Light-Assisted Selective Chemical Synthesis on Plasmonic Nanoparticles: Titanium Dioxide on Gold Nanostars

by

Yujin Kim

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
The Edward S. Rogers Sr.
Department of Electrical & Computer Engineering
University of Toronto

© Copyright by Yujin Kim 2015
Light-Assisted Selective Chemical Synthesis on Plasmonic Nanoparticles: Titanium Dioxide on Gold Nanostars

Yujin Kim

Master of Applied Science

The Edward S. Rogers Sr. Department of Electrical & Computer Engineering
University of Toronto
2015

Abstract

In this thesis, light-assisted crystallization of TiO$_2$ on gold nanostars was investigated by using gold plasmonic nanoparticles as a nano-source of heat to induce forced hydrolysis of TiCl$_4$ precursor. The frequency of localized surface plasmon resonance and absorption cross-sections were investigated using COMSOL. Using a multi-laser Raman setup, in-situ crystallization of TiO$_2$ was observed under various laser frequencies and intensities on four different shapes of gold nanoparticles each with a unique plasmonic resonance frequency. The correlation between laser intensity, precursor concentration, and plasmonic resonance frequency of the nanoparticles with crystallization nature of TiO$_2$ was investigated. Through careful control over the experimental conditions we demonstrate localized crystallization of anatase TiO$_2$ in the valleys of gold nanostars as confirmed by transmission electron microscopy. Our findings offer a new approach to the synthesis of partially covered gold-TiO$_2$ core-shell nanocomposites with promising implications for visible light photocatalytic applications.
Acknowledgments

First, I would like to thank my supervisor, Professor Kherani, who encouraged me throughout the course of my degree with guidance and support. A special thank you to Arthur Montazeri for motivating me with his ideas and passion. I wish to thank Dr. Nastaran Kazemi-Zanjani for her advice on Raman spectroscopy as well as for her great help with organizing the thesis. I also wish to thank J. Kenji Clark for all his efforts with the COMSOL modelling. My deepest gratitude to Navid Soheilnia from the Department of Chemistry for his help with the preparation of TiCl₄ precursor.

I wish to gratefully acknowledge financial support of Natural Sciences & Engineering Research Council, Ontario Research Fund – Research Excellence program, Global Connaught Challenge program, and the Edward S. Rogers Sr. Department of Electrical & Computer Engineering.

Lastly, I would like to thank my colleagues in the APD Labs for providing me with the support, encouragement and enriched graduate school experience.
# Table of Contents

## Contents

Acknowledgments........................................................................................................ iii

Table of Contents........................................................................................................ iv

List of Tables .............................................................................................................. vi

List of Figures ............................................................................................................. vii

List of Abbreviations and Acronyms ........................................................................ xi

Chapter 1 ..................................................................................................................... 1

1 General Introduction ............................................................................................... 1

1.1 Overview .............................................................................................................. 1

1.2 Objective of the thesis ......................................................................................... 4

1.3 Scope of the thesis .............................................................................................. 5

2 Principles and Theory ............................................................................................. 6

2.1 Localized surface plasmon resonance .............................................................. 6

2.1.1 Localized Surface Plasmon resonances in Gold Nanostars ....................... 10

2.2 Thermoplasmonics ............................................................................................ 13

2.2.1 Temperature profile under CW illumination .............................................. 13

2.3 Synthesis of TiO$_2$ via hydrolysis ..................................................................... 16

2.3.1 Crystal structure of TiO$_2$ ......................................................................... 16

2.3.2 Hydrolysis of titanium tetrachloride (TiCl$_4$) ........................................... 17

2.3.3 Nucleation and precipitation of Titanium Dioxide (TiO$_2$) ....................... 19

2.4 Raman spectroscopy .......................................................................................... 22

3 Experimental and Technical Aspects ................................................................. 24

3.1 Experimental Procedures and Characterization .............................................. 24

3.1.1 Au NPs synthesis and solution preparation .............................................. 24
3.1.2 Optical Properties of gold nanoparticles ................................................................. 31
3.1.3 TiO₂ Crystallization ................................................................................................. 33

4 COMSOL Simulation study on gold nanostars .............................................................. 39
  4.1 COMSOL Multiphysics – Wave Optics Module ........................................................ 39
  4.2 Simulation Parameters ............................................................................................ 41
  4.3 Results and discussion ........................................................................................... 42
  4.4 Conclusion ............................................................................................................... 47

5 Plasmonic crystallization of TiO₂ on gold nanoparticles ................................................. 48
  5.1 Raman analysis of TiO₂ plasmonic crystallization ...................................................... 48
    5.1.1 Raman Characterization and Photostability Investigation of AuNSt and TiCl₄ precursor ................................................................. 48
    5.1.2 Effect of laser intensity and illumination duration on crystallization ......................... 49
    5.1.3 Effect of TiCl₄ precursor concentration on crystallization ........................................ 56
    5.1.4 Effect of matching laser wavelength and plasmon resonance frequency on TiO₂ crystallization for various gold nanoparticles ........................................ 61
  5.2 TEM Characterization of plasmonic crystallization of TiO₂ on gold nanoparticles ....... 66
    5.2.1 TEM Characterization of Reference TiO₂ powder (P25) ........................................ 66
    5.2.2 TEM Characterization of Thermally induced TiO₂ crystallization .......................... 68
    5.2.3 TEM Characterization of TiO₂ crystallized on various gold nanoparticles .......... 69
    5.2.4 Thermal stability of l-AuNSt ................................................................................ 81
  5.3 Conclusion ............................................................................................................... 83

6 Conclusions and Outlook ............................................................................................ 84

References ...................................................................................................................... 89

Appendix A: l-AuNSt synthesis .................................................................................... 98

Appendix B: d-spacing of rutile, anatase, brookite, and gold ........................................ 104
List of Tables

Table 2-1 Summary of thermoplasmonic experiments ............................................................. 15
Table 3-1 Structural features of l-AuNSt .............................................................................. 27
Table 3-2 Structural features of AuNFl .................................................................................. 29
Table 3-3 Structural features of s-AuNSt .............................................................................. 30
Table 3-4 Measured power and calculated intensity of lasers in Raman setup ...................... 34
Table 3-5 Normalized laser intensity of lasers in Raman setup ............................................ 35
Table 5-1 Threshold energy for anatase TiO$_2$ formation under 532nm laser, 1M TiCl$_4$, for 20s. 54
List of Figures

Figure 2.1. (a) Normalized extinction spectra of Ag (38nm), Au (25nm) and Cu (133nm). (b) Normalized extinction spectra for Ag wire (90nm diameter with aspect ratio >30), cube (79nm edge), and sphere (38nm). (c) Normalized extinction spectra for Ag nanocubes with increasing size (56nm, 79nm, 129nm). Reprinted by permission from Macmillan Publishers Ltd: [Nature Materials] (47), copyright (2011). ................................................................. 9

Figure 2.2 (a) Absorption and scattering cross-section of gold sphere with respect to the diameter. (b) Absorption and scattering cross-section for 88nm gold sphere with respect to wavelength. Reprinted by permission from John Wiley and Sons [51] .............................................. 10

Figure 2.3 Simulated absorption (closed dot) and scattering (open dot) cross-sections of gold nanostars. For tip aspect ratio of 1.4, core was 24nm in diameter, tip length/base width was 19nm/13.5nm, and number of tips was 8. For tip aspect ratio of 2.2, core diameter was 22nm, tip length/base width was 22nm/10nm, and number of tips was 10. Reprinted with permission from Elsevier [55]................................................................................................................. 11

Figure 2.4 Simulated temperature profile on gold star under 0.22mW laser. Reprinted with permission from [57]. Copyright (2014) American Chemical Society.................................................. 12

Figure 2.5 Crystal structure of TiO$_2$ in (a) rutile, (b) anatase, and (c) brookite. Grey sphere represents Ti atom octahedrally coordinated with O atoms. Reprinted with permission from [69]. Copyright (2006) American Chemical Society................................................................. 16

Figure 2.6 Diagram of the species present in TiCl$_4$ in water system with varying pH and chlorine ion concentration [70]......................................................................................................................... 18

Figure 2.7 Nucleation and growth mechanism for rutile (top) and anatase/brookite (bottom) [70] ........................................................................................................................................... 21

Figure 3.1 (a) prepared Au seed solution (b) TEM image of the Au seed with mean diameter of 11nm ........................................................................................................................................... 25

Figure 3.2 (a,b) TEM images and (c,d) SEM images of the prepared l-AuNSt ......................... 27
Figure 3.3 (a,b) SEM images and (c) TEM image of the prepared AuNFL
Figure 3.4 (a) SEM and (b,c) TEM images of the purchased s-AuNSt
Figure 3.5 TEM image of AuNSp
Figure 3.6 UV-Vis spectrometer (Lambda 1050 from Perkin Elmer)
Figure 3.7 Photograph of AuNSp (60nm diameter), s-AuNSt (127nm tip-to-tip), l-AuNSt (98nm tip-to-tip), and AuNFL (1μm tip-to-tip)
Figure 3.8 Absorbance spectra of l-AuNSt, s-AuNSt, AuNFL, AuNSp
Figure 3.9 Raman experimental setup showing AuNP drop casted on a microscopic glass with TiCl₄ precursor which in turn is held in place by a thin coverslip glass
Figure 3.10 Schematic diagram of experimental setup for TEM grid under Raman
Figure 3.11 Hitachi HF3300 High resolution transmission electron microscope
Figure 4.1 Geometries of simulated gold NPs (a) 35nm diameter sphere (b) 1:1 NS (c) 1:2 NS (d) 1:3 NS (e) Random NS
Figure 4.2 Simulated absorption cross-sections of gold nanostars
Figure 4.3 Calculated extinction (continuous lines) and scattering (dashed lines) spectra of gold nanostar discretized into simplified cone-sphere geometries. Core diameter is 97nm and cone height is 76nm. The green line shows experimental extinction spectrum of gold nanostar. Reproduced from [95] with permission of The Royal Society of Chemistry (RSC)
Figure 4.4 Power loss density maps of 1:3 NS at (A) 785nm and (B) 523nm. Maximum and minimum power loss density values are (A) 1.38x10⁹ W/m³, 127W/m³ and (B) 1.02x10⁶ W/m³, 9281 W/m³, respectively
Figure 4.5 Power loss density distribution of Random NS at (A) 747nm and (B) 519nm. Maximum and minimum power loss density are (A) 1.4x10⁹ W/m³, 222 W/m³ and (B) 1.43x10⁷ W/m³, 1x10⁴ W/m³
Figure 5.1 Raman spectrum of TiCl₄ precursor at t=0 and t=20s of 532nm laser exposure

Figure 5.2 Raman spectrum of P25 and l-AuNST at 100%, 50%, and 25% laser intensity obtained after 20s under 532nm laser in 1M TiCl₄

Figure 5.3 Raman spectra with varying laser intensity for (a) l-AuNST, (b) s-AuNST, (c) AuNSp, and (d) AuNFL. Obtained under 532nm laser after 20s of exposure in 1M TiCl₄

Figure 5.4 Growth rate of 150cm⁻¹ anatase peak for l-AuNST with respect of time for 100%, 50%, and 25% 532nm laser power in 0.2M TiCl₄

Figure 5.5 Raman spectra for (a) l-AuNST, (b) s-AuNST, (c) AuNSp, and (d) AuNFL collected under 532nm laser after 20s exposure at 100% power while varying the precursor concentrations (0.2M, 1M, and 2M)

Figure 5.6 Raman spectrum obtained at the indicated location of l-AuNST by performing a line scan at 1% under 785nm laser after laser irradiation under 785nm laser at 100% for 20s. Green line with (R) marks rutile Raman peaks and black line with (A) marks anatase peaks

Figure 5.7 Raman spectra of (a) AuNSp and (b) l-AuNST under 532nm laser after 20s in 2M TiCl₄

Figure 5.8 Raman spectrum of 2M TiCl₄ precursor under 785nm laser at 100% power at t=0 and t=20s

Figure 5.9 Raman spectra of (a) AuNSp and (b) l-AuNST under 785nm laser after 20s in 2M TiCl₄

Figure 5.10 (A) TEM image of P25 TiO₂ nanopowder. (B) HR-TEM of P25 showing lattice spacing. (C) EELS spectrum of P25

Figure 5.11 (A) TEM image of l-AuNS surrounded by TiO₂ prepared by hot plate heating at 80°C for 1.5hours in 0.2M TiCl₄ solution. (B) and (C) shows HR-TEM image of nanocrystalline precipitate of TiO₂
Figure 5.12 1-AuNSt prepared in 1M TiCl$_4$ under 785nm laser at 100% power. (A) near the centre of laser spot, (B) away from the centre spot, (C) and (D) show EELS spectra of (A) in the range of 230 to 580eV................................................................. 69

Figure 5.13 1-AuNSt prepared in 1M TiCl$_4$ under 785nm laser at 10% power ....................... 71

Figure 5.14 1-AuNS under 638nm laser in 1M TiCl$_4$, 5s (a,b) at 12.5% power and (c,d) at 25% power.................................................................................................................. 72

Figure 5.15 1-AuNSt prepared in 1M TiCl$_4$ under 532nm 10% for 5s. (b) HRTEM image of (a) 73

Figure 5.16 (a,b,c) s-AuNSt in 1M TiCl$_4$ under 638nm at 100% power 5s (d) EELS spectrum of (c) ......................................................................................................................... 74

Figure 5.17 S-AuNSt prepared in 1M TiCl$_4$ under (a) 532nm 50% power, (c,d) 532nm 12.5% power. (b) EELS spectrum of (c,d) .................................................................................................................. 75

Figure 5.18 (a)XEDS mapping of s-AuNSt in 1M TiCl$_4$ under 532nm laser at 12.5% power after 5s (b) corresponding SEM image (c,d,e,f) map of oxygen, gold, titanium, and carbon respectively ................................................................................................................. 76

Figure 5.19 TEM image of s-AuNS in 1M TiCl$_4$ under 785nm laser for 5s (a,b) at 100% power and (c) corresponding EELS spectrum while (d,e) at obtained under 50% power with (f) corresponding EELS spectrum. Inset in (e) is FFT image................................................................. 78

Figure 5.20 TEM images and EELS spectrum of AuNFl in 1M TiCl$_4$ under (a,b,c) 532nm at 10% for 20s, (d,e,f) 638nm at 50% for 5s. (g,h) 785nm at 50% for 5s ................................................. 79

Figure 5.21 (a) AuNSp in 1M TiCl$_4$ under 532nm laser at 5% for 5s and (b) HRTEM image of red square indicated in (a) .................................................................................................................. 80

Figure 5.22 SEM images of l-AuNSt after being subjected in furnace for 5 min at (A) Room temperature, (B) 100°C, (C) 200°C, and (D) 300°C ................................................................................................. 81

Figure 6.1 Simplified diagram of light assisted TiO$_2$ synthesis on AuNS using flow reactor concept ................................................................. 87
List of Abbreviations and Acronyms

$\alpha$ polarizability

$\gamma$ reciprocal of electron relaxation time

$\delta T_{NP}$ temperature increase of nanoparticle

$\delta T(r)$ temperature increase at r distance away from the centre of nanoparticle

$\Delta \omega(T)$ Stokes shift at a given temperature

$\varepsilon(\omega)$ dielectric function

$\varepsilon$ electric constant of medium

$\varepsilon_o$ vacuum permittivity

$\varepsilon_s$ dielectric constant of surrounding medium

$\kappa_s$ thermal conductivity of surrounding medium

$\kappa$ force constant of a particular bond and type of vibration in Raman spectroscopy

$\lambda$ wavelength of light

$\mu$ magnetic constant of medium

$\mu_m$ reduced mass of a molecule

$\nu_0$ frequency of incident light

$\nu_m$ vibrational frequency of molecule

$\rho$ volume density of electric charge in a medium

$\sigma_{abs}$ absorption cross-section

$\sigma_{ext}$ extinction cross-section

$\sigma_{scat}$ scattering cross-section

$\chi$ shape factor of a nanoparticle

$\omega$ frequency of light

$\tilde{\nu}$ wavenumber (Raman shift)

$\omega_p$ plasma frequency
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>symmetric with respect to principal axis and rotation axis</td>
</tr>
<tr>
<td>A₁₉</td>
<td>symmetric with respect to principal axis, rotation axis, and centre of symmetry</td>
</tr>
<tr>
<td>APTES</td>
<td>(3-Aminopropyl) triethoxysilane</td>
</tr>
<tr>
<td>AuNFl</td>
<td>gold nanoflower particles</td>
</tr>
<tr>
<td>AuNP</td>
<td>gold nanoparticle</td>
</tr>
<tr>
<td>AuNSp</td>
<td>spherical gold nanoparticle</td>
</tr>
<tr>
<td>B</td>
<td>magnetic flux density</td>
</tr>
<tr>
<td>B₁₉</td>
<td>Antisymmetric with respect to principal axis but symmetric with respect to rotation axis and centre of symmetry</td>
</tr>
<tr>
<td>c</td>
<td>speed of light</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>CCD</td>
<td>charge-coupled diode</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapour deposition</td>
</tr>
<tr>
<td>CW</td>
<td>continuous wave</td>
</tr>
<tr>
<td>D</td>
<td>electric displacement</td>
</tr>
<tr>
<td>DI</td>
<td>deionized</td>
</tr>
<tr>
<td>E</td>
<td>doubly degenerate vibrations in Raman spectroscopy</td>
</tr>
<tr>
<td>E</td>
<td>electric field strength</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
</tr>
<tr>
<td>E₉</td>
<td>Doubly degenerate vibrations with symmetric centre of symmetry</td>
</tr>
<tr>
<td></td>
<td>magnitude of electric field</td>
</tr>
<tr>
<td>e</td>
<td>charge of an electron</td>
</tr>
<tr>
<td>e-h</td>
<td>electron-hole</td>
</tr>
<tr>
<td>EM</td>
<td>electromagnetic</td>
</tr>
<tr>
<td>F₂</td>
<td>triply degenerate vibrations with antisymmetric rotation axis</td>
</tr>
<tr>
<td>fs</td>
<td>femtosecond</td>
</tr>
</tbody>
</table>
Fwhm  full width at half maximum
H  magnetic field strength
HAuCl₄  chloroauric acid
HRTEM  high resolution transmission electron microscopy
I  irradiance of incoming light
I_{laser}  intensity of laser
\vec{J}(t, \vec{r})  volume density of electric current
k  angular wave number
l-AuNS  long gold nanostar particles
LSPR  localized surface plasmon resonance
m  electron mass
n  free electron density
NP  nanoparticles
n_s  refractive index of surrounding medium
P_{laser}  power of laser
p  electric dipole moment
PML  perfectly matched layer
PR  plasmon resonance
ps  picosecond
PVD  physical vapour deposition
Q  absorbed power by nanoparticle
Q_h  power loss
q(r)  heat power density as a function of radial distance away from the centre of nanoparticle (r)
R  radius of nanoparticle
r  radial distance away from the centre of nanoparticle
s-AuNSt  short gold nanostar particles
SEM  scanning electron microscopy
SERS  surface enhanced Raman spectroscopy
SPR  surface plasmon resonance
T  temperature
$T_0$  reference temperature
t  time
TEM  transmission electron microscopy
TiCl$_4$  titanium tetrachloride
TiO$_2$  titanium dioxide (titania)
V  volume of nanoparticle
XEDS  x-ray energy dispersive spectroscopy
Z  calibration constant for temperature-Stokes shift correlation
Chapter 1

1 General Introduction

1.1 Overview

During the past few decades, the interest in the field of plasmonics has seen a resurgence in part due to the remarkable optical phenomena associated with it and the growing accessibility to nanomaterials synthesis and characterization tools [1]–[5]. When near-infrared (wavelength, $\lambda \sim 700$-1400 nm) and visible ($\lambda \sim 400$-700 nm wavelengths) electromagnetic (EM) radiation is incident on noble metal nanoparticles (NPs) of subwavelength dimensions, multiple fold enhancement in scattering, absorption, and electric field intensity occurs in the near-field, proximal to the metallic nanoparticles, as a result of collective oscillation of the free electrons in the metal, otherwise known as localized surface plasmon resonance (LSPR) [6]. Such plasmonically enhanced optical phenomena have been studied over several decades with well-established applications in surface enhanced Raman spectroscopy (SERS) [7]–[10], sensing [6], [11], [12], and the development of plasmonic antennas [13]. Heat generation as a result of plasmonically enhanced absorption in metal nanoparticles is another recently emerging research area in the field that offers a reliable tool to remotely control the local temperature within nanoscale boundaries suitable for a variety of applications which include photothermal cancer therapy [14]–[16], nanosurgery [17], drug delivery [18], [19], nanoscale temperature control [20], biomedical imaging [21], [22], solar thermal energy harvesting [23]–[25] and nanochemistry [26] applications.

Since most chemical reactions are heavily temperature dependent, plasmonic heating can potentially improve chemical selectivity through intensification of photon/light energy and thereby assist chemical reactions or electron transfer in electrochemical reactions [27]. The incorporation of plasmonics in chemical synthesis has been explored by Cao et al. [26] in 2007 where they reported the growth of carbon nanotubes at room temperature using an optically excited array of gold NP in a gaseous medium. In 2008, Ueno et al.[28] reported localized polymerization of SU8 photoresist polymer within the nanoscale gaps in a periodic array of gold nanostructures where the plasmonic near-field enhancement is the strongest. This experiment not only mapped the near-field distribution around resonating gold structures but also demonstrated
the idea of localized chemical reactions induced by a two-photon absorption process. In 2009, Adleman et al.[29] reported generation of CO₂, CO, and H₂ bubbles using patterned gold NP within ethanol and water containing microfluidic cell under laser irradiation. In 2012, Carlson et al.[30] reported superheating of water in the vicinity of gold nanodots on a thermal sensor up to 594 K under 532nm continuous wave (CW) laser illumination. Plasmonic heat generation on gold nanoparticles, as proposed in this thesis, can be utilized to assist with the synthesis of designer core-shell nanostructures.

The combination of metal and semiconducting material results in unique optoelectrical properties [31] owing to the creation of Schottky barrier - a depletion layer at the metal-semiconductor interface. The Schottky barrier is associated with electronic band bending phenomena the properties of which can be tuned. Further, metal-semiconductor heterostructures/nano-spherical composites have large electronic capacitance due to the large energy difference between the Fermi energy of metal core and conduction band (CB) of the semiconductor shell. This type of electronic structure favours trapping of charge carriers in the core for prolonged periods of time [31]. Schottky junction interfaces may also serve as a space charge layer which enables electron-hole separation with the metallic region serving as a fast lane for charge transfer as well as providing trap centers that function as active sites for photoreactions. These extraordinary properties of metal-semiconductor nanocomposite structures can further help suppress e-h recombination and prolong the lifetime of excited charge carriers which is highly favorable for applications in photocatalysis [32]. In this context, photocatalytic reactions in metal-semiconductor composites can significantly benefit from the prominent feature of LSPR including visible light responsivity, enhanced light absorption, smaller electron-hole (e-h) diffusion length, enhanced local electric field, local heating effect, and molecule polarization effect [32].

An example of a metal-semiconductor structure with outstanding photocatalytic properties in the visible range of light is titanium dioxide (TiO₂) coupled with gold nanoparticles. Photocatalyst, as the name suggests, refers to a type of material which has the ability to transform light energy into chemical energy by generating reductive or oxidative species to participate in a desired chemical reaction [33] and ideally at significantly enhanced kinetics. Among various photocatalysts, TiO₂ (titania) is the most well-researched photocatalytic material due to its abundance, non-toxicity, low cost, and high photocatalytic activity [33]. A few applications of
titania photocatalyst are water/air purification, hydrogen generation by water splitting reaction, self-cleaning paints, sterilization in hospitals, and decomposition of organic compounds [34]. However, TiO$_2$ poses two critical drawbacks: high UV photon energy requirement (<380nm) and high $e$-$h$ pair recombination rate due to volume and surface recombinations [35]. One method of overcoming the large band gap (energy) limitation is by integrating gold NP with titania in order to help absorb visible light via SPR phenomena, thus resulting in an effective Au-TiO$_2$ photocatalyst in the visible – hence, a plasmonic photocatalyst. Au-TiO$_2$ plasmonic photocatalysts have been studied and tested under visible light by several research groups. Hou et al. have demonstrated a 9-fold enhancement in the decomposition of methyl orange with Au films on TiO$_2$ under 532nm laser illumination [36]. Neatu et al. reported detoxification of volatile organic compounds using AuNP/TiO$_2$ powder under visible light [37]. Photoreduction of CO$_2$ has been demonstrated by Hou et al. using AuNP/TiO$_2$ which yields methane under visible light irradiation [38]. Au/TiO$_2$ prepared by a deposition-precipitation method has also showed oxidation of cinnamyl alcohol under visible light [39].

The synthesis of Au-TiO$_2$ plasmonic photocatalysts is commonly categorized into three techniques: deposition-precipitation, photoreduction, and encapsulation [40]. Deposition-precipitation is the most frequently adapted technique where TiO$_2$ powders are added to aqueous solution of HAuCl$_4$ and stirred for ~24hours at a constant pH to deposit Au$^{3+}$ ions on TiO$_2$ [41]. The resulting powder is retrieved and exhaustively washed to remove Cl$^{-}$ ions. Finally, the adsorbed Au$^{3+}$ ions are precipitated into metallic AuNP by thermal treatment under an appropriate reducing atmosphere or in a reducing liquid medium. The method yields very small (~5nm) AuNP with good reproducibility and is a simple procedure. However, the deposition-precipitation method requires careful control over the pH and temperature of the gold precursor solution and is associated with long synthesis time. The photoreduction technique, also known as photodeposition, is carried by dispersing TiO$_2$ powder in aqueous HAuCl$_4$ solution under UV light source. UV light creates excited electrons in the conduction band of TiO$_2$ which reduces Au$^{3+}$ to Au$^0$ leading to the deposition of AuNP on TiO$_2$ surface while alcohols in the solution acts as hole scavengers to prevent positive charge accumulation on TiO$_2$ [41]. Photoreduction method allows for high AuNP loading with less aggregation as there is no thermal treatment step involved, but the approach suffers from low reproducibility [40]. Lastly, the encapsulation technique is used to create more sophisticated composites such as core-shell structures. There are
multiple variations to the encapsulation technique depending on the type of core-shell structure desired. One approach is to start with an organic aqueous medium containing titanium precursor and Au\(^{3+}\) which serves to aggregate TiO\(_2\) precursors into microspheres containing Au\(^{3+}\) via solvothermal treatment [42]. Then following with a hydrothermal treatment induces diffusion of Au\(^{3+}\) to the core while hydrolysis of titanium precursor takes place which forms a shell around the gold core. The Au\(^{3+}\) is reduced in situ to Au\(^0\) by an organic substance during the hydrothermal process. This method yields clusters of AuNP surrounded by a layer of anatase TiO\(_2\) and thus making Au-TiO\(_2\) microspheres. Another encapsulation method was demonstrated by Zhang et al.[43] where 3-Aminopropyl triethoxysilane (APTES) treated silica spheres are coated with AuNP by immersing the silica spheres in a colloidal solution of citrate stabilized AuNP solution. Next, a layer of amorphous TiO\(_2\) was formed by hydrolysis of titanium precursor followed by calcination to obtain anatase TiO\(_2\). Both encapsulation processes, however, require multi-step chemical processes or calcination at high temperature. Also, both techniques result in micro-sized particles which have lower surface area compared to nanoparticles of equivalent weight.

In this thesis, we propose a new core-shell Au-TiO\(_2\) nanoparticle synthesis method which attempts to address the aforementioned disadvantages of conventional techniques. To the best of our knowledge, this is the first study on light-assisted localized synthesis of TiO\(_2\) on gold nanoparticles at ambient pressure and temperature.

1.2 Objective of the thesis

The objective of this study is to explore the use of various gold nanoparticles under continuous laser illumination as a nano-source of localized heat to synthesize crystalline TiO\(_2\) by selective hydrolysis of TiCl\(_4\) liquid precursor. To the best of our knowledge, this is the first study on light assisted localized synthesis of TiO\(_2\) using gold nanoparticles on a surface. We explore a number of shapes and sizes of gold nanoparticles including long-gold nanostar (l-AuNSt), short-gold nanostar (s-AuNSt), gold nanoflowers (AuNF), and gold nanospheres (AuNSp). Considering that the sharp tips of l-AuNSt particles serve as antennas to harvest various wavelengths of light, the focus of the research reported herein is on l-AuNSt featuring sharp tips protruding from a spherical gold core. Naturally, these particles resonate plasmonically under different frequencies and will be subjected under matching or mismatching laser sources to investigate the role of
plasmonic resonance in heat generation and localized crystallization of TiO$_2$ on the surface of the gold nanoparticles. More specifically, our objective is to create designer nanoparticles where the crystallization of TiO$_2$ is localized to the valleys of gold nanostars so as to ensure that the tips of gold particles remained exposed/uncovered. Creating partly-covered gold/TiO$_2$ core-shell structures is a challenging task with the conventional techniques mentioned previously. Thus, by proposing this novel light assisted synthesis method, we aim to investigate this new approach for nano-scale controlled designer particle synthesis and provide a first proof-of-concept within the context of the titania-gold material system.

1.3 Scope of the thesis

The present thesis is organized as follows:

In this first chapter, we have presented a brief overview of the field of plasmonics vis-à-vis thermochemical applications and provided the motivation and objective of the current study. In Chapter 2, background fundamentals will be provided on localized surface plasmon resonance of metal nanoparticles, thermoplasmonics, hydrolysis of titanium tetrachloride (TiCl$_4$) and the resulting precipitation process of titania, and theory of Raman spectroscopy. Chapter 3 presents the synthesis method of gold nanoparticles (AuNP) and corresponding SEM/TEM images of AuNP, experimental setup, and characterization techniques employed in this study. Chapter 4 provides an introduction to COMSOL Multiphysics simulation software and presents COMSOL simulation/modelling data on gold nanostars. Chapter 5 presents the experimental findings of this research. This includes Raman characterization and TEM analysis of Au-TiO$_2$ composite structures and a comprehensive analysis on the crystallization behavior of TiO$_2$ on the four geometries of AuNP. The concluding Chapter 6 provides a summary of the key findings emerging from this research, discusses potential applications of the new synthesized Au-TiO$_2$ structures, and muses on further future research and development of the subject at hand.
Chapter 2

2 Principles and Theory

Successful design of an efficient titania on gold nanoparticle core-shell structure requires a thorough understanding of the underlying phenomena including the plasmonic light absorption and heat generation. A summary of these principles along with a description of the various experimental setups used to characterize the synthesized core-shell material are reported in this chapter.

2.1 Localized surface plasmon resonance

Impinging electromagnetic (EM) radiation incident on subwavelength metallic nanostructures can excite a collective oscillation of the free electrons in metal which is referred to as plasmonic resonance (PR). The plasmonic excitations/resonances follow a cyclic oscillation: Columbic attractive forces between the negatively charged electrons and the positively charged nuclei of metal atoms generate a restoring force that relaxes the electron cloud which was (plasmonically) elongated relative to the nuclei; once the electrons relax back into the ground electronic state, they again undergo plasmonic oscillations/excitations which in turn is followed by another relaxation - all of this happening whilst the incident electromagnetic radiation is present [44].

At the interface between a metal surface and a dielectric material such as air or glass, plasmon resonances take the form of surface plasmon resonances (SPR) [45]. Here the surface plasmons give rise to a collective oscillations of electron density at the metal surface. Plasmonic oscillations at the interface between a metal and a dielectric can significantly enhance the optical near field in close proximity of the metal surface [46]. At the surface of extreme sub-wavelength metal nanoparticles, SPR features intense non-homogeneous oscillating electric fields in the vicinity of metal NP which is termed as localized surface plasmon resonance (LSPR). The enhancement magnitude of electric field may vary from ~10^3 around a single particle to more than 10^6 in the gaps within a nanoparticle array [47].

In the absence or cessation of incident radiation, at the femtosecond timescale surface plasmon resonances decay via two damping mechanisms: radiative damping and non-radiative damping processes [6]. In radiative decay, also known as scattering, the re-emission of photons with energies equal to the energy of the incident photon causes the damping of the plasmonic
oscillations [48]. On the other hand, non-radiative decay is associated with light absorption and consequent heat generation caused by electron-hole pair generation from intraband excitations in the CB or interband transitions from d-band to CB for noble metal NP [49]. As the electrons and holes thermalize as a result of electron-electron scattering, electron-phonon scattering, and surface scattering, heat is generated [3] [50]. The latter process, non-radiative decay, will be discussed in more detail in section 2.2.

The interaction between metals and electromagnetic waves can be understood by looking at how a certain material affects the e-field compared to vacuum, thus giving rise to an important physical property called the dielectric constant ($\varepsilon$) [44]. Dielectric function represents the optical property of a material as a function of the frequency of light. The dielectric function, $\varepsilon(\omega)$, of a material can be represented as:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma \omega} \quad (\text{Eq} \ 2.1)$$

In the above equation, $\omega$ is incident angular frequency of the light, $\gamma$ is the reciprocal of electron relaxation time, and $\omega_p$ is the bulk plasmon oscillation frequency (called plasma frequency) defined as [45]:

$$\omega_p^2 = \frac{n e^2}{\varepsilon_0 m} \quad (\text{Eq} \ 2.2)$$

where $n$ is the free electron density, $\varepsilon_0$ is the vacuum permittivity, $m$ is the electron mass, and $e$ is the electron charge. At room temperature where $\omega >> \gamma$ the real and imaginary parts of the dielectric function can be approximated as:

$$\text{Re}[\varepsilon(\omega)] \approx 1 - \frac{\omega_p^2}{\omega^2} \quad (\text{Eq} \ 2.3)$$

$$\text{Im}[\varepsilon(\omega)] \approx \frac{\omega_p^2 \gamma}{\omega^3} \quad (\text{Eq} \ 2.4)$$
The real part of the dielectric function is responsible for Rayleigh scattering, which is elastic scattering of electromagnetic radiation by particles or molecules much smaller than the wavelength of the radiation. The imaginary component of the dielectric function represents the absorption process. Excited LSPs are responsible for both absorption and scattering effects which can be described by cross-sections as shown below [49]:

\[ \sigma_{\text{abs}} = k \, \text{Im}(\alpha) \quad (\text{Eq } 2.5) \]

\[ \sigma_{\text{scat}} = \frac{k^4}{6\pi} |\alpha|^2 \quad (\text{Eq } 2.6) \]

\[ \sigma_{\text{ext}} = \sigma_{\text{abs}} + \sigma_{\text{scat}} \quad (\text{Eq } 2.7) \]

where \( k \) is the angular wave number in the surrounding medium and \( \alpha \) is the polarizability which for a small spherical particle can be represented as [51]:

\[ \alpha(\omega) = 4\pi R^3 \frac{\varepsilon(\omega) - \varepsilon_s}{\varepsilon(\omega) + 2\varepsilon_s} \quad (\text{Eq } 2.8) \]

\( \varepsilon_s \) refers to the dielectric constant of surrounding medium. Since the origin of plasmonic resonance is the change in electromagnetic dipole, maximum resonance occurs when \( \alpha \) is maximum which happens at \( \varepsilon(\omega) \approx -2\varepsilon_s \). Therefore the plasmon resonance can be expressed as [45]:

\[ \omega_{\text{max}} = \frac{\omega_p}{\sqrt{2\varepsilon_s + 1}} \quad (\text{Eq } 2.9) \]

Thus, it becomes clear that as the dielectric function of the surrounding medium increases the LSPR peak redshifts.

For larger spheres, the above presented dipole approximation method is no longer valid and Mie theory (analytical solutions to Maxwell’s equations) should be used to account for retardation effects [51].

Applying Mie theory, extinction and scattering cross-sections can be represented as [52]:
As demonstrated in the two equations above, the optical properties of the metallic nanoparticles are affected by the shape ($\chi$) and the volume ($V$) of the particles as well as the dielectric of the surrounding medium ($\varepsilon_s$) which has been previously reported in the literature. An example of this is illustrated in Figure 2.1 [47].

Figure 2.1. (a) Normalized extinction spectra of Ag (38nm), Au (25nm) and Cu (133nm). (b) Normalized extinction spectra for Ag wire (90nm diameter with aspect ratio >30), cube (79nm edge), and sphere (38nm). (c) Normalized extinction spectra for Ag nanocubes with increasing size (56nm, 79nm, 129nm). Reprinted by permission from Macmillan Publishers Ltd: [Nature Materials] (47), copyright (2011).

Figure 2.1a illustrates how each type of metal has its own LSPR peak; here silver is more blueshifted compared to gold or copper. The effect of shape on the location of LSPR band is depicted in Figure 2.1b. Regardless of the type of metal, a redshift of LSPR band as well as

\[
\sigma_{\text{ext}} = \frac{18\pi\varepsilon_s^{3/2}V}{\lambda^4} \frac{\text{Im}(\varepsilon)}{\left|\text{Re}(\varepsilon)\chi\varepsilon_s\right|^2 + \left|\text{Im}(\varepsilon)\right|^2} \quad (\text{Eq } 2.10)
\]

\[
\sigma_{\text{scat}} = \frac{32\pi^4\varepsilon_s^2V^2}{\lambda^4} \frac{\left|\text{Re}(\varepsilon)\chi\varepsilon_s - \varepsilon_s\right|^2 + \left|\text{Im}(\varepsilon)\right|^2}{\left|\text{Re}(\varepsilon)\chi\varepsilon_s\right|^2 + \left|\text{Im}(\varepsilon)\right|^2} \quad (\text{Eq } 2.11)
\]

\[\text{Shape factor } (\chi) = 2 \text{ for spheres and can be as large as } 20 \text{ for particle geometries with high aspect ratios. }\chi \text{ can be calculated analytically for spheres or spheroids but numerical methods are required for more complex geometries [53].}\]
increased bandwidth is observed (Figure 2.1c) with increasing particle size because light can no longer polarize the metal homogeneously and the retardation effects results in higher order modes (quadrapole or octapole) [54]. Non-spherical shape typically exhibits more than a single resonance peak due to the varying degree of polarization depending on the direction and location of excited surface plasmon modes.

The ratio of absorption and scattering cross-sections are strongly influenced by size where, for example, gold NPs smaller than 90nm in water show absorption dominant behavior whereas larger particles show scattering dominant properties as shown in Figure 2.2a. At fixed particle size, absorption and scattering cross-sections are influenced by the wavelength as shown in Figure 2.2b [51]. Thus, depending on the desired applications (whether it be maximizing scattering for sensing or absorption for heating) both the particle size as well as the incident wavelength should be carefully selected to obtain desired results.

![Figure 2.2](image)

Figure 2.2 (a) Absorption and scattering cross-section of gold sphere with respect to the diameter. (b) Absorption and scattering cross-section for 88nm gold sphere with respect to wavelength. Reprinted by permission from John Wiley and Sons [51]

### 2.1.1 Localized Surface Plasmon resonances in Gold Nanostars

Since the focus of the present thesis is on gold nanostars, a brief literature review on the previously reported studies on such nanostructures is presented in this section. In a study done by
Yuan et al., finite element method (using COMSOL software) was used to simulate absorption and scattering cross-sections of gold nanostars suspended in water as shown in Figure 2.3 [55]. The reported data shows polarization averaged cross-sections for two different aspect ratios of AuNS particles. This result shows that upon illumination majority of the incoming photons participate in the absorption process which decays as heat. It is due to the unique geometrical structure of the AuNS that it is an efficient light absorber than a scatterer. According to the authors, depending on the aspect ratio of the AuNS, the ratio of $\sigma_{\text{abs}}/\sigma_{\text{scat}}$ can be as high as 10.8 times [55].

Figure 2.3 Simulated absorption (closed dot) and scattering (open dot) cross-sections of gold nanostars. For tip aspect ratio of 1.4, core was 24nm in diameter, tip length/base width was 19nm/13.5nm, and number of tips was 8. For tip aspect ratio of 2.2, core diameter was 22nm, tip length/base width was 22nm/10nm, and number of tips was 10. Reprinted with permission from Elsevier [55]
Rodriguez-Oliveros and Sanchez-Gil have performed numerical calculations on the plasmonic heating effect for gold nanostars using 3D Green’s theorem which calculates the electromagnetic field distribution using surface integral equations [56]. They have found that increasing the number of tips results in red-shifted LSPR peaks with large enhancements of the electric field intensity ($E^2 \sim 10^4$) observed at the vertex. Absorption cross-section also increases with an increase in the number of tips. Increasing the sharpness of the tip also red-shifted LSPR peaks with a larger magnitude absorption cross-section. They also reported that Au nanostars exhibit ~30 fold increase in steady state temperature compared to equivalent spherical particles [56]. In a numerical study done by Ma et al.[57], six branched gold star was simulated for temperature distribution using finite element method (COMSOL) under laser illumination. As seen in Figure 2.4, the maximum temperature (319K) occurred at the centre with lowest temperature at the vertex. It is worthwhile to note that even though the maximum e-field enhancement occurs at the sharp vertex, maximum temperature happens at the core near the troughs between the branches.

![Figure 2.4 Simulated temperature profile on gold star under 0.22mW laser. Reprinted with permission from [57]. Copyright (2014) American Chemical Society.](image)

Plasmonic heat generation around metal nanostructures is described in more detail in the following section.
2.2 Thermoplasmonics

Thermoplasmonics refer to the new sub-field of plasmonics studying the theory and application of plasmonic nanostructures as a source of heat [51]. Even though the optical behaviour of plasmonic nanostructures under EM field is a well-understood subject, determination of near-field temperature distribution largely remains a difficult task [5], [58], [59] as it must encompass heat transfer via conduction, radiation, and convection [60]. The electron dynamic process occurring upon illumination is a multi-step process at femtosecond time scales. First, incident photons create excited electrons which undergo e-e scattering and are at thermal equilibrium within \( \sim 100\text{fs} \) [54]. The electron energy is transferred to the lattice via electron phonon coupling in a few ps. Due to the temperature increase in the NP, the heat is transferred to the surrounding medium via phonon-medium interaction. The last stage in the heat transfer is thermal diffusion within the medium. The complete process of energy transfer from incident photon to surrounding medium as heat happens within a few nanoseconds. Thus, the temperature distribution under continuous or pulsed laser source should be treated differently as is discussed in the following sections.

2.2.1 Temperature profile under CW illumination

Upon illumination, the power absorbed by NPs can be calculated using \( \sigma_{\text{abs}} \) as shown below [51]:

\[
Q = \sigma_{\text{abs}} I \quad \text{(Eq 2.12)}
\]

where \( I \) is the irradiance of incoming light defined as [61]:

\[
I = \frac{n_s c \varepsilon_0 |E_o|^2}{2} \quad \text{(Eq 2.13)}
\]

where \( n_s \) is the refractive index of surrounding medium, \( c \) is the speed of light, \( \varepsilon_0 \) is the vacuum permittivity, \( |E_o| \) is the magnitude of the electric field. This relationship is only valid when the interparticle distance is several times larger than the NP diameter. The absorption cross-section of a spherical particle can be calculated using Mie theory as noted in section 2.1 [62]. However, for complex shapes such as rods, triangles, or dendrites, Mie theory no longer applies and numerical simulation is required to estimate the absorption cross-section.
The heat power (Q) per volume of AuNP can be represented using another parameter called the heat power density $q(r)$ [51]:

$$q(r) = \frac{\omega}{2} Im[\varepsilon(\omega)]\varepsilon_0|E(r)|^2$$  (Eq 2.14)

where $r$ denotes distance away from the centre of NP. From the above relation, it is clear that the heat generation is proportional to the square of the electric field. Assuming spherical NP of radius R, temperature change along the radial distance $r$ can be expressed as:

$$\delta T(r) = \delta T_{NP} \frac{R}{r}, \quad r > R$$  (Eq 2.15)

$$\delta T(r) \approx \delta T_{NP}, \quad r < R$$  (Eq 2.16)

where $\delta T_{NP}$ is the temperature increase of NP. Notice that inside the NP, temperature increase is very uniform unlike the heat power density $q(r)$ which is heavily influenced by the local electric field. This is attributed to much larger thermal conductivity of metals (compared to the surrounding medium) immediately attaining thermal equilibrium within the NP. Other parameters that may affect the temperature increase are absorption cross-section, morphology of NP, thermal conductivity of the surrounding medium, illumination wavelength, and the irradiance of the light source [51]. The temperature increase for a spherical NP can be expressed by [51]:

$$\delta T_{NP} = \frac{Q}{4\pi\kappa_s R}$$  (Eq 2.17)

where Q is the delivered heat power (W), $\kappa_s$ the thermal conductivity (W/m.K) of surrounding medium, and $R$ the radius (m) of spherical NP. For non-spherical NPs, an effective radius is substituted for $R$ in the calculation.

The table below provides an overview of the type of thermoplasmonic experiments and corresponding values of the temperature and laser intensity reported in the literature.
Table 2-1 Summary of thermoplasmonic experiments²

<table>
<thead>
<tr>
<th>Type</th>
<th>Size</th>
<th>Synthesis</th>
<th>Light source</th>
<th>Intensity of light source [W/m²]</th>
<th>Resulting Temp. increase</th>
<th>Observation</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Au thin film</strong></td>
<td>~10-50nm</td>
<td>5nm Au film by e-beam evaporation</td>
<td>532nm CW</td>
<td>1.22x10^{13}</td>
<td>&gt;200°C</td>
<td>Fabrication of Au-Fe₂O₃ composite from iron oxide precursor gas</td>
<td>[63]</td>
</tr>
<tr>
<td><strong>Au sphere</strong></td>
<td>12.7nm</td>
<td>Photothermal</td>
<td>532nm pulse</td>
<td>1.41x10^{12}</td>
<td>500 ± 100°C</td>
<td>Chemical decomposition</td>
<td>[64]</td>
</tr>
<tr>
<td><strong>Au sphere</strong></td>
<td>17nm</td>
<td>Chemical synthesis</td>
<td>514nm CW</td>
<td>4973</td>
<td>~50°C</td>
<td>Ligand polymerization</td>
<td>[2]</td>
</tr>
<tr>
<td><strong>Au sphere</strong></td>
<td>20nm</td>
<td>Block copolymer lithography</td>
<td>532nm CW</td>
<td>6.4x10^8</td>
<td>Δ108°C</td>
<td>Water vapour bubble</td>
<td>[29]</td>
</tr>
<tr>
<td><strong>Au sphere</strong></td>
<td>20nm</td>
<td>Chemical synthesis</td>
<td>532nm CW</td>
<td>5x10^8</td>
<td>Δ7°C</td>
<td>Temperature measurement using photocalorimetry</td>
<td>[65]</td>
</tr>
<tr>
<td><strong>Au islands</strong></td>
<td>~50nm</td>
<td>Annealing evaporated Au film (5nm)</td>
<td>532nm CW</td>
<td>4.9x10^8</td>
<td>&gt;380°C</td>
<td>Growth of Si nanotube</td>
<td>[26]</td>
</tr>
<tr>
<td><strong>Au nanorod</strong></td>
<td>90nm length, 27nm diameter</td>
<td>Chemical synthesis</td>
<td>809nm CW</td>
<td>53800</td>
<td>115 ± 10°C</td>
<td>PDMS microfluidic cell. Water heating</td>
<td>[58]</td>
</tr>
<tr>
<td><strong>Au shell on PS beads</strong></td>
<td>10nm thickness on 150nm PS beads</td>
<td>Sputter</td>
<td>633nm CW</td>
<td>6.5x10^9</td>
<td>&gt;350°C</td>
<td>Crystallization of TiO₂, ZnO, CeO₂</td>
<td>[66]</td>
</tr>
<tr>
<td><strong>Ag shell on silica NPs</strong></td>
<td>150nm thick Ag on 540nm Silica</td>
<td>Nanospheres lithography</td>
<td>Xenon lamp</td>
<td>2x10^4</td>
<td>&gt;230°C</td>
<td>Liquid phase chemical deposition of AuNPs</td>
<td>[67]</td>
</tr>
</tbody>
</table>

²This table serves to give a sense of the laser intensity required to achieve a certain temperature increase on a plasmonic gold/silver nanostructures under illumination. Temperature increase as a result of optical illumination on plasmonic nanostructure resulted in changes which are described in the observation column.
2.3 Synthesis of TiO$_2$ via hydrolysis

As the goal of this work is to demonstrate crystallization of TiO$_2$ via hydrolysis of TiCl$_4$ precursor, a brief introduction on the crystal structure of TiO$_2$ as well as the hydrolysis reaction taking place during crystallization is provided in this section.

2.3.1 Crystal structure of TiO$_2$

Titanium dioxide (titania) is an oxide phase of titanium which is commonly found in one of three crystal structures, namely rutile, anatase, and brookite (Figure 2.5). In all three crystal phases, each Ti atom is surrounded by 6 oxygen atoms with two Ti-O bonds slightly longer than the other four. Rutile is a tetragonal structure consisting of each Ti$^{4+}$ ion being surrounded by six O$^{2-}$ ions [68]. The six oxygen ions form an octahedron which is in contact with ten neighbouring octahedra. Anatase and brookite structure both consist of one octahedron surrounded by eight neighbouring octahedra, four octahedra sharing edges while the other four share corners. Anatase and brookite have more distorted octahedra with lower crystalline symmetry than the rutile structure.

![Image of crystal structures](image)

Figure 2.5 Crystal structure of TiO$_2$ in (a) rutile, (b) anatase, and (c) brookite. Grey sphere represents Ti atom octahedrally coordinated with O atoms. Reprinted with permission from [69]. Copyright (2006) American Chemical Society.
In all three phases of TiO$_2$, rutile, anatase, and brookite, Ti-O bond is a mixed ionic-covalent bond with varying degree of ionicity and covalency depending on the crystal structure and size [70].

### 2.3.2 Hydrolysis of titanium tetrachloride (TiCl$_4$)

Synthesis of titania particles is well-studied and developed over the past few decades. The most common synthesis method for commercial TiO$_2$ production is pyrometallurgical process where TiCl$_4$ is oxidized at high pressure and temperature (1200-1700°C) using oxygen plasma. The equation below describes the process [71]:

$$TiCl_4 + O_2 \rightarrow TiO_2(s) + 2Cl_2 \quad (Eq \ 2.18)$$

In research, various methods, such as sol-gel, hydrothermal, solvothermal, chemical vapour deposition (CVD), electrodeposition, direct oxidation, physical vapour deposition (PVD) and aqueous synthesis, have been studied and used to make TiO$_2$ [70]. CVD is carried in a vacuum chamber at high temperature to vaporize starting precursor(s) which are condensed on a substrate after vapour phase chemical reaction [72]. PVD is similar to CVD except it does not involve a chemical reaction rather it is a straight deposition of vaporized Ti precursor [73]. Both CVD and PVD allow fine control over the shape, thickness, and phase of TiO$_2$ but are slow and costly due to the necessity of high vacuum, high temperature conditions, and complexity of equipment setup. Sol-get method is a solution based TiO$_2$ synthesis method where colloidal suspension of Ti(IV) complex undergoes further polymerization with use of metal organic compound, typically alkoxide [74]. Amorphous titanium oxide after polymerization is further treated to obtain crystalline TiO$_2$. Hydrothermal synthesis involves aqueous solvent processed in an autoclave under a specific pressure and temperature. Solvothermal process is similar to hydrothermal except it uses organic solvent instead of aqueous solvent [75]. These two processes are advantageous as the temperature requirement is not as high as CVD and the reaction completes in a relatively short period of time (~an hour). However, it cannot be carried out at atmospheric pressure. Among the various methods, one particular method will be discussed in depth: aqueous synthesis via hydrolysis of TiCl$_4$. Unlike the above mentioned synthesis methods, aqueous synthesis does not involve the use of autoclave or vacuum chambers. All the reactions can be carried out under atmospheric pressure thus making it a low cost option for synthesis. This
technique is also more environmentally friendly compared to sol-gel or solvothermal which uses organic chemicals as precursor solution.

Aqueous synthesis refers to production of oxide particles via hydrolysis of inorganic precursor solution forced (accelerated) by heating, which is referred to as forced hydrolysis. In the present study, inorganic precursor specifically refers to TiCl$_4$ and the simplified chemical reaction for hydrolysis reaction of TiCl$_4$ can be represented as:

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl \text{ (Eq. 2.19)}$$

Forced hydrolysis can take place at atmospheric pressure and relatively low temperature ($<100^\circ$C) upon reaction of pure liquid TiCl$_4$ with water. Various Ti(IV)-H$_2$O complexes are formed depending on the pH and chlorine ion concentration as shown in Figure 2.6 [70].

![Diagram of the species present in TiCl$_4$ in water system with varying pH and chlorine ion concentration](image)

**Figure 2.6** Diagram of the species present in TiCl$_4$ in water system with varying pH and chlorine ion concentration [70]
Generally, as the chlorine ion concentration increases the number of Cl⁻ attached to Ti(IV) increases (coordination number). But as the pH becomes more basic, those Cl⁻ ions tend to get replaced by hydroxyl groups (OH). However, Ti-Cl-H₂O system is a very complex system sensitive to various factors such as dilution factor, temperature, and pressure and determination of precise type and amount of such Ti(IV) complexes – and to this day remains a difficult system to characterize completely.

### 2.3.3 Nucleation and precipitation of Titanium Dioxide (TiO₂)

Nucleation process of TiO₂ from liquid TiCl₄ is a multi-step chemical process involving deprotonation (hydrolysis), olation and oxolation that remove water molecules and connect multiple octahedral Ti(IV) monomers to form the structures illustrated in Figure 2.7. First, starting with a water solvated [Ti(OH)₆]²⁺ monomer, deprotonation creates hydroxyl group which combines with hydrated metal ion (olation reaction) releasing water as represented by:

\[
Ti \cdot H₂O + Ti \cdot OH \rightarrow Ti \cdot OH \cdot Ti + H₂O \quad \text{(Eq 2.20)}
\]

By repeating deprotonation and olation, a chain of [Ti(OH)₆]²⁺ monomers are created which serves as a building block for further growth. The crystalline phase of the resulting TiO₂ is dependent on which octahedral edge of [Ti(OH)₆]²⁺ monomer is shared to form a nuclei. For example, the rutile phase is formed when equatorial edges are shared while anatase or brookite is formed when apical edges are shared (refer to Figure 2.7). The crystallinity and size of resulting particles are strongly related to the hydrolysis temperature and concentration of solution.

According to Cheng et al. [76], smaller particles with few aggregated TiO₂ clusters are formed at higher temperature (>200°C) and low TiCl₄ concentration (<0.5M). Under lower temperature (<100°C) and high TiCl₄ concentration (>1M), precipitated TiO₂ particles were in micron size range. Kim et al.[77] synthesized TiO₂ powders by autoclaving 0.67M TiCl₄ and reported the effect of hydrolysis temperature on the crystalline phase. For T<65°C and T>155°C, rutile phase TiO₂ was formed. Anatase was obtained at temperature between 70°C and 95°C whereas brookite phase was preferred at temperature between 95-155°C. However, in a similar study done by Addamo et al. [78], poor crystalline quality anatase powders were obtained when the drying temperature was decreased to 60°C compared to 150°C in Kim et al.’s study. Thus, these findings suggest that the drying temperature improves the degree of crystallinity. Effect of both the concentration and temperature was studied by Zheng et al. where they synthesized TiO₂ at
200°C by changing the TiCl₄ concentration from 0.1M to 1M [79]. Under this condition, mixed phase of anatase and rutile was formed with rutile content increasing as the concentration increases. They also studied the effect of temperature at fixed TiCl₄ concentration and reported that increasing the hydrolysis temperature also increases the amount of rutile phase.
Figure 2.7 Nucleation and growth mechanism for rutile (top) and anatase/brookite (bottom) [70]
2.4 Raman spectroscopy

Raman spectroscopy is a highly sensitive and powerful characterization technique for studying vibrational and rotational modes of molecular bonding which can be used as a fingerprint to identify and characterize materials. Upon incidence of a monochromatic light source which is an oscillating electromagnetic wave, molecules in a sample interact with the light resulting in an induced electric dipole moment \( p \) as noted below [80]:

\[
p = p(ν_0) + p(ν_0 + ν_m) + p(ν_0 - ν_m) \quad \text{(Eq 2.21)}
\]

The first term describes the majority of the scattered light which has the same dipole moment as the incident light at frequency \( ν_0 \). This is typically referred to Rayleigh scattering. The second and third term represent inelastic scattering called Raman scattering. More specifically, the second term is called anti-Stokes scattering where the scattered light has higher energy than the incident \( (ν = ν_0 + ν_m) \) where \( ν_m \) refers to the vibrational frequency of the molecule. When the scattered light has less energy, i.e. \( ν_0 - ν_m \), it is termed Stokes scattering. During the Stokes scattering, electrons in the ground state are excited to a higher energy level whereas anti-Stokes scattering takes place at a higher occupied energy level. As the higher energy level is less populated than the ground state, the intensity of anti-Stokes scattering is always less than that of Stokes scattering.

A Raman spectrum typically plots intensity as a function of Raman shift or wavenumber \( \tilde{ν} \) in cm\(^{-1} \) which is the change in frequency between the incident and scattered light:

\[
\tilde{ν} = \frac{ν_m}{c} - \frac{ν_0}{c} \quad \text{(Eq 2.22)}
\]

In the above equation \( c \) represents the speed of light and positive wavenumber is Stokes and negative wavenumber is Anti-Stokes scattering. Raman shift is unique to each vibrational, rotational or stretching mode of molecules and can thus be analyzed to study chemical composition, degree of crystallization, distortion, and even temperature [81]–[83].

Interpretation of Raman spectrum from theoretical perspective is a complex topic that involves quantum mechanics and group theory. Readers interested in quantum mechanical approach and derivation should refer to [80][84]. In brief, not all vibrational modes induce dipole moment.
change and whether a certain mode is Raman active or inactive is determined by the selection rules. The selection rules state that Raman active vibration modes only exist if the polarizability changes with respect to the normal coordinate of the molecule. For inorganic molecules such as crystalline solids, both symmetry of the molecule as well as symmetry of the crystalline structure should be considered. The location of vibrational frequency can be predicted by [84]:

\[ \nu_m = \frac{1}{2\pi} \sqrt{\frac{\kappa}{\mu_m}} \]  

(Eq 2.23)

In the above equation, \( \kappa \) represents the force constant of a particular bond and type of vibration whereas \( \mu_m \) represents the reduced mass of a molecule. Each Raman peak corresponds to a specific mode of vibration and the direction of dipole moment change with respect to the symmetry of the molecule. The symmetrical classification of molecules is out of the scope of this work but the following notations [80],[84] will be used to interpret Raman spectra later in the experimental part of the work, Chapter 5.

A: symmetric with respect to the principal axis of symmetry

B: Antisymmetric with respect to the principal axis of symmetry

E: Doubly degenerate vibrations

F: Triply degenerate vibrations

Subscript g and u: Symmetric or antisymmetric with respect to a centre of symmetry

Subscript 1 and 2: Symmetric or antisymmetric with respect to a rotation axis

\( \nu \): stretching vibration

\( \delta \): bending vibration

\( \rho \): rotational vibration
Chapter 3

3 Experimental and Technical Aspects

In this chapter, procedures for AuNP synthesis along with their SEM/TEM characterization will be presented. Preparation of TiCl$_4$ precursor followed by TiO$_2$ crystallization process is presented. Lastly, a brief overview on the experimental setups used for characterization of the samples is provided.

3.1 Experimental Procedures and Characterization

3.1.1 Au NPs synthesis and solution preparation

For this study, a number of gold nanoparticles of different sizes and shapes have been used. Among them, long gold nanostar (l-AuNS) and nanoflower (AuNF) particles were synthesized while short gold nanostar particles (s-AuNSt) were purchased from Cytodiagnostics (Burlington, Canada). Spherical gold nanoparticles (60nm diameter with optical density 1) were purchased from Ted Pella (Redding, USA).

3.1.1.1 Preparation of Au seed solution

Au seed solution was prepared following the Yuan et al.’s approach [85]. First, 10mM stock solution of chloroauric acid (HAuCl$_4$, Gold chloride hydrate, 99.999% trace metal basis from Sigma-Aldrich) was prepared and stored in a refrigerator for long term storage (up to 6 months). Extra care is required for this process as the original powder form of HAuCl$_4$ is highly corrosive and hygroscopic - readily absorbing moisture from air. By diluting the stock solution, 50ml of 1mM HAUrCl$_4$ solution was prepared in 250ml sized Erlenmeyer flask. The Erlenmeyer flask was pre-treated with a freshly prepared mixture of hydrochloric acid with nitric acid in 3:1 volume ratio (aqua regia) for 15min until a color change of the solution from light yellow to deep orange color is observed. This step is critical for consistent gold nanoparticle synthesis as trace metal residues in glassware can affect the nucleation and reduction process. The pre-treated flask containing HAUrCl$_4$ solution was then immersed in oil bath on hot plate and temperature was brought to 100°C while vigorously stirring the solution using magnetic stirrer. Next, 5ml of 50mM sodium citrate solution (C$_6$H$_8$Na$_3$O$_7$·2H$_2$O, sodium citrate dehydrate ≥99%, Sigma-Aldrich) was added to the boiling HAUrCl$_4$ solution and the mixture was kept under vigorous stirring at boiling temperature for 15 min. The following chemical reaction takes place [86]:
\begin{equation}
6\text{AuCl}_4^- + C_6\text{H}_8\text{O}_7 + 5\text{H}_2\text{O} \rightarrow 6\text{CO}_2 + 24\text{Cl}^- + 6\text{Au}^0 + 18\text{H}^+ \quad (\text{Eq. 3.1})
\end{equation}

Originally pale yellow colored HAuCl₄ solution turned into deep red color after the reaction as is shown in Figure 3.1a. The seed solution was cooled down to room temperature and was filtered using 0.45μm nylon filter to remove any unreacted residues or agglomerates. For long term storage, it was kept refrigerated. As presented in Figure 3.1b, the prepared Au seed solution has been characterized using transmission electron microscopy (Hitachi HF 3300, 300keV) by drop casting the solution on 300mesh carbon Cu grids (from Ted Pella). The gold seeds have an average diameter around 11nm.

![Figure 3.1](image.png)

Figure 3.1 (a) prepared Au seed solution (b) TEM image of the Au seed with mean diameter of 11nm

3.1.1.2 Synthesis of long Au Nanostars (l-AuNSt)

One-step seeded growth was used for nanostar synthesis the method described in Yuan et al. method [85]. This particular synthesis method has been chosen because it does not require the use of surfactant and the chemical reaction takes place at room temperature over a short period of time (~30s). Surfactants in colloidal solution are typically used to ensure long term stability and
prevent agglomeration of particles. However, for our purpose of synthesizing a core-shell material which requires direct contact between the gold and TiCl$_4$ precursor, bare gold NP without surfactant is more desired. 40ml of 0.2mM HAuCl$_4$ solution has been prepared from the stock solution in 100ml sized beaker which has been pre-treated with aqua regia solution. Using micropipette, 20µl of 1M HCl solution was added to the beaker. The beaker was kept under stirring rate of 500rpm during the reaction. 200µl of prepared Au seed solution was added. Next, 200µl of 80mM ascorbic acid (C$_6$H$_8$O$_6$, L-ascorbic acid, Sigma-aldrich) and 400µl of 0.5mM silver nitrate solutions (AgNO$_3$, silver nitrate, ACS reagent $\geq$99.0%, Sigma-aldrich) were added into HAuCl$_4$ solution simultaneously. Immediate color change from light yellow to deep blue suggests formation of gold nanostars. The reaction was carried out for 30s and followed by centrifugation at 6700rpm for 12min to halt further reaction. Supernatant was removed and the pellets were re-dispersed in 10ml of DI water and sonicated back into colloidal form.

Figure 3.2 shows TEM and SEM images of prepared long gold nanostar (l-AuNST) particles. Hitachi S-5200 Scanning Electron Microscope (SEM) from the Centre for nanostructure imaging in Department of Chemistry at U of T was used to characterize morphology of l-AuNST. Colloidal solution of l-AuNST was drop casted on a small piece of silicon wafer and carbon paste was used to fix the sample on an aluminum SEM stub. The particle has a round core with spiky cones around the core creating deep valley regions as well as sharp tips. On average, they have tip-to-tip size of 98nm with 38nm core diameter and sharp spikes with 2.35 aspect ratio (Table 3-1).
Figure 3.2 (a,b) TEM images and (c,d) SEM images of the prepared l-AuNS

Table 3-1 Structural features of l-AuNS

<table>
<thead>
<tr>
<th>l-AuNS</th>
<th>Average</th>
<th>Max</th>
<th>Min</th>
<th>S.D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core size [nm]</td>
<td>38.16</td>
<td>44.64</td>
<td>29.69</td>
<td>4.76</td>
</tr>
<tr>
<td>Tip height [nm]</td>
<td>30.15</td>
<td>50.2</td>
<td>8.056</td>
<td>13.41</td>
</tr>
<tr>
<td>Tip base diameter [nm]</td>
<td>12.92</td>
<td>17.78</td>
<td>9.213</td>
<td>2.69</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>2.35</td>
<td>4.74</td>
<td>0.87</td>
<td>1.06</td>
</tr>
</tbody>
</table>

More detail and analysis on the synthesis and characterization of various types of l-AuNS can be found in Appendix A.
3.1.1.3 Synthesis of Au Nanoflowers (AuNFl)

Synthesis of Au nanoflower (AuNFl) particles is based on the reported method by Yi et al. [7]. In a 20ml scintillation vial, 10ml of 5mM dopamine (dopamine hydrochloride, sigma-aldrich) solution was prepared. By addition of 150μl of 1M HCl, the pH was adjusted at 2.4. In a 50ml falcon tube, 10ml of 1mM HAuCl₄ solution was prepared from the 10mM stock solution. pH adjusted dopamine solution was added into the falcon tube with auric acid and the mixture was vortexed for 1min followed by centrifugation at 7800rpm for 20min. Supernatant was removed and the remaining pellet was re-dispersed in water by sonication.

Shown below (Figure 3.3 (a,b) SEM images and (c) TEM image of the prepared AuNF are SEM and TEM images of gold Nanoflowers (AuNFl) prepared. As seen in the images, these particles have dendritic structures featuring pointy tips as well as grooves similar to l-AuNST. However, due to the large size of the AuNFl (tip to tip size ~1μm) they no longer exhibit surface plasmon resonance as will be discussed in section 3.1.2.
Figure 3.3 (a,b) SEM images and (c) TEM image of the prepared AuNF1

Table 3-2 Structural features of AuNF1

<table>
<thead>
<tr>
<th>AuNF1</th>
<th>Average</th>
<th>Max</th>
<th>Min</th>
<th>S.D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core size [nm]</td>
<td>523.56</td>
<td>666.33</td>
<td>365.57</td>
<td>77.22</td>
</tr>
<tr>
<td>Tip height [nm]</td>
<td>211.88</td>
<td>262.49</td>
<td>133.04</td>
<td>39.89</td>
</tr>
<tr>
<td>Tip base diameter [nm]</td>
<td>164.70</td>
<td>247.79</td>
<td>100.25</td>
<td>40.32</td>
</tr>
<tr>
<td>Aspect ratio</td>
<td>1.32</td>
<td>1.74</td>
<td>0.97</td>
<td>0.25</td>
</tr>
</tbody>
</table>

3.1.1.4 Short Au Nanostar (s-AuNSst)

The purchased s-AuNSst has been examined under SEM and TEM and the corresponding images are shown in Figure 3.4. As seen in Figure 3.4, s-AuNSst have larger core diameter of 81.04nm with shorter tip height compared to l-AuNSst. Instead of having sharp peaks with large aspect ratio shown in l-AuNSst, these particles feature aspect ratio of 1.01 with round tips surrounding the core.
3.1.1.5 Spherical gold nanoparticles (AuNSp)

The AuNSp (purchased from Ted Pella) were examined under TEM and are shown in Figure 3.5. The particles have an average diameter of 54.76 nm with standard deviation of 3.69 measured using an image analysis software called Image J.
3.1.2 Optical Properties of gold nanoparticles

For optical characterization of AuNP, UV-Vis Spectrometer (Lambda 1050 from PerkinElmer) in the Advanced Photovoltaics and Devices group (APD group) was used. An image of the system is shown in Figure 3.6. Prior to measurements, a background scan was performed on DI water filled glass cuvette which is automatically subtracted for the subsequent sample measurements. AuNP dispersed in water was sonicated before measurement to minimize aggregation of particles. The optical properties of the synthesized gold nanospheres are tested by measuring the absorbance of the AuNP suspended in water placed in a glass cuvette. A series of measurements with illumination wavelengths varying between 400nm and 850nm were carried out in wavelength increments of 1nm.

![Figure 3.6 UV-Vis spectrometer (Lambda 1050 from Perkin Elmer)](image)

The four different AuNP, namely l-AuNSt, s-AuNSt, AuNFl, and AuNSp, feature unique optical properties as visually confirmed by varying color of colloidal solutions as shown in Figure 3.7.
Figure 3.7 Photograph of AuNSp (60nm diameter), s-AuNST (127nm tip-to-tip), l-AuNST (98nm tip-to-tip), and AuNF1 (1μm tip-to-tip)

Absorbance spectra of the four AuNP measured using UV-Vis spectroscopy are presented in Figure 3.8.

Figure 3.8 Absorbance spectra of l-AuNST, s-AuNST, AuNF1, AuNSp
AuNSp has a strong and narrow band absorption at 535nm which agrees with what Mie theory predicts. S-AuNS has resonance at 635nm which closely matches the value provided by the supplier (632nm). The l-AuNS has a broadband absorption peak around 800nm. The redshift in maximum absorption peak is due to the plasmon modes along the branches of the l-AuNS as well as the hybridization of plasmons of core and branches. The broad width of the peak is mainly due to the non-uniformity of the synthesized particles with wide distribution in number of branches, aspect ratios, and the angle of branches. Regardless, the location of the peak at 800nm matches both experimental and simulation work reported by Yuan et al. [85]. The AuNF spectrum, on the other hand, does not have an absorption peak due to the large size of the particles. However, as its geometrical cross-section is larger than the other NP, it has higher absorbance compared to non-resonating AuNP.

3.1.3 TiO2 Crystallization

3.1.3.1 Preparation of 2M TiCl4 stock solution

Titanium tetrachloride (TiCl4, ReagentPlus, 99.9% trace metals basis, Sigma-Aldrich) was carefully diluted into 2M stock solution by introducing the original TiCl4 solution into ice-bath cooled DI water in an Erlenmeyer flask while keeping the solution stirred with a magnetic stirrer. This procedure was performed under fume hood as the reaction vigorously releases hydrochloric gas. Prepared solution yielded translucent yellow color and was kept in freezer for long term storage. From this stock solution, further dilution was performed immediately before each experiment to prevent spontaneous hydrolysis which takes place over time forming TiO2.

3.1.3.2 Raman experimental setup used for TiO2 Crystallization and Characterization

Renishaw inVia confocal Raman spectrometer at the Advanced Optical Microscopy Facility (AOMF) within UHN (University Health Network) was used for both the light-assisted synthesis of TiO2 as well as for real time characterization. The Raman setup is equipped with inverted optical microscope (Leica DMI6000) with three separate solid state lasers: 532nm (100mW), 638nm (50mW), and 785mW (250mW). The power delivered at the sample stage is measured using a photodiode power meter from Thorlabs (PM200 with S120C sensor) for each laser and is tabulated in Table 3-4. For data acquisition, 1200 l/mm gratings coupled with 1024x256 deep
depletion silicon RenCam CCD detector were used. Prior to data acquisition, system calibration was performed on a silicon wafer with a strong Raman peak at 520 cm\(^{-1}\).

Table 3-4 Measured power and calculated intensity of lasers in Raman setup

<table>
<thead>
<tr>
<th>Nominal Power Setting</th>
<th>532nm</th>
<th>638nm</th>
<th>785nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Power (mW)</td>
<td>FWHM (μm)</td>
<td>Intensity (W/m(^2))</td>
</tr>
<tr>
<td>100%</td>
<td>19.80</td>
<td>23.98</td>
<td>3.04x10(^7)</td>
</tr>
<tr>
<td>50%</td>
<td>12.30</td>
<td>24.31</td>
<td>1.84 x10(^7)</td>
</tr>
<tr>
<td>25%</td>
<td>5.24</td>
<td>18.99</td>
<td>1.28 x10(^7)</td>
</tr>
<tr>
<td>12.5%</td>
<td>2.94</td>
<td>14.57</td>
<td>1.22 x10(^7)</td>
</tr>
<tr>
<td>10%</td>
<td>2.17</td>
<td>15.05</td>
<td>8.45 x10(^6)</td>
</tr>
<tr>
<td>5%</td>
<td>1.30</td>
<td>14.27</td>
<td>5.63 x10(^6)</td>
</tr>
</tbody>
</table>

The laser intensity is estimated using the equation below assuming Gaussian beam profile [87]:

\[ I_{laser} = \frac{P_{laser}(2.3546)^2}{2\pi(fwhm)^2} \] (Eq. 3.2)

Full width half maximum (fwhm) value was determined using a software called Image J. To do so, laser profile image was captured using the CCD camera built into the Raman set up and a line scan profile across the laser spot using Image J was used to measure the fwhm value. Calculated laser intensity for each wavelength at various optical filters (controlled using percentage value in Raman software) is also presented in Table 3-4. Note that for 785nm laser, filters for 25% or 12.5% are not provided in the setup. Please note that the nominal power setting does not precisely scale with the actual laser intensities shown in Table 3-4. Thus, the actual laser powers presented in Table 3-4 have been normalized and are presented in Table 3-5 below. Further, please note that all the figures in this thesis show the laser intensity in “Nominal Power Setting”.
Table 3-5 Normalized laser intensity of lasers in Raman setup

<table>
<thead>
<tr>
<th>Nominal Power Setting</th>
<th>532nm</th>
<th>638nm</th>
<th>785nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intensity (W/m²)</td>
<td>Normalized Intensity</td>
<td>Intensity (W/m²)</td>
</tr>
<tr>
<td>100%</td>
<td>3.04 x 10⁷</td>
<td>100%</td>
<td>5.75 x 10⁷</td>
</tr>
<tr>
<td>50%</td>
<td>1.84 x 10⁷</td>
<td>60%</td>
<td>2.51 x 10⁷</td>
</tr>
<tr>
<td>25%</td>
<td>1.28 x 10⁷</td>
<td>42%</td>
<td>2.31 x 10⁷</td>
</tr>
<tr>
<td>12.50%</td>
<td>1.22 x 10⁷</td>
<td>40%</td>
<td>1.61 x 10⁷</td>
</tr>
<tr>
<td>10%</td>
<td>8.45 x 10⁶</td>
<td>28%</td>
<td>1.34 x 10⁷</td>
</tr>
<tr>
<td>5%</td>
<td>5.63 x 10⁶</td>
<td>19%</td>
<td>5.48 x 10⁶</td>
</tr>
</tbody>
</table>

For Raman spectroscopy, AuNP were fixed on 3” by 1” Gold Seal® 1mm thick microscopic glass slides purchased from Ted Pella. These glass slides were cleaned by sonication in acetone, DI water, isopropanol, and DI water for 15min each and dried with nitrogen gas. Then a droplet of AuNP solution was drop casted on clean glass slide in a desiccator. A droplet of TiCl₄ precursor was placed on AuNP fixated microscopic glass slide and was covered by a glass coverslip as depicted in Figure 3.9.

Figure 3.9 Raman experimental setup showing AuNP drop casted on a microscopic glass with TiCl₄ precursor which in turn is held in place by a thin coverslip glass
A typical measurement consists of 20 acquisitions at 1s/acquisition to allow for time evolution/progression of the Raman spectrum. 532nm laser and 785nm laser were used for each of the AuNP (I-AuNS, s-AuNS, AuNF, and AuNSp) under 0.2M, 1M, and 2M TiCl$_4$ concentrations. Note that due to system limitations, 638nm laser could not be used for collection of Raman spectra. 638nm laser is equipped with an edge filter that removes signal below 300 cm$^{-1}$ wavenumber disabling observation of the most dominant TiO$_2$ peak located at 150cm$^{-1}$. Most of the Raman acquisition parameters were controlled using software provided by Renishaw (WiRE version 3.3). For examination of the structural change, AuNP fixed on TEM grids were used. In this case, each wavelength of the laser sources were illuminated on the TEM grid sample for a certain duration to induce crystallization of precursor. For the experiments carried on TEM grids, Raman signals acquisition was omitted allowing the use of 638nm which could not be used for signal collection due to the edge filter issue explained previously. The grid was placed such that AuNP are facing the incoming laser as illustrated in Figure 3.10 and were typically exposed for 5s at a single spot. After the optical synthesis using the Raman laser setup, the grid was carefully washed with copious amounts of DI water and dried for subsequent TEM characterization.

![Figure 3.10 Schematic diagram of experimental setup for TEM grid under Raman](image)
3.1.3.3 Transmission Electron Microscope

High resolution transmission electron microscopy (HRTEM) is used to study the AuNP as well as the formation of TiO$_2$ on them. In TEM, high voltage electron beam is transmitted through a thin specimen (such as nanoparticles) thereby producing considerable signals such as secondary electrons, x-rays, Auger electrons, backscattered electrons, elastically scattered electrons, inelastically scattered electrons as well as the transmitted beam [88]. Most of the time, these signals are collected and transformed into images but can also be used to produce electron diffraction patterns or various spectra. Contrary to the light microscope, TEM utilizes electromagnetic lenses aligned in a column along the path of the electron beam in order to shape the beam and hence acquire the image. More detail on the theory and operation of TEM can be referred to a book by Williams and Carter [19].

In this study, HRTEM from Hitachi (HF 3300, Ontario Centre for Characterization of Advanced Materials) was used at 300keV in bright field mode and a photograph of the system is shown in Figure 3.11. HF3300 is equipped with EELS which is discussed in the following section.

Figure 3.11 Hitachi HF3300 High resolution transmission electron microscope
3.1.3.3.1 Electron Energy Loss Spectroscopy

Electron energy loss spectroscopy (EELS) is a technique which can be used to obtain information about band gap, sample thickness, dielectric properties, and identification of elements [88]. Compared to XEDS (x-ray energy dispersive spectroscopy), EELS enables detection of light elements with much better spatial resolution and sensitivity. Upon interaction of the electron beam with the specimen, inelastically scattered electrons are collected using a magnetic prism and are thus transformed in to an energy spectrum.

A typical EELS spectrum can be divided into low energy loss and high energy loss regions. In the low energy loss region, two dominant peaks are present: zero loss peak and plasmon peak. Zero loss peak is due to transmitted electrons that are elastically scattered. Plasmon peaks are formed as the electrons lose energy as a result of plasmon excitation of specimen. Thus, more dominant plasmon peaks are seen for free-electron materials such as Li, Na, Mg, and Al [88]. Low energy loss region spectrum can be used to study dielectric constant, thickness, band gap, and interband transitions. High energy loss region can be used to identify elements by studying ionization edges. Ionization energy refers to the amount of energy required to excite core-shell electrons from its K, L, M, N, ..., shells and is characteristic of a specific element. As the electrons traverse the specimen they lose energy equivalent to the ionization energy and can be seen in the EELS spectrum. However, the intensity for higher ionization edge is very low and becomes even lower for heavier elements. Quantitative analysis for EELS spectrum is also possible but the sample thickness must be thinner than one mean free path of the specimen.

For characterization of Au/TiO$_2$ nanostructures, an EELS spectrometer from Gatan Quantum ERS under accelerating voltage of 300keV in transmission mode was used to obtain the EELS spectra. Fine-tuning and alignment of the aperture, drift tube, and magnetic prism were auto-tuned using Gatan digital micrograph software. Aperture size of 2.5mm and resolution of 0.1eV per channel with a total of 2048 channels were used. Depending on the sample, exposure time was adjusted (typically in the range of 0.1s to 0.5s) and multiple acquisition was performed to improve signal-to-noise ratio. Typical acquisition time for each EELS spectrum was approximately 1min.
Chapter 4

COMSOL Simulation study on gold nanostars

In this chapter we present the use of COMSOL Multiphysics simulation software to numerically calculate the electric field distribution and the plasmonic heat generation on the surface of gold nanostars due to exposure to electromagnetic radiation. Since the thesis is focused on the application of gold nanostars vis-à-vis plasmonic heat generation, the simulation studies presented here mostly concentrate on gold nanostars.

4.1 COMSOL Multiphysics – Wave Optics Module

COMSOL Multiphysics is a computational tool used for studying and modeling various physics-based problems in electrical, mechanical, fluid flow, and chemical applications. To simulate optical properties of l-AuNS, wave optics module [89] was chosen because this module deals with applications that are purely governed by Maxwell’s equations. In this module the power loss of l-AuNS is calculated in the electromagnetic wave frequency domain by solving frequency domain Maxwell’s equations via finite element method.

Finite element method is a semi-numerical method where the area is discretized and the boundary conditions between the discretizing elements in space are exactly determined. In this method Maxwell’s equations are solved approximately for each polygon spatial unit element [90][91].

Maxwell’s equations describe the spatial and temporal variation of the electric field and magnetic field for a given system. An electromagnetic filed in a medium can be described by four vectors: the electric field strength, E, the electric displacement, D, the magnetic field strength, H, and the magnetic flux density, B. These vectors are spatial and temporally differentiable. Maxwell’s equations in the differential form are given below [52]:

\[-\frac{\partial \vec{D}}{\partial t} + \nabla \times \vec{H} = \vec{J}(t, \vec{R})\] (Eq. 4.1)

\[\frac{\partial \vec{B}}{\partial t} + \nabla \times \vec{E} = 0\] (Eq. 4.2)
where \( \rho(t, \vec{R}) \) is the volume density of electric charges in a medium and \( \vec{J}(t, \vec{R}) \) is the electric current density (which is the charge that passes in unit time through a unit area).

More explicitly, Maxwell’s equations can be summarized into the following six equations which relate the various electric and magnetic field vector components [92]:

\[
\frac{\partial \vec{E}_x}{\partial t} = -\frac{1}{\varepsilon} \left( \frac{\partial \vec{H}_z}{\partial y} - \frac{\partial \vec{H}_x}{\partial z} \right) \quad (\text{Eq. 4.5})
\]

\[
\frac{\partial \vec{E}_y}{\partial t} = -\frac{1}{\varepsilon} \left( \frac{\partial \vec{H}_x}{\partial z} - \frac{\partial \vec{H}_z}{\partial x} \right) \quad (\text{Eq. 4.6})
\]

\[
\frac{\partial \vec{E}_z}{\partial t} = -\frac{1}{\varepsilon} \left( \frac{\partial \vec{H}_y}{\partial x} - \frac{\partial \vec{H}_x}{\partial y} \right) \quad (\text{Eq. 4.7})
\]

\[
\frac{\partial \vec{H}_x}{\partial t} = -\frac{1}{\mu} \left( \frac{\partial \vec{E}_z}{\partial y} - \frac{\partial \vec{E}_y}{\partial z} \right) \quad (\text{Eq. 4.8})
\]

\[
\frac{\partial \vec{H}_y}{\partial t} = -\frac{1}{\mu} \left( \frac{\partial \vec{E}_x}{\partial z} - \frac{\partial \vec{E}_z}{\partial x} \right) \quad (\text{Eq. 4.9})
\]

\[
\frac{\partial \vec{H}_z}{\partial t} = -\frac{1}{\mu} \left( \frac{\partial \vec{E}_x}{\partial y} - \frac{\partial \vec{E}_y}{\partial x} \right) \quad (\text{Eq. 4.10})
\]

where \( \varepsilon \) and \( \mu \) denote the electric and magnetic constants of the medium. The six equations above will be solved by COMSOL inside each space unit (finite element) within the simulated domain and averaged over the simulated structure.
4.2 Simulation Parameters

In this study, we investigated five different geometries of gold NP using COMSOL. These are: Sphere, 1:1 NS, 1:2 NS, 1:3 NS, and Random NS as illustrated in Figure 4.1. Sphere is a spherical AuNP of diameter 35nm. “1:1 NS” is a gold nanostar with base diameter to tip height aspect ratio of 1 to 1 and specifically with base diameter of 12nm and tip height of 12nm. Similarly, “1:2 NS” has base diameter of 12nm and tip height of 24nm whereas “1:3 NS” has the same base diameter while the tip height is 36nm. “Random NS” features randomized tip heights ranging from a minimum height of 5nm to a maximum height of 30nm. All the NS particles have same core diameter of 35nm with 14 cone shaped tips protruding from the core. Random NS best resembles the geometry of synthesized l-AuNSl which is the shape of most interest in the present thesis.

![Geometries of simulated gold NPs](image)

**Figure 4.1 Geometries of simulated gold NPs** (a) 35nm diameter sphere (b) 1:1 NS (c) 1:2 NS (d) 1:3 NS (e) Random NS

Next, each type of particle was placed in water with refractive index of 1.33 surrounded by perfectly matched layer (PML) to absorb all the scattered field from the particle under illumination. The PML can be considered to be akin to an anechoic chamber where it is designed to absorb all the radiation and minimize reflected signals. Mathematically, PML is a domain with anisotropic and complex permittivity and permeability to serve as an almost perfect absorbing material. Use of PML allows us to simulate electromagnetic wave propagation in space while keeping the model size small by truncating the domain so as to reduce the computation time. As for the boundary condition, we applied COMSOL’s scattering boundary condition.
Next, the particle geometry is discretized using tetrahedral meshes to be solved for Maxwell’s equations via finite element method. COMSOL automatically generates the mesh with typical mesh size of five second-order elements per wavelength. Finer mesh size is generated for geometries with more complexity such as the tip of a cone.

Next, we set a background field with x-polarized plane wave with electric field amplitude of 1 travelling along the z-axis. The meshed model is placed in the background field which causes scattering of the existing background field. Then COMSOL solver solved for the relative electric field caused by the introduction of gold NP over the frequency range of 273THz to 749THz with step size of 5THz.

The absorption cross-section of each simulated geometry can be calculated as:

\[
\sigma_{abs}[m^2] = \frac{Power \ loss \ [W]}{Intensity \ [W/m^2]} \quad (Eq. \ 4.11)
\]

In the reported simulation the intensity has the following value:

\[
Intensity = \frac{1}{2} c \varepsilon_0 n |E|^2 = 0.001766 \frac{W}{m^2}
\]

where \( c \) is the speed of light (3x10^8 m/s), \( \varepsilon_0 \) the vacuum permittivity (8.854x10^{-12} F/m), \( n \) the refractive index of water (1.33), and \( E \) the electric field (1 V/m).

### 4.3 Results and discussion

The calculated absorption cross-section for each particle geometry has been plotted with respect to the wavelength and is presented in Figure 4.2.
Spherical gold nanoparticle with core diameter of 35nm shows one absorption peak at 532nm with absorption cross section of $2.45 \times 10^{-15} \text{m}^2$. This value is comparable to theoretical value calculated using Mie theory at $2.93 \times 10^{-15} \text{m}^2$ [93]. The experimental UV-Vis spectrum for AuNSp has been plotted as a dashed line showing a slightly red-shifted LSPR peak compared to the simulated Sphere spectrum due to the larger particle diameter (60nm compared to 35nm). Note that the dashed spectrum representing the experimental data serves only as a qualitative guide for comparison of the observed LSPR peak against the simulated data; that is, the vertical axis for the experimental curve is arbitrary (numerical values of absorption cross-section cannot be read off directly from the plot in Figure 4.2). 1:1 NS has one smaller peak at 580nm and one dominant peak at 647nm. This result also closely matched the experimental data for s-AuNST with maximum absorption at 635nm. 1:2 NS has peaks at 620nm, 720nm, and 936nm. 1:3 NS has peaks at 640, 675, 785, and 965nm. According to a study done by Hao et al. using the finite-difference time-domain method [94], it was found that the location of the peak red-shifts with increasing aspect ratio of the tip. Similar trend is found in our study where by increasing the aspect ratio from 1 to 3, we see an overall redshift in the resonance peaks as shown in Figure 4.2.
The peaks at 580, 620, and 640nm for 1:1, 1:2, and 1:3 NS respectively correspond to the hybridized plasmon mode of the gold core with the protruding branches [94]. The strong resonance peak at 936nm and 965nm for 1:2 and 1:3 NS respectively may be due to the perfectly identical branches pointing towards opposite direction. A COMSOL study conducted by Trigari et al., investigated the extinction spectra of gold nanostars by discretizing the complex nanostar shape into a few elementary structures consisting of cones and sphere as shown in Figure 4.3 [95]. Two cones perfectly aligned creating cone-sphere-cone structure supports LSPR in the near IR region similar to absorption cross-section for 1:2 and 1:3 NS reported in Figure 4.2 above.

The Random NS also shows a LSPR peak at 990nm which, however, is not as strong as the 1:2 or 1:3 NS because it does not have the perfect cone-sphere-cone structure.

Figure 4.3 Calculated extinction (continuous lines) and scattering (dashed lines) spectra of gold nanostar discretized into simplified cone-sphere geometries. Core diameter is 97nm and cone height is 76nm. The green line shows experimental extinction spectrum of gold nanostar. Reproduced from [95] with permission of The Royal Society of Chemistry (RSC).

To confirm the accuracy of the results above, we generated power loss density maps for 1:3 NS at two wavelengths, 785nm and 523nm, as graphically presented in Figure 4.4. At 785nm (Figure
4.4a), 1:3 NS shows high power loss density on the cones. Since the plane wave used in the simulation was x-polarized, the four cones located parallel to the x-axis feature the highest intensity compared to the other cones at an angle. This is in good agreement with the established dependency of plasmonic properties to the polarization of the incident light [96]. From this data, it is clear that the resonance at 785nm for 1:3 NS is caused by the tips of the particle. Figure 4.4b illustrates the power loss at 523nm which corresponds to gold core resonance. Contrary to Figure 4.4a where the highest power loss intensities are observed at the tips, at 523nm the core and the trough of cones near the core are resonating. It is worth noting that regardless of which part of the nanoparticle is resonating, the valley region between gold tips exhibit high power loss meaning it is dissipating more heat. This result is in agreement with COMSOL simulation study carried by Ma et al. [57].

![Power loss density maps of 1:3 NS at (A) 785nm and (B) 523nm.](image)

**Figure 4.4** Power loss density maps of 1:3 NS at (A) 785nm and (B) 523nm. Maximum and minimum power loss density values are (A) $1.38 \times 10^9$ W/m$^3$, 127W/m$^3$ and (B) $1.02 \times 10^6$ W/m$^3$, 9281 W/m$^3$, respectively.

Random NS has multiple peaks across a wide range of wavelengths presumably because it contains branches of varying aspect ratios. For example, the LSPR peaks at 640nm is caused by short branches whereas the LSPR peaks at 750nm is due to the longer branches. Also notice that
the magnitude of absorption cross-section for LSPR peaks in Random NS are lower than the peaks found in 1:1NS, 1:2NS, and 1:3NS. It is because the contribution to the LSPR is divided amongst various branch heights for the Random NS resulting in a larger number of LSPR peaks forming with lower magnitude. The formation of numerous LSPR peaks is the basis for the broad LSPR band observed in the experimental UV-Vis spectrum obtained for l-AuNS as depicted by the green dashed line in Figure 4.2. Recall that due to the synthesis method of l-AuNS, the resulting nanoparticles have a wide distribution of geometry in the number of branches, branch height, and tip-to-tip size. The location of LSPR peak is heavily influenced by the aspect ratio of the branch and the fact that these have a wide distribution of aspect ratios, thus resulting in the broadband LSPR peak observed experimentally as depicted by the green dashed line in Figure 4.2 above. Power loss density presented in Figure 4.5 below also supports these observations.

Random NS at 747nm shown in Figure 4.5a features high power loss density at the longest tip in the x-z plane but the shorter tips on the same plane do not exhibit intense power loss. Recall from Figure 4.4a that all the tips on the x-z plane exhibit equally intense power loss behaviour because of the same tip height among them. So at 747nm, only the longest tip in Random NS resonates while the shorter tips are not contributing much to the overall power loss density. This is why we observe a lower magnitude of absorption cross-section for the Random NS compared to the other NS shapes. Random NS at 519nm depicted in Figure 4.5b below shows that now the two short tips are resonating under 519nm plane wave while the longer tips are off-resonance. Thus, each tip with varying height resonates under different frequency and that is the reason why Random NS has numerous resonance peaks appearing in Figure 4.2.
Figure 4.5 Power loss density distribution of Random NS at (A) 747nm and (B) 519nm. Maximum and minimum power loss density are (A) $1.4 \times 10^9$ W/m$^3$, 222 W/m$^3$ and (B) $1.43 \times 10^7$ W/m$^3$, 1$\times$10$^4$ W/m$^3$

4.4 Conclusion

Using COMSOL Multiphysics simulation software, we investigated the power loss and hence calculated the absorption cross-section of gold nanostar particles of varying tip heights. The location of LSPR peak is redshifted as the aspect ratio of tip increases. Random NS, which closely resembles the synthesized gold nanostar (l-AuNS), exhibit numerous LSPR peaks due to its varying branch heights. The modeled results are in a good agreement with the experimental data (UV-Vis spectroscopy) conducted on l-AuNS featuring a broad LSPR band with peak height at 800nm. We have also confirmed that the power loss is generally substantial around the valley region between the branches which may serve as thermal hot spot for localized chemical synthesis.
Chapter 5

5 Plasmonic crystallization of TiO$_2$ on gold nanoparticles

In this chapter, we present data on the crystallization of TiO$_2$ upon the thermochemical reaction between AuNP and TiCl$_4$ precursor under plasmonic heating, and investigate the crystallization efficiency as a result of varying the experimental parameters. The chapter is divided into two sub-chapters: section 5.1 focusing on the Raman study, and section 5.2 focusing on structural analysis using TEM. More specifically, in section 5.1, we will examine the effect of laser intensity, duration, precursor concentration, and the plasmon resonance on the crystallization of TiO$_2$ from liquid precursor. In section 5.2, we narrow down the experimental parameter to 1M TiCl$_4$ concentration while varying the wavelength of laser for each set of AuNP and try to discover the trend between the LSPR and localized titania precipitation. Important findings are summarized at the end of the chapter (section 5.3).

5.1 Raman analysis of TiO$_2$ plasmonic crystallization

5.1.1 Raman Characterization and Photostability Investigation of AuNS and TiCl$_4$ precursor

Prior to the investigation of the optical and thermal interaction between AuNS and TiCl$_4$ precursor, each of them was exposed under 532nm laser at maximum power to observe possible thermal degradation caused by the incident photons. 1M TiCl$_4$ precursor was exposed under 532nm laser for 20s and the resulting Raman spectra are presented in Figure 5.1.
5M TiCl₄ precursor solution has a broad peak at 137 cm⁻¹. Titanium tetrachloride molecules (TiCl₄) have four Raman active vibrational modes at around 389 cm⁻¹ (A₁), 114 cm⁻¹(E), 498 cm⁻¹(F₂), and 136 cm⁻¹(F₂) that correspond to the symmetric stretching in TiCl₄, bending mode of Cl-Ti-Cl, asymmetric stretching of TiCl₄, and bending mode of Cl-Ti-Cl, respectively [97][98].

5.1.2 Effect of laser intensity and illumination duration on crystallization

In this section, the relationship between laser intensity and formation of anatase phase TiO₂ from liquid precursor is investigated.

To monitor the crystallization process, the first series of Raman measurements were conducted on I-AuNSt in contact with TiCl₄ precursor after 20s of 532nm laser irradiation at various laser intensities. The acquired spectra were compared with the Raman spectrum of Degussa P25 powder which is a commercial TiO₂ nanopowder material composed of mainly anatase phase TiO₂. A detailed description of the experimental set-up is presented in section 3.1.3.2 of this thesis. The acquired spectra are presented in Figure 5.2. For convenience, laser intensity is described in percentage while the corresponding intensity values are given in Table 3-4.
Figure 5.2 Raman spectrum of P25 and l-AuNS at 100%, 50%, and 25% laser intensity obtained after 20s under 532nm laser in 1M TiCl₄.

The reference anatase TiO₂ sample (P25) features characteristic anatase TiO₂ peaks at 143cm⁻¹ (E_g) followed by smaller peaks at 395 (B₁g), 514 (A₁g and B₁g), and 637cm⁻¹(E_g) [99]. Interestingly for the TiO₂ produced under 100% laser intensity, a blueshift was observed for the E_g peak from 143cm⁻¹ to 150cm⁻¹ for which we present two possible reasons. The first reason may be due to oxygen deficiencies [100] caused by the nature of experimental set-up which confines the precursor liquid with a coverslip glass preventing contact with atmosphere, a source of oxygen. The second reason for blueshift of E_g peak is potentially due to the phonon confinement effect which becomes more dominant for smaller particles [66]. The blueshift therefore indicates that TiO₂ particles formed in our experiment are much smaller compared to P25 powder. This is in good agreement with the results published by Zhang et al. [99] who reported theoretical calculation of anatase crystallite size to be about 6nm. This statement is confirmed by examining the crystallized TiO₂ and the P25 sample under TEM and will be discussed in section 5.2.
As discussed earlier in section 5.1.1, pure TiCl₄ solution cannot induce anatase TiO₂ formation upon laser irradiation. Thus, the reason behind formation of crystalline TiO₂ must be due to the interaction of l-AuNSt with incoming photons causing the reaction mixture to heat up. Under the plasmonic resonance, excited plasmon modes couple to lattice modes within a few picoseconds resulting in rapid generation of heat [29]. The temperature increase in l-AuNSt results in thermal transport across two types of interfaces: gold/precursor interface and gold/glass interface. The ease of thermal transport across interfaces can be understood using interfacial thermal resistance or also known as Kapitza resistance. Kapitza resistance for gold/glass interface is \(1 \times 10^{-8} \text{m}^2\text{K/W}\) [101] whereas for gold/water interface (as the TiCl₄ precursor is mostly water) is in the range of \(1 \times 10^{-8} \text{m}^2\text{K/W}\) to \(3 \times 10^{-9} \text{m}^2\text{K/W}\) [102]. Gold/water interface having lower interfacial thermal resistance compared to gold/glass interface will have easier heat transfer with a larger amount of heat being transferred to the surrounding aqueous precursor than the glass substrate. Also the thermal coupling between l-AuNSt and glass substrate is very poor (given the lack of intimate contact) such that the heat loss to the substrate via thermal conduction would be negligible compared to the heat transferred to the surrounding precursor.

As the laser intensity decreases, disappearance of anatase peak at 514\,\text{cm}^{-1} indicates low crystallinity compared to that of commercial Degussa P25 powder. At 50\% laser intensity, the first anatase peak at 150\,\text{cm}^{-1} still developed but not as intense as the one at 100\%. Following three peaks at 395, 514, 637\,\text{cm}^{-1} are weak but present as depicted in the inset of Figure 5.2 Raman spectrum of P25 and l-AuNSt at 100\%, 50\%, and 25\% laser intensity obtained after 20s under 532nm laser in 1M TiCl₄.. The intensity and sharpness of the Raman peaks convey information on the crystallinity and degree of symmetry. Sharp and narrow peaks as in P25 implies that this sample is much more crystalline and contains few defects/imperfections compared to l-AuNST/TiO₂ at 100\%. With the laser intensity down at 25\%, no change in the Raman spectrum is observed before and after the laser irradiation. This results suggest that there is a certain threshold intensity that must be provided in order to generate enough plasmonic heating around the l-AuNST to induce forced hydrolysis of TiCl₄ precursor and thus form crystalline TiO₂.
5.1.2.1 Laser intensity threshold for various gold nanoparticles

Similar trend was observed for s-AuNST, AuNFl, and AuNSp and the corresponding spectra are presented in Figure 5.3. At 100% intensity under 532nm laser after 20s, well-defined anatase peaks were observed regardless of the particle shape. However, as the intensity decreased below a certain threshold, three smaller peaks at 395, 514, and 637 cm\(^{-1}\) no longer formed. Table 5-1 summarizes the minimum threshold laser intensity for each particle shape to form anatase TiO\(_2\) with peaks at 150, 395, 514, and 637 cm\(^{-1}\).
Figure 5.3 Raman spectra with varying laser intensity for (a) l-AuNS, (b) s-AuNS, (c) AuNSp, and (d) AuNF. Obtained under 532nm laser after 20s of exposure in 1M TiCl$_4$. 
Table 5-1 Threshold energy for anatase TiO$_2$ formation under 532nm laser, 1M TiCl$_4$, for 20s

<table>
<thead>
<tr>
<th>Shape of AuNP</th>
<th>Threshold laser intensity (%)</th>
<th>Threshold laser intensity (W/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuNSp</td>
<td>10%</td>
<td>$8.45 \times 10^6$</td>
</tr>
<tr>
<td>s-AuNST</td>
<td>12.5%</td>
<td>$1.22 \times 10^7$</td>
</tr>
<tr>
<td>AuNFL</td>
<td>25%</td>
<td>$1.28 \times 10^7$</td>
</tr>
<tr>
<td>l-AuNST</td>
<td>50%</td>
<td>$1.84 \times 10^7$</td>
</tr>
</tbody>
</table>

As indicated above in Figure 5.3 and Table 5-1, each particle has different threshold energy for the formation of anatase TiO$_2$. For example, AuSphere has the lowest threshold at 10% laser intensity meaning it is the easiest among the four particles to assist in TiO$_2$ formation. The main reason behind the AuNSp having the lowest threshold energy comes from the fact that it has matching plasmonic resonance frequency with the incoming laser source at 532nm. Even though the physical size of the AuNSp (60nm diameter) is the smallest among the four, its absorption cross-section under resonance is multiple times higher than the rest of the particles. S-AuNST, with its resonance frequency at 630nm, has the second lowest threshold followed by l-AuNST resonating around 800nm. Even though AuNFL does not have a plasmonic resonance band, it benefits from its large physical size (~0.5μm) by absorbing more photons. The effect of laser wavelength matching with plasmonic resonances of gold nanoparticles will be discussed in more detail in section 5.1.4. It is noteworthy that even when the wavelength of the incident laser does not match the plasmonic resonances of certain gold nanoparticles, enough heat is generated through increasing intensity of the laser toward crystallization of TiO$_2$. This might be due to the fact that not all the synthesised nanoparticles have the same size and shape and that provides a small percentage of gold particles that resonate under the incident 532 nm light.
5.1.2.2 Monitoring the growth rate of TiO₂ crystals

The growth rate of anatase TiO₂ on l-AuNS was studied under three different 532nm laser intensities. Figure 5.4 represents the change in 150cm⁻¹ anatase peak intensity as a function of laser irradiation time. For data processing, software provided by Renishaw (WiRE) was used to measure the Raman intensity from the maximum at 150cm⁻¹ to the baseline such that the background is removed and only the E_g mode Raman signal at 150cm⁻¹ is accounted for.

![I-AuNS: Change in anatase Raman intensity with respect to time](image)

**Figure 5.4 Growth rate of 150cm⁻¹ anatase peak for l-AuNS with respect of time for 100%, 50%, and 25% 532nm laser power in 0.2M TiCl₄.**

First, note that there was no significant change in the peak height for sample irradiated at 25% intensity represented as flat line in the figure. This result agrees with the earlier discussion on the threshold laser power required for formation of titania which was at 50% for 532nm laser. When the intensity of the laser was increased to 50%, number of counts increased linearly with respect to time after 10s suggesting crystallization of liquid precursor to anatase titania. The spectrum for 100% power also suggests steady growth of anatase peak as time progresses. Interestingly the rate of anatase growth (slope of the linear portion of graph) for 50% seems higher than 100%
power. This may be misleading because at 100%, the initial spectrum already had fairly strong anatase peak to begin with. It is caused by the limitation of the Raman instrument set-up where there is a delay of around 3 seconds before the first Raman signals are collected. It is believed that during the first 3 seconds of laser exposure, a significant portion of the titania crystallization process has already taken place for 100% laser intensity.

5.1.3 Effect of TiCl$_4$ precursor concentration on crystallization

As discussed in section 2.3.2, forced hydrolysis of TiCl$_4$ precursor is highly sensitive to the concentration of TiCl$_4$. To study the effect of precursor concentrations on the crystallization of TiO$_2$, Raman experiments were carried out under three different TiCl$_4$ concentrations: 2 M, 1 M, and 0.2 M.

First, we obtained Raman spectra for each type of AuNP under 532 nm laser for 20 seconds at 100% intensity while changing the precursor concentrations. Respective spectra are presented in Figure 5.5.
Figure 5.5 Raman spectra for (a) l-AuNST, (b) s-AuNST, (c) AuNSp, and (d) AuNFL collected under 532nm laser after 20s exposure at 100% power while varying the precursor concentrations (0.2M, 1M, and 2M)
Regardless of the precursor concentrations, l-AuNS has an $E_g$ peak at 150 cm$^{-1}$, a signature peak for anatase TiO$_2$. Differences in $A_{1g}$, $B_{1g}$ and $E_g$ peaks were observed with changing concentration. At 0.2M, those three following peaks were not present. Increasing the concentration to 1M drastically improved the intensity and $A_{1g}$, $B_{1g}$, $E_g$ vibrational peaks appearing at 398, 517, and 641 cm$^{-1}$. However, further increasing the concentration did not aid in having more well-defined anatase structure as shown by the spectrum for 2M with weak intensity. Similar trend was observed with s-AuNS as seen in Figure 5.5. Thus, for l-AuNS and s-AuNS the optimal TiCl$_4$ concentration was at 1M. The following discussion helps better understand the presence of an optimal concentration for hydrolysis of TiCl$_4$.

A possible reason for hindered anatase formation at 2M may be due to its acidic nature compared to 1M solution. Hydrolysis of TiCl$_4$ in water can be represented as:

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl \ (Eq. \ 5.1)$$

After initial hydrolysis, the increase in concentration of $H^+$ and $Cl^-$ is more profound for 2M than 0.2M or 1M, making 2M solution comparably more acidic. To maintain the equilibrium in accordance with Chatelier’s principle, the above hydrolysis reaction would be hindered (less favorable to form TiO$_2$) due to abundant amount of HCl present in the mixture. Another reason may be due to the nature of speciation and precipitation of TiCl$_4$ to TiO$_2$. In order to form TiO$_2$ nuclei, initial Ti(IV)-Cl-H$_2$O complex needs to undergo replacement reaction of Cl$^-$ with hydroxyl group followed by release of water molecules and protons in order to form octahedral structure of Ti-O-Ti complexes. Increasing the initial TiCl$_4$ concentration decreases the amount of water or hydroxyl molecules available to participate in such chemical reaction thus decreasing the likelihood of TiO$_2$ nuclei formation (see Figure 2.6 and Figure 2.7). Thus, for l-AuNS and s-AuNS the ideal precursor concentration for anatase titania precipitation is 1M. However, this trend was not observed for the case of AuNFl and AuNSp.

For AuNFl, spectrum obtained under 0.2M did not indicate any presence of titania. Increasing the concentration produced peaks at 150, 398, 517, and 641 cm$^{-1}$ indicative of anatase formation. The strongest anatase Raman signature was collected under the highest concentration of 2M. With regards to the AuNSp, anatase peaks at 150, 398, 517, and 641 cm$^{-1}$ were present in all three concentrations with varying degree of intensity where higher concentration resulting in sharper and stronger Raman peaks. The main difference between AuNSt and AuNSp is their
plasmonic resonance frequency. In the experiment above, 532nm laser was used which matches the LSPR of AuNSp. AuNFl, even though it lacks any resonance, has a comparably large geometrical cross-section. Thus, the temperature around AuNSp and AuNFl is expected to be higher than l-AuNSt or s-AuNSt. During the nucleation and precipitation reaction, temperature increases the kinetics of Ti octahedral monomer formation. Thus, the higher temperature around AuNFl and AuNSp may balance the hindered chemical reaction that takes place in 2M solution.

To confirm this statement, similar set of Raman experiments were performed on l-AuNSt under its matching LSPR frequency laser (785nm) while changing the TiCl$_4$ concentrations. Each sample was exposed under 785nm at 100% power for 20s to induce titania crystallization. Raman spectrum was obtained by probing it with a low intensity laser (1% power) across the reacted spot to prevent further change in crystalline nature of the sample. Three spectra obtained under 0.2M, 1M, and 2M are shown in Figure 5.6. The optical micrographs of the reacted spot with an arrow indicating the location where the presented spectrum was collected is also presented in this figure.
Figure 5.6 Raman spectrum obtained at the indicated location of l-AuNSt by performing a line scan at 1% under 785nm laser after laser irradiation under 785nm laser at 100% for 20s. Green line with (R) marks rutile Raman peaks and black line with (A) marks anatase peaks.

As shown in Figure 5.6, 0.2M spectrum indicated anatase signature with peaks at 150, 398, 517, and 641 cm\(^{-1}\). The trend we expected to observe was stronger Raman signal with increasing concentrations and indeed 2M spectrum had stronger Raman peaks. However, the peaks appearing in 2M spectrum in Figure 5.6 suggest mixed phase of rutile and anatase TiO\(_2\) with rutile peaks located at 240, 442 (A\(_{1g}\)), and 610 cm\(^{-1}\)(E\(_g\)) and anatase peaks at 143 and 514 cm\(^{-1}\). Spectrum obtained under 1M TiCl\(_4\) precursor also indicated mixed phase titania with peaks at 143, 395, 514, 637 cm\(^{-1}\) for anatase and 240 and 442 cm\(^{-1}\) for rutile. Comparing the 2M and 1M spectra in terms of the Raman peak locations and intensities, 2M sample contains more rutile TiO\(_2\) than 1M sample. Increasing the concentration seems to favour more rutile formation over the dominant anatase formation observed at low TiCl\(_4\) concentration. This result agrees with
Yanqing et al. reporting higher mole fraction of rutile formation over anatase with increasing TiCl₄ concentrations [79].

5.1.4 Effect of matching laser wavelength and plasmon resonance frequency on TiO₂ crystallization for various gold nanoparticles

In this section, the effect of laser wavelength on the crystallization of TiO₂ on l-AuNSt and AuNSp is investigated. As previously reported in section 3.1, AuNSp resonates around 532nm wavelengths whereas the resonance frequency of l-AuNSt closely matches the 785nm laser.

Figure 5.7 illustrates the effect of matching versus mismatching of the incident laser to the LSPR of AuNP. Raman spectra were obtained under the same conditions for both AuNSp and l-AuNSt using 532 nm laser that only matches the plasmonic resonances of the AuNSp.

![Raman spectra](image)

Figure 5.7 Raman spectra of (a) AuNSp and (b) l-AuNSt under 532nm laser after 20s in 2M TiCl₄

The effect of providing a LSPR matching light source for effective heat generation is clearly supported by the Raman spectra of AuNSp (Fig. 5.7a). Reducing the intensity of laser weakens the Raman intensity but the signature anatase Raman peaks at 150, 395, 514, 637 cm⁻¹ remain
present for laser intensity as low as 5% as shown in the inset in Figure 5.7a. When the AuNP are under plasmonic resonance, they exhibit the maximum absorption cross-section as discussed in section 2.2 which leads to maximum temperature increase according to the following equation [51]:

\[ \delta T_{\text{NP}} = \frac{\sigma_{\text{abs}} I}{4\pi \kappa_s R} \]  

(Eq. 5.2)

Another interesting observation is the shift in \( E_g \) peak at 150\,cm\(^{-1}\) with respect to the laser intensity. At 100% power, the \( E_g \) peak maximum was located at 153\,cm\(^{-1}\) which shifted to 150\,cm\(^{-1}\) at 50% power. The shift in Raman peak conveys information on the sample temperature – specifically, the atomic equilibrium positions change as the lattice is heated or cooled. This volumetric expansion or contraction affects the interatomic forces which in turn result in changes in phonon vibrational frequencies represented by the observed Raman shift. The Raman shift can be related to sample temperature using the relationship [103]:

\[ \Delta \omega(T) = Z(T - T_0) \]  

(Eq. 5.3)

where \( \Delta \omega(T) \) is the Stokes shift at a given temperature, \( Z \) is calibration constant, and \( T_0 \) is the reference temperature. According to Raman thermometry study on TiO\(_2\) by Lundt et al. [104], \( E_g \) peak at 153\,cm\(^{-1}\) corresponds to sample temperature of 180°C whereas 150\,cm\(^{-1}\) corresponds to temperature of 120°C. Our observations agree with the delta T equation above and suggest that the temperature increase is proportional to the intensity.

Contrarily, NP under non-resonating conditions are not an efficient source of heat as supported by the trend seen in Figure 5.7b for l-AuNS. Anatase was only formed under 100% power which is 20 times more intense than what is required for anatase formation on AuNSp under 532nm, LSPR matching laser. The \( E_g \) peak was located at 150\,cm\(^{-1}\) at 100% intensity as compared to 153\,cm\(^{-1}\) at 100% intensity for AuNSp. The blueshift in \( E_g \) peak indicates higher sample temperature as discussed in the previous paragraph and thus we deduce that AuNSp induce higher temperature increase than l-AuNS under 532nm laser.

Under the same laser intensity (I), thermal conductivity of medium (\( \kappa_s \)), and similar effective particle radius (R), Eq. 5.2 predicts a higher temperature increase for AuNSp compared to l-AuNS which would correlate with a higher absorption cross-section. From the absorption cross-
section simulation reported in Chapter 4, \( \sigma_{\text{abs}} \) of 1-AuNS (referred to as Random NS in simulation) is 1.52x10\(^{-15}\)m\(^2\) while Mie theory predicts \( \sigma_{\text{abs}} \) of 1.11x10\(^{-14}\)m\(^2\) for 60nm diameter spherical Au particles at 532nm. Hence, 7.3 times higher absorption cross-section of AuNSp under resonance would result in higher temperature increase and allows for anatase formation under lower laser intensity - being compensated by its higher absorption cross-section.

In the next series of Raman measurements, a 785nm laser source was used which matches the plasmonic resonances of 1-AuNS. Prior to the crystallization experiment, photostability of TiCl\(_4\) was tested by acquiring its Raman spectrum with 20s exposure time under 100% power. Two spectra obtained in \( t=0 \) and \( t=20s \) are presented and compared in Figure 5.8.

![Figure 5.8 Raman spectrum of 2M TiCl\(_4\) precursor under 785nm laser at 100% power at \( t=0 \) and \( t=20s \)](image)

As presented in Figure 5.8, there is a peak at 107cm\(^{-1}\) which will be observed for 785 nm laser regardless of the composition of the sample. This peak is the plasma line caused by the probe laser that results from the non-lasing transition of laser diode [100]. As it is due to the probe laser (785nm), this peak is disregarded as it does not contain information about the sample. The peaks at 134 and 335cm\(^{-1}\) are caused by bending of Cl-Ti-Cl bond in TiCl\(_4\) and [TiCl\(_6\)]\(^{2-}\) and [TiCl\(_3\)]\(^{-}\) intermediate species [70]. Over the 20s exposure under 100% intensity 785nm laser, no change
in Raman spectrum was observed for 2M TiCl₄ solutions. Thus, we can be assured that any development of Raman peak with AuNP in TiCl₄ is caused by AuNP.

After the photostability of the precursor was tested, the Raman spectra of 2M TiCl₄ in contact with AuNSp and l-AuNST were acquired after 20s exposure to 785nm laser with varying intensities as presented in Figure 5.9.

![Raman spectra](image)

**Figure 5.9** Raman spectra of (a) AuNSp and (b) l-AuNST under 785nm laser after 20s in 2M TiCl₄

As shown in Figure 5.9a, AuNSp shows two dominant peaks at 135cm⁻¹ and 274cm⁻¹ regardless of the laser intensities. 135cm⁻¹ is caused by bending mode of Cl-Ti-Cl in TiCl₄ precursor thus it indicates that the precursor did not undergo crystallization to anatase [70]. One possible source for the Raman peak at 276cm⁻¹ could be the vibration of Ti-O bonds in sodium titanate structure which might be formed as an intermediate species during the crystallization process as reported by Kim *et al.*’s [83] and Gao *et al.*’s [105] Raman studies on sodium titanate and hydrogen titanate [105]. Another possible reason for the peak at 274cm⁻¹ is due to intermediate species such as [TiO₂Cl₄]⁻⁴ or [TiOCl₃]⁻ [70]. In general, the exact cause of the peak at 274cm⁻¹ is unclear but it is likely to be a signature of an intermediate titanium oxy-chloride species that
forms in the process of deprotonation and hydrolysis reaction of TiCl$_4$ precursor. However, lack of any TiO$_2$ Raman signature indicates that AuNSp under non resonating laser cannot induce crystallization of TiO$_2$ from the starting precursor solution.

On the other hand, l-AuNSt whose LSPR peak matches the incoming laser source at 785nm indicated presence of TiO$_2$ as observed in Figure 5.9b. The spectrum obtained under 100% laser power contained rutile peaks located at 240, 442 (A$_{1g}$), and 610 cm$^{-1}$ (E$_g$) and anatase peak at 150cm$^{-1}$ (E$_g$). As previously reported in this chapter, under 532nm laser illumination at 100% intensity, l-AuNSt showed complete anatase signature. By changing the laser to 785nm, in other words by matching the laser to the particle resonance frequency, we obtained a mixed phase of both rutile and anatase TiO$_2$. The transition temperature from anatase to rutile varies depending on the synthesis method and other parameters such as pressure, precursor concentration, and acidity but the general trend is that rutile phase requires higher annealing temperature than the anatase [106]. Matching the laser to the resonance of l-AuNSt resulted in mixture of rutile and anatase implying that the temperature increase was greater under 785nm (matching resonance) than 532nm (non-matching). Thus, we conclude that plasmonic resonance plays an important role in heat generation and plasmonically excited NP which are tailored to match the radiant frequency are an efficient means of generating heat to induce crystallization of TiO$_2$. 
5.2 TEM Characterization of plasmonic crystallization of TiO$_2$ on gold nanoparticles

In this section, TEM characterization of the TiO$_2$ crystals formed through exposing TiCl$_4$ precursor and gold nanoparticles to laser light is presented, complementing the Raman observations presented in previous section. As described in Chapter 3, TEM grids with AuNP situated on them were placed in 1M TiCl$_4$ solution and subsequently exposed to a laser source to initiate the TiO$_2$ crystallization; the TEM grids are then examined under a transmission electron microscope.

In the following sections, we first present TEM images of commercial P25 titania powder. Next we discuss the structural features of Au/TiO$_2$ nanocomposite particles obtained via light assisted heating of gold NPs. We also present and discuss a similar l-AuNS/t/TiCl$_4$ mixture synthesized on a hot plate which serves as a control sample in contrast to the samples from the proposed light assisted synthesis method.

5.2.1 TEM Characterization of Reference TiO$_2$ powder (P25)

As shown in Figure 5.10a, P25 is made of irregular shaped particles with a wide size distribution. Under high resolution TEM, the lattice structure of anatase TiO$_2$ can be clearly seen as shown in Figure 5.10b. The measured interplanar spacing (d-spacing) was 0.35nm which matches well with the anatase (101) plane [107]. For reference, d-spacing values of anatase, rutile, brookite, and gold has been provided in Appendix B.

As mentioned in Chapter 3 the TEM setup that was used in this thesis was equipped with electron energy loss spectroscopy (EELS) therefore the majority of the TEM imaged results reported in this section include the corresponding EELS spectra. EELS spectrum for P25 is shown in Figure 5.10c. The four peaks in the energy range 455-465eV represent the Ti L-edge which matched well with the Gatan atlas provided by the manufacturer as well as other studies on EELS analysis of TiO$_2$ [108] [109]. Two peaks observed near 530eV corresponds to O K-edge [109]. The lattice spacing value and EELS spectrum obtained from P25 TiO$_2$ nanopowder will serve as a reference for the optically synthesized TiO$_2$ around AuNP in the following section.
Figure 5.10 (A) TEM image of P25 TiO$_2$ nanopowder. (B) HR-TEM of P25 showing lattice spacing. (C) EELS spectrum of P25
5.2.2 TEM Characterization of Thermally induced TiO$_2$ crystallization

To investigate the role of the solution temperature (bulk heating) on the crystallization of TiO$_2$, we conducted a control experiment by heating the precursor-L-AuNSt mixture solution on a hot plate. L-AuNSt dispersed in 0.2M TiCl$_4$ solution was placed on a hot plate at 80°C for 1.5 hours while keeping the solution stirred at 500 rpm. Then the particles were centrifuged and re-dispersed in DI water. TEM images of the prepared sample are shown in Figure 5.11.

![TEM images of L-AuNS surrounded by TiO$_2$](image)

**Figure 5.11** (A) TEM image of L-AuNS surrounded by TiO$_2$ prepared by hot plate heating at 80°C for 1.5 hours in 0.2M TiCl$_4$ solution. (B) and (C) shows HR-TEM image of nanocrystalline precipitate of TiO$_2$

The darker particles are L-AuNSt surrounded by a bulky matrix of titania. It was found that after 1.5 hours of hot plate heating at 80°C, the L-AuNSt has undergone thermal deformation losing its original spiky/prickly shape and turning into a spherical shape as seen in Figure 5.11a. HRTEM images reveal multicrystalline TiO$_2$ nanoparticles surrounding L-AuNSt with d-spacing values of 0.35 and 0.32 nm corresponding to anatase (101) and rutile (110). Synthesis of rutile titania using forced hydrolysis of TiCl$_4$ on a hot plate has been reported under 1M TiCl$_4$, at 80°C, for 5 hours [70]. Even though the reaction time for our study was shorter (1.5hrs), decrease in TiCl$_4$ concentration also decreases the required time to induce crystallization and precipitation of titania [70]. Thus, this sample prepared using hot plate heating likely contain mixed phase (rutile and anatase) titania. However, it is noteworthy to mention that this method produces non-localized and bulky titania precipitation and causes thermal destruction of L-AuNSt particles. Therefore, this method does not allow for fine control over the location and thickness of TiO$_2$ crystallization.
5.2.3 TEM Characterization of TiO$_2$ crystallized on various gold nanoparticles

5.2.3.1 l-AuNST

In this section, we examine the morphology of TiO$_2$ formation around l-AuNST under optical heating by observing the resulting structure under HRTEM. Figure 5.12 below illustrates the l-AuNST irradiated under 785nm laser that matched the plasmon resonance for 5s at 100% power in 1M TiCl$_4$ concentration.

Figure 5.12 l-AuNST prepared in 1M TiCl$_4$ under 785nm laser at 100% power. (A) near the centre of laser spot, (B) away from the centre spot, (C) and (D) show EELS spectra of (A) in the range of 230 to 580eV
As presented in Figure 5.6, laser irradiation often results in micron sized crater formation. As the TEM technique requires transmission of electron beam through a specimen, the centre of the crater could not be analyzed under TEM. As we move away from the centre, thermally deformed 1-AuNSt surrounded by a layer of titania was observed as seen in Figure 5.12a. The temperature in this region is estimated to be over 300°C according to the thermal stability experiment which will be discussed in section 5.2.4. This type of particle reshaping is due to the metastable nature of 1-AuNSt where high temperatures promote surface and bulk diffusion of gold atoms resulting in the transformation to a stable spherical shape. Also, notice that the crystallization of TiO₂ is not localized but rather encapsulates the entire gold core. This is because of the continuous laser source matching LSPR and thus resulting in intense heat generation. Upon absorption of photons, electron-electron scattering results in drastic temperature increase of the electron cloud at femtosecond timescales which in turn results in lattice heating due to electron-phonon coupling [54]. The temperature gradient between the heated gold lattice and the cold surrounding medium convectively heat up the liquid precursor until thermal equilibrium is reached. This multi-step thermal transfer process occurs simultaneously under CW laser which results in bulk heating of the precursor considering that the time required to reach thermal equilibrium is a lot longer than the fast electron dynamic processes occurring in the plasmonically resonating gold NP. As a result, 1-AuNSt undergoes surface and bulk diffusion and turns into spherical particles while the bulk heating of TiCl₄ precursor serves to completely cover the particles with titania.

Moving further away from the centre, we observe 1-AuNSt with titania crystallite size less than 10nm forming around the branches of 1-AuNSt as shown in Figure 5.13b. As this particle was not under direct illumination, the particle still maintained its sharp features. The lattice spacing value of 0.34nm closely matches (101) plane of anatase which is further strengthened by the EELS spectrum in Figure 5.13c,d. Figure 5.13d shows Ti L3 at 458eV and L2 edge at 466eV corresponds to interband transition from 2p1/2 and 2p3/2 to unoccupied 3d orbital [108]. Oxygen K-edge peak around 530eV was also observed. However, the location of anatase precipitation was mostly around the tip of 1-AuNSt rather than the valley. This result is different from what we expected as discussed in Chapter 4 where higher temperature increase was expected around the valley forming localized TiO₂ precipitates. It is speculated that this is likely caused by the simultaneous contribution of different heating mechanism(s) in the sample. Given the high temperature increase in the centre of the sample due to laser irradiation (and associated Gaussian
beam profile), it is reasonable to expect conductive heat transfer to the bulk TiCl₄ medium in the surrounding region which would accordingly contribute to heating up the l-AuNST.

It is noteworthy that with 10% laser intensity, localized polymerization of the precursor was observed in the valley region of the l-AuNST as seen in Figure 5.13. However, due to the low laser power intensity anatase crystallization was not observed.

![Figure 5.13 l-AuNST prepared in 1M TiCl₄ under 785nm laser at 10% power](image)

To understand the effect of plasmonic resonance on the l-AuNST/TiO₂ nanostructure, similar experiments were conducted using 638nm and 532nm laser. Figure 5.14 illustrates l-AuNST in 1M TiCl₄ under 638nm at 12.5% (Figure 5.14a,b) and 25% (Figure 5.14c,d) laser power. Under 12.5% power, it precipitated TiO₂ localized in the valley of l-AuNST while exposing the tips. From the HRTEM image in Figure 5.14b, we confirmed lattice spacing of 0.35nm matching to the (101) plane of anatase titania. Further increasing the power to 25% resulted in partial particle reshaping and complete encapsulation of the gold particles by a matrix of titania as seen in Figure 5.14c. Higher power appears to cause more thermal damage and results in larger titania shell thickness with less localized crystallization behaviour. In Figure 5.14d, we measured the lattice spacing value to be 0.26nm which closely matches (101) plane of rutile titania. This observation may suggest that higher power not only increases the shell thickness but also undergoes phase transformation from anatase to rutile.
Figure 5.14 1-AuNS under 638nm laser in 1M TiCl₄, 5s (a,b) at 12.5% power and (c,d) at 25% power

Next, we conducted the same experiment under 532nm laser which is completely mismatched from the LSPR peak of 1-AuNST. The results are shown in Figure 5.15.
Theoretically the absorption cross-section at mismatched wavelength should be several times smaller than when it is at resonance. However, Figure 5.15 shows formation of nanocrystallite titania with lattice spacing of 0.35nm corresponding to (101) anatase phase. The likely reason for this may be due to the presence of unreacted gold seed in the synthesized l-AuNS. Due to the nature of the seeded growth method employed for synthesis of l-AuNS, unreacted gold seeds whose LSPR resonance at 532nm may contribute to heating under laser irradiation thus increasing the overall temperature of the TiCl₄ precursor in the vicinity of the nanoparticles. Further, due to bulk thermal diffusion, crystallization of titania is not localized and also causes particle reshaping as seen in Figure 5.15a (turning the l-AuNS into a more round shaped particle). The crystallization in this case is not localized inside the valleys of the gold nanostars, indicating the contribution of other thermal effects in this system.
5.2.3.2 S-AuNST

In this section, TEM images of s-AuNST with optically synthesized TiO$_2$ under 100% intensity of 638nm laser in 1M TiCl$_4$ solution are presented in Figure 5.16.

![TEM images](image)

**Figure 5.16** (a,b,c) s-AuNST in 1M TiCl$_4$ under 638nm at 100% power 5s (d) EELS spectrum of (c)

Under the resonating laser (638nm), we were able to produce Au/TiO$_2$ nanocomposite particles with localized anatase titania as confirmed by Figure 5.16b under HRTEM showing the (101) anatase structure. The crystallite was composed of sub 10nm sized nanocrystals as seen in Figure 5.16c. We also collected EELS spectrum over the sample as shown in Figure 5.16c and confirmed Ti L-edge peaks around 460eV followed by O K-edge around 530eV confirming the presence of titania.

Next, the TiO$_2$ crystallization on the s-AuNST was investigated under non-resonating laser wavelengths. The TiO$_2$ crystals that are synthesized from 1M TiCl$_4$ under 532nm laser at 50%...
power and at 12.5% power are shown in Figure 5.17 (a,b) and (c,d,e), respectively. Once again, the central irradiated region results in a micron-sized crater and hence cannot be TEM characterized, however, the presented images are taken from near the edge of the crater.

Figure 5.17 S-AuNST prepared in 1M TiCl₄ under (a) 532nm 50% power, (c,d) 532nm 12.5% power. (b) EELS spectrum of (c,d)

As shown in Figure 5.17a and Figure 5.17b, under 50% power the s-AuNST particles turn completely into spherical particles with a few particles showing crystallite formation on the surface with lattice spacing of 0.29nm. This value does not coincide with any of the possible hkl planes of either rutile or anatase titania and it is hard to conclude what is the crystalline nature of this precipitate. To minimize the thermal damage, we reduced the laser power to 12.5% and observed s-AuNST with a large precipitate as depicted in Figure 5.17c. EELS spectrum of this precipitate shown in Figure 5.17e did not indicate presence of titania. The lattice spacing value read from Figure 5.17d closely matched (111) plane of gold. However, EELS is not a practical method for identification of heavy elements like gold. Thus, to confirm, we conducted a mapping
scan of the area using x-ray energy dispersive spectroscopy (XEDS) and the results are presented in Figure 5.18.

Figure 5.18 (a) XEDS mapping of s-AuNS in 1M TiCl₄ under 532nm laser at 12.5% power after 5s (b) corresponding SEM image (c,d,e,f) map of oxygen, gold, titanium, and carbon respectively
Figure 5.18b shows a SEM image of s-AuNS with the unknown precipitate with lattice spacing of 0.23nm to the left side of s-AuNS. From analyzing the elemental map shown in Figure 5.18c,d,e, and f, we observed that the s-AuNS has surface adsorbed titanium and oxygen as well as carbon possibly from the carbon TEM grid or other sources of contamination. The precipitate on the s-AuNS indicated presence of titanium, carbon, and oxygen but no sign of gold. Thus, even though it has a lattice spacing of (111) gold, XEDS results suggests that it is probably a mixture of Ti, O, and C. However, from EELS and XEDS we cannot identify the substance.

Regardless of the identity of this substance, we can make a statement about the polymerization of TiCl$_4$ around s-AuNS under 532nm. Under 532nm laser, changing the laser power results in different degree of gold thermal damage and different structure of the precipitate but in either case we did not observe titania formation. This result seems to contradict the Raman spectra for s-AuNS where we observed anatase titania formation under 532nm laser with intensity as low as 12.5% (refer to Figure 5.3b). The contradiction is caused by the different probing locations used for Raman and TEM characterization. Under Raman spectroscopy setup, Raman signals are collected from the centre of irradiation with the highest temperature increase. However, exposing the sample under CW laser source for 20s results in heat diffusion with temperature inversely proportional to the radial distance away from the centre (Eq 2.15). As the TEM images were obtained near the edge of the bulky crater where the temperature increase would have been much smaller than the centre of irradiation, it is difficult to directly correlate the two results obtained from Raman and TEM.

Lastly, we observe the morphology of Au/TiO$_2$ nanocomposite synthesized under 785nm laser in 1M TiCl$_4$. Figure 5.19a and b illustrates TEM images of s-AuNS at 100% laser power after 5s. (101) plane anatase nanocrystals were clearly observed under HRTEM image as well as EELS spectrum (Figure 5.19b,c). Structurally, the anatase titania completely surrounded the s-AuNS making a fully covered core-shell nanoparticle. Reducing the power to 50% does not yield titania but rather forms a precipitate in a corner of s-AuNS as seen in Figure 5.19d. Fast fourier transform (FFT) image of the precipitate presented as an inset in Figure 5.19e seems to suggest (111) and (220) plane of gold (for complete d-spacing value of gold, refer to Appendix C). This precipitate has a similar structure as the one observed in Figure 5.17d. Again, it is hard to make a firm conclusion about this precipitate however from the EELS spectrum with lacking Ti L-edge peaks we conclude that at 50% power no TiO$_2$ precipitates.
Figure 5.19 TEM image of s-AuNS in 1M TiCl$_4$ under 785nm laser for 5s (a,b) at 100% power and (c) corresponding EELS spectrum while (d,e) at obtained under 50% power with (f) corresponding EELS spectrum. Inset in (e) is FFT image
5.2.3.3 AuNFl

AuNF\textsubscript{l} has a tip-to-tip diameter of $\sim 1\mu m$ with the largest geometrical cross-section. Although the studied gold nanoflowers do not exhibit plasmonic resonances under the visible lasers that are used in this thesis, they yield anatase TiO\textsubscript{2} crystals as shown in Figure 5.20.

![TEM images and EELS spectrum of AuNF\textsubscript{l} in 1M TiCl\textsubscript{4} under (a,b,c) 532nm at 10\% for 20s, (d,e,f) 638nm at 50\% for 5s. (g,h) 785nm at 50\% for 5s](image)

Figure 5.20 TEM images and EELS spectrum of AuNF\textsubscript{l} in 1M TiCl\textsubscript{4} under (a,b,c) 532nm at 10\% for 20s, (d,e,f) 638nm at 50\% for 5s. (g,h) 785nm at 50\% for 5s
More specifically, Figure 5.20a was synthesized under 532nm laser at 10% power. In this case, a large precipitate formed at a corner of one AuNF and a HRTEM image was obtained from the edge of this precipitate as the centre was too thick to be resolved under a 300keV electron beam. FFT image provided as an inset in Figure 5.20b shows a diffuse ring pattern rather than a diffraction spot suggesting the amorphous nature of the precipitate with the lattice spacing value closely matching the (101) anatase titania. EELS spectrum of the corresponding sample (Figure 5.20c) indicated presence of Ti L-edge and O K-edge. Complete encapsulation of AuNF by TiO₂ was observed when the AuNF/TiCl₄ mixture was exposed under 638nm laser at 50% (Figure 5.20d) and under 785nm laser at 50% (Figure 5.20g).

5.2.3.4 AuNSp

AuNSp was irradiated by its matching resonance laser (532nm) at 5% power for 5s in 1M TiCl₄ solution and the resulting structure is presented in Figure 5.21 below.

Figure 5.21 (a) AuNSp in 1M TiCl₄ under 532nm laser at 5% for 5s and (b) HRTEM image of red square indicated in (a)

It appears that the AuNSp particle is completely surrounded by a shell of thickness varying from 10nm to 75nm. Near the surface of the shell, a small crystal was observed and HRTEM image is presented in Figure 5.21b. The precipitate had a partial lattice structure with measured d-spacing value of 0.36nm in close accordance with (101) anatase phase of TiO₂. Previously from section
5.2.1, we estimated the minimum threshold energy for TiO\(_2\) formation around AuNSp under 532nm laser to be 10\% of the power. It is speculated that because the precipitate size is so small that the Raman signal was too low to be resolved. The fact that we observe anatase formation under such low intensity demonstrates that the AuNSp particles are an efficient means of heating due to the increased temperature contribution by the well-matched LSPR.

### 5.2.4 Thermal stability of l-AuNSt

Since the deformation of the l-AuNSt particles were observed on several occasions during the range of experiments reported here, we studied the thermal stability of the synthesized l-AuNSt in the following experiment. L-AuNSt fixed on small pieces of silicon wafer were placed in a furnace for 5min under temperatures of 100\(^\circ\)C, 200\(^\circ\)C, and 300\(^\circ\)C. Each of the samples were characterized under SEM and the corresponding images are shown in Figure 5.22.

Figure 5.22 SEM images of l-AuNSt after being subjected in furnace for 5 min at (A) Room temperature, (B) 100\(^\circ\)C, (C) 200\(^\circ\)C, and (D) 300\(^\circ\)C
As seen in Figure 5.22, no visible change in shape was observed at 100°C. With the heat treatment at 200°C, we observe that the longer branches are still present however the shorter tips have started to turn more blunt as seen in Figure 5.22c. At 300°C, the l-AuNSt has completely undergone thermal transformation into a spherical shape losing all its sharp branched structures. These results serve as a reference tool to estimate the temperature of the TiO$_2$ containing AuNSt mixtures studied by TEM and reported in the foregoing sections of this chapter.
5.3 Conclusion

In this section, we present a summary of the Raman and TEM characterization of TiO$_2$ crystallization on plasmonic gold nanoparticles.

With regards to Raman analysis, we observed anatase titania formation under 532nm laser regardless of the particle shape. However, depending on the geometrical cross-section and location of the LSPR band each particle varied in the minimum threshold laser power required to form titania from TiCl$_4$ precursor. In 1M TiCl$_4$ solution under 532nm, AuNSp required the minimum laser power followed by s-AuNST, AuNFI, and l-AuNST. The optimal TiCl$_4$ concentration for AuNSp and AuNFI was 2M whereas 1M resulted in more intense and sharp anatase peak for l-AuNST and s-AuNST.

To study the role of plasmonic resonance, we compared and contrasted AuNSp with resonance frequency at 535nm and l-AuNST with resonance frequency at 800nm. Under 532nm laser, resonating AuNSp induced anatase crystallization at a laser power as low as 5% whereas non-resonating l-AuNST required 100% power. Contrarily, under 785nm laser resonating l-AuNST exhibited mixed phase (rutile and anatase) titania formation under 100% power. Non-resonating AuNSp, however, did not result in any titania crystallization. From the above observations, we concluded that matching the laser source to the LSPR frequency of the nanoparticle aid in crystallization of TiO$_2$ by lowering the required energy and by maximizing the absorption cross-section to generate heat around the AuNP.

HRTEM and EELS spectra revealed the structural features of optically synthesized Au/TiO$_2$ nanocomposite. With regards to the l-AuNST, careful control over the laser intensity is required as the particles tends to turn into spherical shapes due to the metastable nature of pointy tips. By fine tuning the laser intensity (638nm, 12.5% power, 5s), we have successfully created Au/TiO$_2$ core-shell nanoparticles with localized TiO$_2$ on the valleys while exposing the gold tips. Similar semi-covered core-shell structure was observed for s-AuNST prepared under 638nm laser at 100% power for 5s. Light assisted TiO$_2$ synthesis was also achieved using AuNFI and AuNSp but did not yield a localized titania precipitation but rather forming a bulky shell encapsulating the gold particles.
Chapter 6

6 Conclusions and Outlook

This thesis proposes a novel core-shell nanoparticle synthesis method by exploiting the heat generation around plasmonically excited gold nanoparticles. We explored four different shapes of gold nanoparticles, mainly focusing on the sharp tipped nanostar particles referred to as l-AuNS. The main emphasis was to optically excite the plasmonic resonances of the AuNP so that the coupled resonance and hence the generated heat at the particle surface can be transferred to the immediate surrounding TiCl4 precursor so as to aid in localized crystallization of titania around the valleys (resonating hot spots) of l-AuNS. The resulting semi-covered core-shell nanoparticles show promise for photocatalytic reaction applications in the visible range. Such plasmonically induced localized crystallizations offers a reliable alternative for traditional composite nanostructure synthesis methods such as deposition-precipitation, photoreduction, and encapsulation.

For the synthesis of the structured Au nanoparticles, we employed the seeded growth chemical synthesis method which provided significant control over the production of l-AuNS which had the desired sharp pointy nanostar shape and corresponding optical resonances.

The light assisted synthesis of TiO2 was conducted using a Raman experimental characterization facility equipped with three wavelengths of CW lasers: 532nm, 638nm, and 785nm. The choice of AuNP (AuNSp (sphere), l-AuNS (long nanostar), s-AuNS (short nanostar), AuNFL (nanoflower)) were based on their plasmonic resonance peaks so as to match the available laser sources in order to study the role of plasmonic resonance in heat generation and thus chemical synthesis of titania. The Raman facility was used for both light-assisted plasmonic synthesis as well as Raman characterization. Complementary TEM studies were carried out to characterize the crystallized phases and location. To gain insight into the resonances of the Au nanostars, COMSOL Multiphysics modelling was also carried out.

A summary of the important findings and conclusions emerging from this thesis are presented:

- We performed a numerical simulation study using COMSOL to understand the optical behaviour of gold nanostars and the role of gold tip height on the location of LSPR peaks.
By solving for power loss density we obtained absorption cross-section values for gold nanostars with varying tip aspect ratios in the wavelength range from 400nm to 1000nm. It was found that the LSPR peak is strongly dependent on the tip height and specifically increasing the tip height caused a redshift in the LSPR peak. From power loss density mapping, we confirmed that the long branched tips in gold nanostar particles were responsible for the LSPR in near-IR region whereas the shorter branches and the spherical core were responsible for the small LSPR peak near 530nm. The heat dissipation at the valley region between two branches, in general, was less affected by the incoming light frequency and remained high thus supporting the proposed design of creating localized titania formation in the valley regions.

- Raman spectroscopy and TEM were used to characterize TiO$_2$ crystallization under various experimental conditions. By carefully controlling the laser wavelength and intensity, which are essential to preventing nanoparticle deformation, we demonstrated successful light assisted core-shell nanoparticle synthesis with localized TiO$_2$ crystallization. We observed that under laser irradiation at wavelengths differing from that of the plasmonic resonance of AuNP, higher intensity were required to induce titania crystallization. In addition, some experiments under non-resonant laser light conditions did not yield any titania. On the other hand, matching the laser source to the LSPR wavelength required lower laser intensity for titania formation which is indicative of enhanced degree of heat generation under plasmonic resonance.

- By conducting Raman spectroscopy, formation of anatase phase titania was confirmed with 532nm laser on all AuNP (l-AuNSt, s-AuNSt, AuNSp, and AuNFl) in 1M TiCl$_4$ precursor. Laser intensity required for anatase formation was lowest with AuNSp followed by s-AuNSt, AuNFl, and l-AuNSt. Under 785nm laser, only plasmonically resonating l-AuNSt induced crystallization of titania. By increasing the TiCl$_4$ concentration to 2M, we were able to obtain mixed phase titania containing both anatase and rutile phases.

- Due to the limitation of CW source lasers with long exposure times compared to the timescale of thermal transfer within the lattice from $e$-$e$ scattering and $e$-phonon coupling, the heat affected zone was rather large as a result of bulk thermal diffusion within the
medium. The obtained Au/TiO$_2$ core-shells varied in structure depending on the comparative distance from the centre of laser irradiation. Regardless of the limitations and difficulties in this first investigation, we have successfully demonstrated the viability of the proposed new approach in core-shell nanoparticle synthesis.

- In a controlled experiment, we also prepared and examined 1-AuNSt/TiO$_2$ nanocomposite structures synthesized by conventional heating of TiCl$_4$ mixture rather than plasmonically generated heat. These experiments showed the thermal sensitivity of the spiky nanostar to deformation, transforming into the thermodynamically stable spherical shape, and also accompanying crystallization of a bulky matrix of TiO$_2$ covering the entire l-AuNSt. These experiments showed that deformation of the nanostars begins to occur at approximately 80°C under prolonged heating (1.5hrs) or above 200°C under short heating (5min).

From an application perspective, one promising application of the semi-covered Au/TiO$_2$ core-shell nanoparticles synthesized using the proposed method is for the development of efficient visible light photocatalysis. Photocatalysis refers to the use of a particular type of material which has the ability to transform light energy into chemical energy by generating reductive or oxidative species which can participate in a desired chemical reaction [33]. Efficient photocatalysts can be used in a wide range of applications such as water/air purification, hydrogen generation by water splitting reaction, self-cleaning paints, sterilization in hospitals, and decomposition of organic compounds [34]. With the synthesized semi-covered Au/TiO$_2$ core-shell structure, the exposed gold tips can serve as nano-antennas to collect the incoming light source. The expected benefits of Au nanostars are: direct charge injection from gold to TiO$_2$ and enhancement of $e$-$h$ formation in TiO$_2$ by increasing the local intensity of the electric field [47]. Direct charge injection mechanism, is similar to dye sensitization in solar cells, where gold nanostars would act as tuned optical plasmonic light absorbers and transfer the energetic electrons to TiO$_2$. Due to the electronic band alignment of gold and TiO$_2$, electrons are favorably transferred from gold to TiO$_2$ which is desired for the hydrogen-evolution reaction requiring electrons to complete the reduction of hydrogen ions [47].
Even though we have only explored the light assisted optical synthesis of TiO\textsubscript{2} on AuNP fixed on a substrate with the experimental setup of Raman lasers, the proposed synthesis method can easily be scaled up for mass production using a flow reactor as shown in Figure 6.1.

**Figure 6.1 Simplified diagram of light assisted TiO\textsubscript{2} synthesis on AuNS using flow reactor concept**

Chemically prepared AuNS can be mixed into a batch of TiCl\textsubscript{4} solution which is directed through a transparent pipe connected with a pump. As the AuNS/TiCl\textsubscript{4} mixture flows, it is exposed under resonating laser induced localized crystallization of TiO\textsubscript{2} which can be collected in another batch. Resulting Au/TiO\textsubscript{2} nanoparticles can be washed and dried to obtain composite nanopowders or be fixed on various types of substrate for use in specific applications. By controlling the concentration of TiCl\textsubscript{4}, anatase or mixed phase of anatase and rutile can be achieved. This type of flow reactor synthesis is possible because the LSPR on AuNS is not polarization dependant, meaning the AuNS in precursor mixture can freely flow in random orientation with respect to the incoming laser source. Unlike the traditional hydrothermal synthesis method, proposed scheme only requires a few seconds for completion of reaction thus increasing the throughput. Another advantage of this flow reactor design other than mass production is the finer control over the laser exposure duration by controlling the flow rate of the
attached pump. Even continuous laser source on a flow reactor could act as a pulsed laser source since the laser irradiation time on a single nanoparticle is constrained by the flow rate.

In order to take full advantage of localized heating behaviour of gold nanoparticles under plasmonic resonance, use of a pulsed laser is much more desirable than CW source. Pulsed laser would enable fine control over not only the synthesized shell thickness and location but also the crystalline phase of the material which is determined by the synthesis temperature. A pulsed laser provides further confinement of spatial temperature distribution which would allow for better control over the thickness of TiO$_2$ shell. This type of confinement of temperature achieved under pulsed laser opens up possibilities for other application involving control over pressure [110], [111], superheating of liquid, bubble generation, metal ablation [112], [113], or stress wave generations [114]. The proposed light assisted synthesis method can also be applied to a wide range of precursor solutions for synthesis of various types of core-shell nanoparticles of interest.
References


[54] S. Hashimoto, D. Werner, and T. Uwada, “Studies on the interaction of pulsed lasers with plasmonic gold nanoparticles toward light manipulation, heat management, and


Appendix A: I-AuNSt synthesis

In this section, we investigate the gold nanostar synthesis in more detail. As explained in section 3.1.1, one-step seeded growth method has been adapted to chemically synthesize AuNSt particles. Here, the effect of varying the concentration of auric acid, silver nitrate, hydrochloric acid, and the amount of seed solution will be presented. For all the experiments, aqua regia treated beakers were used to carry chemical synthesis with a magnetic stirring set at 500rpm. We varied the concentration of the chemical solutions but the volume of the solutions were kept constant at 40ml, 0.4ml, 0.2ml for HAuCl₄, AgNO₃, and ascorbic acid solutions respectively.

A1. Effect of HAuCl₄ concentration

While the other parameters were kept constant, we varied the concentration of HAuCl₄ to study the effect of HAuCl₄ on the morphology of resulting AuNSt. As the molar ratio between HAuCl₄ and ascorbic acid play an important role on the sharpness of the peaks as reported by Yuan et al., the concentration of ascorbic acid was adjusted accordingly to keep the molar ratio at 1:2. Table A 1 summarizes the experimental parameters.

<table>
<thead>
<tr>
<th></th>
<th>HAuCl₄</th>
<th>Ascorbic Acid</th>
<th>AgNO₃</th>
<th>Seed</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1-1</td>
<td>0.1mM</td>
<td>40mM</td>
<td>1mM</td>
<td>0.2ml</td>
<td>40μl</td>
</tr>
<tr>
<td>A1-2</td>
<td>0.25mM</td>
<td>100mM</td>
<td>1mM</td>
<td>0.2ml</td>
<td>40μl</td>
</tr>
</tbody>
</table>

Hitachi S5200 scanning electron microscope was used to image the obtained I-AuNSt and the images are shown in Figure A1 below.
Figure A 1. SEM images of synthesized l-AuNS of (a) A1-1 (lower HAuCl₄ concentration) and (b) A1-2 (higher HAuCl₄ concentration)

The tip-to-tip diameter of the particles were similar for both A1-1 and A1-2. However, overall uniformity in particle size distribution was better for A1-2 synthesized in 0.25mM HAuCl₄ solution thus following experiments were performed at 0.25mM HAuCl₄ solution while varying the other parameters.

A2. Effect of gold seed amount

In this section, we performed two sets of experiment: one with filtered or unfiltered gold seeds and the other with changing the amount of seed solution. Filtration was carried using a 0.45μm nylon filter which removes any unreacted residues or agglomerates. Table below summarizes the experimental parameters.

Table A 2. Chemical synthesis parameters with varying amount of gold seed solution

<table>
<thead>
<tr>
<th></th>
<th>HAuCl₄</th>
<th>Ascorbic Acid</th>
<th>AgNO₃</th>
<th>Seed</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2-1</td>
<td>0.25mM</td>
<td>100mM</td>
<td>0.03mM</td>
<td>0.4ml filtered</td>
<td>40μl</td>
</tr>
<tr>
<td>A2-2</td>
<td>0.25mM</td>
<td>100mM</td>
<td>0.03mM</td>
<td>0.4ml unfiltered</td>
<td>40μl</td>
</tr>
<tr>
<td>A2-3</td>
<td>0.25mM</td>
<td>100mM</td>
<td>1mM</td>
<td>0.8ml filtered</td>
<td>40μl</td>
</tr>
<tr>
<td>A2-4</td>
<td>0.25mM</td>
<td>100mM</td>
<td>1mM</td>
<td>0.2ml filtered</td>
<td>40μl</td>
</tr>
</tbody>
</table>
The obtained l-AuNST was washed by centrifugation, re-dispersed in DI water and examined under SEM as shown in Figure A2.

**Figure A 2.** SEM images of (a) A2-1, (b) A2-2, (c) A2-3, (d) A2-4

By comparing Figure A2a and A2b, the effect of filtering the gold seed solution is clear. Unfiltered seed has more number of gold seeds as well as residues and agglomerates with wide particle size distribution compared to the filtered seed. Filtering the seed solution (Figure A2-a) resulted in a slightly larger nanoparticles with sharper spikes compared to the unfiltered one (Figure A2-b). Reducing the number of seed resulted in more spiky nanostar particles. When the seed solution was increased to 0.8ml, no nanostar formation was observed as depicted in Figure A2-c. When the seed amount was further reduced to 0.2ml, high aspect-ratio nanostar particles were obtained as shown in Figure A2-d.
A3. Effect of silver nitrate solution (AgNO₃)

This section presents the effect of changing silver nitrate solution on the morphology of l-AuNST. The concentration was varied from 0.1mM up to 5mM as summarized in Table A3. Corresponding SEM images are presented in Figure A3.

Table A3. Chemical synthesis parameters with varying AgNO₃ concentrations

<table>
<thead>
<tr>
<th></th>
<th>HAuCl₄</th>
<th>Ascorbic Acid</th>
<th>AgNO₃</th>
<th>Seed</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3-1</td>
<td>0.25mM</td>
<td>100mM</td>
<td>0.1mM</td>
<td>0.15ml</td>
<td>40μl</td>
</tr>
<tr>
<td>A3-2</td>
<td>0.25mM</td>
<td>100mM</td>
<td>0.5mM</td>
<td>0.15ml</td>
<td>40μl</td>
</tr>
<tr>
<td>A3-3</td>
<td>0.25mM</td>
<td>100mM</td>
<td>1mM</td>
<td>0.15ml</td>
<td>40μl</td>
</tr>
<tr>
<td>A3-4</td>
<td>0.25mM</td>
<td>100mM</td>
<td>5mM</td>
<td>0.15ml</td>
<td>40μl</td>
</tr>
</tbody>
</table>

Figure A3. SEM images of (a) A3-1, (b) A3-2, (c) A3-3, and (d) A3-4
At low AgNO$_3$ concentration, dendritic nanostar formation did not occur as shown in Figure A3-a. The seed solution, originally ~13nm, grew in size to 60nm diameter but no peaks were developed. At 0.5mM AgNO$_3$ concentration, the peaks started developing as shown in Figure A3-b. Most well-defined dendritic gold nanostar shape was achieved using 1mM AgNO$_3$ solution with tip-to-tip diameter of 122nm. Further increasing the concentration to 5mM yielded smaller tip-to-tip diameter (84nm) however the aspect ratio of the peaks formed was not as high as the nanostar synthesized using 1mM solution.

**A4. Effect of acidity**

Here, we report the effect of acidity on the morphology of resulting l-AuNSt. While keeping the other parameters constant, the amount of 1M hydrochloric acid was changed from 20μl to 10μl as summarized in Table A4 and the resulting nanostar particles were examined under SEM as presented in Figure A4.

**Table A 4. Chemical synthesis parameters with varying amount of HCl**

<table>
<thead>
<tr>
<th></th>
<th>HAuCl$_4$</th>
<th>Ascorbic Acid</th>
<th>AgNO$_3$</th>
<th>Seed</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A4-1</strong></td>
<td>0.25mM</td>
<td>100mM</td>
<td>1mM</td>
<td>0.1ml</td>
<td>20μl</td>
</tr>
<tr>
<td><strong>A4-2</strong></td>
<td>0.25mM</td>
<td>100mM</td>
<td>1mM</td>
<td>0.1ml</td>
<td>10μl</td>
</tr>
</tbody>
</table>

**Figure A 4. SEM images of (a) A4-1 (more acidic) and (b) A4-2 (less acidic)**

Lowering the pH by addition of 20μl HCl resulted in more spiky shaped nanostar compared to synthesis carried in higher pH environment with 10μl of HCl. This results agrees with the
observation made by Yuan et al. reporting more redshifted gold nanostar synthesized using higher amount of HCl corresponding to higher aspect ratio nanostar particles.
## Appendix B: d-spacing of rutile, anatase, brookite, and gold

<table>
<thead>
<tr>
<th></th>
<th>Rutile</th>
<th></th>
<th>Anatase</th>
<th></th>
<th>Brookite</th>
<th></th>
<th>Gold</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>hkl</td>
<td>d (Å)</td>
<td>hkl</td>
<td>d (Å)</td>
<td>hkl</td>
<td>d (Å)</td>
<td>hkl</td>
<td>d (Å)</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>3.247</td>
<td>101</td>
<td>3.52</td>
<td>120</td>
<td>3.512</td>
<td>111</td>
<td>2.355</td>
<td></td>
</tr>
<tr>
<td>101</td>
<td>2.487</td>
<td>103</td>
<td>2.431</td>
<td>111</td>
<td>3.465</td>
<td>200</td>
<td>2.039</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>2.297</td>
<td>004</td>
<td>2.378</td>
<td>121</td>
<td>2.9</td>
<td>220</td>
<td>1.442</td>
<td></td>
</tr>
<tr>
<td>111</td>
<td>2.188</td>
<td>112</td>
<td>2.332</td>
<td>200</td>
<td>2.729</td>
<td>311</td>
<td>1.229</td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>2.054</td>
<td>200</td>
<td>1.892</td>
<td>012</td>
<td>2.476</td>
<td>222</td>
<td>1.177</td>
<td></td>
</tr>
<tr>
<td>211</td>
<td>1.6874</td>
<td>105</td>
<td>1.6999</td>
<td>201</td>
<td>2.409</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>1.6237</td>
<td>211</td>
<td>1.6665</td>
<td>131</td>
<td>2.37</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>002</td>
<td>1.4797</td>
<td>213</td>
<td>1.493</td>
<td>220</td>
<td>2.344</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>310</td>
<td>1.4528</td>
<td>204</td>
<td>1.4808</td>
<td>211</td>
<td>2.332</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>221</td>
<td>1.4243</td>
<td>116</td>
<td>1.3641</td>
<td>040</td>
<td>2.296</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>301</td>
<td>1.3598</td>
<td>220</td>
<td>1.3378</td>
<td>112</td>
<td>2.254</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>112</td>
<td>1.3465</td>
<td>107</td>
<td>1.2795</td>
<td>022</td>
<td>2.244</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>311</td>
<td>1.3041</td>
<td>215</td>
<td>1.2649</td>
<td>221</td>
<td>2.133</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>1.2739</td>
<td>301</td>
<td>1.2509</td>
<td>032</td>
<td>1.9685</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>202</td>
<td>1.2441</td>
<td>008</td>
<td>1.1894</td>
<td>231</td>
<td>1.8934</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>212</td>
<td>1.2006</td>
<td>303</td>
<td>1.1725</td>
<td>132</td>
<td>1.8514</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>321</td>
<td>1.1702</td>
<td>224</td>
<td>1.1664</td>
<td>212</td>
<td>1.8332</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>1.1483</td>
<td>312</td>
<td>1.1608</td>
<td>240</td>
<td>1.7568</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values obtained from 2015 International Centre for Diffraction Data