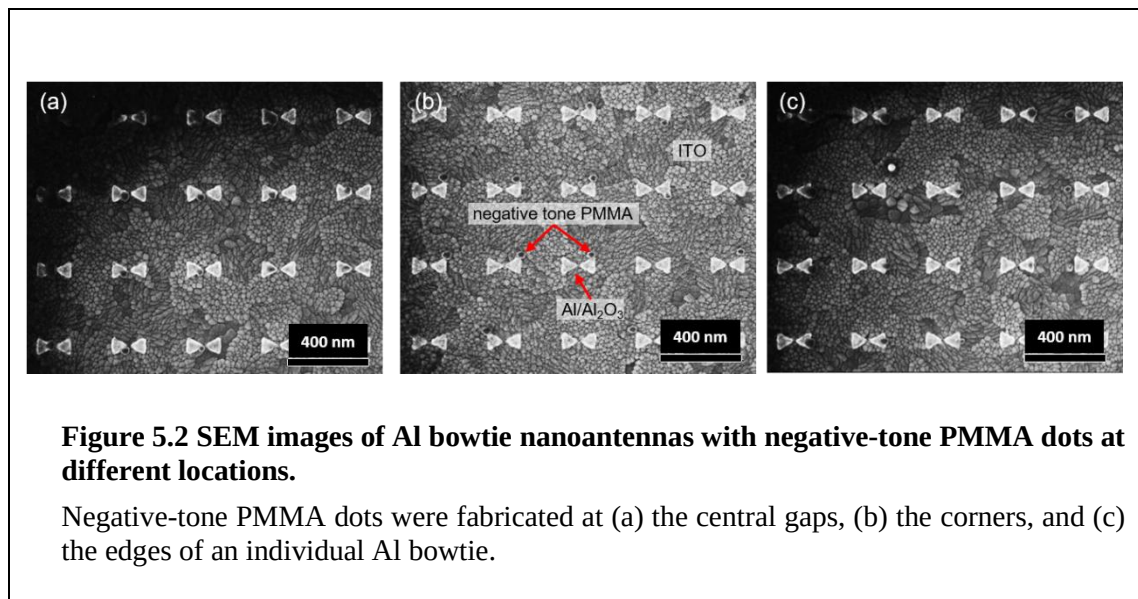


Figure 5.2 displays SEM images of arrays of Al bowtie nanoantennas with negative-tone PMMA dots (black dots) at different locations. The SEM images were acquired after developing the sample in acetone. An in-lens mode with an electron beam operating at an acceleration voltage of 10 keV was employed for imaging.

5.1.5 Polarization dependence of SERS signals

FDTD simulations were performed for a single Al bowtie antenna, as illustrated in Figure 5.3(a, b). A maximum field intensity of $|E|^2 \approx 180$ was calculated in the central gap of the bowtie when illuminated by an excitation wavelength at 532 nm polarized along the x -axis, compared to $|E|^2 \approx 60$ at the four outer corners of the bowties when illuminated by light polarized along the y -axis.

In SERS, the intensity of Raman signals for adsorbates can be greatly enhanced by orders of magnitude and is often observed at sharp features or within narrow gaps between metal surfaces.^{133,134,136,142} The light incident on these features can couple with the surface plasmon resonances which leads to the generation of an enhanced optical field over the metal surfaces. The enhanced electric field can then excite resonance Raman modes of the molecules being studied, leading to an increase in the Raman scattering signals.

According to the electric field distribution maps calculated from FDTD simulations, demonstrated in Figure 5.3(a, b), the locations of the enhanced near-field intensity or plasmonic hotspots are sensitive to the polarization direction of the incident light. To probe the locations of hotspots, negative-tone PMMA dots were used as a nanoscale probe. A dot of negative-tone PMMA was fabricated at three different locations *i.e.* the central gap, the corner, and the edge of the Al bowtie (see Figure 5.3(e-g)), corresponding to regions of different electric field intensities.

Figure 5.3(c) and (d) show the Raman scattering spectra of Al bowtie antennas with a negative-tone PMMA dot at different locations. Raman measurements were performed with *x*- and *y*-polarization directions, corresponding to the polarization directions illustrated in Figure 5.3(a, b). A 532 nm CW excitation wavelength was used to excite the LSPR of the Al structures. The laser was focused on a bowtie nanoantenna using a 100 $\times$ (0.90 NA) objective. The beam diameter was calculated as 720 nm ($1.22 \lambda/\text{NA}$) and a laser power of 2.6 mW was measured at the focal point. The Raman spectrum was acquired using a point exposure and an integration time of 5 s. The measurement was repeated and Raman spectra with pronounced fingerprints were used to plot the graphs.

As described in Chapter 4, negative-tone PMMA exhibits graphitic properties as observed in Raman fingerprints. Figure 5.3(c) shows Raman spectra of Al antenna with a negative-tone PMMA dot. The spectra were obtained using a 532 nm CW laser polarized along the *x*-axis. The prominent Raman peaks at around 1350 cm^{-1} and 1588 cm^{-1} , corresponding to D- and G-bands appear when a negative-tone PMMA dot was located within the gap. In contrast, Raman intensities of D- and G-bands obtained from an Al bowtie with a negative-tone PMMA dot at the corner and edge are much lower.

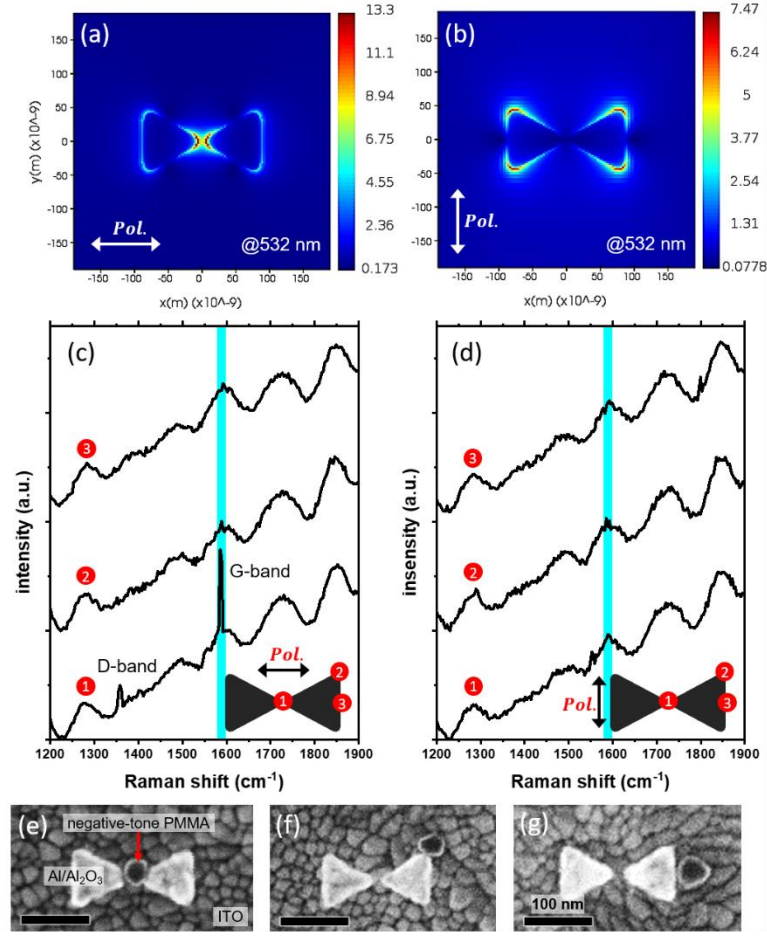


Figure 5.3 Electric field distribution maps of a single Al bowtie nanoantenna simulated using FDTD method. Raman spectra of Al bowties with negative-tone PMMA deposited at different locations and SEM images of the related structures.

(a, b) Near-field distribution maps of a single Al bowtie made of 15 nm separated equilateral triangles of 85 nm side length and 20 nm thickness, on an ITO-coated glass substrate, calculated using FDTD method, when illuminated by light at 532 nm with different polarization directions, indicated by the white arrows. The electric field strength is in the units of [V/m]. (c, d) Raman spectra of Al bowties/negative-tone PMMA dots at different locations, indicated by the red circles, when measured using 532 nm CW laser polarized parallel and perpendicular to the connecting axis of the bowties (see the insets). D- and G-bands appear with high Raman intensities when the negative-tone PMMA dot is located in the central gap and is excited by the laser polarized parallel to the connecting axis of the bowtie, correlating with the maximum field intensity calculated by FDTD. Spectra are scaled and shifted for clarity. (e-g) SEM images of a single Al bowtie with a negative-tone PMMA dot at the central gap, corner, and edge, respectively.

In Figure 5.3(d), Raman fingerprints for D- and G-bands are relatively low and are not significantly larger than background signals. Nevertheless, among these spectra, the G-band observed for Al antenna with a negative-tone PMMA dot at the corner has a higher Raman intensity compared to the background spectra.

The intensities of the G-band (indicated by the solid vertical cyan-coloured line in Figure 5.3(c, d)) in the Raman spectra for single Al bowties with a negative-tone PMMA dot located at different positions were compared. The difference in Raman intensities was compared with the near-field intensities calculated from FDTD simulations. When the antenna is excited by the laser polarized along the x-axis, the maximum field enhancement occurs in the gap region, causing the Raman modes of the nanoscale probe to be enhanced, resulting in the sharp G-peak in the Raman spectrum. Similar results are observed in the Raman spectrum when a negative tone dot was located at the corner of the bowtie and was excited by light polarized along the y-axis. The G-peak can be identified, however, the intensity is much lower than the previous case because the enhanced field intensity observed at the corner is expected to be three times lower than that in the central gap ($|E|^2 = 60$ vs 180).

5.1.6 SERS enhancement factor

5.1.6.1 Theory

Resonance Raman scattering is typically weak due to the small scattering cross-section of analyte molecules. However, in surface-enhanced Raman scattering (SERS), the signals of Raman scattering can be amplified by placing probe molecules near metallic nanostructures. SERS enables single-molecule detection and can be used to determine the enhancement factor (EF). Two mechanisms that give rise to enhancement in Raman scattering have been widely proposed in the literature including: (1) the electromagnetic (EM) enhancement due to plasmonic effects^{143,144} and; (2) chemical enhancement that involves the excitation of charge transfer between the analyte molecules adsorbing on the surface of the metal and metallic nanostructures.^{145–147} In this context, only EM enhancement will be discussed in detail.

In electromagnetic (EM) enhancement, the incident light (laser) excites the localised surface plasmon resonances of the metal, giving rise to concentrated light

(EF_{ext}) on the surface of the metal that subsequently enhances Raman scattering fields (EF_{scat}). The total EM enhancement factor (EF) can be expressed in equation 5.1.

$$EF = EF_{\text{ext}} \times EF_{\text{scat}} = \frac{|E_{\text{SPR}}(\omega)|^2}{|E_0|^2} \times \frac{|E_{\text{SPR}}(\omega - \omega_s)|^2}{|E_0|^2} \quad 5.1$$

Where ω is the frequency of the incident light and ω_s refers to the frequency due to Stokes-shifted Raman scattering. E_{SPR} is the enhanced electric near-field around the surface of the metal. E_0 is the electric field of the incident light. For simplicity, in most calculations, E_0 is set to one. Because EF_{ext} and EF_{scat} are approximately the same. Therefore, equation 5.1 can be simplified as:

$$EF = |E_{\text{SPR}}|^4 \quad 5.2$$

Equation 5.2 is a more popular form that is used to calculate the SERS enhancement factor.^{143,148} The EF can greatly be enhanced by many orders of magnitude when SERS substrates/nanostructures possess surface plasmon resonances matching the frequency of the excitation laser.

In experimental practice, the EF for a single molecule of an analyte can be calculated from the ratio between SERS and normal Raman scattering normalized by the number of probe molecules. The correlation¹³⁵ can be expressed as:

$$EF = \frac{I_{\text{SERS}}}{I_{\text{NRS}}} \times \frac{N_{\text{NRS}}}{N_{\text{SERS}}} \quad 5.3$$

Where I_{SERS} and I_{NRS} are the intensities of SERS and normal Raman scattering, respectively. N_{SERS} is the number of probe molecules located in the vicinity of LSPRs of the SERS nanostructures. N_{NRS} refers to the number of probe molecules in the volume excited by the incident laser used in the normal Raman scattering measurements *i.e.* in the absence of plasmonic nanoantennas.

5.1.6.2 Experimental results

To determine the SERS enhancement factor as expressed in equation 5.3, it is important to acquire Raman intensities for the negative-tone PMMA taken on (I_{SERS}) and off (I_{NRS}) the bowtie nanoantenna site. These intensities can be calculated from the area under the peak intensity at a wavenumber of interest from a Raman spectrum. The number of molecules of negative-tone PMMA dots on and off the bowtie antenna site is defined as N_{SERS} and N_{NRS} , respectively.

A normal Raman scattering spectrum was acquired from a square array of negative-tone PMMA dots with a period of 380 nm, fabricated using EBL with a high electron dose of 180 [mC/cm²]. The dots were deposited on an ITO-coated glass substrate away from Al bowtie antenna site. An average surface area of the dots was calculated using image processing software – ImageJ. Figure 5.4 compares the structures of the dots before and after image processing. The average result of the top surface area calculated for 15 dots was $(3.02 \pm 0.13) \times 10^4$ nm².

For a fair comparison, an average top surface area of negative-tone PMMA dots deposited on the Al antenna site was also calculated using image processing while the circularity was set between 0.75 and 1 in order to remove interferences from the grains of the ITO substrate, thus improving the accuracy of the measurement. Image processing for calculation of the surface area of the dots is illustrated in Figure 5.5. For statistical purposes, 6 dots were employed to calculate the top surface area. The average result was statistically measured $(5.03 \pm 1.78) \times 10^2$ nm².

To calculate N_{SERS} and N_{NRS} , it is safe to consider only the volume of the nanoscale probe contained within the volume (a cylindrical shape) of the laser spot size. The 532 nm laser was focused on the sample by a 100× objective with NA = 0.9 to a diffraction-limited spot with a lateral diameter $d = 1.22\lambda/NA \approx 720$ nm. The depth of the cylindrical volume of the laser was determined as a thickness of PMMA which is 42 nm (measured by an ellipsometer on a silicon substrate). Considering the cylindrical volume of these two parameters, at least 5 negative-tone PMMA dots on areas of the substrate far from the Al antenna site were detected for the normal Raman scattering measurement (see Figure 5.4). Therefore, the volume of negative-tone PMMA dots without Al nanoantenna (V_{NRS}) contained in the laser volume is $(6.34 \pm 0.05) \times 10^6$ nm³.

To determine the total volume of negative-tone PMMA on the antenna site (V_{SERS}) within the volume of the laser spot, we did a careful analysis based on the Gaussian distribution of a laser spot. Figure 5.6 illustrates a spherical Gaussian beam of a 532 nm laser spot. For an actual beam diameter of 720 nm, the intensity of the laser is accounted for $1/e^2 = 0.135$ of the intensity maxima.¹⁴⁹ This means that regions illuminated by the edges of the laser beam can contribute less to the Raman signals. Therefore, by considering this condition together with the perfect alignment of the step size in Raman measurements, a single Al bowtie nanoantenna with a nanoscale probe for each measurement was used for calculating V_{SERS} . Because the G-band can be detected when the dot is located in the central gap of the Al bowtie nanoantenna. Therefore the dimensions of the dots in the central gap of Al bowties were used in the calculations. The average volume of negative-tone PMMA dots (V_{SERS}) located in the central gap of Al bowtie antennas is calculated to be $(2.11 \pm 0.75) \times 10^4 \text{ nm}^3$.

To calculate the number of probe molecules on- and off-antenna site, in most studies, a solution-based analyte is typically used. Therefore, chemical properties including the Avogadro's constant, packing density, molecular weight, and the volume (for normal Raman scattering) or the surface area (for SERS) of the analyte are required. However, in this study, the analyte is in the solid phase and is specifically located in the vicinity where the LSPR exists and not only on the surface of the antennas. Therefore, equation 5.3 can be simplified as:

$$EF = \frac{I_{SERS}}{I_{NRS}} \times \frac{V_{NRS}}{V_{SERS}} \quad 5.4$$

I_{SERS} and I_{NRS} were calculated from the integrated areas under the G-peak (centred at around 1588 cm^{-1}) in the Raman spectra, as illustrated in Figure 5.7(a) and (b), respectively. To exclude background signals, the peak tails were in the range of $1580\text{-}1600 \text{ cm}^{-1}$ (*i.e.* assigned to the G-mode of graphitic materials).^{115,124,150}

Detailed calculations of the Raman intensities and the calculation of the enhancement factor with the propagation of uncertainty are provided in Figure A-6, Appendix A, page XXII. The EF based on equation 5.4 is $(0.55 \pm 0.11) \times 10^3$.

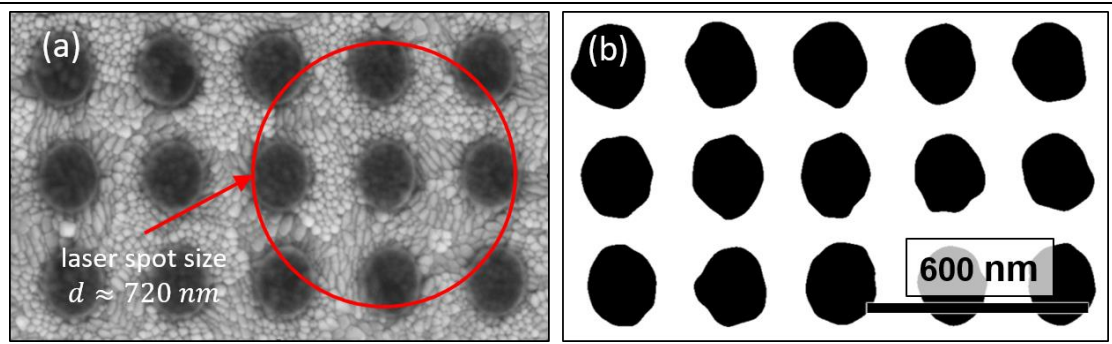


Figure 5.4 SEM image of negative-tone PMMA dots on ITO substrate (off Al bowtie nanoantenna site) and an output of the image processing obtained from the SEM image.

Image processing and statistical analysis of the surface area of negative-tone PMMA dots were carried out using software – ImageJ. The average result of the top surface area of the fifteen dots is $(3.02 \pm 0.13) \times 10^4 \text{ nm}^2$. The maximum number of PMMA dots contained in the volume of the laser spot (indicated by the red open circle) is approximately 5.

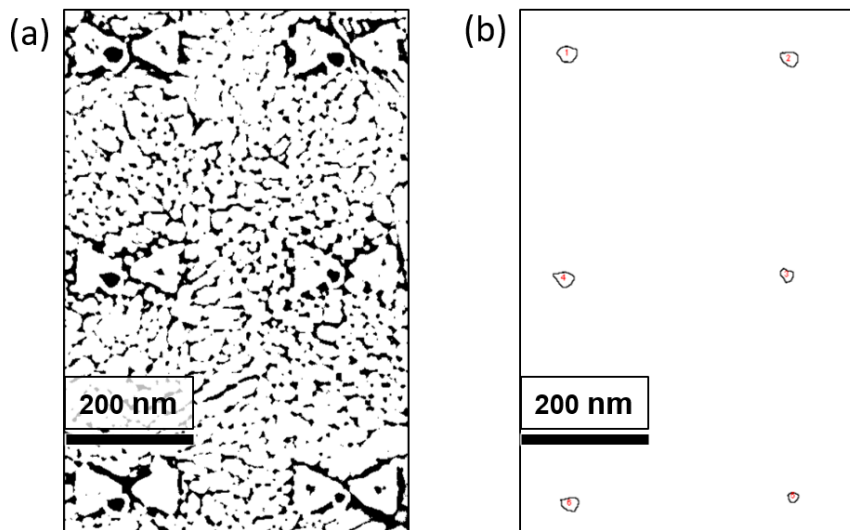


Figure 5.5 Images illustrating before and after image processing for calculating surface area of negative-tone PMMA dots located on the antenna site.

The image processing and statistical analysis of the surface area of negative-tone PMMA dots were carried out using software – ImageJ. The circularity of the dots was set from 0.75-1 to eliminate unrelated particles such as grains of ITO. The average area of the six dots is calculated to be $(5.03 \pm 1.78) \times 10^2 \text{ nm}^2$.

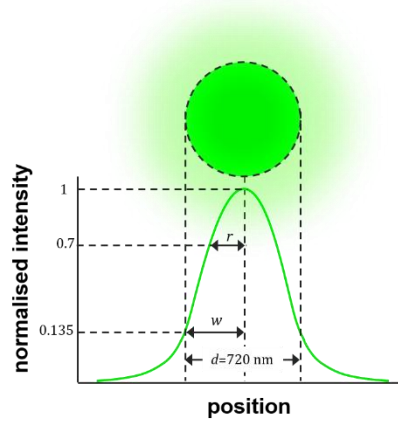


Figure 5.6 Gaussian distribution of a laser spot

The beam diameter (d) of a laser is defined as the location where the intensity is 13.5% of the maximum value.

It should be noted that the enhancement factor of $(0.55 \pm 0.11) \times 10^3$ was experimentally acquired for a single Al bowtie antenna where the field enhancement occurs in the central gap. The experimental EF is smaller than the EF obtained from the theoretical calculations (*i.e.* $|E|^4$) which can range from (0.63×10^3) to (2.86×10^4) , relatively depending on the positions in the plasmonic hotspots, as indicated in the colour bar of the electric field strength in Figure 5.3.

The relatively large error reflects various uncertainties. For example, there may be a spectral mismatch in which the centre of the laser spot was not well aligned to the centre of the Al bowtie antenna. Such mismatch can result in a decrease in laser intensity which subsequently reduces the enhancement factor.

The locations where the negative-tone PMMA dots were deposited can also cause the variation in Raman scattering intensities. Since the average diameter of the dots located in the central gap of Al bowties was measured (25 ± 5) nm, the ultimate volume for a dot can then occupy the cylindrical volume of the gap, whose diameter was measured (17 ± 3) nm, where the maximum field enhancement exists. As a consequence, the Raman scattering intensities obtained from the experiment are smaller than the Raman scattering intensities from the simulation results.

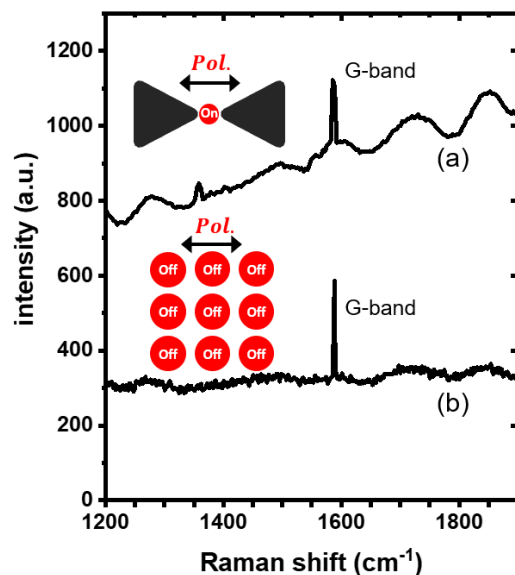


Figure 5.7 SERS and normal Raman scattering spectra.

Raman spectra were acquired from (a) on and (b) off Al bowtie antenna samples with the corresponding layouts of the experimental configuration. The measurements were carried out when the laser was polarized along the connecting axis of the bowtie (indicated by the arrows).

In Figure 5.7, although the Raman intensity for the G-band obtained from the off-nanoantenna site (Figure 5.7(b)) has a signal-to-noise ratio greater than that obtained from the on-nanoantenna site (Figure 5.7(a)), the background signals *e.g.* multiple peaks at 1276 cm^{-1} , 1490 cm^{-1} , and 1724 cm^{-1} that may be originated from residuals of PMMA^{151,152} can clearly be identified using the on-nanoantenna substrate. Such experimental results confirm the role of Al bowtie nanoantennas as a sensitive tool for SERS applications that require the excitation wavelength in the visible region of the spectrum.

5.1.7 Conclusion

In this work, we demonstrated the possibility to probe the locations of hotspots around a single Al bowtie nanoantenna using Raman spectroscopy. The locations around an Al bowtie nanoantenna associated with different levels of electric near-field intensities were probed using a 532 nm CW laser together with negative-tone PMMA dots as an analyte being deposited at selective locations. The experimental results suggested that the highest

Raman intensity occurred when the analyte was located in the central gap of the Al bowtie nanoantenna, associating with the maximum field intensity observed in the simulations. The location in the hotspot has also confirmed to produce the enhancement factor as high as $(0.55 \pm 0.11) \times 10^3$, suggesting that an Al bowtie nanoantenna is an effective, sustainable, and low-cost SERS substrate for visible excitation wavelengths.

5.2 Designing Al plasmonics for sensing applications

5.2.1 Introduction

Metallic nanostructures have been widely exploited for biomedical and biosensing applications.¹⁵³ These applications take advantage of surface plasmon resonance bands and the enhanced electric near-fields due to the excitation of charge density oscillations by light. Biosensing applications can be classified into three main categories including surface-enhanced Raman scattering (SERS), refractive index (RI) biosensing, and surface-enhanced fluorescence (SEF).⁷⁵

5.2.1.1 Plasmonic sensing

In SERS applications, the confined sub-wavelength volume of light over the surface of metallic nanostructures can be used to amplify the Raman scattering of the nearby analyte down to a single-molecule level.

While SERS applications exploit the near-field enhancement and charge carrier injection mechanism¹⁵⁴, RI biosensing utilises the change in surface plasmon absorption bands to monitor biomolecules adsorbed on the metal surface. Because the LSPRs are typically excited at the interface between the metal and a dielectric, hence the maximum field intensity can be generated at the metal-dielectric interface, while the evanescent field penetrates both the adjacent media. The evanescent field is extremely sensitive to the refractive index of the dielectric near the metal surface. The changes in the refractive index of the local surrounding environment can alter the positions of the LSPR peaks. Such a vital feature enables real-time and label-free detection of biomolecules with known refractive indices adjacent to the metal surface.^{155–157}

Fluorescence-based sensing is very important in biological applications. Conventional biosensing that makes use of bare fluorophores suffers from a low rate of

fluorescence emission.^{71,158,159} However, the fluorescence rate can be improved through the use of plasmonic nanostructures. Increased absorption in fluorophores in the near-field of plasmonic nanoparticles can lead to enhancement in fluorescence rates and a decrease in molecular excited-state fluorescence lifetimes.

Although plasmonic nanostructures have shown great promise to improve performance for many biological sensing applications, they suffer from intrinsic optical losses including Landau damping that is caused by the interband and intraband excitations (absorption) and radiative loss. A number of strategies to suppress or mitigate losses have been proposed. These strategies include: (1) implementing highly-doped semiconductor nanocrystals as alternatives to conventional plasmonic noble metals¹⁶⁰; (2) innovating fabrication techniques for ultra-smooth metal surfaces with reduced losses^{50,161}; (3) employing a gain-medium to amplify the resonant emission of surface plasmons¹⁶²; and (4) using high-refractive-index dielectric resonators¹⁶³. However, these approaches rely on multiple steps and often make nanofabrication a cumbersome task.

The loss rate is associated with the spectral linewidth of the surface plasmon resonances. Individual metallic nanoantennas typically produce large resonance linewidths associated with short plasmon lifetimes due to non-radiative and radiative losses. Non-radiative damping can be reduced by the choice of metals while radiative loss can be mitigated by arranging metallic nanoantennas in a periodic lattice that supports SLRs. The origin of SLRs comes from the coupling of LSPRs of individual metallic nanoantenna (plasmonic mode) to in-plane orders of diffraction modes of the array (photonic mode) – known as *Rayleigh anomalies*. Such a hybrid mode results in ultra-narrow resonance linewidths which exhibit remarkably high-quality factor resonances.

5.2.1.2 Recent advancement in Al-based sensing with high Q factors

An ultra-narrow resonance linewidth down to 3 nm can be achieved using Ag and Au nanoantenna arrays.^{50,51,161,164} Au and Ag nanostructures have long been widely studied for biosensing applications. However, due to their optical and chemical properties, Au can only be tailored across the visible range, extending to the infrared regions of the spectrum, while Ag offers tunable LSPRs across the UV to NIR, yet suffers from

degradation due to sulfidation by sulfur compounds in the air which degrade plasmonic properties over time.

Al plasmonics has recently been developed in both fundamental studies as well as on-demand biosensing applications, towards low-cost, sustainable, and high performance. Nanoantenna arrays are open cavities that are easy to fabricate. Therefore, particular attention has been paid to designing and engineering Al structures and geometries.

Al nanodisks arranged in a hexagonal lattice fabricated on a stretchable substrate (polydimethylsiloxane: PDMS) have been reported to support SLRs with a narrow resonance linewidth as low as 5 nm over the entire visible wavelength range. Such a platform offers tunable and reversible plasmon resonances on a single system.⁵³ Another study has demonstrated that the narrow spectral resonance linewidth can be extended to the NIR range by thermally annealing Al nanodisks in a square lattice at a high temperature (620°C). The heating treatment resulted in increased grain sizes in Al, leading to the improvement of spectral linewidths from 14 nm to 4 nm while maintaining the same SLR peak in the NIR region.¹⁶¹

In addition to nanodisk arrays, other structural frameworks such as nanohole, nanoslit, nanostrip, and nanodisk arrays have been studied for sensing devices.^{51,165–169} In this work, we focus on Al bowtie nanoantenna arrays with varying periodic distances as a potential platform to support high-quality sensing. An ultra-narrow resonance linewidth down to 3 nm as well as multipolar resonances can be achieved with this platform. These remarkable features provide the opportunity for next-generation multifunctional devices that require multi-resonance transmission spectra with high Q factors.

5.2.2 Al nanoantenna arrays with tunable SLRs

Al bowtie nanoantenna arrays on an ITO-coated glass substrate were fabricated using the nanofabrication technique described in section 2.3. The same platform consisted of several arrays of Al bowtie nanoantennas. All arrays were separated by a distance of 50 μm to minimise the probability of interference of surface plasmon resonances between neighbouring arrays. Each array contained multiple Al bowtie nanoantennas arranged in a square lattice from 114×114 to 192×192 elements, to cover a square area of $50 \times 50 \mu\text{m}^2$.

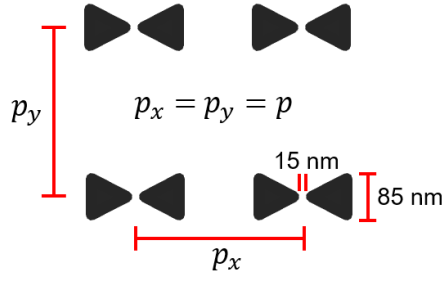
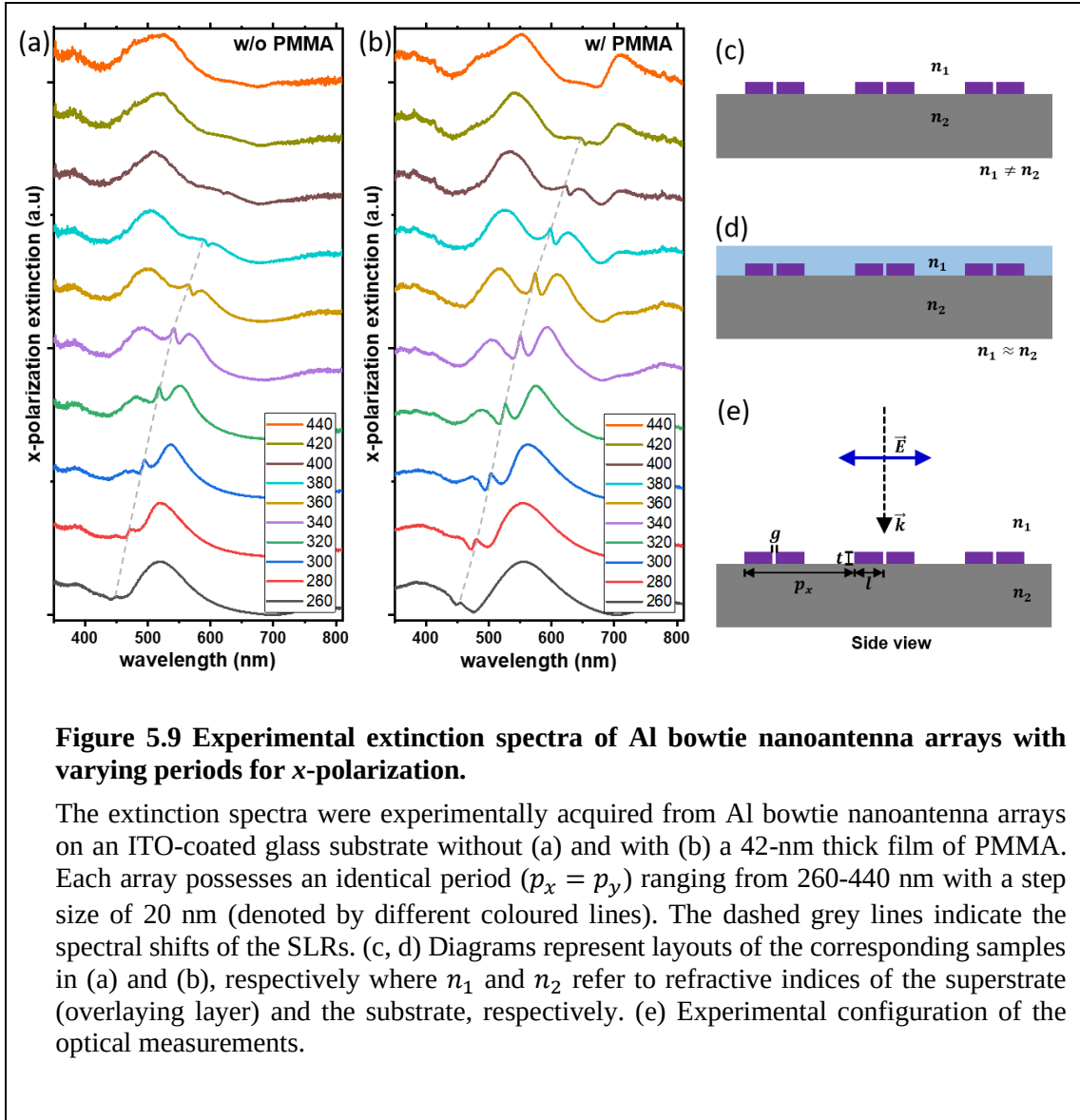


Figure 5.8 Structural arrangement of Al bowtie lattice array.

An Al bowtie nanoantenna possessed a side length of 85 nm, a central gap of 15 nm, and a thickness of 20 nm. The periodic distances along the x - and y -axes are defined as p_x and p_y , respectively. Each array had identical periodic distances $p_x = p_y$.

To study the effect of SLRs produced from Al bowtie structures, we considered a single Al bowtie (consisting of two tip-to-tip triangles with a gap of 15 nm, a side length of 85 nm, and a thickness of 20 nm) as a group of an individual nanoantenna. The antennas were designed to have equal periodic distances in the x - and y -directions, *i.e.* $p_x = p_y$, while each array had different periodic distances from one to another starting from 260 to 440 nm with a step size of 20 nm. The design layout of Al lattice arrays is demonstrated in Figure 5.8.

Figure 5.9(a) illustrates experimentally measured optical spectra of Al bowtie nanoantenna arrays with different periodic spacings on the asymmetric environment (*i.e.* the refractive index of the substrate (n_2) is not equal to the refractive index of the overlying layer (n_1)). Light incident perpendicular to the plane of the substrate with a polarization direction along the x -axis was employed in the optical measurements. For such a condition, SLR peaks can be observed in arrays having periodic distances from 260 to 400 nm. Narrow resonance linewidths (FWHM) can be identified for periods from 280 to 360 nm while the smallest spectral linewidth of 7 nm occurred for a period of 340 nm. In addition to the presence of SLRs that gives rise to narrow resonance linewidths, spectral shifts to longer wavelengths with respect to an increase in periodic spacings can be recognised.



To study the effect of the surrounding medium ($n_1 \approx n_2$) on the SLRs, we spin-coated a thin layer of PMMA (~ 40 nm) to cover the entire surface of the sample and measured optical responses of the nanoantenna arrays. As demonstrated in Figure 5.9(b), we discovered that in addition to the red-shift in the SLR peaks (~ 30 nm) the resonance linewidths narrowed and a small resonance linewidth of 6 nm can be achieved with an array period of 380 nm.

In the asymmetric environment in which $n_1 \neq n_2$, the radiation pattern in the overlying layer tends to be highly asymmetric with most of the scattered light in the substrate, leading to a weak angular overlap of diffracted orders. Contrastingly, in the

symmetric environment where $n_1 \approx n_2$, the radiation pattern is likely to be symmetric with most of the in-plane diffracted waves, resulting in a highly coupled mode which yields much sharper resonances compared to the asymmetric system.^{49,170} This is why setting an adapted lattice is necessary, yet not sufficient to observe the high Q factor resonance modes. Nonetheless, in many practical sensing applications, plasmonic sensors are exploited in liquid environments which possess a refractive index that can match the refractive index of the substrate.

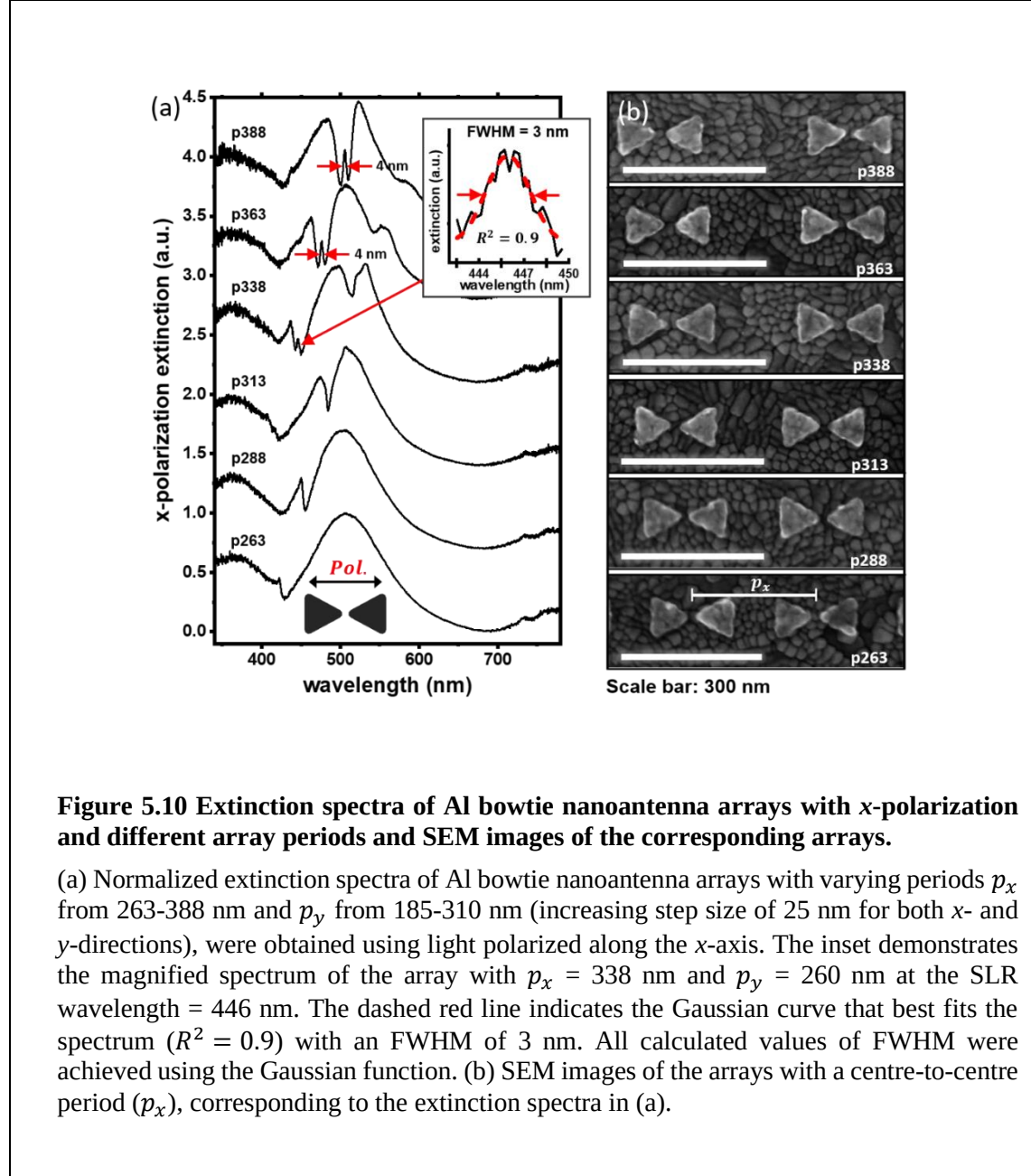
Al bowtie nanoantenna arrays in the symmetric system cannot only exhibit highly sharp resonance linewidths, but also offer multipolar plasmon resonances due to coupling modes of SLRs and LSPRs which cover the entire visible region of the spectrum. This phenomenon can be useful for next-generation multi-functional applications that require low-loss light-harvesting across the visible range such as biomedical sensing, surface-enhanced Raman spectroscopy on a single chip, and optical filters.¹⁶⁸

5.2.3 Al structures with ultra-narrow resonance linewidths

SLRs in Al bowtie nanoantenna arrays can be identified for periods between 260 and 400 nm. Therefore, we further investigated the presence of the SLRs in this periodic range. In this experiment, we varied edge-to-edge spacings in the arrays from 100-225 nm in the x - and y -directions, corresponding to periods of, p_x from 263-388 nm and p_y from 185-310 nm. The spacings were increased with a step size of 25 nm. Fabricated Al bowtie nanoantennas are shown in Figure 5.10(b).

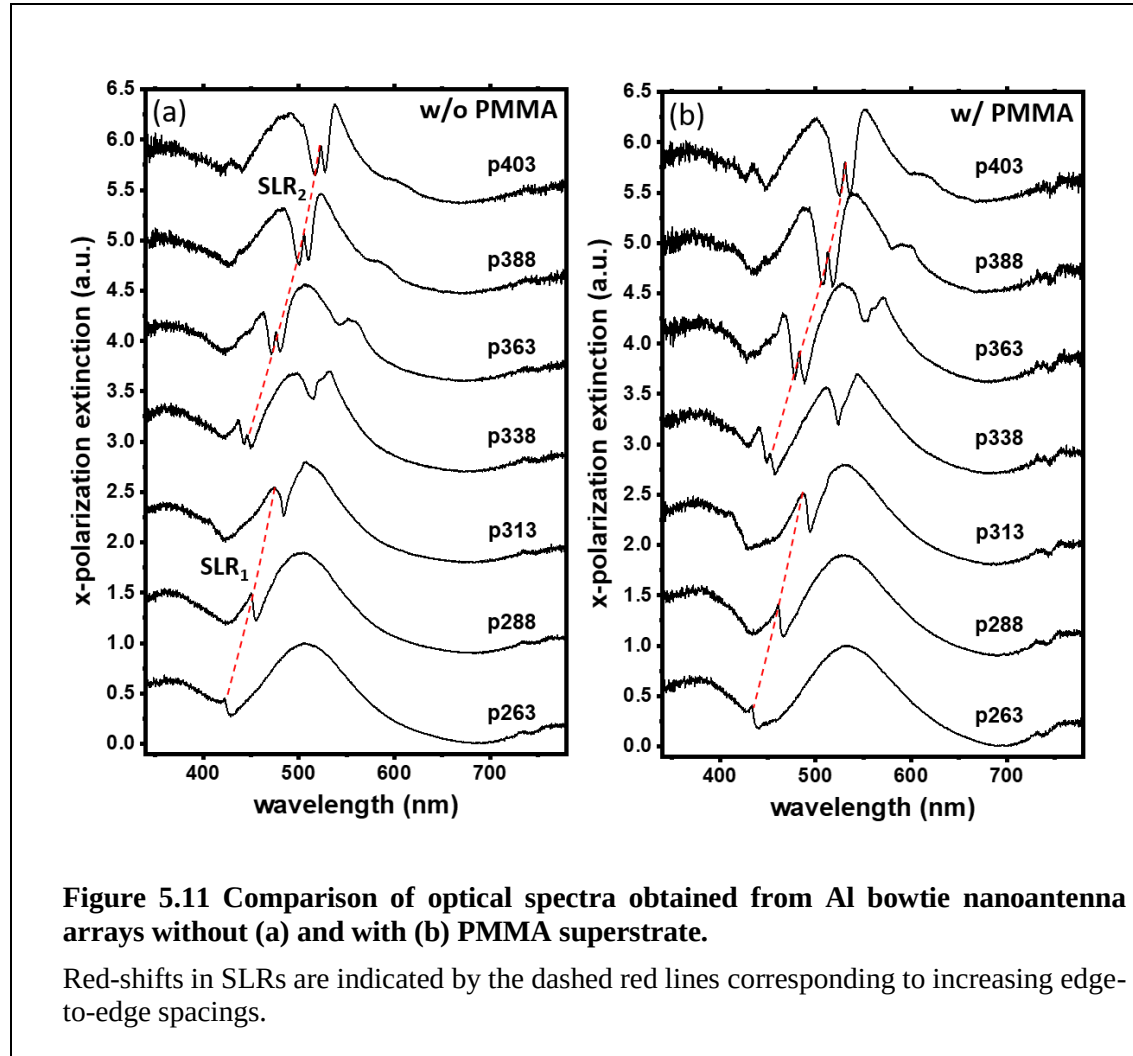
Figure 5.10(a) shows the experimental x -polarization extinction spectra of Al bowtie nanoantenna arrays with different edge-to-edge spacings, $p_x = 263$ -388 nm and $p_y = 185$ -310 nm (step size of 25 nm). For periods $p_x = 263$ -313 ($p_y = 185$ -235 nm), in the visible spectrum, two main peaks occur while the sharp peaks associated with SLRs are red-shifted as periods increase. For the periods $p_x = 338$ -388 nm ($p_y = 260$ -310 nm), the extinction spectra become complicated with the existence of multiple resonance peaks as a result of SLRs and LSPRs. However, for these periods, ultra-narrow resonance linewidths at FWHM (best fit to a Gaussian function) can be observed from 3.2-4.3 nm with the SLR peaks of 446, 476, 505 nm, respectively. The ultra-narrow spectral linewidth as low as 3 nm with the SLR peak of 446 nm associated

with the quality factor of ~ 150 (i.e. $446 \text{ nm} / 3 \text{ nm}$) in the asymmetric system ($n_1 \neq n_2$) is among the best reported for Al nanoantenna arrays in the UV to NIR region.^{53,161,171} Such a high-quality factor is much greater than the quality factors observed for isolated plasmonic nanoantennas which are in the order of 10, as demonstrated in Figure 1.7 in Chapter 1.



It should be noted that in this experiment, each array had periodic conditions where $p_x \neq p_y$, which are distinct from the conditions demonstrated in section 5.2.2. The

asymmetric periodic conditions, therefore, result in multiple resonance peaks in addition to non-consecutive shifts in SLR peaks when the period increased, p_x from 263-388 nm and p_y from 185-310 nm. The observed non-consecutive shifts in SLR peaks *i.e.* SLR₁ (with a Fano line-shape) and SLR₂ are indicated by the dashed red lines in Figure 5.11(a).



A 40-nm thick PMMA was deposited on the same sample to entirely cover Al bowtie nanoantenna arrays to produce a systematic system where the substrate refractive index matches closely to that of the overlying layer ($n_1 \approx n_2$). The measured x -polarization extinction spectra of the arrays are illustrated in Figure 5.11(b). The same effect *i.e.* non-consecutive shifts in SLR peaks (SLR₁ and SLR₂) can be observed in the systematic environment, as indicated by the dashed red lines. Although the high refractive

index of PMMA yields sharp lattice modes, the resonance linewidths (FWHM) associated with the periods $p_x = 338\text{-}388$ ($p_y = 260\text{-}310$ nm) remain the same *i.e.* ~ 4 nm, suggesting that for these periodic conditions ($p_x \neq p_y$), small resonance linewidths as low as 4 nm can be achieved in both asymmetric and symmetric platforms. The ultra-narrow resonance linewidth can also be tuned in the wavelength range from 445-523 nm for asymmetric system and 452-530 nm for the symmetric system. These spectral ranges are favourable to commonly used fluorophores in biosensing applications whose excitation wavelengths are in the UV to the visible region of the spectrum.^{71,75}

5.2.4 Conclusion

The SLR of Al bowtie nanoantenna arrays can be tuned across the visible region of the spectrum when the lattice periods arranged in the x - and y -directions are equal. By changing the local surrounding environment of the superstrate to relatively match optical properties of the substrate, SLR peaks can be improved, resulting in narrower resonance linewidths. This advantage allows Al bowtie nanoantenna arrays to be a sensitive platform for biosensing applications that particularly work in high refractive index environments.

When arranging Al bowtie nanoantennas in a square lattice in which the period distances in the x - and y -directions are different (*i.e.* edge-to-edge spacings are equal), ultra-narrow resonance linewidths as low as 4 nm can be achieved in the wavelength range that favours the excitation wavelengths of most commonly used fluorophores.^{71,75} With such engineering conditions, it suggests that Al bowtie nanoantenna arrays can potentially be a sensitive platform that offers widespread use in surface-enhanced fluorescence applications.

Moreover, it is evident that the ultra-narrow resonance bandwidth as low as 3 nm can be achieved in this system. To the best of our knowledge, Al bowtie nanoantenna arrays fabricated on a rigid substrate can produce a 3-nm ultra-narrow resonance linewidth, associated with a high Q factor of ~ 150 in the visible range of the spectrum, comparable to the best values reported using a flexible substrate.^{53,171} The achievable 3-nm resonance linewidth on a rigid substrate in addition to the presence of multipolar plasmon resonances can potentially be exploited for sustainable multi-functional devices that require multi-resonance modes.

Aluminium was previously considered an “*inferior*” plasmonic material in the visible regime compared to gold and silver²⁷. However, when arranged in a periodic array with rigorous conditions, particularly Al bowtie nanoantenna arrays in a square lattice could suppress radiative losses of the structures, yielding highly sharp and narrow resonance linewidths with a tunable wavelength, especially in the visible region. This remarkable property of Al bowtie nanoantenna arrays may offer a promising approach for cost-effective and sustainable ultrasensitive label-free biosensing applications.^{50,75}

CHAPTER 6

Germanium Growth Induced by Localised Surface Plasmon Resonance

6.1 Introduction

Semiconductor nanocrystals or quantum dots (QDs) have attracted much attention due to their size-dependent optical and electrical properties, which potentially have a wide range of applications in areas such as biomedical sensing, bioimaging, nanoscale light sources, energy storage and conversion, and field-effect transistors.¹⁷² Commonly known QD materials such as CdSe, GaAs, PbS, and PbSe have been reported to offer a broad range of spectral absorption, which enables facile spectral tuning, high luminescence quantum yields, short fluorescence lifetimes and exceptional chemical stability. Nevertheless, concerns regarding their hazardous chemical properties and toxicity to living organisms make them less favourable for biomedical applications.¹⁷³ Therefore, developing alternative QDs with low toxicity while offering beneficial optical and electrical properties is an intriguing topic in the research field.

Ge nanocrystals with size-dependent optical and electrical properties have been studied for nearly four decades.¹⁷⁴ Ge nanocrystals have advantages over classical compound semiconductor nanocrystals in terms of low toxicity and biocompatibility. Typically, Ge nanocrystals can be synthesized by physical or chemical methods. However, in most cases, extreme pressures and temperatures together with the use of reducing agents are required, hence costly and not environmentally friendly.

In this chapter, the growth of Ge nanocrystals driven by surface plasmons in Au nanoantennas with distinct shapes and geometries was studied. Formation of Ge nanocrystals from diphenylgermane was observed on Au nanoantennas where localised surface plasmon resonances were present.

6.1.1 Germanium nanocrystals

In a bulk semiconductor, atomic orbitals overlap resulting in continuous band structures *i.e.* the valence band and conduction band. For such materials, excitons (electron-hole pairs) can be generated when an electron is excited from the valence band to the conduction band when external energy greater than the bandgap energy is supplied. During this process, the vacancy in the valence band leads to the generation of a positively charged hole.

However, if the size of the semiconductor decreases, the number of atoms in the material is reduced, resulting in the emergence of discrete energy levels and an increase in the bandgap. In this case, the energy required to excite an exciton is larger than in the bulk material. This phenomenon is known as “*the quantum confinement effect*” and occurs when the size of the semiconductor is close to or below the exciton Bohr radius. The exciton Bohr radius can be approximated using equation 6.1.

$$r_B = \frac{\hbar^2 \epsilon_r}{e^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \quad 6.1$$

Where r_B is exciton Bohr radius, $\hbar$ is the reduced Planck's constant, ϵ_r is the relative permittivity of the material, e is the charge of the electron, while m_e^* and m_h^* represent the effective masses of the electron and hole, respectively.

Considering equation 6.1, it can be seen that ϵ_r , m_e^* , and m_h^* play a vital role in determining the exciton Bohr radius. Ge has a higher value of ϵ_r and lower values of m_e^* and m_h^* , compared to Si. The most reportedly calculated exciton Bohr radius for Ge is 24.3 nm which is much larger than the well-known exciton Bohr radius of Si (4.5 nm).¹⁷³ The large exciton Bohr radius of Ge allows the observation of quantum confinement effects in Ge nanomaterials at larger dimensions than for the case of Si.

6.1.2 Synthesis and fabrication of germanium nanostructures by light

Ge nanocrystals can be synthesized by either physical or chemical approaches. Chemical synthesis is commonly used to produce Ge nanocrystals because it holds great promise for scalable commercial production. However, hostile synthesis conditions such as elevated temperatures and the use of strong reducing agents are required to facilitate the growth of Ge nanocrystals.¹⁷³ A number of physical synthesis methods to produce Ge nanocrystals have also been reported, including laser ablation, sputtering, chemical vapour deposition, gas-phase pyrolysis, plasma techniques, etching, and ion implantation followed by high-temperature annealing.^{173,175–177}

Both chemical and physical approaches often involve mechanisms associated with phase change in which a precursor in either liquid or vapour phase dissociates at a catalyst to promote nucleation of Ge nanocrystals. These synthetic approaches include solution-liquid-solid (SLS), supercritical fluid-liquid-solid (SFLS), vapour-liquid-solid (VLS) and vapour-solid-solid (VSS) methods.

Many studies^{178–180} have shown that the use of metal nanoparticles as seeds (catalysts) can promote scalable production of Ge nanocrystals through the formation of a eutectic of the metal and the semiconductor. For example, in VLS, an Au catalyst is heated to form a liquid phase which can then rapidly adsorb a vapour phase precursor to supersaturation levels, thus mediating the growth of Ge nanowires. The idea under the growth of Ge nanowires is to heat the entire sample to the Ge:Au eutectic temperature of $\sim 360^{\circ}\text{C}$.¹⁷⁹ This mechanism not only limits the choice of substrates and device integration routes that support high operating temperatures, but also restricts a precise arrangement of the growth of semiconductor nanocrystals at exact locations.

Advanced applications such as nanolasers for ultra-fast optoelectronics require hybrid systems based on plasmonic antennas and semiconductor nanocrystals. To efficiently obtain a strong near-field coupling of a semiconductor nano-emitter to the antenna mode, it is crucial to place the nano-emitter at a position of high electric field intensity *i.e.* plasmonic hotspot. Several approaches have been attempted to position semiconductor nano-emitters at local hotspots. One technique utilised an atomic force microscope to selectively move Au nanoparticles from a substrate surface to the targeted locations of emitters.¹⁸¹ While another technique is based on a stochastic approach where

semiconductor nano-emitters are dispersed on a large number of Au nanoparticles and subsequently coupled emitter/antenna pairs are identified.¹⁵⁸ However, these techniques face limitations in terms of low reliability, poor reproducibility, and can be cost- and time-consuming. With these restrictions, the fabrication of semiconductor nano-emitters at plasmonic hotspots with high accuracy remains challenging, yet is an ongoing topic.

Plasmon-induced chemical vapour deposition (CVD) has recently been developed by the Baumberg group to selectively control the growth of Ge nanowires on individual Au nanoparticles.¹⁷⁸ The study showed that by using a laser that is frequency matched to the surface plasmon resonance of an individual Au catalyst nanoparticle, selective growth of a Ge nanowire due to local heating can be achieved, even at low laser power (0.6 mW). In contrast, when using off-resonant laser wavelengths, much higher laser power was needed to trigger the catalytic Ge growth. This technique highlights the capability to selectively control Ge growth at specific locations based on the near-field enhancement of plasmonic Au nanoantennas.

In this chapter, we studied laser-driven catalytic Ge growth on Au bowtie and Au rod dimer nanoantenna arrays in the liquid system. The laser illumination with a wavelength matching that of the surface plasmon resonance of Au nanoantennas was used to trigger the catalytic process. Nucleation of Ge nanocrystals locally on Au nanoantennas was observed when nanoantennas were optically excited at the frequency of an LSPR and the synthesized Ge was analysed using Raman and EDX spectroscopies.

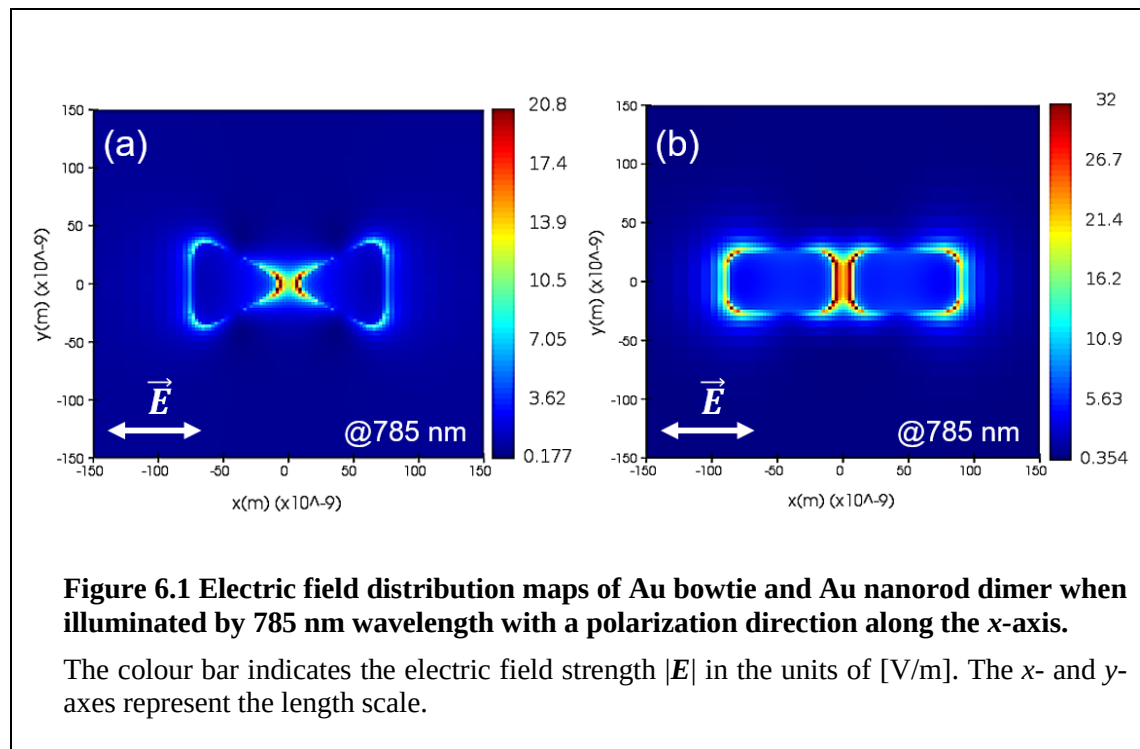
6.2 Optical responses of Au nanoantennas

Au nanoantennas with two distinct geometries including bowties and rod dimers were designed to have an LSPR close to 785 nm matching the excitation wavelength. FDTD simulations were performed to determine suitable geometries and dimensions for the nanoantennas. An Au bowtie consisted of two opposing equilateral triangles with a thickness of 20 nm, a side length of 70 nm, and a tip-to-tip separation distance of 15 nm. An Au rod dimer was composed of two identical nanorods having a width of 50 nm, a length of 80 nm, a thickness of 20 nm, and a central gap of 15 nm.

These individual nanoantennas were arranged with an equal separation distance of 250 nm for both vertical and horizontal directions to perform multiple antennas in a

square array of $50\ \mu\text{m} \times 50\ \mu\text{m}$. These structures were simulated such that the top surfaces were exposed to air and the bottom surfaces were on a 100-nm thick ITO layer on a bulk glass substrate. An additional adhesion layer of 1-nm thick Ti was also inserted between Au and ITO.

To minimise the simulation time, a unit cell of a single nanoantenna was calculated. Periodic boundary conditions were implemented for the x - and y -directions while perfectly matched layers (PML) were implemented at the upper and lower sides of the simulation cell in the z -direction. A plane wave light source with a spectral range of 400-850 nm was launched from the air above a unit cell of the nanoantennas at normal incidence following the experimental configuration, with the polarization along the x -axis. A mesh unit of $2.5 \times 2.5 \times 2.5\ \text{nm}^3$ was used in the simulations to generate the electric field distribution maps. The refractive index of ITO was taken from material data available from Sopra Material Database⁹⁸ which provided the best fit to the experimental results. The optical properties of other materials can be found in section 3.1.1.2.



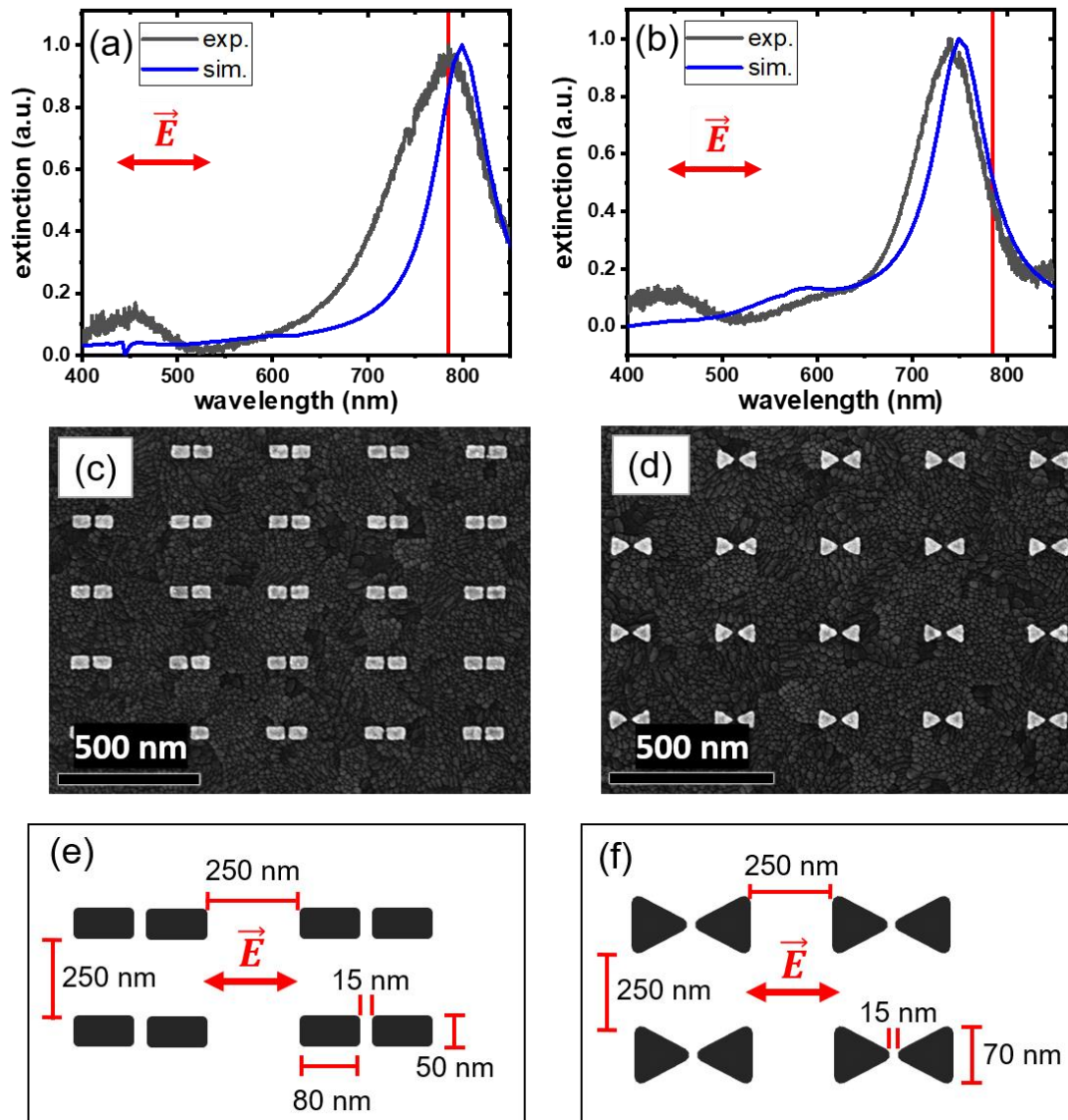


Figure 6.2 Calculated and experimental optical spectra of Au nanorod dimer and Au bowtie nanoantenna arrays and their corresponding topography and arrangement diagram.

Simulated (blue line) and experimental (grey line) extinction spectra of (a) Au nanorod dimer array and (b) Au bowtie nanoantenna array collected using x-polarized light (indicated by the red arrows). The red solid lines indicate the wavelength at 785 nm used in the Raman system. The spectra were acquired before SEM imaging (shown in c, d) in order to eliminate spectral shifts due to carbon residues deposited during SEM. (e, f) Diagrams of 2D pattern of Au rod dimer array and Au bowtie nanoantenna array, respectively.

Figure 6.1(a) and (b) show electric field distribution maps for an Au bowtie and an Au rod dimer, respectively when illuminated by a 785 nm excitation wavelength along the x-polarization direction. The maximum field intensities of both structures occur in the gap while the rod dimer exhibits a greater maximum field intensity ($|E|^2 \approx 1000$) compared to that of the bowtie ($|E|^2 \approx 430$). The difference in the electric field intensities correlates well with the optical spectra presented in Figure 6.2(a, b) where Au rod dimers are resonant at 785 nm and Au bowtie antennas are a slightly off-resonance. The enhanced electric fields in narrow gaps or at sharp features, known as hotspots, are regions of interest and can locally promote decomposition of diphenylgermane to produce Ge nanocrystals.

In Figure 6.2(a, b), the calculated extinction spectra (blue) of Au nanorod dimer and Au bowtie nanoantenna arrays are compared with the experimental extinction spectra (grey). Both calculated and experimental spectra of Au nanorod dimer array have a resonance peak close to 785 nm (indicated by the vertical red line) whereas those of Au bowtie nanoantenna array have a resonance at a slightly lower wavelength. The similar features for Au bowtie nanoantenna array are also seen in the simulations in which diphenylgermane (DPG) liquid precursor ($n = 1.6$)¹⁸² was added (see Figure A-7(a, b) in Appendix A), following the experimental configuration (see Figure 6.3). Although multiple plasmon peaks are observed when the top surfaces of Au bowtie nanoantenna arrays are surrounded in the uniform liquid precursor, one of the peaks appears close to 785 nm. The locations of hotspots around Au nanoantennas with the presence of DPG precursor was also investigated. According to the electric field distribution maps based on this condition, the locations of hotspots were similar to those observed in air *i.e.* in the gaps and around curvatures. Details of the simulations are provided in Appendix A, Figure A-7(c, d).

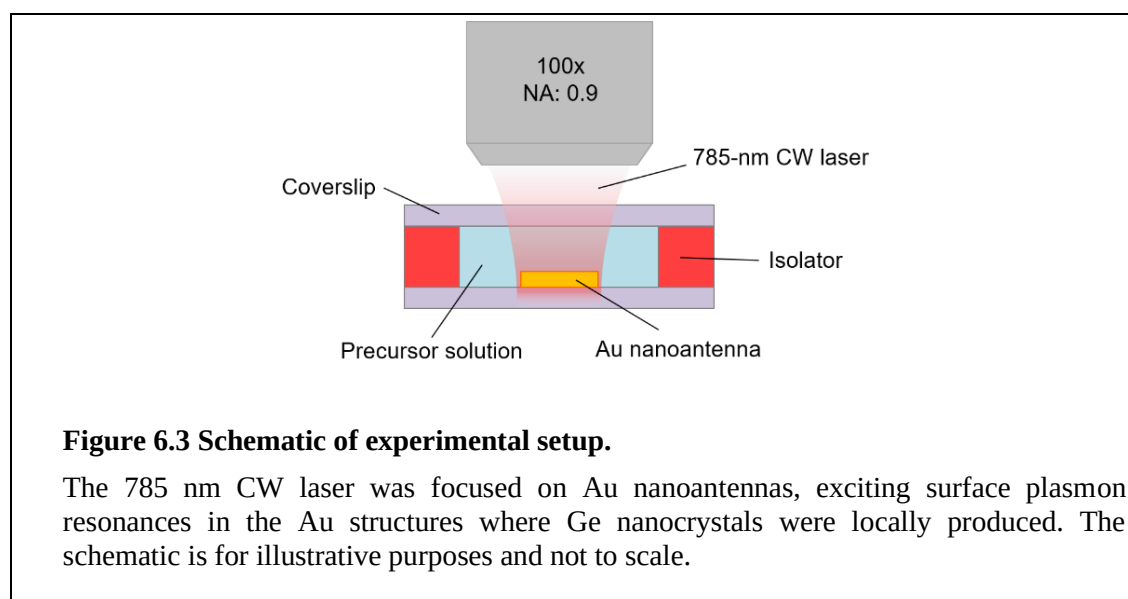
In Figure 6.2(b), Au bowtie nanoantenna arrays possess a plasmon resonance peak centred at ~ 750 nm in the experiment (~ 740 nm in the simulation) while half of the optical peak has an intensity overlapping with the excitation wavelength at 785 nm. When particularly considering plasmon resonance mode, Au bowtie nanoantennas with these dimensions are less ideal for the 785 nm excitation. However, because Au bowtie nanoantennas possess multiple sharp apexes. Sharp features of metals have been demonstrated to produce an extra enhancement over the plasmon resonance background.

The phenomenon arises from a non-resonant *lightning-rod effect* which can occur at sharp terminations regardless of excitation wavelengths.^{183,184} For this reason, it is worth investigating the influence of the lightning-rod effect, though with low responses of the LSPR effect at the 785 nm excitation wavelength.

Au bowtie and Au rod dimer nanoantennas were fabricated on an ITO-coated glass substrate by EBL followed by metal evaporation (as described in section 2.3.1). SEM micrographs of Au nanoantenna arrays and their designed dimensions are illustrated in Figure 6.2(c-f). Au rod dimers had measured length and width of (78 ± 2) nm and (56 ± 3) nm, respectively with a gap of (20 ± 1) nm while Au bowtie nanoantennas had a side length of (70 ± 1) nm with a gap of (18 ± 3) nm. These nanoantennas were arranged in a square array manner with an edge-to-edge spacing measured (249 ± 3) nm for Au rod dimer arrays and (251 ± 6) nm for Au bowtie arrays. Detailed calculations can be found in Appendix A, Table A-4.

6.3 Laser-driven catalytic Ge growth on Au nanoantennas

Laser irradiation and selective absorption based on the near-field enhancement of Au nanoantennas were used to locally heat and trigger chemical reactions on a germanium precursor supported catalyst Au nanoantennas in a liquid system. The experiment was carried out under ambient conditions *i.e.* at room temperature and atmospheric pressure.



A sample consisting of arrays of Au bowtie and Au rod dimer nanoantennas fabricated on an ITO-coated glass substrate was immersed in a liquid-phase diphenylgermane ($\text{Ge}(\text{C}_6\text{H}_5)_2\text{H}_2$) precursor in a close system. A configuration of the experimental setup is illustrated in Figure 6.3.

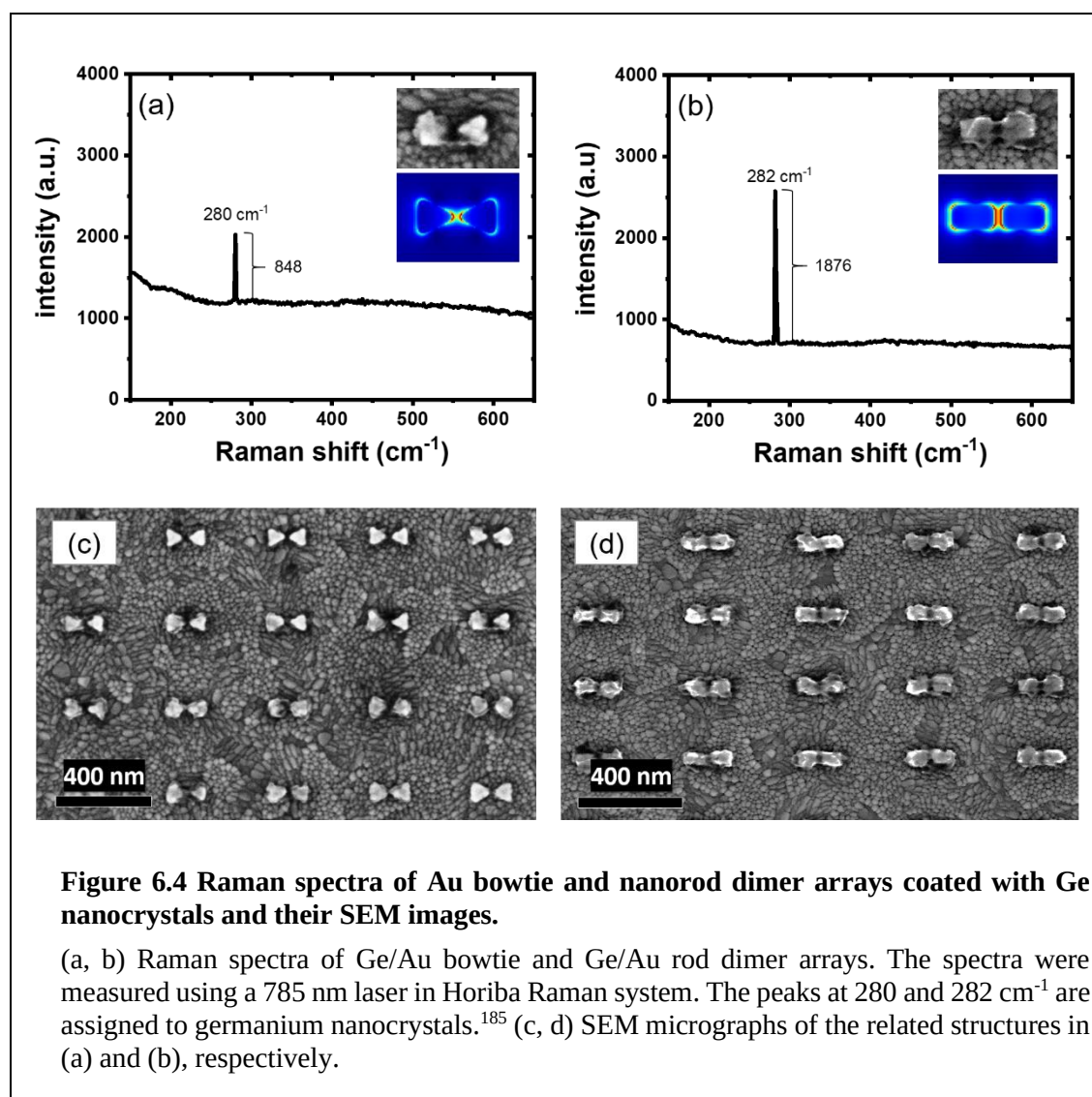
In Figure 6.3, a silicone gasket with a thickness of 1 mm and an opening with a diameter of 7 mm was placed on top of the surface of the sample to create a well for the liquid-phase precursor. 2.5 μL of germanium precursor (diphenylgermane: DPG, purchased from Fluorochem Ltd.) was introduced into the well to entirely cover the arrays of Au nanoantennas. A coverslip was placed over the top of the gasket to create a closed system. The sample was mounted under a $100\times$ objective lens ($\text{NA} = 0.9$) while the 785 nm excitation laser was focused on the arrays with a measured power of 27 mW. The laser with a spot size of approx. 1 μm was scanned in a raster manner with an exposure time of 5 s and a step size of 300 nm in a square area of $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$.

Excitation of the LSPR in Au nanoantennas leads to optical field enhancement at specific regions on the nanoantenna surface. For instance, laser illumination with polarization along the x-axis results in the near-field enhancement in the gap of the Au bowties and Au rod dimers. Such optical enhancement can potentially lead to heat generation in the metal and surrounding media. Locally heating DPG with temperatures greater than the Au:Ge eutectic at 360°C can cause DPG to undergo redistribution to germane (GeH_4) in solution and subsequently decompose to germanium atoms.¹⁷⁹ These Ge atoms can diffuse through Au and eventually crystallise to form Ge nanocrystals.

Figure 6.4(c) and (d) illustrate SEM images of the sample after laser illumination. It can be seen that Ge nanocrystals were formed on Au nanoantennas and at the regions where the optical field intensities are high *e.g.* in the gap. The transformation of DPG to Ge nanocrystals is indicated in the Raman spectra as shown in Figure 6.4(a, b) in which the sharp peaks around 280 cm^{-1} are assigned for Ge nanocrystals.¹⁸⁵

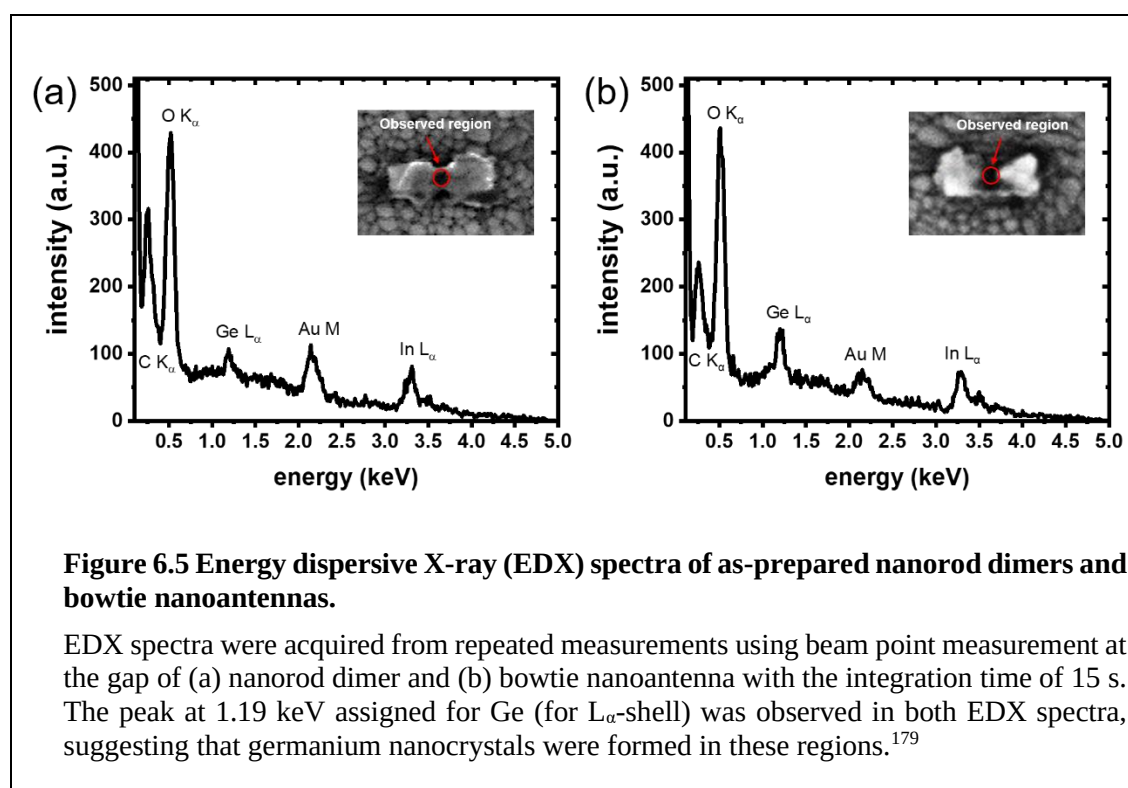
In Figure 6.4(a, b), it is clear that the Raman fingerprint assigned for Ge nanocrystals obtained from Au rod dimer array possesses a higher intensity (1876) compared to that (848) acquired from Au bowtie nanoantenna array. The difference in the Raman intensities for both structures correlate well with the simulation results. According to the simulated electric field distribution maps and optical spectra, Au rod

dimer array demonstrates the LSPR that best fits with the 785 nm excitation wavelength. In contrast, Au bowtie nanoantenna array was less favourable when particularly considering resonant effects of the surface plasmons. Therefore, when a 785 nm excitation wavelength was employed, the laser-driven catalytic Ge growth was more efficient for Au rod dimer array than for Au bowtie nanoantenna array. As illustrated in the Raman spectra (Figure 6.4(a, b)), a higher Raman intensity for Ge was found in Au rod dimer array whereas the Raman peak for Ge was lower in Au bowtie nanoantenna array.



Although the LSPR of Au bowtie nanoantenna arrays did not exactly match the 785 nm excitation wavelength, the production of Ge nanocrystals was observed. This may be due to a non-resonant lightning-rod effect which occurs at sharp curvatures of conductive materials. Studies^{183,184,186} have shown that small curvatures of metal terminations can induce charge accumulation at their ends, known as the lightning-rod effect, which is responsible for an extra field enhancement over that of the localised surface plasmon resonance. An Au bowtie nanoantenna consists of several sharp tips in addition to a small gap where two tips are placed close together. Such a gap mode of Au bowtie can produce charge accumulation which leads to an extra field enhancement and results in the highest electric field compared to other regions. The gap region has shown to play a vital role in initiating catalytic Ge growth. This is illustrated in the inset of Figure 6.4(a). The production of Ge nanocrystals occurred in the gap mode (black region) of the Au bowtie nanoantenna corresponding to the region with the highest electric field enhancement.

6.4 Elemental analysis



The nucleation of Ge nanocrystals was also observed under EDX spectroscopy. An electron beam with an energy of 5 keV was used to stimulate X-ray emission characteristic of elements in the sample.

Figure 6.5 shows EDX spectra of Au nanoantennas after laser illumination. For comparison, an electron beam was focused on the central gap of either a bowtie or a rod dimer. It is clear that the characteristic X-ray of Ge at the energy of 1.19 keV (for L_{α} -shell) can be detected for both Au bowtie and Au rod dimer nanoantennas. Additional characteristic X-ray peaks are assigned to Au in the nanoantennas and the indium tin oxide-coated substrate.

6.5 Conclusion

Au bowtie and Au rod dimer nanoantennas were successfully fabricated. The structures comprised of two identical nanoantennas placed close to one another, leaving a small gap in between. Such a small gap allows light to be concentrated and the electric field intensity is amplified. In the gap, Au rod dimers can produce an electric field intensity approximately 2 times greater than that of Au bowtie nanoantenna array when illuminated by a 785 nm wavelength. However, evidence in the Raman spectra reveals that the catalytic Ge growth can be observed in both structures in the plasmonic hotspots. The catalytic Ge growth may be due to the contribution of both localised surface plasmon resonance and the non-resonant lightning-rod effect, especially in the case of Au bowtie nanoantenna array. The contribution may thereafter potentially lead to thermal distribution that could trigger phase changing mechanisms corresponding to the Ge:Au eutectic temperature as already been purposed in various studies.¹⁷⁸ However, additional investigation is further required to confirm the thermal distribution process. In this chapter, Raman spectra and EDX analysis have confirmed that Ge nanocrystals could be synthesized at the local hotspots around Au nanoantennas.

CHAPTER 7

Conclusion

7.1 Thesis summary

The objective of this thesis was to investigate chemical and physical mechanisms of energy transfer from nanostructured metals, focusing on Al and Au. The generation of hot carriers, near-field enhancement, thermal decay, and radiative relaxation are known as competitive dephasing mechanisms of surface plasmon resonances. Many modern methods have been proposed to qualitatively and quantitatively study energy transfer in plasmonic systems. However, many of these techniques rely on complex setups and acquiring experimental results can be a cumbersome task.

Chapter 4 demonstrated that by using a simple Raman spectroscopy setup, energy transfer in Al plasmonic nanostructures can be observed. Al bowtie nanoantennas and Al nanodisks were used as models to produce localised surface plasmon resonances (LSPRs) matching the excitation wavelength in a Raman microscope. Polymethylmethacrylate (PMMA) was used as a photosensitive probe whose chemical structure was modified by energy transfer from the Al nanostructures. The chemical structure of PMMA was observed to change from sp^3 -hybridization to sp^2 -hybridization as indicated in the Raman fingerprints, suggesting that the energy transfer from Al nanostructures was sufficient to modify the structure of PMMA. Additionally, it is evident that the increasing volume of decomposed PMMA around Al nanodisks with respect to the incident power of the laser correlated well with a two-photon absorption mechanism as described by the Beer-Lambert law. This observation highlights that a two-photon absorption mechanism enabled by excitation of the LSPRs could cause chain scission in PMMA that subsequently leads to chemical transformations.

Many studies have shown that PMMA can be converted into graphitic materials when exposed to focused beams of high-energy electrons having kinetic energies on the order of kilo-electronvolts and post-exposure thermal annealing (800°C).^{113,114} These techniques allow the long polymer chain of PMMA, $(C_5O_2H_8)_n$ to break down into smaller fragments while volatile groups such as CO_2 , H_2 , and CH_3O can be removed by the vacuum system, resulting in the formation of carbon networks possessing graphitic properties. In Chapter 4, it is evident that the LSPRs of Al nanoantennas assist the change in the hybridization of carbon in PMMA from sp^3 -hybridization to sp^2 -hybridization (*i.e.* from PMMA to graphitic carbon) which completely altered chemical and electrical properties. The change of the chemical structure of PMMA into graphitic materials was identified by Raman fingerprints. In the presence of Al nanoantennas D- and G-peaks could be observed in the Raman spectra of PMMA films, suggesting that graphitic carbon was produced. In contrast, D- and G-peaks were not observed in the absence of Al nanoantennas. The findings show that aside from the techniques employing an electron, the excitation of the localised surface plasmon resonances can also result in the production of graphitic materials or carbon dots. The plasmon-assisted graphitization in PMMA paves the way for direct fabrication of metal-semiconductor hybrid materials which can potentially be useful for photocatalysis, biosensing, plasmon-enhanced spectroscopy, and solar cells.

In Chapter 5, section 5.1 showed that a combination of electron-beam lithography and SERS can be used to identify the locations of hotspots around Al bowtie nanoantenna at the single nanoantenna level. To probe the locations of hotspots, an analyte – negative-tone PMMA nanodots with graphitic properties – was selectively formed at different locations correlating with different electric near-field intensities produced due to the excitation of the LSPRs of an Al bowtie nanoantenna in response to the 532-nm-wavelength laser. Prominent fingerprints for D- and G-peaks were observed when the analyte was located in the central gap of an Al bowtie while these peaks appeared with lower intensities or were not observed when the analyte was located at the corner or edge associated with low electric near-field intensities as predicted by simulations. The sensitivity of the SERS effect from an Al bowtie depends significantly upon the polarization direction of the excitation laser. For example, when an Al bowtie was illuminated by light polarized along the connecting axis of the bowtie, the most

significant field enhancement occurred in the central gap. On the other hand, when the antenna was excited by light polarized vertical to the connecting axis of the bowtie, the electric near-fields were enhanced at the corners of the bowtie. However, when considering these two cases, the central gap was observed to generate higher near-field intensities compared to those at the outer corners of the bowtie.

By using electron beam irradiation to selectively deposit an analyte at desired locations, it is also feasible to determine the SERS enhancement factor (EF) at certain locations. With an analyte located in the central gap of an Al bowtie, the results demonstrated that an EF as high as $(0.55 \pm 0.11) \times 10^3$ could be generated. This method not only offers a reliable means to probe the locations of hotspots, but also allows one to quantify the EF at particular locations. Although this technique provides great benefits, there are limitations that may diminish overall performance. First, the resolution of the image was restricted by the diffraction limit of the conventional optical microscope integrated with the Raman spectroscopy system. Moreover, the minimum step size in Raman maps limits control over the placement of the laser beam with respect to the nanoantennas. Therefore, it is challenging to precisely align the centre of the laser spot to a specific particle of interest. The misalignment between the centre of the laser spot and the location where the field enhancement occurs may result in a reduction in the measured SERS EF relative to the maximum EF. Secondly, the precise deposition of an analyte requires electron-beam lithography and careful control over the electron beam exposure position. In this investigation, negative-tone PMMA was manually fabricated using a beam spot exposure. The technique was restricted by many factors such as slight variation in the duration of exposure time for each fabrication of a carbon nanodot and misalignment of the electron beam with respect to the nanoantennas. These parameters could result in non-uniform shapes of the carbon nanodot analyte, which subsequently complicates the calculation of an exact SERS EF.

Aluminium was previously considered as an “*inferior*” plasmonic material in the visible regime compared to gold and silver²⁷ due to loss associated with an interband transition in the NIR region of the spectrum. However, the results in Chapter 5, section 5.2 demonstrated that Al bowtie nanoantenna arrays, arranged in a periodic square lattice, supported by a rigid platform – an ITO-coated glass substrate – could greatly suppress the radiative loss of the nanostructures, yielding sharp and narrow resonance linewidths

with a tunable wavelength in the visible region. A narrow resonance linewidth as low as 3 nm associated with a high-quality factor of 150 was achieved for Al bowtie nanoantenna arrays. The Q factor of 150 is much larger than typical Q factors of LSPRs which are on the order of tens.¹⁸⁷ This achievement was attributed to a hybrid mode of the LSPRs of individual Al bowties and diffracted waves in the lattice array, known as surface lattice resonances (SLRs). In addition to ultra-narrow resonance linewidths, multiple surface plasmon resonances were also observed. The findings presented in Chapter 5 suggest that Al bowtie nanoantennas can potentially be exploited for use in ultrasensitive label-free biosensing applications towards low-cost, sustainable, and high-performance sensors.^{50,75}

Because Al bowtie nanostructures were fabricated on a conductive glass substrate containing indium doped tin oxide, possessing n-type semiconductor characteristics, optical properties of the sample must be carefully investigated. Further studies could support the development of devices based on SLRs in Al bowtie nanoantenna arrays. Examples include investigations of: (1) the effect of semiconductor nanostructures on the surface plasmon resonances of Al bowtie nanoantennas; (2) the influence of the thickness of the ITO semiconductor layer on the optical responses of Al bowtie nanoantennas; and (3) types of a semiconductor platform (*e.g.* TiO₂ versus ITO) that can influence the optical responses of Al bowtie nanostructures.

Chapter 6 investigated laser-driven catalytic Ge growth on Au bowtie and Au rod dimer nanoantenna arrays. Au rod dimer and Au bowtie nanoantenna arrays were designed to produce LSPRs that were resonant with the excitation laser at 785 nm. Au rod dimer had an LSPR centred at 785 nm while Au bowtie nanoantenna array had an LSPR at a slightly lower wavelength (centred at 750 nm). When the structures immersed in diphenylgermane precursor solution were illuminated by the excitation laser matching their LSPRs, Ge nanocrystals formation was observed. The Ge growth on Au nanoantennas was identified in Raman spectra as well as in EDX spectra. The production of Ge nanocrystals was sensitive to the polarization direction of the incident light and only occurred at the locations of plasmonic hotspots. We concluded that the Ge growth on Au nanoantennas occurred due to the contribution of both localised surface plasmon resonance and the non-resonant lightning-rod effect, particularly for the case of Au bowtie nanoantenna array whose LSPR was less favourable to the 785 nm excitation. The contribution can thereafter potentially lead to thermal plasmon decay that could trigger

phase changes as a result of the Ge:Au eutectic temperature which has already been reported in several studies.^{178,179} However, to confirm this mechanism additional investigation regarding thermal distribution is further required.

Au nanoparticles have long been recognized as a catalyst for synthesizing (seeding) Ge nanowires or nanoparticles.¹⁷⁹ In a recent study, controlling the growth of Ge nanocrystals by light at certain locations based on the near-field enhancement of Au nanoparticles was achieved using a vapour phase Ge precursor. The technique is known as plasmon-induced vapour deposition (CVD). The synthesis procedure took place in a vacuum chamber with a base pressure ($\sim 10^{-7}$ mbar) to facilitate the inclusion of a gas precursor. It is understood that the technique relies on advanced equipment operating under high vacuum with a gas flow controller system in addition to the use of hazardous vapour-phase precursor. In contrast, Chapter 6 highlights that the nucleation and growth of Ge nanocrystals at local plasmonic hotspots based on the polarization direction of the excitation wavelength could be achieved in a simple system containing liquid phase Ge precursor and Au catalysts. The findings in Chapter 6 serve as a novel method for producing nanoemitters and nanoabsorbers strongly coupled with plasmonic near-fields which can lead to the creation of new plasmonic hybrid nanostructures with potential applications in plasmon-based catalysis, nanoscale light sources, and photovoltaic devices.

7.2 Future directions

7.2.1 Fabrication of metallic nanoantennas

Complex metallic nanostructures with multiple sharp features have shown great promise for ultrasensitive biosensing applications owing to an intensified light-matter interaction. Structures such as nanostars and nanourchins can easily be produced using bottom-up chemical synthesis approaches. Despite several advantages, chemical synthesis of metallic nanoparticles suffers from irregular positioning, resulting in challenging optical characterisation experiments requiring single-particle spectroscopy. The use of electron beam lithography reported throughout this thesis offers precise high-resolution nanofabrication. However, the technique is time-consuming, expensive, and has a serious throughput constraint for mass production. Fabricating substrate-bound metallic

nanostructures with low production cost and high reproducibility for large-scale commercial applications is desired.

Nanofabrication techniques combining ultraviolet nanoimprint lithography and tilted evaporation methods have been reported for the fabrication of Au nanocrown arrays with high reproducibility.¹⁸⁸ The technique not only offers large-scale production with great reproducibility, but also paves the way for fabricating three-dimensional nanostructures. Therefore, the technique is promising for the fabrication of Al nanostructures with complex features towards low-cost and high-performance plasmonic applications.

7.2.2 Simulations

The FDTD method was used in this work. The method facilitates theoretical calculations of electromagnetic fields as a result of light-matter interactions. All simulations presented in this thesis were performed using material data available in the literature^{95,96,98} while a physical parameter *i.e.* the thickness of a substrate was taken from the data provided by the commercial supplier. These parameters could influence the theoretical calculations. Although simulation results were found to match well with experimental observations, the input dielectric properties of the materials are considered as one source of potential error in the calculated spectra.

To acquire accurate simulation results, it is crucial to measure the optical properties (*i.e.* refractive indices) of materials, especially of ITO-coated glass substrates used in the experiments. The optical constants of an ITO substrate could be determined using spectroscopic ellipsometry. Ellipsometry measures the amplitude ratio and phase difference between p- and s-polarizations. These parameters provide information regarding the refractive index and extinction coefficient of a material which can be exploited in the simulation method.^{50,98,189} Knowing optical parameters of materials being investigated not only improves the accuracy in numerical simulations, but also gives insight into light-matter interaction of the materials without practical fabrications.

7.2.3 Experimental analysis

In Chapter 4, although the graphitization of PMMA was characterised by Raman spectroscopy while prominent graphitic properties were observed, identifying the

topography or locations where the graphitization was formed requires additional techniques. For example, by using high-resolution transmission electron microscopy (HRTEM), the crystallization of the graphitic materials based on the selected area electron diffraction pattern could be observed.¹¹³ This method not only gives details of crystallization of the graphitic materials but also assists in identifying the locations where the graphitic materials were produced. HRTEM analysis of nanostructures in this work would necessitate fabrication of nanoantennas on ultrathin membranes that support characterisation by HRTEM.

Tip-enhanced Raman spectroscopy (TERS), combining a single metal SERS nanoparticle and a scanning probe microscope, is another powerful technique that can be used to characterise the chemical, electrical, and topological properties of a single molecule. Applying this technique for future research could help detect molecules of the graphitic materials produced by metallic nanoantennas for further insight into the energy transfer in plasmonics in addition to understanding the conductivity of the hybrid materials.^{190,191}

In Chapter 6, plasmon-driven catalytic Ge growth was characterised by Raman spectroscopy and EDX spectroscopy. Although the techniques could identify the formation of the Ge nanocrystals due to the LSPRs of Au catalysts, the optical properties of Ge nanocrystals as a result of shape and size have not been characterised. Photoluminescence (PL) spectroscopy is a typical technique that has been widely used to characterise the optical properties of semiconductor nanomaterials. For Ge nanocrystals with unknown dimensions, high energy excitation wavelengths, typically in the UV region, are used.¹⁷³ It is also possible to measure PL spectra using a Raman spectroscopic system. However, by using this method, distinct lower excitation wavelengths must be applied such that the Raman peaks (that vary depending on the excitation wavelengths) are shifted to lower wavelengths, being further away from the PL emission to be measured. Because the PL emission of a semiconductor does not change when the excitation wavelength is changed, therefore by comparing the spectra obtained from various lower excitation sources, the peak that remains the same in all spectra could indicate the PL emission of Ge nanocrystals. Unfortunately, our Raman spectroscope does not have multiple excitation sources in the UV region, thus not sufficient to characterise the PL of Ge nanocrystals. In addition, a photodetector that is sensitive to

the PL emission in a broad wavelength regime from visible to NIR would be beneficial for this characterisation technique.

In Chapter 6, although we have demonstrated that the localised surface plasmon resonance and a non-resonant lightning-rod effect could contribute to the generation of Ge nanocrystals on Au nanoantennas, it is also worth studying the *in-situ* real-time chemical evolution of diphenylgermane precursor to Ge nanocrystals. This work could be achieved using electrochemical TERS.¹⁹² As already reported in several studies, Ge nanocrystals can be formed on Au catalysts by phase-changing mechanisms when the catalysts are heated to the Au:Ge eutectic temperature above 360°C. However, in this chapter, we have not yet confirmed these processes. Therefore, in future work, thermal analysis involving computational methods and simulations would be beneficial to verify the phase-changing mechanisms of Ge on an Au catalyst.

7.3 Final remarks

Plasmonics is a modern and flourishing field of science that holds great promise for various applications such as nano-optics, biosensing, biomedical treatment, as well as solar cells. Numerous theoretical and experimental approaches have been implemented to gain insight into fundamental mechanisms of energy conversion that arises from plasmon excitation. This thesis has investigated promising physical and chemical mechanisms of LSPR-related energy transfer from Al and Au plasmonics at the single nanoantenna level. These mechanisms were found to facilitate chemical transformations of the surrounding medium *i.e.* from non-conductive to conductive materials at the enhanced local electric fields, leading to the generation of new plasmonic hybrid materials. The novel plasmonic hybrid nanostructures can potentially be exploited for next-generation plasmonic applications. In the author's opinion, special attention for future work should not only be paid to the fundamental progress, but also the development of existing applications with purposes of further improvement in efficiencies and large-scale commercialisation whose performances rely on design and engineering of metal structures.

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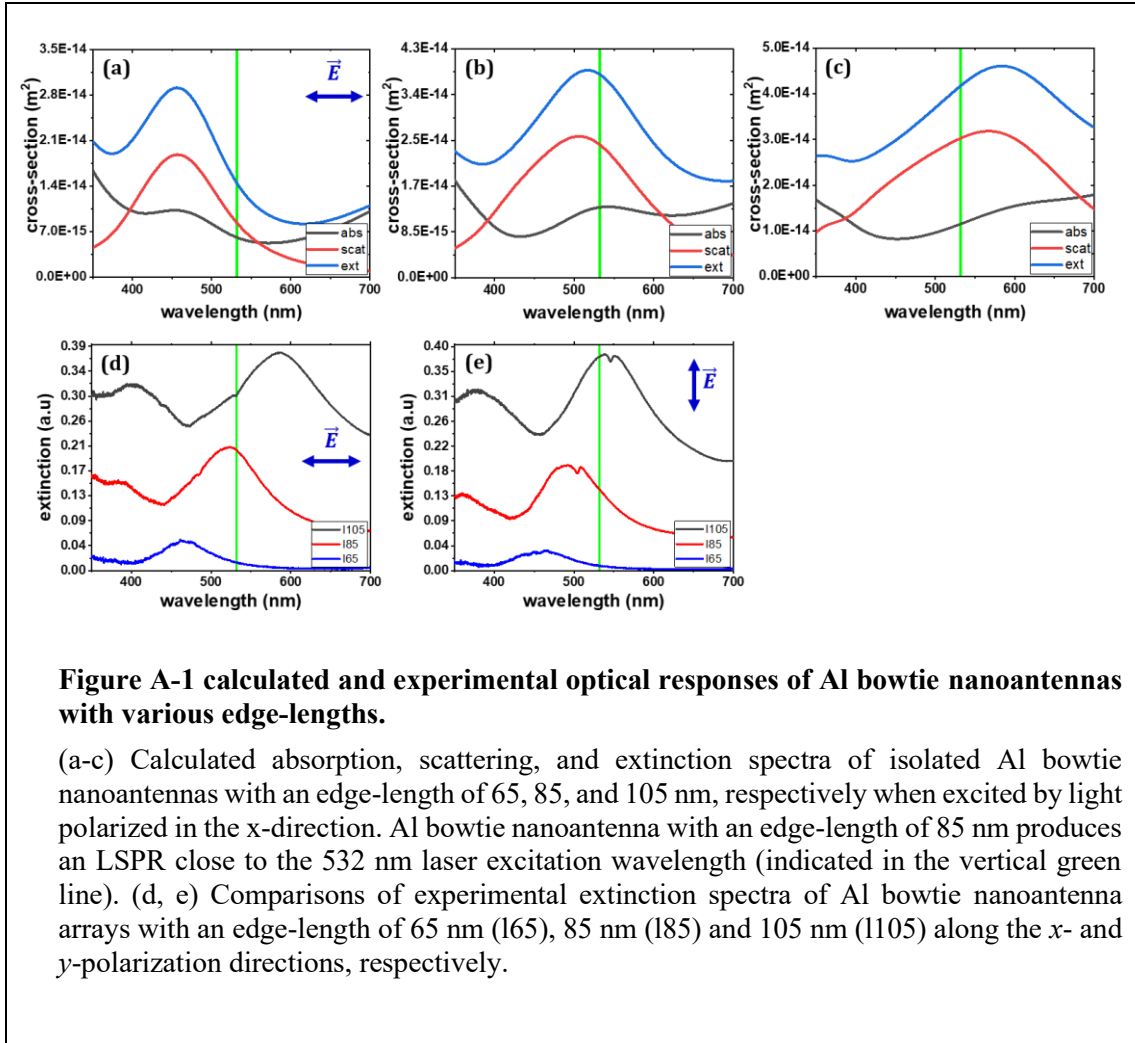
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Appendix A



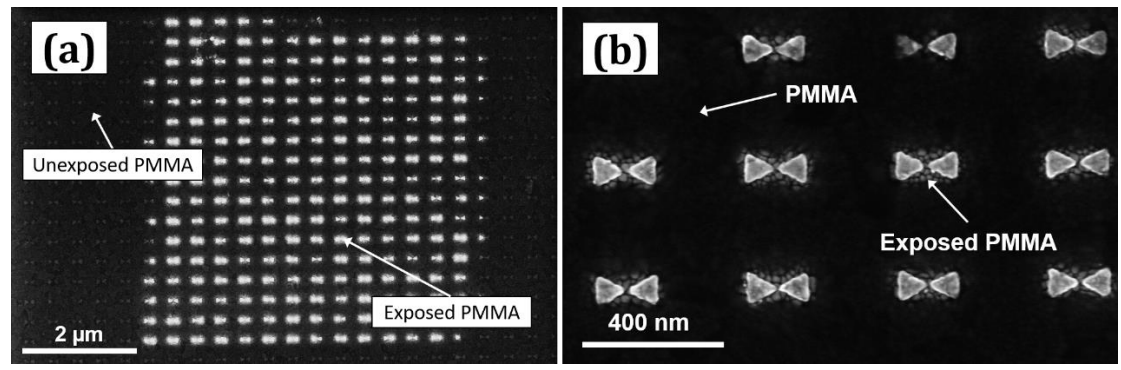


Figure A-2 SEM images of exposed and unexposed PMMA supported by Al bowtie nanoantennas having a 15 nm gap and an 85 nm side length after laser exposure and development.

(a) Low and (b) high magnifications of SEM images illustrating exposed and unexposed regions of PMMA around Al bowtie nanoantennas.

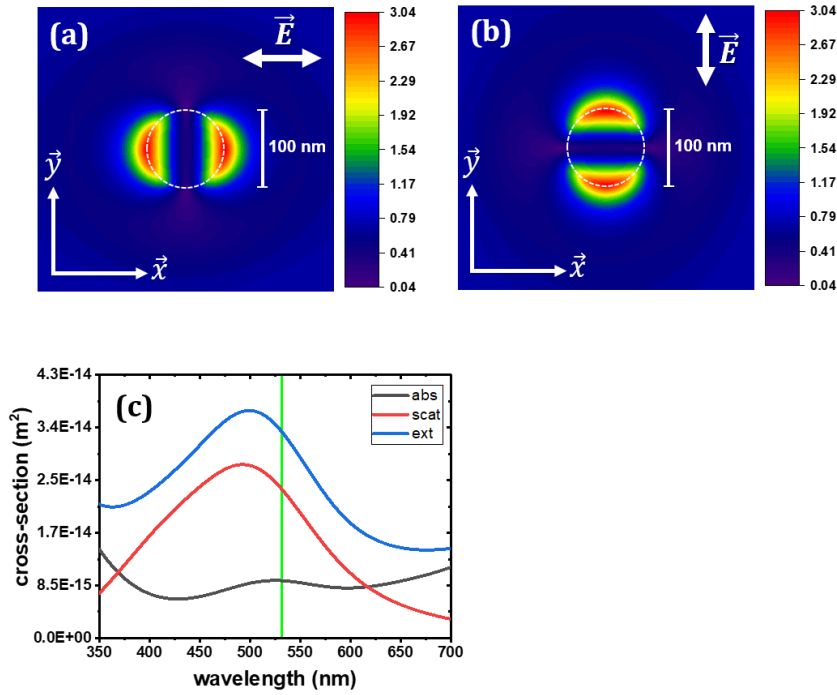


Figure A-3 FDTD simulations of electric field distribution maps of an isolated Al nanodisk with respect to x - and y -polarizations and cross-section spectra.

(a, b) Electric field distribution maps of an isolated Al nanodisk when illuminated by light polarized along the x - and y -axes, respectively. (c) Cross-section spectra of the related structure. The vertical green line indicates the 532 nm excitation wavelength.

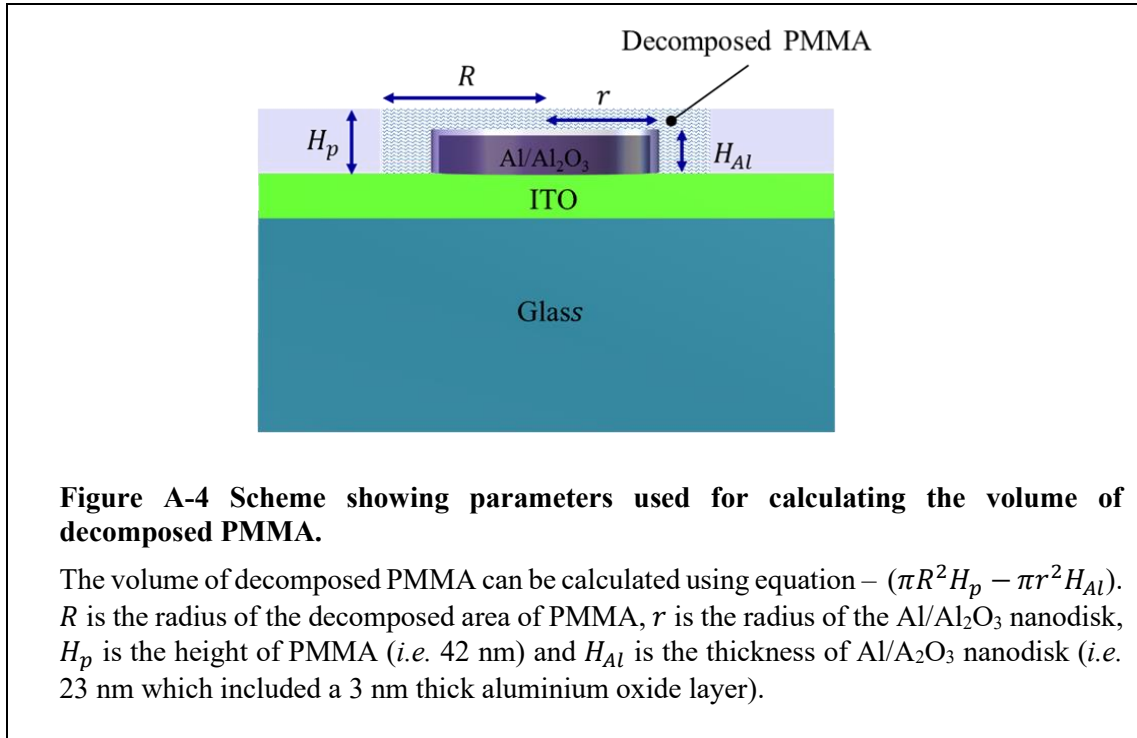


Table A-1 Diameters of decomposed PMMA at different power levels. The data were manually measured using the Straight Line tool in the software ImageJ 1.51j8.

Power (mW)	17.1	15.8	14.7	12.1	11.3	10.1	9.6
D 1 (nm)	333.33	239.92	210.35	181.33	157.66	154.00	166.4
D 2 (nm)	283.65	231.79	197.59	192.03	173.52	150.83	154.0
D 3 (nm)	241.63	208.06	211.54	173.80	171.02	167.05	155.7
D 4 (nm)	275.87	225.88	196.70	185.67	178.67	170.96	161.7
D 5 (nm)	245.61	235.85	196.76	163.91	172.48	174.37	159.9
D 6 (nm)	244.64	251.99	199.68	201.38	163.00	160.20	161.5
D 7 (nm)	249.68	226.74	180.93	166.08	163.46	158.00	155.9
D 8 (nm)	280.49	240.00	189.89	193.68	195.78	148.66	132.9
D 9 (nm)	214.20	209.52	214.73	185.99	180.27	154.09	143.8
D 10 (nm)	250.47	227.56	209.06	188.41	151.34	171.67	161.6

Table A-2 Calculated areas of decomposed PMMA at different power levels. The data were generated using Microsoft Excel 2010.

Power (mW)	17.1	15.8	14.7	12.1	11.3	10.1	9.6
A 1 (nm ²)	3665115.03	1898767.15	1459566.33	1084621.30	819939.58	782312.46	913586.85
A 2 (nm ²)	2654021.16	1772263.10	1287860.22	1216401.56	993202.68	750437.05	782718.91
A 3 (nm ²)	1925930.06	1427959.84	1476127.28	996410.62	964789.59	920516.90	800501.60
A 4 (nm ³)	2510427.91	1683039.71	1276284.59	1137161.85	1053033.24	964112.74	862606.17
A 5 (nm ²)	1989898.36	1834892.25	1277063.32	886236.65	981332.75	1002957.06	843615.14
A 6 (nm ²)	1974211.79	2094620.83	1315248.88	1337739.28	876423.50	846571.86	860367.23
A 7 (nm ²)	2056393.94	1695879.89	1079841.39	909857.71	881377.16	823479.85	802043.94
A 8 (nm ²)	2595216.36	1900033.63	1189441.24	1237395.00	1264373.70	728999.22	583326.17
A 9 (nm ²)	1513483.66	1448070.73	1520982.63	1141084.99	1071977.63	783227.12	682208.27
A 10 (nm ²)	2069427.60	1708168.29	1441719.25	1170972.52	755520.52	972137.33	861539.64

Table A-3 The calculated volume of decomposed PMMA at different power levels. The data were calculated with Microsoft Excel 2010 using equation explained in Figure A-4.

Power (mW)	17.1	15.8	14.7	12.1	11.3	10.1	9.6
V 1 ($\times 10^{-4} \mu\text{m}^3$)	34.24	16.57	12.18	8.43	5.78	5.41	6.72
V 2 ($\times 10^{-4} \mu\text{m}^3$)	24.13	15.31	10.46	9.75	7.52	5.09	5.41
V 3 ($\times 10^{-4} \mu\text{m}^3$)	16.84	11.87	12.35	7.55	7.23	6.79	5.59
V 4 ($\times 10^{-4} \mu\text{m}^3$)	22.69	14.42	10.35	8.96	8.12	7.23	6.21
V 5 ($\times 10^{-4} \mu\text{m}^3$)	17.48	15.93	10.36	6.45	7.40	7.62	6.02
V 6 ($\times 10^{-4} \mu\text{m}^3$)	17.33	18.53	10.74	10.96	6.35	6.05	6.19
V 7 ($\times 10^{-4} \mu\text{m}^3$)	18.15	14.54	8.38	6.68	6.40	5.82	5.61
V 8 ($\times 10^{-4} \mu\text{m}^3$)	23.54	16.59	9.48	9.96	10.23	4.88	3.42
V 9 ($\times 10^{-4} \mu\text{m}^3$)	12.72	12.07	12.80	9.00	8.31	5.42	4.41
V 10 ($\times 10^{-4} \mu\text{m}^3$)	18.28	14.67	12.00	9.30	5.14	7.31	6.20
Average	20.54	15.05	10.91	8.70	7.25	6.16	5.58
STD	5.65	1.94	1.33	1.37	1.38	0.95	0.93

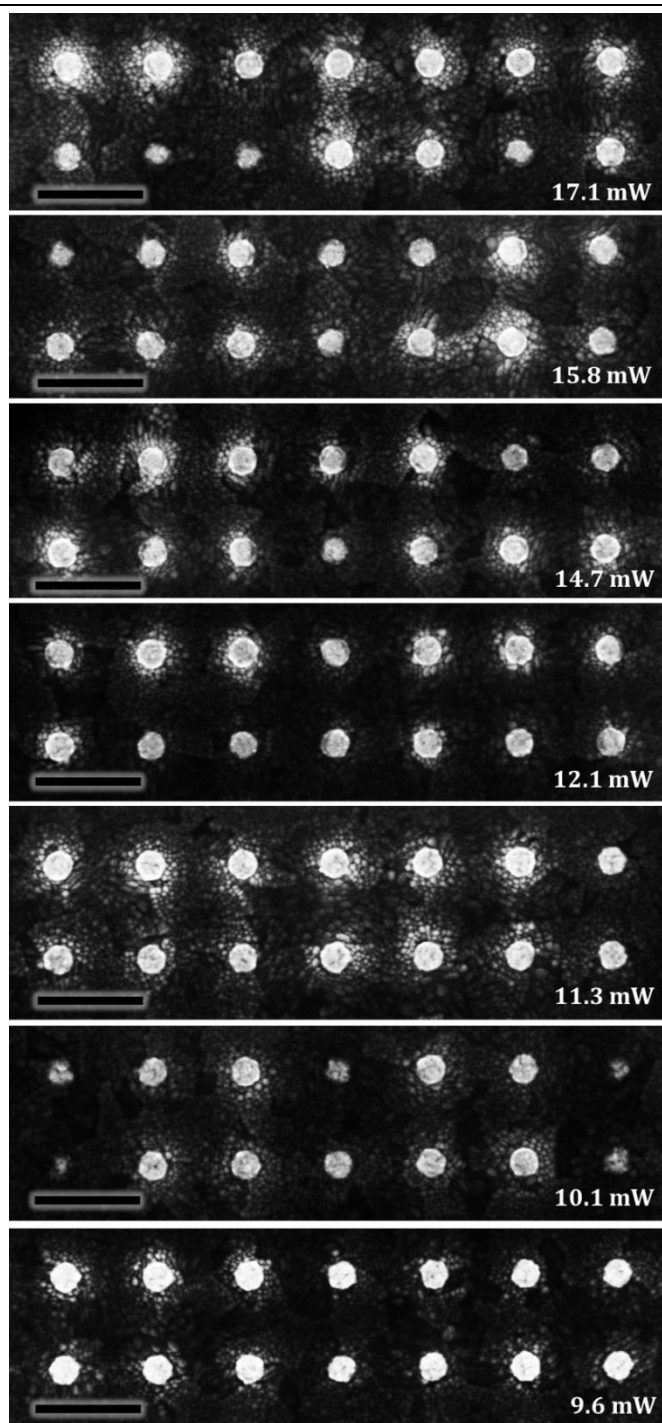


Figure A-5 SEM images illustrating areas of decomposed PMMA around Al nanodisks when excited by different excitation power levels. The scale bar is 400 nm.

The SEM images were obtained using an in-lens detector with an acceleration voltage of 5 kV.

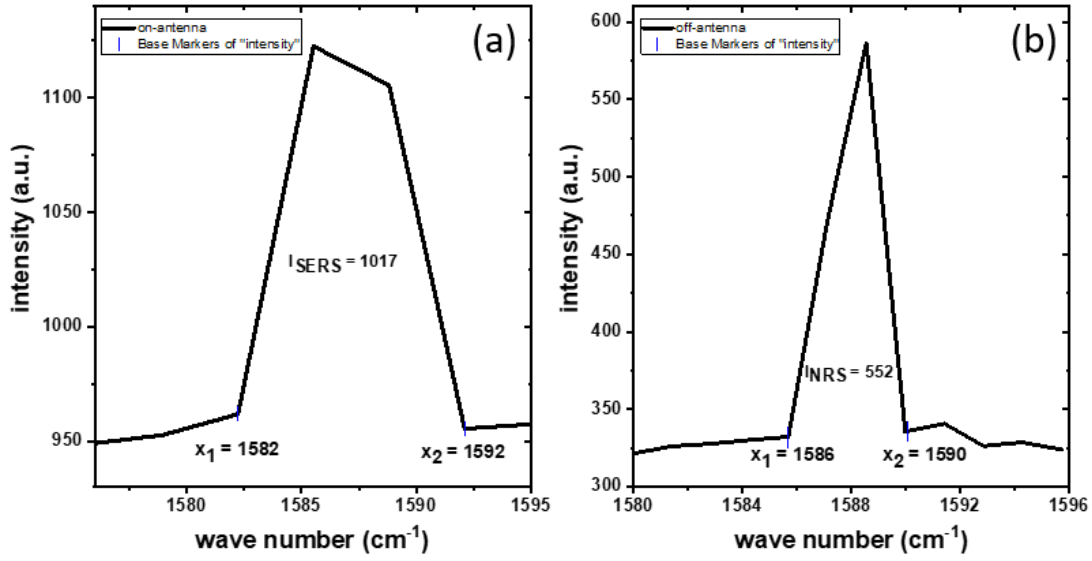


Figure A-6 Raman spectra and parameters used to calculate Raman intensities for on- and off-antenna samples.

Raman spectra obtained from the sample (a) on- and (b) off-antenna sites. The area under the peak (centred at around 1588 cm⁻¹) of each spectrum was used to calculate Raman intensities (I_{SERS} and I_{NRS}), while the peak tails (x_1 - x_2) were in the range 1580-1600 cm⁻¹ which have been assigned to the G-mode of graphitic materials in the literature.^{115,124,150}

The calculation of the enhancement factor with propagation of uncertainty

$$EF = \frac{I_{SERS}}{I_{NRS}} \times \left[\frac{N_{NRS} \pm \delta x}{N_{SERS} \pm \delta y} \right]$$

$$EF = \left(\frac{I_{SERS}}{I_{NRS}} \times \frac{N_{NRS}}{N_{SERS}} \right) \pm \left[\left(\frac{N_{NRS}}{N_{SERS}} \right) \times \sqrt{\left(\frac{\delta x}{N_{NRS}} \right)^2 + \left(\frac{\delta y}{N_{SERS}} \right)^2} \right]$$

$$EF = \left(\frac{1017}{552} \times \frac{6.34 \times 10^6}{2.11 \times 10^4} \right) \pm \left[\left(\frac{6.34 \times 10^6}{2.11 \times 10^4} \right) \times \sqrt{\left(\frac{0.05 \times 10^6}{6.34 \times 10^6} \right)^2 + \left(\frac{0.75 \times 10^4}{2.11 \times 10^4} \right)^2} \right]$$

$$EF = (0.55 \pm 0.11) \times 10^3$$

Table A-4 Statistical measurements of dimensions of Au bowties and Au rod dimers. L, W, G, and S represent the length, width, gap, and edge-to-edge spacing.

NO.	bowtie (nm)		rod dimer (nm)			Bowtie		Rod dimer	
	L	G	L	W	G	S(x)	S(y)	S(x)	S(y)
1	72	18	82	57	17	249	260	247	247
2	67	19	79	59	22	243	262	252	249
3	68	13	79	54	17	242	254	247	249
4	69	16	74	59	23	243	256	242	249
5	70	18	76	55	22	243	254	247	247
6	69	21	76	54	15	249	254	250	252
7	69	17	79	60	20	249	258	245	250
8	70	22	79	52	17	251	253	247	252
9	70	15	79	57	22	247	256	249	245
10	71	19	77	52	20	245	258	257	247
11	71	19	79	54	22	245	256	251	250
12	72	21	77	54	20	242	261	252	247
average	70	18	78	56	20		251		249
STD	1	3	2	3	3		6		3

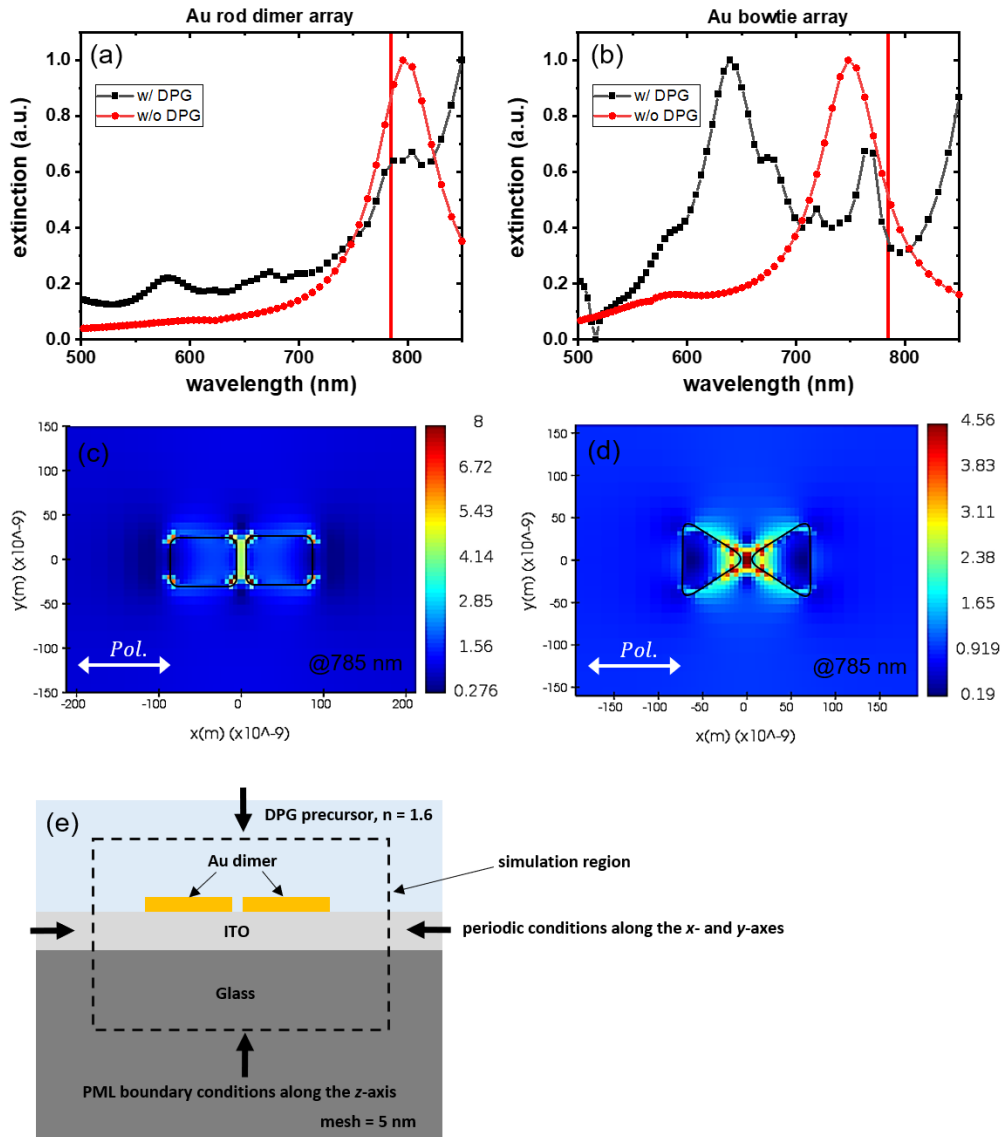


Figure A-7 Simulated extinction spectra of Au rod dimer and Au bowtie nanoantenna arrays with and without diphenylgermane (DPG) precursor solution and a simulation diagram.

(a, b) Calculated optical spectra of Au rod dimer and Au bowtie nanoantenna arrays with (black) and without (red) DPG liquid precursor. The vertical red lines indicate a 785 nm excitation wavelength. (c, d) Electric field distribution maps of Au rod dimer and Au bowtie nanoantennas with DPG precursor, simulated with x-polarized light, indicated by the white arrows. (e) Diagram illustration of a simulation region (dashed line). PML boundary conditions were employed in the z-direction. Periodic boundary conditions were used in the x- and y-directions to include plasmonic coupling effects. The refractive index of DPG was 1.6. The mesh unit was $5 \times 5 \times 5 \text{ nm}^3$.

Appendix B

Table B-1 Nomenclature: optics

Symbol	Definition
$\vec{E}$	electric field
$\vec{H}$	magnetic field
E	amplitude of electric field
$\varepsilon(\omega)$	dielectric constant of a material
$\varepsilon_i(\omega)$	imaginary part of the dielectric constant
$\varepsilon_r(\omega)$	imaginary part of the dielectric constant
ε_m	dielectric constant of the surrounding medium
ε_0	permittivity of a vacuum
ω	angular frequency
$\vec{k}$	wavevector
λ_{LSPR}	wavelength of LSPR
λ_{SPP}	wavelength of SPP
λ	wavelength
$\vec{\mu}$	dipole moment
α	static polarizability
$\vec{r}$	distance from original coordinates
r	radius
x, y, z	Cartesian coordinates
ω_p	plasma frequency
ω_{LSPR}	resonance plasma frequency
τ	relaxation time
n_e	number density of electrons
e	electron charge
m^*	effective mass of an electron
c	velocity of light
C_{ext}	extinction cross-section
$\sigma_{abs}(\lambda)$	absorption cross-section
$\sigma_{scat}(\lambda)$	scattering cross-section
$\hbar$	reduced Planck constant = $(\frac{h}{2\pi})$
h	Planck constant
N	number of particles
$\vec{A}_{ij}$	array of matrix $(i \times j)$
α	polarizability
S	dipole sum
θ	angle
$S(\lambda)$	incident photon flux
$\eta(\lambda, \varphi_{SB})$	probability of hot electron injection
A	area
N_c	hot carrier density
V_{MFP}	volume of the integrated field enhancement

Continued next page

Symbol	Definition
$q(r)$	heat power density
Q	heat power
V	volume of plasmonic material
λ_{ab}	wavelength of the absorption
λ_{em}	wavelength of the emission
γ_{rad}	radiative decay rate
$\gamma_{non-rad}$	non-radiative decay rate
γ_{exc}	excitation rate
$ E ^2$	plasmon-enhanced field intensity
T	transmittance
A	absorbance
P	power
R	reflection
γ	reflection coefficient
δ	film phase factor

Table B-2 Nomenclature: solid-state physics

Symbol	Definition
E_F	Fermi energy level
E_c	conduction band energy
E_v	valence band energy
E_g	energy bandgap
ϕ_{SB}	Schottky energy barrier
ϕ_M	work function of the metal
χ_s	electron affinity of the semiconductor
j_{sc}	metal-to-semiconductor hot-electron photo-current

Table B-3 Nomenclature: electron interaction with matter

Symbol	Definition
d	beam diameter
i	beam current
B_o	source brightness
B_i	image brightness
α	convergence angle
E_m	dissipation energy
E_i	incident electron energy
E_d	displacement energy
A_t	atomic number
r	distance from the point of electron incidence
η	backscattering coefficient
δ	secondary electron coefficient
α	forward scattering range parameter
β	backscattering range parameter
R_t	resist thickness
V_e	beam voltage
D_f	effective beam diameter

About the Author

The author, Kamonpan Chumpol, obtained a bachelor's degree in physics from Srinakharinwirot University, Thailand. Shortly after graduation, she joined the National Insitute of Metrology, Thailand where she worked as a metrologist in the Photometry and Radiometry department.

In 2015, she was awarded a fully-funded UCD Global Excellence Scholarship – Her Royal Highness Princess Maha Chakri Sirindhorn's (of Thailand) Scholarship – to pursue her master's degree in NanoBio Science at University College Dublin. Chumpol's MSc thesis focused on the design and fabrication of high-performance solar energy harvesting devices using plasmonic bio-inspired features. After completion of her master's degree in 2016, she joined Professor Richard Hobbs' group in the School of Chemistry at TCD. Her research interests were investigations of plasmon-mediated energy transfer at the single nanoantenna level for photochemistry and photocatalysis.

During the PhD programme, Chumpol had published a first-authored article in a peer-reviewed journal (Multiphoton Absorption and Graphitization in Poly(methyl methacrylate)-Coated Aluminum Nanoantenna Arrays. *J. Phys. Chem. C* **124**, 8930–8937 (2020).), details of which are included in chapter 4 in this PhD dissertation, while the research results in chapters 5 and 6 are under preparation for future publications.

In addition to publications, Chumpol had demonstrated ability to disseminate research results by attending a Third-Year Presentation programme organised by the Dublin Chemistry Graduate Programme. She received an overall Honours grade in her talk. Furthermore, her conference paper entitled Plasmon-Assisted Chemical Changes in Poly(methyl methacrylate) was also evaluated and accepted by SPIE Europe for the conference Nanophotonics VIII.

Chumpol had also engaged in a Transition-Year Nanoscience programme organised by TCD and CRANN. She acted as a workshop presenter to help students gain practical knowledge of nanotechnology in everyday life as well as encourage them to become next-generation scientists.