Modeling and analysis of post plasmonic effects in optically excited metal nanosystems

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Abstract

Plasmonic nanoparticles such as gold (Au) and silver (Ag) with their heterogeneous nanocomposite structures have aggrandized in multitude of applications including biomedical imaging (optical, photoacoustics (PA), dark field, etc.), sensing techniques including wavelength shift Local Surface Plasmon Resonance (LSPR) bands and Surface Enhanced Raman Spectroscopy (SERS), photothermal therapy, and drug delivery. Their usage is made plausible by optical excitation of suitable wavelength and subsequently triggering LSPR. To manipulate LSPR, this field of nanotechnology requires appropriate modification and design of nanostructures in terms of size, shape, surface functionalization, coating, interparticle coupling, etc. These modifications are inevitable to achieve better performance and sensitivity via one or more of these objectives: 1) higher absorption, 2) field enhancement and 3) thermodynamic stability.

Though the unique capabilities of coatings/shell on nanomaterials are quite promising, post effects of optical excitation intuitively can be claimed to disturb the core-shell nanostructures. There are few possible intermediate phenomena like electric field enhancement, thermal expansion, heat generation, gas evolution, boiling, ablation, breakdown, and plasma formation which can cause this. This thesis investigates the cause of perturbations in such nanostructures via few of the above effects (ther-

mal expansion & electric field enhancement). These mechanisms occur under specific conditions of temperature, irradiation timing, laser intensity, nanoparticle shape, environment matrix, pulse duration, beam diameter, etc. In addition to the investigation on structural damage, the thesis also investigates the formation of plasmonic coupling via optical excitation as a stimulus to build nanostructures and the effect of a conductive interface in such coupled systems. There have been studies reported about melting and reshaping of metal nanoparticles, damage caused by plasmonic precursors embedded in a dielectric via heat or field enhancement), etc. However, an understanding of the stability of a standalone hetero-nanostructure under laser excitation has not been reported yet. Hence this work provides an understanding of plasmonic excitation and subsequent transfer of energy affecting the stability of a hetero-nanostructure which depends on size and shape of the plasmonic material. This will aid the modeling and designing of nanostructures, especially for biomedical applications.

In this thesis, we have explored several mechanisms which induce morphological or structural change on composite hetero - nanostructures with a dielectric coating on gold nanoparticles. We used finite element method (FEM), MATLAB and theoretical analysis to numerically compute and predict the intensity range where a breakdown is expected. First, we explored structural damage on smaller nanoparticles like silica coated spherical Au nanoparticles (AuNP@SiO_2). Using a nanosecond pulsed laser we have shown the possibility of structural breakdown which was characterized using Transmission Electron Microscopy (TEM) images and Scanning Electron Microscopy images (SEM). An intensive literature and theoretical model backup the fact that structural failure in these core-shell nanospherical structures happens due to the differential thermal expansion of core-shell pair and that rupture or deformation happens

throughout the silica coating.

Following this, we extended our study towards silica coated Ag nanoprism (AgNPr@SiO_2) which exhibits a different breakdown mechanism. Due to the triangular geometry and high scattering of Ag than that of Au, a low input intensity could create a field enhancement near the corners causing damage to be initiated at the corners. Numerical models were used to analyze the localization of intensity near corners and estimate the range of values for the breakdown. Thus, a more controlled breakdown is achieved and with a low laser fluence. These nanosystems are anticipated to have a significant impact on biomedical applications, providing futuristic possibilities for non-invasive methods as suitable agent carriers. These agents can be injected non-invasively and be remotely activated to respond to external stimuli at convenient sites inside a real-life sample.

Finally, we have investigated the effect of optical excitation on plasmonic clusters connected covalently by a conductive inter-particle interface. For this, we have selected spherical gold nanoparticles (AuNPs) and gold nanoprisms (AuNPrs) and modified their surface with a synthetically modified diacetylene monomer. Upon exposure to ultra-violet light (254 nm), the diacetylene undergoes photopolymerization to polydiacetylene resulting in the formation of interparticle assembly and initiate clustering. We anticipate that the interface comprising of conductive polymers allows interparticle plasmonic exchange upon suitable light excitation.

Theoretical simulation and experimental findings suggested that upon suitable optical excitation, plasmonic nanosystems including core-shell analogs as well as interparticle clusters undergo various changes. The resultant transformation in these nanosystems varies for different

structures depending on factors such as size, shape, coating, and nature of laser used for excitation. The study presented in this thesis will provide insight into plasmon interactions based structural instabilities and changes in plasmonic nanomaterials during interaction with electromagnetic (EM) waves.

Contents

Acknowledgements	i
Abstract	iii
List of Abbreviations	xi
List of Figures	xiii
List of Tables	xix
1 Introduction and Literature Review	1
1.1 Plasmonics and Metal Nanoparticles	2
1.2 Modeling	3
1.3 Plasmonic Nanostructures in Biomedical Engineering	8
1.4 Plasmonic Effects in Nanostructures	10
1.4.1 Disruptive Effects of Electromagnetic Interaction	11
1.4.2 Constructive Effects of Electromagnetic Interaction	14
1.5 Motivation and Objective	15

2	Optically Induced Rupture in Gold-Silica Nanostructures	17
2.1	Introduction	18
2.2	Mutually Dependent Variables During Plasmonic Interaction	19
2.2.1	Temperature Dependence of Variables	19
2.2.2	Model for Temperature Dependent Dielectric Constant	22
2.3	Quasi Static Temperature of Nanoparticle under Pulsed Ir- radiation	25
2.3.1	Analytical Estimation of Quasi Static Temperature .	25
2.3.2	Convergence by Iteration on Analytical Model for Quasi Static Temperature	27
2.3.3	Finite Element Method Simulation	31
2.4	Optical Excitation of Gold Nanoparticles	32
2.4.1	Theoretical Analysis	32
2.4.2	Experimental Analysis	44
2.5	Summary and Conclusion	49
3	Light Intensity Field Enhancement (LIFE) Induced Localized Edge Abrasion of Silica-Coated Silver Nanoprisms	53
3.1	Introduction	54
3.2	Radius of Curvature (ROC) Analysis - Corner and Edge Smoothing	57

3.2.1	Geometry - ROC Analysis	57
3.2.2	Absorption Spectrum - ROC Analysis	59
3.2.3	LIFE Profile - ROC Analysis	59
3.2.4	ROC Analysis - Summary	60
3.3	LIFE Induced Edge Abrasion	61
3.3.1	Theoretical Analysis	61
3.3.2	Experimental Analysis	69
3.4	Conclusion	77
4	Investigation on Conductive Polymer Mediated Plasmonic Coupling and Charge Transfer Plasmons	79
4.1	Introduction	80
4.1.1	Formation of Plasmonic Clusters	80
4.1.2	Charge Transfer Plasmons (CTP)	82
4.2	Conductive Coupling of Gold Nanospheres	83
4.2.1	Theoretical Analysis	83
4.2.2	Experimental Analysis	85
4.3	Conductive Coupling of Gold Nanoprisms	89
4.3.1	Theoretical Analysis	89
4.3.2	Experimental Analysis	92

4.4	Conclusion	96
5	Conclusions and Future Work	97
5.1	Conclusions	97
5.2	Future Work	99
A	Laser Irradiation Setup and Fluence Calculation	103
A.1	Laser Setup	103
A.2	Fluence Calculation	104
A.2.1	Gaussian Beam Propagation	104
A.2.2	Depth Resolved Fluence	108
A.2.3	Transmission Coefficient	109
B	Optical Parameters of the Materials Used for the Study	111
B.1	Silica	111
B.2	Gold	112
B.3	Silver	113
B.4	Graphene Oxide	113
B.5	Polyacetylene	113
	Bibliography	116

List of Abbreviations

AuNP	Gold Nanoparticle
AuNR	Gold Nanorods
AgNPr	Silver Nanoprism
DLT	Drude-Lorentz-Temperature (DLT)
TTM	Two-Temperature Model
OTM	One-Temperature Model
DDA	Discrete Dipole Approximation
MMP	Multiple Multipole
FDTD	Finite Difference Time Domain
AuNP@SiO ₂	Silica coated Gold Nanoparticle
AgNPr@SiO ₂	Silica coated Silver Nanoprism
GNR	Gold Nanorod
PEN	Plasmonically Engineered Nanoprobes
GO	Graphene Oxide
GO-AgNPr@SiO ₂	Graphene Oxide wrapped Silica coated Silver Nanoprism
UV	Ultra-Violet
VIS	Visible
NIR	Near Infra-Red
EM	Electromagnetic
FEM	Finite Element Method
SERS	Surface Enhanced Raman Scattering
SPR	Surface Plasmon Resonance
LSPR	Local Surface Plasmon Resonance
DOS	Density of States
FWHM	Full Width Half Maximum
SEM	Scanning Electron Microscopy
FE-SEM	Field Emission Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
PA	Photoacoustics

PAI	Photoacoustic Imaging
TEOS	Tetraethyl Orthosilicate
ROC	Radius of Curvature
LIFE	Light Intensity Field Enhancement
LIDT	Laser Induced Threshold
MPI	Multiphoton Ionization
CW	Continuous Wave
ND-Filter	Neutral Density Filter
CTP	Charge Transfer Plasmon
BDP	Bonding Dimer Plasmon
SBDP	Screened Bonding Dimer Plasmon
dAc	Diacetylene
pAc	Polydiacetylene
PDT	1,2-Phenylenedimethanethiol
PBS	Phosphate Buffered Saline
OD	Optical Density

List of Figures

1.1	Comparison of Drude, Drude-Lorentz & Critical point analysis for gold	5
1.2	Plasmonically engineered nanoprobcs (PENs) for biomedical applications	9
1.3	Schematic illustration of possible plasmonic sources of damage	12
2.1	Illustration of the mutually dependent variables	20
2.2	Plot: Absorption cross section of silica coated gold α_{abs} vs refractive index of silica n_{silica}	21
2.3	Flowchart of iterative algorithm for temperature estimation .	29
2.4	Plot: Absorption cross section of gold α_{abs} vs temperature T	30
2.5	Plot: Temperature profile (T) of gold vs input fluence	31
2.6	Simulated power absorption & temperature of AuNP@SiO ₂	33
2.7	Theoretical temperature profile T_{iter} & simulated temperature profile T_{sim} of AuNP@SiO ₂	35

2.8	Expected thermal stress profile	39
2.9	Simulation: Maximum Light Intensity Field Enhancement inside silica dielectric	43
2.10	Simulation: Intensity enhancement map of AuNP@SiO ₂ at 526 nm	43
2.11	Transmission electron microscope (TEM) images of AuNP@SiO ₂ (ca. 30 nm silica shell thickness)	46
2.12	Scanning electron microscope (SEM) images of AuNP@SiO ₂ (ca. 30 nm silica shell thickness)	46
2.13	Transmission electron microscope (TEM) images of AuNP@SiO ₂ (ca. 30 nm silica shell thickness)	47
2.14	Fluence vs thermal stress & fluence vs maximum tempera- ture for AuNP@SiO ₂	48
2.15	Schematic illustration of the optically induced structural in- stability in AuNP@SiO ₂	50
3.1	Schematic illustration of the LIFE induced localized edge abrasion of AgNPr@SiO ₂	56
3.2	Geometry of AgNPr with different corner ROC & edge ROC	58
3.3	Simulation: Absorption profile of AgNPr & AgNPr@SiO ₂ vs ROC	59
3.4	Simulation: Maximum LIFE of AgNPr & AgNPr@SiO ₂ with ROC	60

3.5	Absorption peak & intensity enhancement peak of AgNPr & AgNPr@SiO ₂ vs ROC	60
3.6	Simulation: Estimated LIFE in AgNPr@SiO ₂ nanoparticles at 900 nm	62
3.7	Illustration of the interaction of EM field with graphene oxide wrapped nanosphere & nanoprism	64
3.8	Simulation: Reduction of LIFE near corners of AgNPr@SiO ₂ up on GO wrapping	65
3.9	Simulation: Comparison of absorption spectra & LIFE changes of AgNPr, AgNPr@SiO ₂ & GO-AgNPr@SiO ₂	65
3.10	AgNPr@SiO ₂ samples before & after irradiation	72
3.11	GO-AgNPr@SiO ₂ samples before & after irradiation	72
3.12	Measured absorption of AgNPr@SiO ₂ & GO-AgNPr@SiO ₂ before & after irradiation	73
3.13	Transmission electron microscope (TEM) images of AgNPr@SiO ₂ nanoprisms before & after irradiation	74
3.14	Raman spectra of AgNPr@SiO ₂ & GO-AgNPr@SiO ₂ be- fore & after 1800 s irradiation	75
3.15	Field emission scanning electron microscope (FE-SEM) im- ages of AgNPr@SiO ₂ & GO-AgNPr@SiO ₂	76
3.16	Transmission electron microscope (TEM) images of GO- AgNPr@SiO ₂ nanoprisms before & after irradiation	76

3.17 Box plot comparing the damage ratio of AgNPr@SiO ₂ using TEM images	78
4.1 Simulation: Absorption & extinction spectra of the coupled AuNPs	85
4.2 Schematic representation of coupling by UV irradiation . . .	86
4.3 Transmission electron microscope (TEM) images of polydiacetylene mediated conductive coupled AuNPs	87
4.4 Measured absorption spectra of AuNP solution & polydiacetylene assisted conductive coupled AuNP system	88
4.5 Measured absorption spectra of polydiacetylene layer . . .	89
4.6 In plane excitations to trigger the dominant longitudinal dipole resonance	90
4.7 In plane excitations to trigger intermediate longitudinal quadrupolar resonance	90
4.8 Out of plane excitations to trigger the weak lateral quadrupolar resonance	91
4.9 Average absorption & extinction spectrum	91
4.10 Simulation: Absorption & extinction spectra of the coupled AuNPrs	93
4.11 Transmission electron microscope (TEM) images of polydiacetylene mediated conductive coupled AuNPrs	93

4.12 Transmission electron microscope (TEM) images of polydiacetylene mediated conductive coupled AuNPrs-doubled the amount of polydiacetylene	94
4.13 Transmission electron microscope (TEM) images of polydiacetylene mediated conductive coupled AuNPrs-reduced stirring speed while photopolymerization	94
4.14 Measured absorption spectra of AuNPr solution & polydiacetylene assisted conductive coupled AuNP system	95
5.1 Schematic of drug release upon laser excitation	100
5.2 Schematic summary of dielectric/polymer coated plasmonic nanostructures in controlled drug delivery & other applications (imaging & photothermal therapy)	101
A.1 Schematic of laser irradiation setup.	103
A.2 An illustration to estimate fluence on the sample	106
A.3 Comparison of Gaussian beam in air for 526 nm & 900 nm & their change when propagating through AuNP@SiO ₂ & AgNPr@SiO ₂ sample columns respectively	107
A.4 Region of propagation through which Gaussian beam propagates through AuNP@SiO ₂ & AgNPr@SiO ₂ solutions . . .	109
B.1 Refractive index of fused silica measured at 20°C	111
B.2 Dielectric constant & refractive index fit of Au to Otter's data	112

B.3	Dielectric constant of silver thin film measured by spectroscopic ellipsometry at 300 K	113
B.4	Dielectric constant of single/multiple layers of graphene oxide determined by imaging ellipsometry	113
B.5	Dielectric constant of polyacetylene	114

List of Tables

4.1	Irradiation time vs percentage of dimers	96
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Chapter 1

Introduction and Literature Review

Last decade witnessed research producing a multitude of possibilities in the domain of plasmonics based on the physics of surface plasmon resonance and local surface plasmon resonance. This unique phenomenon is made plausible by the interaction of electromagnetic field with free electrons on metal surfaces in nanoscale. The result of this interaction can be tuned to appear as heat and photothermal effect, photoacoustic effect, surface enhanced Raman scattering, enhanced field, metal enhanced fluorescence, dark field light scattering, photodynamic effect, etc. where they find many biomedical applications such as nano-resolution bio-imaging, biosensors, photothermal therapy, therapeutic and theranostic diagnosis in medicine. In order to make them biocompatible and thermodynamically stable, at the same time to enhance performance, several modifications on metal nanoparticles with shapes, coatings and heterostructures have been proposed and studied.

1.1 Plasmonics and Metal Nanoparticles

The mathematical theory and analysis developed from Maxwell's equations for a simple observation of scattering and attenuation of gold colloids by Gustav Mie in 1908, after several decades developed into a more complex domain of plasmonics with the discovery of lasers and evolution of more sophisticated computers and numerical methods [1]. However, the theory was generalized for all metallic particles whose valence band let alone their free electrons to interact with the incoming electromagnetic (EM) field to form quantum of collective excitation of free electrons called plasmons. Experiments and modeling have been carried out on metallic colloidal solutions in vis (visible) and ultra-violet (UV) ranges [2]. They have shown that among the metals of the second and third transition series which commonly form molecular metal clusters compounds, only gold (Au) and silver (Ag) offer the possibility of exhibiting absorption bands due to plasma resonances from free electron, whilst for other d-block metals it is due to predominant interband transitions. Later, studies on single metal nanoparticles (NPs) were initiated where particles were sufficiently far apart in monodisperse solutions to prevent inter particle interaction [3]. This paved the way to design and modify NPs forming combined and hetero-nanoparticles while studying and analyzing them as single nanostructures. Hence, optical excitation using a pulsed laser of suitable wavelength on plasmonic nanomaterials subsequently trigger local surface plasmon resonances (LSPR), where surface plasmon resonance (SPR) waves are confined and propagated within nano-sized geometrical domains. Metallic nanoparticles using gold (Au) and silver (Ag) are the base candidates owing to their availability of free electrons and ease of tunability of their LSPR response over a wide range of wavelengths from visible to near infra-red (NIR) [4, 5]. The unique prop-

erty of gold and silver to show plasma oscillations [2] especially in visible and higher range made them preferable candidates to be exploited in their light matter interaction studies. With the progress of nanotechnology and nano-optics we are attaining control over optic energy in sub-wavelength structures and nanophotonics beyond diffraction limit in such metallic NPs [6].

1.2 Modeling

The Mie's solution gives exact solution for spherical particles. However, Mie theory can be oversimplified for cross sectional calculations for spherical particles by some approximations and considering Rayleigh limit sizes of only up to 200 nm [1]. Also, the assumption of optical constants of metals like dielectric permittivity in nanoscale is same as that of bulk was made [1]. The foremost required property to carry out theoretical analysis and modeling is the dielectric permittivity of the metal. Drude model (Equation Eq. 1.1) is a very good approximation for the complex dielectric permittivity due to free electron contribution below the onset of interband transition in longer wavelengths. Whereas, in some metals, for shorter wavelengths due to extra contribution from inner orbital electrons via interband transitions Lorentz-Drude model and various experimental data have to be depended upon making model complex. Drude model for intraband transition is given as:

$$\epsilon_{Drude}(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \quad (\text{Eq. 1.1})$$

where ω_p is the plasma resonance frequency, ω is the excitation frequency, γ is the effective electron-phonon relaxation frequency. For bulk, it is the inverse of electron-phonon relaxation time τ_{e-ph} [7]. But,

in nanoscale, when mean free path is limited by the size, the relaxation frequency due to scattering on the particle surface becomes a function of size as Av_F/R where A is a proportionality constant that depends on electron surface interaction [3, 8, 9] ($A = 1$ for isotropic scattering [10]), v_F is the Fermi velocity, $R = 4V/S$ is effective dimension of the particle or path length of electrons, V is the particle volume and S is the particle surface area, [8, 9]. Hence the effective relaxation frequency or electron-phonon damping constant becomes size dependent and is given as [9, 11–15]:

$$\Gamma = \frac{1}{\gamma_{e-e-ph}} + Av_F/R \quad (\text{Eq. 1.2})$$

The analytical model used for intraband modeling in our studies is given as:

$$\epsilon_{Inter-Band}(\omega) = K \int_{\omega_g}^{\infty} \frac{\sqrt{y - \omega_g}}{y} (1 - f(y, T)) \left[\frac{\omega^2 - y^2 - \gamma_{e-e}^2 + i2\omega\gamma_{e-e}}{(\omega^2 - y^2 - \gamma_{e-e}^2)^2 + 4\omega^2\gamma_{e-e}^2} \right] \quad (\text{Eq. 1.3})$$

where $f(y, T) = 1/(1 + e^{(E_y - E_F)/(k_B T)})$ is the Fermi distribution of quasi-particle states, $\omega_g = E_g/\hbar$, E_g is the interband gap energy at the tail, $E_y = y\hbar$ is the electron energy of state, E_F is the Fermi energy, k_B is the Boltzmann constant, γ_{e-e} is the damping frequency due to electron-electron scattering of inter-band electrons and K is a constant given by $8\mu^2 e^2 m_e^* \sqrt{2m_e^*} / \pi \hbar^3 m_e^2$ [16], where μ is the dipole moment which is supposed wave vector independent for all transitions, e is the electron charge, m_e is the electron mass and m_e^* is the effective electron mass in the metal.

Early studies pertaining to the importance of interband term for metals were done on bulk and thin films showing the plasma resonances deviates from expected for visible and near UV [17, 18]. The measure-

ments done by Johnson and Christy for the optical constant [18] is one of the most widely used and reliable data set in room temperature.

When it comes to analytical representation, Drude model fairly approximates optical properties of silver in near UV-visible region and several parametrization have appeared in literature [19, 22]. Representing analytical models for optical properties of gold is more challenging because lower threshold for onset of interband transitions. Attempts have been made for gold to fit best known Johnson and Christy's data [19]. In 1998 Rakic and team have combined several oscillators in Lorentzian model to reproduce the absorption peaks due to interband transitions up to 5 eV [20]. Figure 1.1 shows a comparison plot for the Drude, Drude-Lorentz & Critical point analysis for interband transitions models for the room temperature dielectric permittivity of gold.

Some of the more sophisticated models give very precise behavior by including quantum effects and non-locality. Density functional theory (DFT) is a very suitable model to incorporate all the quantum effects [23]. However, the nanoparticles they used was of size less than

Figure 1.1: Comparison of dielectric permittivity models for gold: Drude, Drude-Lorentz & Critical point analysis for interband transitions. Red line denotes Critical point analysis fit to Johnson and Christy' data [19]. b) Green line denotes the Drude model alone and c) blue line denotes the Drude-Lorentz model by Rakic [20, 21].

5 nm. For greater sizes as the number of electrons increases, the DFT calculations will become enormously heavy with huge memory and run-time. Hydrodynamic model is another approach which is well known and has been in use for more than a decade [24]. It was successful in reflecting the non-locality arising from electron response smearing over the Thomas-Fermi screening length. Over the years, the model was modified and alternatives were introduced. One such successful model is Local Analogue Model (LAM) [25] to mimic the non-locality by geometry modification. These models also efficiently incorporated size effects which is due to size dependent damping.

But all the models lacked temperature dependence and becomes even more complex when temperature dependence is involved. It is necessary to have a temperature dependent model because, every EM wave interaction with free electrons is followed by a series of processes involving initial energy absorption by electrons, electron-electron scattering and electron phonon scattering giving energy to lattice and heating it [9,26,27]. This is a classical phenomenon where the structure expands by raising the temperature of lattice. This temperature variation alters the optical properties [28] and thus the interaction of EM wave with metals is to be modeled as a bidirectional coupled dynamic process. Temperature dependence of dielectric permittivity have been tried to model analytically while most of the early studies focus only on imaginary term [29]. A previous report [21] shows an analytical model named Drude-Lorentz-Temperature (DLT) model for the same in the range 292-1188 K for gold nanosphere using the Drude-Lorentz model at room temperature as a reference. Another work [10] on gold nanospheres tried to model temperature dependence using simplified interband term (Equation Eq. 1.3) from Random Phase Approximation (RPA) and hyperbolic band structure [15, 16, 30] and have compared it with Otter's data [31] on bulk gold. Their analytical models

used parameters to fairly fit Otter's data. Also since Johnson and Christy's data were measured by more sophisticated methods (but measured only for room temperature), it was more accurate than that of Otter's data [27]. When the analytical models described by Equations Eq. 1.1-Eq. 1.3 are truly temperature dependent, it is the scattering/damping terms $\gamma_{e-e}(T)$ and $\gamma_{e-ph}(T)$ which mainly contributes to the temperature dependency. Other factors which are functions of these damping terms can also contribute to it, like thermal expansion coefficient, size of the particle and hence electron concentration, environment refractive index, specific heat capacity of the particle etc [32]. Even for silver, not too detailed analysis has been carried including the whole complex term with interband term. It was in 2013 a very detailed analysis of silver dielectric permittivity with measurement and modeling of different parameters was done but was limited only up to 650K. However, earlier temperature dependent models [28] did proceed with some approximations like one electron model without electron-electron or electron-phonon interaction as opposed to later studies [15, 16, 33–35] after 1974 on metallic NPs showing the importance of such intermediate quasiparticle collision and cooling terms in confined metallic nanostructures. This is named as two-temperature model (TTM) but is shown that it is accurate only for femto- and short pico-second laser pulses [36]. Finally, apart from all these analytical methods today we have more sophisticated numerical and computational methods like discrete dipole approximation (DDA) [37, 38], boundary element method (BEM) [38, 39], finite element method (FEM) and finite difference time domain (FDTD) method [38, 40], multiple multipole (MMP) method [41], T matrix method [42], etc. to carry out simulations and visualize the results.

1.3 Plasmonic Nanostructures in Biomedical Engineering

In regard with light absorption and scattering various applications have branched such as in detecting fluorescence of single molecules [44, 45], enhance Raman scattering [46], resonantly transfer energy of excitons [47], create nanosized quantum amplifiers of optical energy [48], sensing techniques [49, 50], light manipulation for solar energy technologies [51], biomedical applications [52] such as high resolution bio-imaging, light activated cancer treatments, and so on [53]. However, most research outputs from plasmonic nanomaterials channels towards biomedical field. The three main bio applications of plasmonics include 1) sensor devices for diagnostics; 2) in vitro imaging and diagnosis; and 3) in vivo imaging, diagnosis and theranostics [54, 55]. Additionally, in biomedical engineering, plasmonic nanomaterials are widely employed as exogenous contrast agents in thermal expansion based techniques such as photoacoustic (PA) imaging [56–62] and photoacoustic guided drug delivery [60–62]. A summary of applications of plasmonic nanoparticles in biomedical engineering is represented in 1.2. Photoacoustic technique is based on generation of acoustic signals on irradiation of pulsed laser energy, which results due to thermal expansion followed by an initial pressure distribution. When the pressure wave propagates omnidirectional as ultrasonic waves through medium of analysis, signals could be detected with the help of suitable transducers. On the other hand, with a sufficiently high conversion of light into thermal energy, it is also possible to use the same contrast agents as theranostic agents to conduct thermal therapy [59, 62]. Even though the time to time discoveries on plasmonics are new and not yet completely understood, we are gaining more control over the explored physics like plasma resonance, absorption, scattering,

Figure 1.2: Plasmonically engineered nanoprobes (PENs) for biomedical applications. (A) Tuning and combining plasmonic building blocks, non-plasmonic building blocks, and modulators and formation of PENs via engineering particle morphology, particle composition, assembled structure, hybrid structure, surface modification, and bioconjugation. (B) Representative biomedical applications of PENs (Reprinted (adapted) with permission from [43]. Copyright (2016) American Chemical Society.)

intensity enhancement, etc. by manipulating morphologies like shape, size, combination of materials on the nanostructure, environment conditions like irradiating laser fluence, pulse duration, surrounding medium

and with proper theoretical as well as numerical modeling and simulation. Over the years, nanoparticle designs have undergone many studies in terms of shape, size, coupled structures, coated structures, etc. to manipulate LSPR and achieve better performance in terms of sensitivity and biocompatibility. Hence, along with their heterogenous hybrid analogues [63–69], plasmonically coupled crystals [70–73] and aggregates [74, 75], their use has been aggrandized in a multitude of applications ranging from biomedical imaging (optical, dark field, photoacoustic, etc.), sensing techniques including wavelength shift LSPR bands and surface enhanced Raman spectroscopy (SERS), photothermal therapy, drug delivery, etc.

1.4 Plasmonic Effects in Nanostructures

Plasmon excitation was first observed by Wood [76] in the beginning of 20th century and the technique was later developed and demonstrated by Kretschmann [77] and Otto [78] on thin metal films. The plasmon waves excited on surface of metal films and called SPR. Instead of using a metal film, if metal nanoparticles/nanostructures whose size is less than the wavelength of EM wave is used so that the surface waves cannot propagate but localized, we get LSPR. LSPR offers much smaller sensing volumes due to the short EM decay length [79, 80] and greater spatial resolution than SPR [50]. Since then research on single metal nanoparticles and LSPR advanced. As an attempt to develop composite nanostructures for various factors as already mentioned such as attaining thermodynamic stability, biocompatibility, prevention of aggregation, etc, core-shell nanostructures began to gain attention. Of such nanostructures silica coating is very common and efficient. Since our study focus on electromagnetic interaction and plasmonics mediated optically

induced effects, damage on these nanostructures was our primary concern. LSPR is triggered via laser irradiation of suitable wavelength and intensity. Hence, the question arise on laser interaction with core metal as well as silica coating. On the other hand, electromagnetic interaction was also used for building nanostructures and forming coupled particles. By forming coupling, the sensitivity of these nanostructures to absorption and extinction can be highly designed and tuned to suit desired application.

1.4.1 Disruptive Effects of Electromagnetic Interaction

1.4.1.1 Laser interaction with metal nanoparticles

Plasmonic interaction of metal nanoparticles with EM waves can induce different pressure generating physical phenomena. The light absorption and plasmon resonance can cause heat generation, thermal expansion, melting, evaporation, Coulomb explosion and plasma formation, etc. These generated pressure propagate and captured as photoacoustic (PA) signal as well depending on the efficiency of light to pressure conversion or coupling [81]. Apart from absorption, scattering, modification of photon density of states (DOS) and wave shortening at the metal-surrounding interface can cause light field enhancement depending on the size and shape of the nanoparticle. Several studies have been reported on the observed effects on bare nanoparticles. They include size reduction and shape changes on gold nanoparticles (AuNPs) [82–84], gold nanorods (AuNRs) [85] and silver nanoparticles (AgNPs) [83]. All the results were explained by thermal melting or thermal evaporation of the nanoparticle. These thermal mechanisms are the only possible explanation for nanosecond pulse and longer pulse irradiations which is explained using one temperature model (OTM). At the same time, sub-picosecond and shorter pulse irradiations will lead to Coulomb explosion as the cause

which is explained by two temperature model (TTM) [86].

Figure 1.3: Schematic illustration of possible plasmonic sources of damage. (T_l is the lattice temperature, T_e is the electron temperature, τ_e is the fragmentation temperature and $T_{b.p.}$ is the boiling point.)

1.4.1.2 Laser interaction with silica

Damage by direct irradiation: Under nominal energy range, silica is transparent to EM waves under region of interest (UV-vis-NIR). This is evident from the absorption spectrum of the silica as well as the optical parameter of silica. The imaginary part of the dielectric constant is zero making the loss term inside the silica zero and hence no absorption. However, beyond certain intensity, the electric field can be brought as high enough to induce dielectric breakdown. There has been several reports on laser induced dielectric breakdown of silica. Using single nanosecond pulses the threshold fluence ranged from high values as $3050 \pm 600 \text{ J/cm}^2$ (1064 nm, 13 ns) [87] to $3858 \pm 85 \text{ J/cm}^2$ (1064 nm, 8 ns) [88]. However, we are not interested in such direct laser induced damage as

the laser intensity which is directly irradiating on silica must be extremely high. Since the nanostructures and plasmonics we study are for biomedical purpose, the energy and intensity of laser cannot be in the above referenced ranges. Even though the above studies have showed threshold reduction using multiple pulse damage, the order of required fluence does not go down by more than one which is far out of the limits for biomedical applications. At the same time, sub-picosecond and femtosecond pulses bring down the threshold to the range of 1 J/cm^2 [89] but at the cost of high intensity due to short pulse width. It is to be noted that the threshold measurements in all the above studies were done on microscopic scale. If the damage initiation was to be considered on nanoscale level, the threshold is defined in even lower range. It was reported that using nanosecond pulse and fluence in the range of 10 J/cm^2 , silica nanoballs were etched out [90].

Changes/damage by plasmonic interaction mediated: Plasmonically active materials like Au and Ag when combined with silica can act as a bridge between them to induce plasmonic effects in plasmonically passive dielectric silica. There have been several reports on laser induced subsurface cracks by nano-inclusions and laser ablation of fused silica films by embedded gold nanoparticles [91–94]. For small size particles thermal mechanisms were explained as the cause for silica damage [92, 94]. Bonneau *et al.* concluded melting and ejection of gold ($\text{AuNP} < 5 \text{ nm}$) embedded in silica as the source of damage [92]. Whereas in bigger particles ($\text{AuNP} \sim 600 \text{ nm}$), electric field amplification and subsequently induced local ionization in silica was involved [91]. Additionally, the effect of presence of crack was studied stating that pre-existing cracks in silica can amplify the damage effect by either trapping the nano-inclusions or by field amplification [93]. A study on intensity modulation by spherical inclusions shows that intensity enhancement by particles greater than 40

nm is significant [95]. However, these studies use direct fluence in the range of 4 J/cm^2 and above or intensity in the corresponding range for nanosecond pulsed irradiation. The size of damages used for modeling analysis were observed on microscopic level. Additionally, the dielectric silica were used as films and thin layers.

As mentioned already, silica in nanoscale form as coatings and shell structures with metallic nanoparticles is widely studied and employed in different shapes and sizes, especially pertaining to biomedical applications. Similar to the subsurface and layers of dielectric embedded by nano-inclusions is prone to damage by their close contact, the silica-metal hetero-nanostructures are prone to damage or in other words, change in morphology. In thesis, we initially investigate few cases of plasmonic effects on such structures where we have conducted theoretical and simulations modelings with experimental proofs to explain how the sources of disturbances vary case by case in nanosecond regime.

1.4.2 Constructive Effects of Electromagnetic Interaction

Engineering nanoparticles to form dimers, trimers, chain structures, etc in a controlled manner is of significant interest because of the high field enhancement that can arise in the nanogaps between nanoparticles. Due to high intensity, it can be used for imaging, surface enhanced Raman spectroscopy (SERS), and due to its sensitivity to changes in medium it has promising application in sensing. To form coupled structures, methods such as self assembly as well as stimulus induced have been reported. For stimulus responsive methods, pH and temperature are the mostly used stimuli for studies. However, an optical stimulus have not been used much in this regard. Only study reporting optical means to cou-

ple nanoparticles was when laser excitation was shown to form an optical micro-cage trapping the AuNPs in the focal spot to form aggregates [96]. But, this formed clusters rather than coupled systems. Additionally, recent studies in making the nanogap to form conductive coupling has proved tunability of the collective plasmon resonance that could arise from the formed whole structure. Thus arising charge transfer is known as the charge transfer plasmon (CTP) which shows good response in the NIR region of the absorption/extinction spectrum. It is a highly tunable mode with tremendous opportunities in sensing and building artificial and active nanodevices [97, 98].

1.5 Motivation and Objective

Plasmonically engineered nanoprobe (PENs) have gained a significant spot of attention in biomedical engineering. The plasmonic activities are triggered by the electromagnetic interaction. However, the mechanisms triggered can activate the core plasmonic nanoparticle as well as transfer energy to the non-plasmonic materials like dielectrics and polymers used to engineer the PEN which are attached to the plasmonically active materials. Despite the advantages of the newly developed and developing PENs, the conditions for their plasmonic activation and usage varies depending on material properties, size and shape which has not been defined properly yet. Therefore, the scope of this thesis was to model plasmonic excitation and analyze the mode of energy transfer. Towards this goal, the main focus of the thesis address the following:

- (i) Possibility of a structural damage - As mentioned above, plasmonically active nanoparticles can transfer its energy to nearby materials by different methods and affect them. In this work, we intend to prove

the possibility of a structural damage due to this coupling using a simple nanoparticle structure (a nanospherical core-shell structure).

- (ii) Controlled damage - After proving the possibility of damage, our next aim was to show the damage can be executed in a controlled manner.
- (iii) Nature of damage and threshold - As mentioned earlier, the energy transfer from plasmonically activated nanoparticles can happen via many mechanisms like lattice vibrations and temperature to form heat flow, wave shortening and energy accumulation to form field enhancement, pressure waves, etc. These can happen simultaneously as well, but the primary cause for the damage can vary depending on the size and shape of the nanoparticle like nanospheres, nanorods, nanoprisms, etc. Once the primary cause and mode of energy transfer is identified, the appropriate design parameters and irradiation conditions can be determined from the model to withstand the disturbance.
- (iv) Building nanostructures - Contrary to above works, electromagnetic interaction can also be used constructively to build and couple nanostructures. In this preliminary study, we tried to bind and couple nanoparticles using optical stimulus. Rather than forming aggregates or big clusters, it is anticipated that irradiation conditions can be optimized to control the size of coupled systems and shape of formed structures.

Chapter 2

Optically Induced Rupture in Gold-Silica Nanostructures

In this chapter we report a study which shows that drastic structural defects such as rupture and breakdown can be mimicked by simple optical pulse irradiation. This happens because of the heat and pressure waves generated in these hybrids. The structural differential expansion of constituent materials induces a thermal stress in the system which causes a structural instability and ultimately ruptures the coating. To demonstrate this phenomenon a comprehensive theoretical and experimental study has been conducted on silica coated gold nanoparticles, with diameter ca.80 nm. The heat and pressure waves generated due to the irradiation initiate a crack in the silica coating and ruptures the structure eventually. The mechanism of this phenomenon has also been elucidated via theoretical and experimental means.

2.1 Introduction

A silica encapsulation on plasmon absorption based contrast agents such as gold nanoparticles (AuNPs) offer options for surface functionalization in addition to good thermodynamic stability and biocompatibility [99, 100]. For example, a coating of mesoporous silica on gold nanorods (GNRs) simultaneously reduces toxicity and provides high drug loading capacity to extend its applications in photothermal therapy and developing new approaches for targeted drug delivery applications [101, 102].

In this context, though the unique capabilities of silica coating on nanomaterials are quite promising, optical irradiations are known to cause perturbations in their bulk and surface morphologies [93]. Several studies have been conducted previously that focused on the laser induced damages on polished bulk silica surface in various nanoparticle inclusions [94]. However, such experiments were performed in bulk silica interfaces where damages within the pre-existing silica cracks and the effects on thermal parameters of the material were focused. Therefore, we anticipate that, by modeling a hybrid system in nano-dimensions that consists of silica coated gold nanoparticle (AuNP@SiO_2) with no inherent cracks and a study of its interaction with pulsed laser irradiation of suitable wavelength would be of great importance. Furthermore, it would hint about the effect of surface plasmon resonance (SPR) of AuNPs [2, 82] and the generated photoacoustic (PA) waves, on the structure and stability of the hybrid silica-AuNP system [103].

Herein, we have studied and analyzed the effect of optically induced heating in nanoscale dimensions and investigated the cause of generated pressure using AuNP@SiO_2 hybrid as a model system. We

have elucidated the effect of various physical parameters that have the potential to induce defects and cracks in the system. We aim to investigate the optical irradiation induced structural/morphological changes in a spherical core shell system via a theoretical approach and later corroborate the findings with experimental studies.

2.2 Mutually Dependent Variables During Plasmonic Interaction

2.2.1 Temperature Dependence of Variables

In order to theoretically compute the effect of optical irradiation, we have considered an AuNP core of ca.10 nm radius (R_s) and a silica shell of thickness (d) ca.30 nm in water medium. We have considered a 526 nm nanosecond pulse of energy E_p and a laser beam diameter B_d as the excitation source. Figure 2.1 illustrates the possible temperature dependency of variables during 526 nm laser excitation.

The first relation of temperature T with size R_s (radius) is derived from temperature rise assisted thermal expansion. This increase in R_s (expansion) negatively affects both heat relaxation τ_r (B from Equation Eq. 2.13, when including the effect of density change with size) and the temperature rise (Equation Eq. 2.15) with a cyclic feedback as shown in Figure 2.1 and tends to attain a stable state.

The second relation comes from thermal expansion as explained in Equation Eq. 2.17 and Equation Eq. 2.18 which has an overall positive effect on thermal stress at the interface. Here β_{Au} is the temperature dependent expansion coefficient of gold and ε is the thermal strain, the relative change in size of the particle.

The third relation derives the temperature dependence of refractive index of silica n_{silica} whereby the refractive index of fused silica was reported to increase with temperature. However, the expected change in refractive index of silica near 1000 K is only up to 1% [104, 105]. Additionally, absorption cross section α_{abs} of AuNP for 526 nm excitation increases when a temperature dependent variation of local refractive index of silica occurs. The rise in α_{abs} with n_{silica} is shown in the Figure 2.2 which was computed using the following equation [27]:

$$\alpha_p = 4\pi(R_s + d)^3 \left[\frac{(\epsilon_s - \epsilon_m)(\epsilon_c + 2\epsilon_s) + (\frac{R_s}{R_s+d})^3(\epsilon_c - \epsilon_s)(\epsilon_m + 2\epsilon_s)}{(\epsilon_s + 2\epsilon_m)(\epsilon_c + 2\epsilon_s) + (\frac{R_s}{R_s+d})^3(\epsilon_c - \epsilon_s)(2\epsilon_s - 2\epsilon_m)} \right]$$

$$\alpha_{abs} \approx \alpha_{ext} = k \text{Im}(\alpha_p)$$

(Eq. 2.1)

where $k = 2\pi n/\lambda$ (wavenumber) of the ambient medium, n is the refractive index of the ambient medium, $\lambda = 526$ nm, α_{ext} is the extinction cross

Figure 2.1: Illustration of the mutually dependent variables (each variable elaborate below). Dotted lines denote equivalent variables. Double sided solid arrow indicates non-monotonic relation.

section and α_p is the polarizability. ϵ_c , ϵ_s , ϵ_m are the dielectric constants of gold, silica and water respectively. The values for ϵ_c and ϵ_s are obtained from as per reported [18, 106] while R_s is radius of AuNP and d is shell thickness of silica. Equation Eq. 2.1 has been computed using a dipolar approximated simplified version of MIE theory for the Rayleigh limit where particles size is very small (radius < 20 nm) compared to the wavelength of light, which further supports the approximation $\alpha_{abs} \approx \alpha_{ext}$ [27, 56].

Figure 2.2: Plot of change in absorption cross section of silica coated gold α_{abs} (at 526 nm) with arbitrary change in refractive index of silica n_{silica} (due to the change in temperature).

Hence, effectively a thermal stress enhancement could be anticipated. Since, no previous experimental studies on refractive index of fused silica for higher temperatures have been conducted, we have omitted this effect in our studies. Additionally, analysing these values, the overall effect of change in refractive index of silica was estimated to be negligible [107].

The fourth relation reflects positive temperature dependence of specific heat capacity of AuNP as shown in Equation Eq. 2.2 [26]:

$$c_0(T) = 109.579 + (0.128)T - (3.4 \times 10^{-4})T^2 + (5.24 \times 10^{-7})T^3 \\ - (3.93 \times 10^{-10})T^4 + (1.17 \times 10^{-13})T^5 \quad (\text{Eq. 2.2})$$

The increment in $c_0(T)$ positively affects heat relaxation τ_r (B from Equation Eq. 2.13) and the temperature rise (Equation Eq. 2.15).

The final relation of dielectric permittivity (ϵ) with temperature is primarily due to the change in size of the particle and factors such as damping as well as scattering rate among electrons and phonons. The electron density varies with respect to change in size of AuNP that alters the interaction of electrons with the incoming electromagnetic wave. Additionally, along with the change in size, an increase in temperature determines extent of collision and scattering within electrons and phonons and thus results in temperature damping. Due to these complex phenomena and temperature dependent changes, the absorption cross section of AuNP and the mathematical factors of the corresponding physics are further explained in the following section.

2.2.2 Model for Temperature Dependent Dielectric Constant

The temperature dependence of dielectric constant has been theoretically modeled and studied in previous studies [10, 15, 16, 30, 107]. The unique temperature term T we mention here represents both electron and lattice temperature due to the equilibrium between the electron and lattice temperature. However, it is to be noted that electron-electron scattering, electron-phonon scattering and Fermi distribution are a function of

electron temperature, while electron-phonon scattering also depends on lattice temperature in general. The dielectric function of gold can be represented as contribution from response of free conduction electrons by the Drude model and inter-band transition. Drude model is a good approximation for long wavelength excitation. But for visible region and lower, the effect of inter-band transition from 5d to 6sp conduction band of Au is dominant. Therefore, the dielectric function $\epsilon(\omega, T)$ at excitation ω and temperature T can be expressed as:

$$\epsilon(\omega, T) = \epsilon^D(\omega, T) + \epsilon^{IB}(\omega, T) \quad (\text{Eq. 2.3})$$

where Drude term from Equation Eq. 1.1 gets modified to,

$$\epsilon^D(\omega, T, R) = 1 - \frac{\omega_p^2}{\omega(\omega + i\Gamma(T, R))} \quad (\text{Eq. 2.4})$$

where $\Gamma(T, R) = \Gamma_{e-e-ph}(T) + Av_F/R$ is the damping frequency, $\omega_p = \sqrt{n_0 e^2 / \epsilon_0 m_e}$ denotes the plasma frequency, $\Gamma_{e-e-ph}(T)$ is the damping frequency due to electron-phonon and electron-electrons scattering of conduction electrons, v_F is the Fermi velocity, A is a proportionality constant ($A = 1$ for isotropic electron scattering), $R = 4V/S$ is the effective dimension of the particle or path length of the electrons, V is the particle volume, S is the particle surface area, n_0 is the electron density, e is the charge of electron, ϵ_0 is the permittivity of free space and m_e^* is the effective electron mass in the metal ($0.99m_e$ for gold and $0.96m_e$ for silver) [18].

The inter-band term from Equation Eq. 1.3 gets modified to,

$$\epsilon^{IB}(\omega, T) = K \int_{\omega_g}^{\infty} \frac{\sqrt{y - \omega_g}}{y} (1 - f(y, T)) \left[\frac{\omega^2 - y^2 - \Gamma_{e-e}^2(T) + i2\omega\Gamma_{e-e}(T)}{(\omega^2 - y^2 - \Gamma_{e-e}^2(T))^2 + 4\omega^2\Gamma_{e-e}^2(T)} \right] \quad (\text{Eq. 2.5})$$

where $f(y, T) = 1/(1 + e^{(E_y - E_F)/(k_B T)})$ is the Fermi distribution of quasi-particle states, $\omega_g = E_g/\hbar$, E_g is the interband gap energy of 1.8 eV at the tail, $E_y = y\hbar$ is the electron energy of state, y is their corresponding frequency, E_F is the Fermi energy, k_B is the Boltzmann constant, $\Gamma_{e-e}(T)$ is the damping frequency due to electron-electron scattering of inter-band electrons and K is a constant. The above model can be tuned to fit Otter's experimental data by tuning the parameters. Fitting of these parameters to fit Otter's data was adopted from previous report [10]:

$$\begin{aligned}\Gamma_{e-e-ph}(T) &= 6.1 \times 10^{11} + 2.97 \times 10^{11}T \\ \Gamma_{e-e}(T) &= 2.75 \times 10^{14} + 5.35 \times 10^{10}T \\ K &= 2.65 \times 10^{24} s^{-3/2} \\ E_F &= 2.55 eV\end{aligned}\tag{Eq. 2.6}$$

However, the above fitting was found to produce good fitting only for higher temperatures (>1200 K). Hence, the same set of parameters were tuned to fit (Appendix section B.2) for lower temperatures as follows:

$$\begin{aligned}\Gamma_{e-e-ph}(T) &= 6.1 \times 10^{11} + 0.3 \times 10^{11}T \\ \Gamma_{e-e}(T) &= 3.64 \times 10^{14} + 4.02 \times 10^{10}T \\ K &= 2.87 \times 10^{24} s^{-3/2} \\ E_F &= 2.62 eV\end{aligned}\tag{Eq. 2.7}$$

Finally, we obtained the temperature profile T_{iter} with maximum temperature T_{max} of 1059 K using an analytical estimation and iterative approach in MATLAB R2014a which is explained in following section 2.3. We have also obtained a temperature profile T_{sim} from simulation using Finite Element Method solver COMSOL multiphysics 4.4 with maximum temperature T_{max} of 1032 K.

2.3 Quasi Static Temperature of Nanoparticle under Pulsed Irradiation

2.3.1 Analytical Estimation of Quasi Static Temperature

Temperature of a nanoparticle under nanosecond pulsed irradiation follows quasi static profile and can be analytically estimated with some approximations. Due to the high conductivity of gold metal nanoparticle (AuNP), temperature at any time instant t can be assumed to be uniform $T(t)$ throughout the sphere. The non-uniformity was found to be negligible as reported previously [26, 108, 109]. The heat equation which describes the heating of a particle with radius R_s was shown to be [108]:

$$\rho_0 c_0 V_0 \frac{dT}{dt} = \frac{1}{4\pi R_s^2} I_g(t) \alpha_{abs} S_0 - J_\epsilon S_0 \quad (\text{Eq. 2.8})$$

with initial condition $T(t = 0) = T_\infty$, where $S_0 = 4\pi R_s^2$ is the surface area of the particle, $V_0 = \frac{4}{3}\pi R_s^3$ is the volume of the particle, $I_g(t)$ is the Gaussian profile intensity profile, T_∞ is the ambient temperature 293.15 K, $c_0(T)$ is the specific heat capacity of bulk gold [26] (agrees with that of the nanoparticle estimated at 532 nm excitation [109]), α_{abs} is the absorption cross section of AuNP and J_ϵ is the energy loss from the particle. J_ϵ is composed of loss due to conduction J_c and radiation cooling J_r .

$$J_\epsilon = J_c + J_r \quad (\text{Eq. 2.9})$$

Since heat loss due radiation was negligible [108],

$$J_\epsilon = J_c = - \left(k(T) \frac{dT}{dr} \right)_{sp} \quad (\text{Eq. 2.10})$$

where $k(T) = k_\infty \left(\frac{T}{T_\infty} \right)^a$ is the temperature dependent coefficient of thermal conductivity of surrounding medium where a denotes material dependent constant. Here, sp means that calculation is done at the surface of particle. For temperature independent case, $a = 0$ and thus $k(T) = k_\infty$. Then the heat flux for quasi-stationary scenario was described by [108]:

$$\begin{aligned} J_\epsilon = J_c &= \frac{k_\infty T_\infty}{(a+1)R_s} \left[\left(\frac{T}{T_\infty} \right)^{a+1} - 1 \right] \\ &= \frac{k_\infty T_\infty}{R_s} \left[\left(\frac{T}{T_\infty} \right) - 1 \right] \end{aligned} \quad (\text{Eq. 2.11})$$

Substituting Equation Eq. 2.11 in Equation Eq. 2.8 and with rearrangement of terms delivers:

$$\frac{dT}{dt} + \frac{4\pi k_\infty R_s}{\rho_0 c_0 V_0} T = \frac{I_g(t) \alpha_{abs}}{\rho_0 c_0 V_0} + \frac{4\pi k_\infty R_s}{\rho_0 c_0 V_0} T_\infty$$

Or

$$\frac{dT}{dt} + C_1 T = C_2 I_g(t) + C_1 T_\infty \quad (\text{Eq. 2.12})$$

where $C_1 = (4\pi k_\infty R_s)/(\rho_0 c_0 V_0)$ and $C_2 = \alpha_{abs}/(\rho_0 c_0 V_0)$ substitutions are made assuming all parameters involved in C_1 and C_2 are constants. Equation Eq. 2.12 is a linear first-order ordinary differential equation with a solution:

$$\mathbf{T}(t) = \mathbf{T}_\infty + \mathbf{A} e^{-Bt} \int_0^t \mathbf{I}_g(\mathbf{x}) e^{Bx} d\mathbf{x} \quad (\text{Eq. 2.13})$$

where $A = (3\alpha_{abs})/(4\pi R_s^3 c_0 \rho_0)$, $B = (3k_\infty)/(c_0 \rho_0 R_s^2)$ which is the inverse

of the characteristic heat relaxation time τ_r , I_g is the Gaussian laser input intensity given as:

$$I_g(t) = \frac{4E_p}{\pi B_d^2 t_p} e^{\frac{-4 \log(2)(t-t_0)^2}{t_p^2}} \quad (\text{Eq. 2.14})$$

where E_p is the pulse energy, t_p is the pulse duration at full width half maximum (FWHM), B_d is the laser beam diameter and t_0 is a time offset used before starting the irradiation in simulation in COMSOL Multiphysics 4.4. Also an estimate for maximum temperature was given in a previous literature [27] as:

$$T_{max-rise} = \frac{\max(I_g) \alpha_{abs}}{4\pi R_s k_\infty} \quad (\text{Eq. 2.15})$$

where $\max(I_g)$ = maximum intensity $I_{(g_{max})}$. Here temperature of gold nanoparticle was estimated assuming with a matrix of silica surrounding. Additionally, the temperature profile $T(t)$ estimated in Equation Eq. 2.13 assumed some parameters to be constant for solving the differential equation. Therefore, the mutual dependency of variables explained in section 2.2 are ignored. To solve this, the analytically estimated $T(t)$ is subjected to a more comprehensive iterative algorithm to incorporate those effects.

2.3.2 Convergence by Iteration on Analytical Model for Quasi Static Temperature

After analytically estimating the temperature profile as explained in above section 2.3.1, the assumed constant parameters are subjected to temperature dependence and set to the new values of analytically estimated temperature. Again the temperature is analytically estimated using these new sets of parameters as constants. This is continued till the

convergence (refer to the below algorithm 1 and flowchart Figure 2.3) is achieved. We have used MATLAB 2014b to implement the above. The Matlab algorithm to converge the temperature (owing to mutual dependency of variables) at each time step proceeds as follows:

Algorithm 1 Iteration to converge Temperature $T(t)$ of the nanoparticle at each time step t

```

1: procedure TEMPERATURE( $T(t)$ )
2:   Set the initial conditions particle dimensions (core radius  $R_s$ , core
   volume  $V_p$ ), core density ( $\rho_0$ ), and particle temperature  $T_\infty$  for the cur-
   rent time instant.
3:   Set  $T_i = T_\infty$  and change in temperature  $dT = T_i - 0$  where  $i = 1$ .
4:   while convergence not achieved, i.e.,  $dT/T_i < 0.1\%$  do
5:     Evaluate absorption cross section  $\alpha_{abs}$  using Equation Eq. 2.1.
6:     Evaluate  $T_{i+1} = T(t_n)$  using Equation Eq. 2.13.
7:     Evaluate  $c_0(T_{i+1})$  using Equation Eq. 2.2.
8:     Evaluate  $\beta_{Au}(T_{i+1})$  using Equation Eq. 2.17.
9:     Estimate change in volume  $dV_p = 3 \times \beta_{Au}(T_{i+1}) \times V_p \times (T_{i+1} - T_i)$ .
10:    Update  $V_p = V_p + dV_p$ .
11:    Update  $R_s$  from new volume  $V_p$ .
12:    Update  $\rho_0$  from new volume  $V_p$ .
13:    Update  $\epsilon(\omega, T + i + 1)$  using Equations Eq. 2.3-Eq. 2.7.
14:    Update  $dT = T_{i+1} - T_i$ .
15:  end while
16:  Assign  $T_{iter}(t_n) = T_{i+1}$ .
17:  Repeat steps from 2 to 16 for each time instant  $t_n$ .
18: end procedure

```

Steps 2 and 3 initialize all the variables which are expected to converge owing to mutual dependency. Steps 4 to 16 define iteration and run through temperature convergence. Step 5 covers the temperature dependency of α_{abs} . Step 6 address the temperature dependency of τ_r and T_{max} . Step 8 covers the temperature dependency of β_{Au} and ϵ . Step 14 covers the temperature dependency of $\epsilon(\omega, T)$. The steps are presented in a flow chart (Figure 2.3).

Thus we obtained T_{iter} . Using this algorithm, a trend in absorp-

Figure 2.3: Iteration to converge the analytically estimated temperature profile $T(t)$

tion cross section (α_{abs}) (at 526 nm) vs temperature was verified (Figure 2.4). The absorption was observed to decrease for higher temperatures. A reduction in absorption would effect the rise of temperature and thus explains the final and non-positive relation between temperature, dielectric permittivity and absorption cross section in Figure 2.1. This dependence of absorption is directly reflected in the evolution of temperature for an input fluence (Figure 2.5). The temperature instead of rising will start to fall in value with input fluence.

Assumptions and approximations for theoretical calculation:

Heat loss due to radiation is neglected and effect of silica thickness was not taken into account.

Figure 2.4: Plot of change in absorption cross section of gold α_{abs} (at 526 nm) with temperature T.

Figure 2.5: Plot of change in temperature profile (T) of gold with input fluence for 526 nm.

2.3.3 Finite Element Method Simulation

To verify the estimated range of temperature under specified conditions, a Finite Element Method numerical calculation was performed. We used COMSOL Multiphysics 4.4 for the calculation. The methodology for COMSOL simulation was taken from literature [110]. First a gold nanosphere with silica coating in water as medium was geometrically modeled and meshed accordingly. For simulation of the physics in COMSOL we made use of 1) electromagnetic wave and 2) heat transfer inbuilt modules.

Electromagnetic wave: The source laser was modeled as a linearly polarized plane wave of required wavelength (526 nm). The module uses the Helmholtz equation to estimate the electric field distribution

inside and outside the structure. The energy absorbed by the particle is calculated as the resistive heating in AuNP. Using the pulse duration, average power absorbed can be estimated for a suitable laser pulse (Gaussian pulse). This laser pulse is used in the next heat transfer module.

Heat transfer: Heat diffusion equation is accounted with heat source as energy absorbed (resistive heating) from the aforementioned module and the temperature profile (T_{sim}) in AuNP is estimated.

Assumptions and approximations for FEM:

Due to the inability to couple frequency domain module electromagnetic wave and time domain module heat transfer, the temperature dependency in optical property (here dielectric permittivity of gold) is omitted.

2.4 Optical Excitation of Gold Nanoparticles

2.4.1 Theoretical Analysis

2.4.1.1 Simulation and Analytical

A Gaussian beam profile with temporal intensity $I_g(t)$ and full width at half maximum (FWHM) t_p of 9 ns duration was employed for this study. Water and silica remain transparent when being irradiated with 526 nm pulsed laser excitation while the absorption cross section (α_{abs}) of the AuNP core at 526 nm was estimated to be 570 nm^2 using MIE theory simulator (nanoComposix). The estimated parameters were in agreement with the results obtained from our simulations (using COMSOL multiphysics 4.4) as shown in the power absorption profile of the AuNP@SiO₂ (Figure 2.6) and dipolar approximated simplified MIE theory calculation for small sized (radius < 20 nm) particles (Equation Eq. 2.1 in section 2.2.1). The power absorbed by the particle comprises mainly of resistive heat-

ing of the particle during the laser irradiation [110] which was found by $P_{abs} = I_g \alpha_{abs}$ [26] and subsequently led to a temperature rise inside the AuNP.

Figure 2.6: Simulated power absorption profile of AuNP@SiO₂. Temporal profile of power absorbed by the AuNP@SiO₂ (black line) and the resultant temperature profile T_{sim} (red line). Inset: The simulated 3-D cross section of the temperature distribution throughout the core-shell structure at time instant 45.5 ns (marked blue) where maximum core temperature rises to 1032 K. Input fluence = 0.2 J/cm², pulse duration = 9 ns.

For AuNP@SiO₂ nanostructure, the pulse duration t_p is longer than the heat relaxation time τ_r (ca.60 ps) as computed from the parameter B in Equation Eq. 2.13. Upon irradiation of pulsed excitation to silica coated AuNP, the temperature distribution gives a quasi-stationary profile [108]. This may vary when we consider contributions from coating properties as well as the property of surrounding medium. Thus, the quasi-static temperature profile for an arbitrary laser pulse intensity $I_g(t)$ can be derived as Equation Eq. 2.13, whose derivation is elaborated in section 2.3.1.

$$T(t) = T_{\infty} + Ae^{-Bt} \int_0^t I_g(x)e^{Bx} dx$$

where $A = (3\alpha_{abs})/(4\pi R_s^3 c_0 \rho_0)$, $B = (3k_{\infty})/(c_0 \rho_0 R_s^2)$ which is the inverse of the characteristic heat relaxation time τ_r , I_g is the Gaussian profile, T_{∞} is the ambient temperature, ρ_0 is the density and c_0 is the specific heat capacity of gold. Specific heat capacity of AuNP at 532 nm was reported to be in good agreement with bulk gold (0.149 J/g K) [109]. Since our case requires a temperature dependent specific heat capacity, we used $c_0(T)$ for bulk gold used in previous reported calculations [26]. The maximum rise in temperature attained by the Au core was computed by the Equation Eq. 2.15 [27, 108]. However, both Equations Eq. 2.13 and Eq. 2.15 neglect the radiation effects and suffer from bidirectional dependency of multiple inherent variables due to temperature dependent parameters (section 2.2).

Therefore, to include bidirectional variable dependency, Equation Eq. 2.13 was subjected to more comprehensive iterative approach to find the temperature profile T_{iter} (section 2.3) implemented in MATLAB R2014a. Additionally, upon considering bidirectional dependency, radiation effects and thickness of shell, T_{sim} (section 2.3) was computed by simulation using Finite Element Method solver (COMSOL multiphysics 4.4). The methodology for COMSOL simulation was adopted as per explained in literature [110]. In silica AuNP hetero-nanostructure, the thermal expansion and increasing electron-phonon scattering is the dominant mechanism that causes shifting and broadening of SPR in AuNP core when compared to the change in dielectric permittivity of the surrounding silica matrix [107]. Therefore, an approach with additional intra-band (Drude model) and inter-band model from previous literature were used to fit Otter's experimental data (section 2.2.2) [10, 15, 16, 30]. Similarly, since

the rise in temperature positively affects refractive index of silica matrix at core-shell interface [104, 105], a simultaneous hyperchromic effect on absorption of AuNP as well as increase in the particle temperature may occur (section 2.2.1).

Figure 2.7 shows the absorbed power intensity profile $P_{abs} = I_g \alpha_{abs}$, iteratively estimated T_{iter} and simulated value of temperature profile as T_{sim} .

Figure 2.7: Intensity profile of power absorbed P_{abs} (black line) by the hybrid (AuNP@SiO₂). Theoretically obtained temperature profile T_{iter} (dotted blue line) and simulated temperature profile T_{sim} (solid blue line). Inset graph: Comparison between the simulated and theoretically obtained temperature profile. Input fluence = 0.2 J/cm², pulse duration = 9 ns.

The maximum temperature estimated using Equation Eq. 2.15 was ~ 1054 K. After subjecting $T(t)$ (Equation Eq. 2.13) to iterative method we got T_{iter} whose maximum was ~ 1059 K. At the same time the simulation results a maximum temperature ~ 1032 K. The simulated temperature

attained a maximum whose value is different than theoretical (T_{iter}) due to the assumptions and approximations mentioned above. The theoretical value had a deviation $\sim 2.6\%$ from the simulated value.

2.4.1.2 Thermal Stress Analysis

The thermal stress developed in the metal-coating interface was estimated using Equation Eq. 2.16,

$$\frac{\sigma}{\varepsilon} = B_M \quad (\text{Eq. 2.16})$$

where $B_M = 180$ GPa is the bulk modulus of gold, σ is the thermal stress, $\varepsilon = \beta_{Au}(T)(T(t) - T_\infty)$ is the thermal strain, $\beta_{Au}(T)$ is the temperature dependent expansion coefficient [26] given by:

$$\begin{aligned} \beta_{Au}(T) = (12.00269 \times 10^{-6}) + (0.00953 \times 10^{-6})T + (8.4 \times 10^{-12})T^2 \\ + (5.43 \times 10^{-15})T^3 \quad (\text{Eq. 2.17}) \end{aligned}$$

Using maximum temperature $T_{max} = \max(T_{sim})$ in thermal expansion coefficient in Equation Eq. 2.17, the maximum expected strain for gold nanosphere:

$$\begin{aligned} \varepsilon_{Au} &= 3\beta_{Au}(T_{sim})(T_{sim} - T_\infty) \\ \varepsilon_{Au_{max}} &= 3\beta_{Au}(T_{max})(T_{max} - T_\infty) \\ &= 3 \times 18.86 \times 10^{-6}(1032 - 293.15) \\ &= 0.0481 \end{aligned} \quad (\text{Eq. 2.18})$$

The expansion of silica was calculated using the silica temperature of immediate surrounding at the interface. Assuming continuity in temperature at interface, the maximum expected strain for hollow sphere:

$$\begin{aligned}
 \varepsilon_{silica} &= 3\beta_{silica}(T_{max})(T_{max} - T_{\infty}) \\
 &= 3 \times 0.55 \times 10^{-6}(1032 - 293.15) \\
 &= 0.0012
 \end{aligned}
 \tag{Eq. 2.19}$$

From Equation Eq. 2.18 and Equation Eq. 2.19, the ratio r of maximum expected expansion:

$$\begin{aligned}
 r &= \frac{\varepsilon_{Au}}{\varepsilon_{silica}} \\
 &= 34.83
 \end{aligned}
 \tag{Eq. 2.20}$$

When we use theoretical temperature T_{iter} instead of simulated T_{sim} in Equations Eq. 2.18-Eq. 2.20, we will get ratio $r=33.31$. Thus expansion of silica is ≈ 35 less than gold and neglected to calculate thermal stress using Equation Eq. 2.16. Then, for simulated T_{sim} the maximum expected thermal stress at maximum temperature was calculated using Equation Eq. 2.16 as:

$$\begin{aligned}
 \sigma &= \varepsilon B_M \\
 \sigma_{max} &= \varepsilon_{Au_{max}} B_M \\
 &= 0.0418 \times 180 \text{ GPa} \\
 &= 7.524 \text{ GPa}
 \end{aligned}
 \tag{Eq. 2.21}$$

Similarly, applying Equation Eq. 2.21 using theoretical temperature profile

T_{iter} , we get $\sigma_{max} = 7.794$ GPa shows a deviation of $\sim 3.6\%$ from the simulated value.

The effect of the thermal stress developed within the nanostructure can be analyzed by performing stress analysis on the core-shell structure. For this, a homogeneous hollow spherical shell of silica was considered where the thermal stress arising from the core was replaced by an internal pressure P_i . The external pressure P_o (atmospheric pressure) was neglected during calculation as the value was negligible compared to P_i . On the silica structure, the radial stress σ_r and circumferential stresses σ_θ , σ_ϕ ($\sigma_\phi = \sigma_\theta$ due to spherical symmetry) were developed as functions of internal pressure P_i . According to Von-Mises criterion for stress in a plastic-elastic hollow sphere, the structure begins to yield when $(\sigma_{vm} = \sigma_\theta - \sigma_r) \geq \sigma_y$. Therefore, as the internal pressure was increased, a plastic deformation followed by threshold pressure (P_e) (Equation Eq. 2.22) evolve from the interior towards exterior, until a pressure of P_p (Equation Eq. 2.23) [111]:

$$P_e = \frac{2}{3} \left(1 - \frac{R_s^3}{(R_s + d)^3} \right) \sigma_y \quad (\text{Eq. 2.22})$$

$$P_p = 2\sigma_y \ln \left(\frac{R_s + d}{R_s} \right) \quad (\text{Eq. 2.23})$$

The silica-AuNP hetero-nanostructure are therefore expected to deform or completely disassemble near threshold pressure P_e owing to the brittle nature of silica nanoshell. Figure 2.6 shows the power absorbed and the corresponding temperature rise in AuNP core for a fluence of 0.2 J/cm^2 . Correspondingly, using aforementioned iterative approach on Equation Eq. 2.13, the maximum temperature attained was estimated to be $\sim 1059 \text{ K}$ and was found to agree with the simulated value of

Figure 2.8: Expected thermal stress profile before failure (solid line) in proportion with temperature of core using stress-strain relation in Eq. 2.16. The failure point $P_e = 5.24$ GPa (marked in red circle).

1032 K. The deviation of $\sim 2.6\%$ between estimated and simulated value arise due to the radiation loss and the effect of silica thickness. Assuming a continuous temperature profile across the structure, the strain relation gives the ratio $\sim 35:1$ between maximum expected expansion of solid core (here Au) to that of hollow expansion of the silica shell. Evidently, this implies that there exists a restricted expansion and thus induces a thermal stress. However, according to previous reports [112], the temperature profile loose continuity at the gold silica interface which simultaneously increase the ratio and induce a higher stress in the system. Bulk silica remains brittle in nature with a characteristic 1D (one dimensional) tensile yield limit (σ_y) of 45-155 MPa. At the same time, ductile nature of silica with an ability to withstand tensile stress up to few GPa (~ 8 GPa) can be observed at nanoscale, if the strain rate is very low [113, 114]. How-

ever, when the strain is increased, the silica at nanoscale (reported using nanorod) broke without elongating exhibiting a clear brittle nature but still with high yield strength of $\sigma_y \approx 8$ GPa, which we used in our calculations. Using simulated value of temperature, the maximum thermal stress evolved due to expansion was estimated from Equation Eq. 2.16 to be 7.52 GPa as shown in Figure 2.8. Correspondingly, the theoretical analysis gave a slightly different value of 7.79 GPa with a 3.6% deviation. This high stress was formed in a very short duration of picoseconds and hence imposed a very high strain rate on the nanosystem resulted in reducing the ductility and tending the system towards a brittle nature [113, 114]. The threshold stress P_e in this case was estimated to be 5.24 GPa ($< P_i$) and was sufficient enough to collapse the structure. Therefore, once crack due to the stress is triggered, resultant failure of structure would occur.

2.4.1.3 Possible Sources of Disturbance

In this context, it must be noted that, PA signal generation followed by pulsed laser irradiation on nanoparticles possibly generates various physical phenomena due to the pressure disturbances as explained in section 1.4. The pressure wave generation from the target due to PA is governed by the fundamental relation $P_0 = \eta \Gamma A_e$, where P_0 = initial pressure, η is the heat conversion efficiency due to the intermediate mechanisms which includes thermal expansion, gas evolution, ablation, breakdown and plasma formation, [81] Γ = Grueneisen parameter and A_e = heat absorbed [60, 81, 115–117]. However, this relation holds true only when the stress and thermal confinement conditions are satisfied by the target object (silica-AuNP hybrid) [115, 117, 118]. The confinement conditions require the laser pulse duration t_p to be less than the acoustic confinement time which is less than the thermal confinement time. Additionally, this can be mathematically stated as $t_p < R_s/v_s < R_s^2/4\alpha_{th}$, where R_s is the

dimension of optically absorbing target, v_s is the speed of sound through the same target object and α_{th} is the thermal diffusivity. These expressions intuitively explain the condition that the irradiating laser pulse should be with very small duration than the time taken by either acoustic wave or the heat to traverse away from the target of interest. Since nano-sized targets fail to satisfy the confinement criteria [118, 119] within a nanosecond pulsed laser excitation, these targets act mainly as a local heating source. This implies that the rate of heat transfers to the surrounding medium and the resultant vapour bubble formation becomes the primary source for PA signal generation and hence, for a coated nanostructure it depends mainly on the shell thickness [118–121]. However, in such nanosystems the PA signal generated can be evaluated to be of the order of few pascals to kilopascals whose magnitude negligibly affect the structural stability of the system. In the current investigation, the possibility of supplementary phenomena such as surface evaporation and light intensity modulation effect is eliminated. Light intensity modulation effect occurs strongly upon interference of the incident light with scattered or reflected light from the particle. An eventual strong enhancement of the electromagnetic field in interference points resulting in damage of silica lattice pattern. However, considering the case of nano sized AuNP (radius < 40nm), the effect of this field intensity modulation is insignificant [95]. Figure 2.9 shows the maximum Light Intensity Field Enhancement (LIFE) profile in the dielectric with the wavelength. Figure 2.10 shows the LIFE ($|E/E_0|^2$) and corresponding electric field magnitude (E) at 526 nm, where E_0 is the incident ambient electric field. It can be seen that at 526 nm the enhancement is very low (~ 45) making an electric field of ~ 63 MV/m which is not sufficient to induce a breakdown in silica dielectric (Refer chapter 2 for more on LIFE and LIFE induced damage on silica). Next, surface evaporation is another possible phenomenon that reduces the size of a bare nanopar-

ticle by evaporation due to heat deposition on the lattice but this occurs only near boiling point of the nanoparticle. Additionally, the evaporation is inhibited by the solid silica matrix around core Au. Therefore, under normal conditions, a primary source of pressure generation can always be assigned to the thermal expansion of nanostructure. Coulomb explosion of AuNP upon interaction with pulsed laser excitation is an extreme condition which might occur with a femtosecond regime [86]. Coulomb explosion happens when ejection of a batch of electrons due to the absorbed heat and charge repulsion to generate multiple ionized nanoparticles to undergo spontaneous fission [86]. This is mainly due to the high power from short duration pulse which rapidly raises the temperature of electron gas leading to ultra-slow heat damping and thus attain an equilibrium with lattice by electron-phonon scattering. Additional possibility of laser force induced elongation and change in shape of AuNP is a process to be considered only near the melting point of gold in the hybrid nanostructure [85, 122]. Thus, for a nanosecond pulse that generates AuNP core temperature less than the melting point of gold, the sole reason for interface stress remains thermal expansion.

The optical excitation of silica-AuNPs at a given pulse initially transfer energy to surface electrons (e-) of the Au core followed by attenuation within few hundreds of femtoseconds by e - e collision. Thus formed hot electron gas release its energy into the lattice through electron-phonon scattering [9,26,27]. The effect of this energy transfer and release was reflected as thermal expansion which occur within few picoseconds (ca. 10ps) range [9, 26, 27]. This rapid expansion was also supported by the time required to traverse the absorber, $\tau_c = 2R_s/v_s$ (ca.6ps), (v_s is the speed of sound in the absorber) [123] which concludes the assumption that the thermal expansion eventuates prior to any other mechanisms including the heat release as well as generation of PA pressure

Figure 2.9: Maximum Light Intensity Field Enhancement inside silica dielectric.

Figure 2.10: Intensity enhancement map of AuNP@SiO₂ at 526 nm.

as mentioned earlier. It was also noted that the magnitude of heat loss to intake by the Au core, within a laser pulse, varies in the order of 10^5 [82] and the volumetric thermal expansion coefficient (β_{Au}) of gold was greater than that of silica (β_{silica}) by a factor of ~ 26 . Therefore, the mechanical

strength of the structure was expected to be affected by multiple factors such as the rapid thermal expansion, slow heat release from the core to shell and the low thermal expansion coefficient of silica than the core. Additionally, in a silica coated AuNP structure, the thermal expansion of the gold sphere was also restricted by the silica shell structure. As a result, a thermal stress was developed in the metal-coating interface.

2.4.2 Experimental Analysis

2.4.2.1 Preparation of AuNP@SiO₂

Gold nanoparticles (radius ca.10 nm) and tetraethyl orthosilicate (TEOS) were purchased from Sigma-Aldrich and used without further purification. The AuNP@SiO₂ nanoparticles were prepared by a process developed, based on the Stöber method involving tetraethyl orthosilicate (TEOS) [124]. In a typical synthesis, AuNP solution (3 mL) was concentrated by centrifugation at 6000 rpm for 15 min. The concentrated AuNPs were then dispersed in ultrapure water (0.5 mL) followed by addition of isopropyl alcohol (2.5 mL) containing 4-mercaptopbenzoic acid (5 mm, 5 mL) under vigorous vortexing. After incubating under room temperature without stirring for 30 min, tetraethyl orthosilicate (TEOS, 1.2 mL) and ammonia solution (90 mL) were added for condensation. After 15 min, APTES (0.5 mL) was added into the solution and then the mixture solution was incubated at room temperature overnight in order to ensure complete encapsulation. Further purification was carried out before using AuNP@SiO₂ for the next step. The amount of APTES was varied to obtain different shell thicknesses of silica (AuNP@SiO₂-30 nm and AuNP@SiO₂-15 nm). The as-synthesized hybrids were taken in aqueous solution which had a measured optical density (OD) of 10 cm⁻¹ and particle density of 6×10^{12} particles/mL. The metal volume fraction (p)

was tuned to $\sim 0.25\%$ ($\ll \sim 13\%$) which minimized the interaction between metal spheres and thus provided a solution which was similar to an isolated single structure system, as assumed in the computational analysis [125]. The laser irradiation was setup as shown in Appendix section A.1. The laser fluence upon irradiation on the sample was estimated by considering factors like propagation of Gaussian beam, reflection at interfaces, depth-resolved optical fluence distribution within sample columns [116], etc. Using this an average fluence of $F_{av} = 0.2 \text{ J/cm}^2$ inside the sample was obtained. Hence the solution was irradiated with single laser pulse with fluence of 0.2 J/cm^2 and a pulse duration of 9 ns at a wavelength of 526 nm. To monitor the changes in the morphology several electron microscopic images were captured at two stages, before and after the irradiation.

2.4.2.2 Imaging and Characterization

For a given radius of R_s (ca.10 nm), after establishing the theory that predicts the failure of AuNP@SiO₂, we verified this phenomenon using an experimental setup. The transmission electron microscope (TEM) images of the silica coated AuNPs (Figure 2.11a) showed a clear core-shell morphology. The radius of gold nanoparticles and silica coated AuNPs was ca.10 nm and ca.40 nm respectively. After optical irradiation, it was very clear from the TEM image that the silica coating around the gold nanoparticle was ruptured (Figure 2.11b).

To further visualize the rupture of silica coating, SEM images were also obtained to characterize the 3D morphology of particles before and after irradiation (Figure 2.12). The SEM images clearly illustrate the rupture of the silica coating and further show the spherical nature of AuNP@SiO₂ being destroyed. In this experimental setup the pulse was

Figure 2.11: Transmission electron microscope (TEM) images of AuNP@SiO₂ core-shell structure in solution a) before and b) after being exposed to one laser pulse. Fluence for the irradiation was 0.2 J/cm² AuNP@SiO₂ with pulse duration of 9 ns and wavelength of 526 nm.

Figure 2.12: Scanning electron microscope (SEM) images of AuNP@SiO₂ core-shell structure in solution a) before and b) after being exposed to laser pulse. Fluence for the irradiation was 0.2 J/cm² with pulse duration of 9 ns and wavelength of 526 nm.

sufficient to rupture the coating as the fluence (0.2 J/cm²) was sufficiently higher than the threshold (0.16 J/cm²). The experiments were repeated for a different set of samples with lower silica thickness (ca. 15 nm) and as expected for same fluence the TEM images (Figure 2.13) reveals increased damage intensity than that of 30 nm thickness silica shell. Overall, the theory of silica bursting by optical irradiation was strongly corroborated.

Figure 2.13: TEM images of a) AuNP@SiO₂ with overall silica thickness of ca.15 nm, b) a single particle before irradiation. (c, d) Morphology changes observed after irradiation. Fluence for the irradiation was 0.2 J/cm² with pulse duration of 9 ns and wavelength of 526 nm.

rated with experimental results.

The transmission electron microscopy (TEM) analyses were performed on a FEG-TEM (JEM-2100F, JEOL, Japan) operated at 200 kV. Field emission scanning electron microscope images were taken using JEM-2100F, JEOL, Japan operated at 5.0 kV.

In addition, a threshold for fluence and maximum temperature

was also predicted by estimating a stress vs fluence and maximum temperature vs fluence profile as shown in Figure 2.14. It is simulated that a fluence of $\sim 0.16 \text{ J/cm}^2$ (Figure 2.14a) is necessary to attain threshold thermal stress $P_e = 5.24 \text{ GPa}$. At the same time from theoretical estimated temperature, this threshold was found to be $\sim 0.15 \text{ J/cm}^2$ with a percentage error of $\sim 3.7\%$. Even though the maximum temperature shows a linear relationship with fluence, the stress profile is slightly deviated due to the non-linear temperature dependent thermal expansion coefficient $\beta_{Au}(T)$ and dielectric permittivity $\epsilon(T)$. The required temperature can also be traced from the graph and found to be $\sim 850 \text{ K}$ for both theoretical and simulation. Three different fluence were used verify the results; two values above the estimated threshold where rupture was observed and a low fluence below the threshold where the structure remained intact (Figure 2.14).

Figure 2.14: a) Fluence vs thermal stress developed inside the silica-AuNP nanostructure. b) fluence vs maximum temperature attained by AuNP core. The corresponding threshold points required for the rupture of silica coating are marked by squares. Blue stars indicate results obtained and verified experimentally.

2.5 Summary and Conclusion

Based on the experimental observations and theoretical computations, the overall scheme of this phenomenon has been illustrated in the Figure 2.15. The schematic presentation clearly elucidates the internal changes occurring in the hybrid structure due to the optical irradiation. The differential thermal expansion (Figure 2.15c) initiates a crack on the silica-gold interface which gradually leads to a structural collapse of the silica coating (Figure 2.15d). The mechanism has been shown in 3 proposed stages. The entire process is a continuous regime which has been divided into stages for clear understanding. Stage 1, irradiation of laser on the particle, stage 2, initiation of a crack due to thermal stress and finally stage 3, structural collapse of silica coating. The optical pulse irradiation in the experimental setup and in the theoretical computation was tuned to have a sufficiently high fluence to cause the bursting.

Interestingly, while considering a core-shell nanostructure with perfectly plastic features, Equations Eq. 2.22 and Eq. 2.23 shows that the stability for a given core size is minimal when the shell thickness (d) remains minimum and subsequent stability increases almost linearly with respect to d . At the same time, for a brittle system, the structure stability depends only on initial threshold P_e (Equation Eq. 2.22). From the expression for P_e it can be concluded that the stability deteriorates directly in proportion with the shell thickness. To corroborate this theory pertaining to the effect of irradiation on hybrids with different shell thickness, another set of experiments with a smaller shell thickness (ca. 15 nm) were conducted (Figure 2.13) under similar conditions. The effect of irradiation on the hybrid was greater than the previous case due to the reduced stability. This can be evidently observed in the TEM images and hence, supports the theory of optically induced structural collapse of hybrids as proposed

Figure 2.15: Schematic illustration of the optically induced structural instability in AuNP@SiO₂ nanoparticles. a) Representation of AuNP@SiO₂ (silica coated AuNPs), b) Stage 1: optical irradiation (526 nm, 9 ns laser) on AuNP@SiO₂, c) Stage 2: differential thermal expansion initiating a crack at the gold-silica interface and d) Stage 3: structural deformation (bursting) of the silica coating eventuating within few hundreds of picoseconds to few nanoseconds.

on the basis theoretical studies.

However, there are other possible ways to cause this effect where, the primary requirement is to induce a high internal pressure that is capable of initiating a crack at the interface. The variation of parameters like pulse duration and pulse repetition rate are some of the future investigative goals. According to the theory, reducing the pulse width duration may raise the temperature of the system by increasing the power delivery. A multiple pulse irradiation may cause repeated thermo-elastic expansion of the AuNP which may lead to a fatigue and eventually leading to de-

formation and rupture of the coating. The pulse repetition rate may play a role in this phenomenon. The frequency of laser pulses would significantly aid in providing a higher repetition rate which in turn would offer enough relaxation gap for the AuNP to release heat and return to its normal state. Such a relaxation resulting from a similar pulse irradiation that occurs within a time delay of approximately 1 ns between pulses would induce disturbance in surface coated silica shell.

In conclusion, we have shown that a pulsed laser excitation of silica coated AuNPs, upon satisfying specific conditions would lead to structural instability of the silica shell coating. Further, after considering effect of several variables, this study concludes that the primary source of disturbance in gold-silica core-shell nanostructure arise due to the thermal expansion induced thermal stress development. Depending on the mechanical strength (yield stress and fracture toughness) of silica shell at nanoscale, this thermal expansion initiates cracks and cause damage to the nanostructure. In addition, the stability of hybrid also depends on the shell thickness of the hybrid and decreases with decrease in shell thickness which was verified by theoretical and experimental studies. Future studies may be directed to carry out detail investigation on the effect of parameters like pulse width and pulse repetition rate of laser excitation, to control the extend of structural rupture which is promising in biomedical and clinical applications. Another possible extension of this study is to fabricate yolk-shell like structure or materials and test their enhanced catalytic activity after irradiation as it would expose most of the core material to surface. Overall, the experimental and theoretical computations in this report provide a profound insight on the mechanism of the optically induced structural instability and would also help to conduct investigative studies for further functional applications.

Declaration:

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Chapter 3

Light Intensity Field Enhancement (LIFE) Induced Localized Edge Abrasion of Silica-Coated Silver Nanoprisms

Silver nanoprisms (AgNPrs) exhibit localized surface plasmon resonance (LSPR) in the near infrared (NIR) region of electromagnetic spectra. LSPR driven electric field enhancement around AgNPr edges have been subjected to various studies. A coating of dielectric materials such as silica on the surface of AgNPrs is employed to extend the application of these nanoparticles in biocompatible conditions and to increase the thermal stability. Upon interaction with optical excitations (pulsed laser excitation), AgNPrs undergo light intensity field enhancement (LIFE) at the corners. In the case of a hybrid hetero-nanostructure of AgNPr with silica coating (AgNPr@SiO₂), LIFE leads to a nano-structural deformation. In this

study, we demonstrate that depending on the intensity of light excitation, medium properties and geometrical sharpness of corners of the prisms, LIFE could induce localized damage or abrasion at the edges of immediate dielectric contact, here silica coating. A theoretical study was conducted to establish the influence of finite radius of curvature (ROC) of corners upon plasmonic interactions to generate a LIFE during appropriate optical excitations. Experiments were performed in AgNPr@SiO₂ using nanosecond pulsed laser excitation at 900 nm and electron microscopic analysis of nanostructures revealed a localized 'edge abrasion of silica at the prism corners. Further to study the effect of direct plasmonic excitation during LIFE, pulsed laser excitation on ultra-thin graphene oxide (GO) wrapped AgNPr@SiO₂ (GO-AgNPr@SiO₂) was conducted. Due to GO wrapping and subsequent change in light absorption, the extent of LIFE at corners diminishes which leads to structural stability and preserving hetero-nanostructure morphology. This study paves the way to a unique approach for the development of new hetero-structured plasmonic hybrid materials as active agents for bio-related applications based on optical techniques.

3.1 Introduction

Among single nanoparticle structures, Ag nanoprisms (AgNPrs) have been studied extensively in past years owing to its promising potential in chemical, biomedical and clinical applications. Van Duyne and Schatz [126–129] have conducted several pioneering studies with AgNPrs for sensitive nanoscale affinity LSPR biosensors [130]. They were related to streptavidin sensing [128], anti-biotin sensing [131], diagnoses of Alzheimer's disease [132], etc. Moreover, the large extinction spectrum and efficient scattering of triangular AgNPrs also make them better con-

trast agents in general and has gained widespread attention [130, 133–136]. AgNPs can be made to have larger sensing volumes by far reaching electromagnetic (EM) fields if the nanoprisms are sufficiently thin [79, 80]. Further, the triangular geometry of the AgNPs makes it slow to penetrate into tissues, than rod or sphere and the shape dependent bactericidal activity, reduces system toxicity [137]. As explained in chapter 1 over the years, nanoparticle designs have undergone many studies in terms of shape, size, coupled structures, coated structures, etc. to manipulate LSPR and achieve better performance in terms of sensitivity and biocompatibility. There are numerous hybrids and coatings for nanoprisms reported previously. These include highly stable polymer coating as contrast agents for bio-imaging [64], silica coated gold nanoplates as stable photoacoustic contrast agents [65], Ag-Au core-shell hybrid for hydrogen sulfide detection [67], gold quantum cluster capped with lipoic acid for fluorescence imaging based tumor detection [66], heterometallic Au-Ag hybrids for near-field fluorescence microscopy [68], Ag-Ag₂S hybrid nanoprisms [69], etc. A silica coating or silica shell offers post-surface functionalization possibilities and thus a convenient approach for enhancing thermodynamic stability and biocompatibility [99, 100, 138]. Additionally, core-shell structures have advantages of preventing agglomeration and oxidation of metal core.

As proved in our previous study [32] and explained in chapter 2, in spite of several benefits of dielectric coating like silica shell on plasmonic nanomaterials, optical excitation and subsequent plasmonic interaction invoke numerous possibilities to disturb the core-shell nanostructure which cause perturbations in their bulk and surface morphologies. Thus as mentioned in previous chapters upon light excitation, plasmonic hetero-nanostructures may suffer geometrical instabilities owing to possible intermediate phenomena such as electric field enhancement, thermal

Figure 3.1: Schematic representation illustrating the experimental process and LIFE induced localized edge abrasion of AgNPr@SiO₂ nanoparticles and resultant structural changes.

expansion, heat generation, gas evolution, boiling, ablation, plasma formation, Coulomb explosion, etc. [81]. In this study, we investigate the effect of light intensity of LSPR on a plasmonic hetero-nanostructure to understand the extent of structural instability arise due to localization of surface plasmons at the edges. To prove the concept, a nanosystem comprising of a plasmonic core with uniform silica coating, multiple edges and plasmon absorption in NIR region is preferred. AgNPrs with uniform silica coating (AgNPr@SiO₂) and plasmon absorption maximum between 800-950 nm satisfy requisites above. First, we analyzed the effect of field intensity enhancement in a theoretical model of silver-silica core-shell structure using finite element method (FEM) simulation. We have proved that light intensity field enhancement (LIFE) may lead to structural instability in core-shell nanoprisms. The results were further corroborated using ultra-dilute solutions of AgNPr@SiO₂ by excitation using 900 nm nanosecond pulsed laser source confirming localized edge abrasion of silica coating upon post irradiation. Figure 3.1 depicts LIFE induced localized edge abrasion in AgNPr@SiO₂ core-shell nanostructures.

3.2 Radius of Curvature (ROC) Analysis - Corner and Edge Smoothing

3.2.1 Geometry - ROC Analysis

Analytical models and solutions of scattering and absorption of electromagnetic (EM) waves can be estimated only for simple and symmetric particles like spheres [139]. For nanoparticles like rods and prisms, numerical techniques should be used. In such studies with nanoparticle models using ideal sharp edges in numerical calculations were proven to produce erroneous results against nanoparticle models with corner and/or edge smoothing [139–141]. Even though only the finite radius of curvature (ROC) at the three corners was considered in few of these studies [140, 141], the melting ice model [139] which considered smoothing of both the corners as well as edges was close to the real case. So, we initially performed a simulation analysis of corner and edge smoothing individually on the AgNPr@SiO₂ to relate the significance of edge smoothing in numerical calculations. This in turn helped to understand what roundness values are to be given to get realistic values, thereby to get simulation values close to that of real nanoprisms. The FEM simulations were conducted using COMSOL Multiphysics 4.4. Details of the analysis can be found in the following sections (3.2.2 - 3.2.4).

A 10 nm thick silica coated silver nanoplate (AgNPr@SiO₂) of 110 nm side (10 nm thickness) and using different ROC combinations of corners and edges were considered for our study. Figure 3.2 shows different geometries of AgNPr used as core structures in our hetero - nanostructures. We have considered a nanosecond pulse of duration t_p (7 ns) and fluence 7 mJ/cm² as the excitation source. The absorption profile

Figure 3.2: Geometry of AgNPr with corner ROC and edge ROC formatted as $(ROC_{corner}, ROC_{edge})$ nm: (a) (3,1.5) nm, (b) (3,3) nm, (c) (3,5) nm, (d) (10,1.5) nm, (e) (10,3) nm and (f) (10,5) nm.

and intensity enhancement of the nanostructure is then numerically calculated using FEM and estimated parameter is power absorbed (P_{abs}). The power absorbed by the particle comprises mainly resistive heating of the particle during the laser irradiation [110], which is directly proportional to the absorption cross section (α_{abs}) by $P_{abs} = I_g \alpha_{abs}$ [26], where I_g is the light intensity. Similar to the observations from previous studies [139–141] our calculations show a reduction in absorption with smoothing or increasing ROC. Figure 3.3 shows the calculated absorption profile of bare AgNPr and AgNPr@SiO₂ respectively. In addition to the proportional reduction in absorption, a blue shift is clearly visible from the full absorption spectra profile and can be attributed to the reduction in effective side length of the nanoprism as the ROC is increased for our specific triangular geometry. We also studied the variation of light intensity field enhancement (LIFE) in these nanostructures (Figure 3.4). It is defined as the ratio of electric field intensity ($|E|^2$) inside the nanostructure when laser irradiated to that of ambient medium electric field intensity ($|E_0|^2$) used to excite the nanoparticle. The maximum LIFE can be observed near the corners which is corresponding to the hotspot formed.

Figure 3.3: Absorption profile of (a) AgNPr and (b) AgNPr@SiO₂ calculated using FEM.

3.2.2 Absorption Spectrum - ROC Analysis

Absorption profile of the bare silver nanoprism (AgNPr) and silica coated silver nanoprism (AgNPr@SiO₂) were calculated for different corner ROC and edge ROC using finite element method (FEM). Figure 3.3 shows the comparison of power absorbed by these nanostructures. A blue shift with increasing ROC_{corner} and ROC_{edge} is obvious. But the effect of increasing ROC_{corner} is dominant than that of increasing ROC_{edge} .

3.2.3 LIFE Profile - ROC Analysis

LIFE of the bare silver nanoprism (AgNPr) and silica coated silver nanoprism (AgNPr@SiO₂) were calculated for different corner ROC and edge ROC using finite element method (FEM). Figure 3.4 shows the comparison of maximum LIFE, which is near the corners of the nanostructures. Similar to that of absorption, a blue shift with increasing ROC_{corner} and ROC_{edge} can be seen while the effect of increasing ROC_{corner} being dominant than that of increasing ROC_{edge} .

Figure 3.4: Maximum LIFE of (a) AgNPr and (b) AgNPr@SiO₂ calculated using FEM.

3.2.4 ROC Analysis - Summary

Figure 3.5: Comparison of (a) absorption peak and (b) intensity enhancement peak of AgNPr and AgNPr@SiO₂ nanostructures with varying ROC_{corner} and ROC_{edge} .

Figure 3.5(a) and (b) shows the variation of absorption and LIFE peaks with smoothing. It can be seen that, both corner and edge smoothing simultaneously reduce the absorption and LIFE, which lead to decreasing the hot-spot intensity. At the maximum finite radius of curvature at edges (ROC_{edge}), which is half the maximum of the thickness of the core silver, the hetero-nanostructure is assumed to be similar in geometry to the real nanoparticle studied later. It was estimated previ-

ously that upon exposure of silica nanoparticles (5-30 nm radii) to 12 ns pulsed laser excitation at 1064 nm, damage thresholds range from 11.2 to 16.8 J/cm² [90]. A threshold electric field generated for the above case was estimated (using Equation Eq. 3.1 obtained from Poynting vector relation $I_{av} = (E \times H^*)/2$) as ~ 70 -85 MV/m, which would lead to damage. The Poynting relation is translated as follows:

$$I = \frac{E^2 n c \epsilon_0}{2} \quad (\text{Eq. 3.1})$$

where, n is the refractive index of silica at irradiating wavelength, c is the speed of light, ϵ_0 is the permittivity of free space and I is the intensity of laser (fluence per unit pulse width), Using intensity I from the irradiating conditions mentioned above and n as the refractive index of water, we get an input ambient electric field (E_0) of 2.4 MV/m.

3.3 LIFE Induced Edge Abrasion

3.3.1 Theoretical Analysis

3.3.1.1 Silica Coated Silver Nanoprisms - FEM Simulation

To theoretically compute the electric field enhancement, we have considered the core-shell nanosystem AgNPr@SiO₂ with following specifications. (a) A silver core with length of 110 nm and thickness of 10 nm, (b) silica coating of 10 nm thickness and radius of curvature at a dimension of 10 and 5 nm for corners and edges respectively and (c) a 900 nm linearly polarized light with a fluence of 7 mJ/cm² and 7 ns duration pulse width. For simulation, the optical parameters of Ag and SiO₂ were taken from previously reported ellipsometric and experimental data [29, 106]. Figure 3.6 shows the electric field intensity enhancement of AgNPr@SiO₂

Figure 3.6: Estimated LIFE in AgNPr@SiO₂ nanoparticles (irradiation at 900 nm) using FEM simulation. A linearly polarized light ($\vec{E}$ in the y-direction) propagating in the x-direction is selected as the excitation source. a) & c) shows LIFE in AgNPr@SiO₂ at the half and quarter cross-section respectively. b) & d) shows phantom images after removing Ag core from original models a & c.

models satisfying specifications above a-c. Figure 3.6a and c display field intensity localization at edges of plasmonic Ag core. A cross section map projecting towards the point of view (Figure 3.6c) indicates LIFE localization at edges. A phantom representation was then displayed after removing Ag core to clearly visualize LIFE localization in the dielectric contact (here silica). The resultant electric field due to plasmonic localization at the edge was calculated as ~ 155 MV/m which is ca. 65 times higher than the input ambient electric field 2.4 MV/m (section 3.2.4). Hence, it is reasonable to anticipate that LIFE leads to the high electric field at the edges which would eventually result in destabilizing silica coating at the edges. The above observation could be explained by analyzing possible perturbations in the metal and silica shell interfaces on account of LIFE. One way to study this aspect could be by reducing efficient plasmonic absorption in Ag core of AgNPr@SiO₂ nanoparticles. For this, we have

simulated graphene oxide (GO) coating on AgNPr@SiO₂, and calculated the changes in plasmon absorption and corresponding LIFE variations.

3.3.1.2 Graphene Oxide Wrapping on Silica Coated Silver Nanoprisms - FEM Simulation

Recently, graphene and GO based hybrids via wrapping on nanomaterials have attracted broad interest as a potential strategy to enhance biocompatibility and thus apply for applications including bio-imaging and drug delivery [103, 142–149]. Similar to plasmonic metals like Au and Ag, GO has a complex dielectric permittivity [150] which produce a finite absorption spectrum in the UV-Vis and infra-red region. To estimate the effect of GO wrapping on plasmonic absorption, we considered a 1 nm thick GO in the surface of AgNPr@SiO₂ core-shell structure. Figure 3.9a shows the simulated absorption spectra of individual Ag, AgNPr@SiO₂, as well as GO, wrapped AgNPr@SiO₂ hybrids. In contrary to previous reports on spherical nanohybrids [103], triangular shaped AgNPr@SiO₂ exhibits a red shift of absorption with a quenching upon GO wrapping. Similarly, a GO wrapping on AgNPr@SiO₂ induces a decrease in the LIFE. A contour intensity profile of LIFE intensity with respect to wavelength (Figure 3.9b) illustrates the corresponding decrease with respect to wavelength. Therefore, in a nanoprism-silica hybrid, wrapping of an extra layer of GO comprises of significant light scattering when compared to perfectly symmetrical systems.

For a sphere, the effective bending and change in propagation direction of the EM wave caused by the ambient environment (GO coating) would not change the polarizability of the nanoparticle. The symmetry of the sphere in all directions will produce the same dipole moment for EM waves incident from any direction. The propagation and direction of

incidence should not be misinterpreted as classical ray optics but rather a change in direction of electric field oscillation and an effective change in propagation direction for only a small space where nanoparticle exists. For a nanoprism, due to its non-symmetrical/non-spherical geometry, the bending of field (bending expected to be high due to the high value for real part of refractive index of GO coating) as mentioned before will cause a change in polarizability due to its change in shape and effective area the field propagates through. An illustration of above explanation can be found in Figure 3.7. Here, line n corresponds to the direction of electric field oscillation incident on nanoparticle normally and thus without any bending. Meanwhile, the line o corresponds to the direction of electric field oscillation incident at an oblique angle which has changed its direction of oscillation. Moreover, the presence of GO (complex dielectric permittivity) may induce scattering. For a large size particle as a nanoprism, the role of extra layer of GO as a scatterer might be significant compared to that of small spherical nanoparticles. Figure 3.8 shows the FEM simulation of LIFE reduction near silver-silica corners upon GO wrapping.

Three observations were derived from the theoretical simulations

Figure 3.7: Illustration of the interaction of EM field with GO wrapped (a) nanosphere and (b) nanoprism. ($\vec{E}_n$) is the field incident normal to the structure and ($\vec{E}_o$) is the field incident at an oblique angle. Line n and Line o shows the corresponding direction of polarization.

Figure 3.8: FEM simulation results illustrating the reduction in LIFE near corners between silver-silica interface when wrapped with GO. (Excitation at 900 nm). The images correspond to (a) AgNPr@SiO₂ and (b) GO-AgNPr@SiO₂.

Figure 3.9: Comparison of simulated absorption spectra and LIFE changes of AgNPr, AgNPr@SiO₂, and GO-AgNPr@SiO₂. a) Simulated absorption spectra. b) A contour intensity profile showing LIFE variation among pristine and hybrid core-shell systems.

performed above. (a) LIFE undergoes variation upon smoothing corners as well as edges of a nanosystem with triangular geometry. (b) plasmonic localization mediated LIFE leads to electric field large enough to destabilize silica in the AgNPr@SiO₂ system. (c) Wrapping of an ultra-thin layer of GO decreases LIFE at edges and thus was failed to reach threshold electric field to damage silica coating. We then conducted ex-

periments to validate the theoretical postulate using silica coated AgNPr and GO wrapped hybrids.

3.3.1.3 Laser Induced Damage on Silica

The laser induced damage on silica can be either by direct irradiation or by foreign material inclusions induced via plasmonic interaction. Numerous studies have been conducted extensively on laser induced damage and dielectric breakdown on silica and other oxides since decades [88, 151–155]. There are several proposed postulates for the damage process including avalanche ionization (impact ionization), multiphoton ionization (MPI), tunneling, etc. The foremost proposed theory is avalanche which can happen in thin oxides under the influence of electric field and short pulse regime where as in ultrashort pulse regime like femtosecond pulses, multiphoton ionization alone is capable of producing high electron density to reach plasma critical density [152]. Mechanisms for optical breakdown for sub-picosecond pulses are well known and laser induced damage thresholds (LIDT) provide deterministic values as the lattice has no time to respond during the pulse [152, 155–157]. Hence, no effect of lattice scattering, thermal or mechanical stress is accountable in this case [152]. On the contrary, for longer pulses like nanosecond and continuous wave (CW), threshold estimation is not reliable and vary by a factor of more than 100 [88]. Here the mid-gap states due to defects plays a role where these states get occupied when the material relaxes during long pulses [156]. Additionally, little is known about the optical properties of these defects [89]. Moreover, all the above studies observe the damage process on a microscopic scale on bulk surfaces or thin films. This may be the reason of very high but inconsistent values of reported threshold fluence of the order 10^4 J/cm². The onset of damage on nanoscale might give even less varying LIDT.

3.3.1.4 Challenges in Determining a Threshold (LIDT)

Practically, there are many possibilities to be considered which might raise a challenge in finding an exact threshold where the silica material breakdowns. The laser induced damage on silica has never reported a reliable threshold for nanosecond pulses due to mid-gap defect states. In nanoparticles, we do not have much information about the number of defect states and thus their effects during nanosecond and longer pulses. The interface between the metal and the silica shell are likely to have defects, especially near the corners due to high probability for imperfections. Moreover, the damage threshold can be shape and size dependent. In our studies, the effect of electric field is on localized spots of triangle shell shaped silica. Another factor which poses the challenge is the deviation of estimated shape by corner and edge smoothing using ROC from the synthesized nanoprisms. Finally, the difficulty in theoretical estimation also arises from coupling several significant temperature dependent phenomena which are dependent on each other as elaborated in our previous studies [32].

3.3.1.5 Laser Induced Damage Mechanism in Nanoparticles (Silica Coated Silver Nanoprisms)

As mentioned earlier, the metal-silica interface is highly likely to contain defect states near the corners. Initially, for a transparent solid like silica, the charge carrier density can be assumed to be around at least 10^8 cm^{-3} at room temperature [158]. But this means only a negligible amount of initial seed electrons to initiate the damage process in the silica nanovolume. In spite of the large fluence threshold of order 10^4 J/cm^2 reported in literature and models fits based on damages observed on microscale, a low threshold of order 10 J/cm^2 was used to etch out sil-

ica nanoballs which is an observation of damage in nanoscale triggered with lower fluence [90]. This is an indication that MPI can be initiated in this range. In our studies, we also estimated an equivalent fluence of the same order ($7.3\text{-}14.6\text{ J/cm}^2$) corresponding to the enhanced field near the corners. So, from this observation, we propose that fluence of order 10 J/cm^2 is enough to initiate MPI to seed avalanche. Additionally, upon irradiating 7.3 mJ/cm^2 fluence, the temperature of the metal can rise up to 600 K , which was found using FEM method (COMSOL Multiphysics). This temperature exists nearby the metal nanoparticle can control conduction band (CB) electrons from relaxing down to deep traps or valence (VB), reducing the threshold for remaining pulse. Then for the remaining pulse duration as well as further pulses, impact ionization seeded by these electrons can raise the electron density in the CB to reach critical density. As well known, once the critical density is reached, the plasma frequency matches the laser frequency making the material strongly absorbing. This enables the easy deposit of energy altering the properties of material [89]. Furthermore, we continued to repeat the experiment using longer irradiation time allowing more pulse to excite the nanoparticles. Here, the TEM images of 3.6 mJ/cm^2 irradiated sample still showed no changes. At the same time, 7.3 mJ/cm^2 irradiated sample had undergone structural changes, but the impact was higher than the previous results. Silica shell was damaged and ruptured. Moreover, as the irradiation time is increased, the damage impact was observed to increase due to decreasing threshold. It is known that multiple exposures will lower the threshold damage, which might be due to incubation [89]. This phenomenon implies laser induced modifications like the introduction of more defects and occupying existing defects and traps, weakening the system to further pulses.

3.3.2 Experimental Analysis

3.3.2.1 Materials and Methods

The nanoparticle (AgNPr@SiO₂) samples were obtained from the commercial supplier Nanocomposix and used as received. The laser excitation experiment was conducted using Opolette tunable laser (Opotek Inc. Tunable Laser Systems, Canada) as the excitation source and Thorlabs optical setup (lens, mirrors and optical table). Electronic absorption spectra were recorded on a Shimadzu UV-3101 PC NIR scanning spectrophotometer. TEM images were captured by JEOL 2010 TEM at 200kV. Zeta potential was measured by Mavern Nanosizer. Raman spectra of the nanoparticles on cleaned silicon substrate were measured with a Raman microscope (LabRAM HR, Horiba Yvon). The excitation wavelength of the irradiating light was 633 nm (He-Ne Laser, Melles Griot) and signals were collected by using a $\times 100$ objective lens.

GO was prepared by a modified Hummer's method [159]. At first, graphite (0.5 g) was suspended in concentrated H₂SO₄ (15 mL) under ice bath. KMnO₄ (1.5 g) was gradually added to the suspension with constant stirring. The mixture was stirred at 50 °C for 3h, followed by the addition of distilled water (35 mL). After stirring for another 15 min, distilled water (150 mL) was added to terminate the reaction. 10 mL, 30% H₂O₂ was added to the suspension and the color of solution turned into bright yellow. The mixture was then washed by HCl solution (250 mL, 10%) and distilled H₂O. In order to exfoliate the oxidized graphite, the product was treated with an ultrasonic probe at 250W for 1h and centrifuged at 8000 rpm for 30 min. The supernatant was collected. The process was repeated three times and the supernatant (600 mL) was collected as GO stock suspension. GO stock suspension (100 mL) was mixed with NaOH (5 g), sodium

monochloro acetate (5 g), and the mixture was sonicated for 2h to convert the OH groups into COOH groups. The mixture was then washed repeatedly with distilled water until well dispersed GO-COOH suspension was obtained. The solvent of GO-COOH suspension was changed into DMF by centrifugation and then the solution was treated with ultrasonic probe at 250 W for 1h in order to break GO sheets into a proper size for the nanoparticle wrapping application.

The surface of AgNPr@SiO₂ nanoparticle was modified with 3-aminopropyltriethoxysilane (APTES) and electrostatic GO wrapping was carried out following previously reported procedures [103, 145]. To prepare GO-AgNPr@SiO₂, a GO suspension in DMF was added with constant stirring to AgNPr@SiO₂-NH₂ (1 mg/mL in water) at room temperature for 24 h to complete wrapping process. The GO-AgNPr@SiO₂ was then collected using centrifugation and washed thoroughly to remove excess GO residues. The surface potential variations in the nanoparticles were investigated by ζ -potential measurements in distilled water. AgNPr@SiO₂-NH₂ shows a ζ -potential 26 ± 5.1 mV due to the presence of amino groups on the surface, while upon GO wrapping the value changes to -35.1 ± 8.1 mV confirming surface covering with negatively charged GO sheets. The strong electrostatic interactions between charged GO surface and amino-modified AgNPr@SiO₂-NH₂ surfaces trigger formation of GO wrapped AgNPr@SiO₂. From the Raman spectrum, a combination of peaks characteristic to GO ('D' band and 'G' band at 1350 and 1597 cm⁻¹ respectively) also confirm completion of GO wrapping on AgNPr@SiO₂ (Figure 3.14). Figure 3.12 shows corresponding changes in the absorption spectrum of GO wrapped hybrid. Figure 3.15b shows field emission scanning electron microscope (FE-SEM) image and Figure 3.16a shows the TEM image of a single GO wrapped AgNPr@SiO₂ nanoparticle.

The purchased AgNPr@SiO₂ was of concentration 1 mg/mL with OD 93.47 cm⁻¹. Upon dilution to 0.05 mg/mL OD reduces 20 times to 4.6734 cm⁻¹ by Beer Lambert's law ($\mu_a \propto$ concentration of the solution). The metal volume fraction (p) was found to be $\sim 0.0144\%$ ($\ll \sim 13\%$) which minimized the interaction between metal spheres and thus provided a solution which was similar to an isolated single structure system, as assumed in the computational analysis [125]. The laser irradiation was setup as shown in Appendix section A.1. The laser fluence upon irradiation on the sample was estimated by considering factors like propagation of Gaussian beam, reflection at interfaces, depth-resolved optical fluence distribution within sample columns [116], etc. Using this an average fluence of $F_{av} = 7.3$ mJ/cm² inside the sample was obtained. This is for the case where ND filter is not used in the setup. By using an ND filter of 50% transmission as shown in Figure A.1 we obtained a fluence of 3.6 mJ/cm², which is around half of the initial fluence. We conducted our experiments using these two values of fluence. Using the intensity (I) as fluence per unit pulse width and Equation Eq. 3.1, the ambient electric field (E_0) in each of the irradiating cases (3.6 mJ/cm² and 7.3 mJ/cm²) were calculated as 1.47 MV/m and 2.09 MV/m respectively.

Figures 3.10 and 3.11 shows the samples used for the study to compare the visible changes before and after irradiation. AgNPr@SiO₂ show the plasmon absorption maximum at 904 nm with a shoulder band around 613 nm (Figure 3.12(a)). A dilute AgNPr@SiO₂ solution (0.05 mg/mL) under constant stirring of 500 rpm was first irradiated with a laser pulse of 7 ns, 20 Hz repetition rate and fluence of 3.6 mJ/cm² and 7.3 mJ/cm² for 300 seconds.

Figure 3.12 clearly shows a change in the absorption spectra of AgNPr@SiO₂ and GO wrapped AgNPr@SiO₂. The change in shape and

Figure 3.10: (a) AgNPr@SiO₂ before irradiation, (b) AgNPr@SiO₂ after irradiation (3.6 mJ/cm² fluence, 7 ns pulse at 900 nm wavelength) for 900 s and (c) AgNPr@SiO₂ after irradiation (7.3 mJ/cm² fluence, 7 ns pulse at 900 nm wavelength) for 900s.

Figure 3.11: (a) AgNPr@SiO₂ before irradiation, (b) GO-AgNPr@SiO₂ before irradiation and (c) GO-AgNPr@SiO₂ after irradiation (7.3 mJ/cm² fluence, 7 ns pulse at 900 nm wavelength) for 900 s.

broadening of spectrum of silica coated silver nanoprism (Figure 3.12(a)) can be attributed to the change in refractive index which occurred due to the damage of environment silica matrix. Meanwhile, the preserved shape of spectrum for GO wrapped nanostructure sample (Figure 3.12(b)) clearly indicates that no damage has occurred by laser irradiation. However, the reason for reduced value of the spectrum is unknown.

Figure 3.12: Comparison of measured absorption spectra (a) AgNPr@SiO₂ and (b) GO wrapped AgNPr@SiO₂ before and after irradiation (900 s exposure) with 7 ns pulse of fluence 7.3 mJ/cm² at 900 nm wavelength.

3.3.2.2 Imaging and Characterization (AgNPr@SiO₂)

Transmission electron microscopy (TEM) analyses were then carried out for the AgNPr@SiO₂ samples. Figure 3.13 shows TEM images of samples irradiated with nanosecond pulse laser irradiation at time intervals of 0, 300, 900 and 1800 seconds. The TEM image of pristine AgNPr@SiO₂ (Figure 3.13a) remains intact with well-defined Ag-silica boundaries and a completely contacted area at the edges (Figure 3.13a-inset, high-resolution image). AgNPr@SiO₂ irradiated with 7 ns pulsed laser at 900 nm with an estimated fluence (based on Equation Eq. A.9) of 7.3 mJ/cm² for 300 s shows clear initiation of dielectric breakdown at the edges (Figure 3.13b & high-resolution image). Similarly, upon increasing the irradiation time (900 s) expansion of initially seeded dielectric breakdown occurs at the edges of the core-shell nanoprisms (Figure 3.13c & high-resolution image). For the next sample, the irradiation for 1800 s leading to a complete morphological imbalance in the Ag-silica (plasmon-dielectric) interface was observed (Figure 3.13d). This shows that exposure to more number of pulses or longer irradiation time reduces the

Figure 3.13: TEM images of AgNPr@SiO₂ nanoprisms before and after LIFE mediated edge abrasion. a) A pristine AgNPr@SiO₂ nanoprism and a high-resolution image showing dielectric silica edge with no defects before pulsed laser irradiation. b) & c) TEM images of AgNPr@SiO₂ nanoprisms showing edge abrasion after irradiation with 7.3 mJ/cm² nanosecond pulsed laser for a period of 300 & 900 s respectively. Right side lane of both images shows high-resolution image visualizing localized abrasion at edges. d) TEM images of AgNPr@SiO₂ nanoprisms after irradiation for a period of 1800 s.

threshold of localized breakdown which is in line with the theory. It must be noted that samples irradiated with a fluence of 3.6 mJ/cm² undergo no structural damages to the core-shell nanoprisms. Therefore, optimum external fluence to initiate dielectric damage could be between 3.6-7.3 mJ/cm².

From FEM simulation, the intensity enhancement factor $|E/E_0|^2$ was calculated as ~ 2000 at 900 nm irradiation, and the enhanced electric field ' E ' around the corners was estimated as 65.74 MV/m (for fluence 3.6 mJ/cm²) and 93.47 MV/m (for fluence 7.3 mJ/cm²). Using Equation

Figure 3.14: Raman spectra of AgNPr@SiO_2 (Blue curve), GO-AgNPr@SiO_2 before irradiation (red curve) and after 1800 s irradiation (black curve).

Eq. 3.1, this enhanced electric field mediated effective fluence in the corners of Ag-silica nanoprisms is estimated as 7.2 J/cm^2 and 14.6 J/cm^2 respectively. It was reported previously that a fluence of the order 10 J/cm^2 would lead to structural collapse and damage in silica samples with nanometer dimensions [90]. Thus, the observed damage is attributed to the laser induced damage via plasmon assisted LIFE at the Ag-silica interfaces at the corners of AgNPr@SiO_2 nanoprisms. More details on the laser induced dielectric breakdown and damage of silica are explained in section 3.3.1.3

3.3.2.3 Imaging and Characterization (GO-AgNPr@SiO_2)

Next, the effect of GO wrapping on the LIFE mediated localized edge abrasion was experimented. Irradiation of GO-AgNPr@SiO_2 was carried out using a pulsed laser at 900 nm with a fluence of 7.3 mJ/cm^2 which induces profound LIFE mediated damage at the edges in case of

Figure 3.15: Field emission scanning electron microscope (FE-SEM) images of AgNPr@SiO₂ and GO wrapped AgNPr@SiO₂. Red arrow indicates wrapped GO on single nanoprism surface.

Figure 3.16: TEM images of GO-AgNPr@SiO₂ nanoprisms before (a) and after (b) pulsed laser irradiation at a fluence of 7.3 mJ/cm² for 1800 s. White arrows points GO coating.

AgNPr@SiO₂ particles. We have observed that profound irradiation of pulsed laser irradiation on GO wrapped nanohybrids fails to induce damage selectively at the edges as observed with AgNPr@SiO₂. Figure 3.16a and 3.16b shows the TEM image of a GO wrapped AgNPr@SiO₂ before and after irradiation for 1800 s.

3.4 Conclusion

FEM simulation and experiments with AgNPr@SiO₂ clearly support electric field intensity and plasmonic hot-spot localization at the edges. The LIFE generated at the plasmonic edge of a dielectric coated nano prism would lead to structural damage at the edges significantly. Irradiation of an ultra-dilute solution of (0.05 mg/mL) AgNPr@SiO₂ at different time intervals with a fluence of 3.6 mJ/cm² induces no structural damages in both pristine as well as GO wrapped hybrids. Similarly, the irradiation using a 7-ns pulse with fluence 7.3 mJ/cm² induces LIFE mediated edge damage for AgNPr@SiO₂ particles significantly. The changes are visible for samples irradiated at 300 and 900 s respectively. The extent of irradiation for a longer period (1800 s) effectively destabilizes the full nanohybrid architecture leading to bleaching of dielectric silica coating from the surface. Using image analysis on TEM images, a damage ratio (damage area to silica area) 0.0372 and 0.2167 was obtained corresponding to 300 s and 900 s of irradiations respectively (3.17). Analysis for 1800 s irradiation is insignificant since the damage area could not be properly segmented. Wrapping of ultra-thin layer of GO on AgNPr@SiO₂ reduces the light absorption by active plasmonic core due to the broad absorption of GO in the UV-vis and near-IR spectral region. GO wrapping experiments proves the influence of LIFE in edge damaging of silica on Ag-silica interfaces.

In conclusion, herein we have demonstrated light intensity field enhancement (LIFE) mediated damage of dielectric coating on silver-silica nanoprisms upon excitation using nanosecond pulsed excitation. FEM simulation study was first conducted using models of silica coated silver nanoprisms (AgNPr@SiO₂) and established a geometry dependent localization of LIFE would lead to hot-spot generation at the corners. In a real

Figure 3.17: Box plot comparing the damage ratio of 300 s and 900 s irradiations on AgNPr@SiO₂ using 5 areas of TEM images. The results marked in black corresponds to 300 s irradiations and red corresponds to 900 s irradiations. The right image shows 2 pairs of TEM image of (a, c) 300 s irradiation and (b, d) 900 s irradiation. The abrasions are highlighted in yellow. Values estimated using ImageJ software.

sample, it was confirmed that tuning and controlling the input irradiation fluence could cross the breakdown threshold and trigger the damage in the immediate dielectric surrounding of metal nanoparticle via LIFE. During the study, we achieved a breakdown using a low external laser fluence of 7.3 mJ/cm². Further, to prove the LIFE process, an ultrathin GO coated hybrid was exposed to same laser fluence and found no effect on dielectric damage at the corners. We envisage that the advantage of LIFE mediated controlled structural collapse opens opportunities in biomedical applications including design and development of new smart remote-controlled drug carrier vehicles with enhanced drug delivery efficacy.

Declaration:

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Chapter 4

Investigation on Conductive Polymer Mediated Plasmonic Coupling and Charge Transfer Plasmons

Plasmonic coupling of nanoparticles (NPs) have been known to show more interesting and unique characteristics than single NPs. Plasmonic coupling includes dimers, trimers, tetramers and complicated clusters of higher order. The resultant signature observations are spectroscopic enhancement and spectral shifts. Coupling can be achieved using different nanoparticles like nanospheres, nanorods, nanoprisms, etc., via self-assembly and stimulus responsive methods. Hence, the absorption and scattering can be tuned to the desired range. Due to the triangular shape of nanoprisms, the field enhancement between the corners of two or more coupled nanoprisms is shown to have a higher value than spheres. More-

over, these couplings require a capacitive medium between them. A conductive interface enables charge transfer between the particles introducing new coupling behavior. We herein report a preliminary study on the stimulus responsive plasmonic clustering of gold nanoparticles (AuNPs) and gold nanoprisms (AuNPrs) assisted by the photopolymerization of diacetylene (dAc) upon exposure to ultraviolet (UV) light forming conductive polydiacetylene. Additionally, the conductive polydiacetylene layers between the particles is shown to introduce new peaks of charge transfer plasmons (CTP) which is analyzed by the FEM method and later corroborated using UV-visible spectrum characterization and microscopic imaging.

4.1 Introduction

4.1.1 Formation of Plasmonic Clusters

Plasmonically coupled metal nanoparticles of gold (Au) and silver (Ag) are characterized by unique properties and functionalities through which their applications can be extended beyond that of single nanoparticles. Plasmonic coupling happens when two or more plasmonically active particles are brought together to interact. They can be engineered and designed to have desired properties if the plasmonic resonance can be tuned by controlling number of particles in the plasmonic clusters, inter-particle separation, coupling orientation, and dielectric environment. The resultant high spectroscopic enhancement and spectral shifts allows novel applications and smart device development [160]. Controlling the number of particles in a cluster as well as bringing them close enough to couple efficiently has been a challenging problem. There have been several techniques reported including stimulus responsive [96, 161–168] as well

self-assembled aggregates [71, 72, 169–179]. Most of the self-assembled aggregates are achieved on spherical Au nanoparticles (AuNPs) [71, 172, 175–177, 179] or nanorods (AuNRs) [72, 169–174, 179]. Although many studies focus on forming long chains, few reports focus on controlling the number of particles in the end to end assembly. Chain length of AuNR assembly from dimer to long chains were reportedly controlled using concentration of binding ligand 1,2-Phenylenedimethanethiol (PDT) [72]. Cluster of AuNP of different particle numbers were obtained by drying nanoparticle containing droplets technique [176]. In another study, 3D clusters with different particle numbers of AuNP were obtained via DNA directed [71] and Pluronic F-68 bonding [177]. Most of the stimulus responsive research dealt with spherical AuNPs [96, 161, 163–168] with few of them experimenting on AuNRs [162]. These stimulus responsive studies were reversible and the stimuli were either pH, temperature, or both. Another interesting study was using photo-stimulus where laser excitation was shown to form an optical micro-cage trapping the AuNPs in the focal spot to form aggregates [96]. However, stimulus responsive studies showed less progress on control on nanoparticle numbers and coupling orientation.

For nanoprisms, coupling was initially realized by using only electron beam lithography. Few recent report shows the formation of dimers and long chains of Ag nanoprisms (AgNPrs) by polymer directed self-assembly method [179, 180]. In these studies, even though long chains were not formed limiting the particle number to form only small clusters, they lacked control on cluster sizes. However, many theoretical works show that the nanogap between nanoprism can produce high electric field enhancement which can be used for imaging, sensitive bio-sensing, surface enhanced Raman spectroscopy (SERS), etc. Herein, we report a preliminary study on optical stimulus responsive plasmonic cluster forma-

tion of Au nanoparticles (AuNPs) and nanoprisms (AuNPrs). We used diacetylene (dAc) grafting over nanoparticles which polymerizes to polydiacetylene (pAc) upon exposure to UV light. The polydiacetylene grafted on the nanoparticle acts as an interface between two interacting particles and will help the particles to maintain a nanogap between them.

4.1.2 Charge Transfer Plasmons (CTP)

All the above mentioned couplings and assemblies of nanosystems are mediated by non-conductive agents forming capacitive couplings. However, these coupled systems can be formed by conductive interfaces giving rise to conductive coupling [97, 98, 181–184]. Capacitive coupling is when the nanogap medium is capacitive like air or water. Conductive coupling is when plasmons are allowed to interact through the nanogap via quantum effects such as tunneling or when the charges are allowed to conduct and pass through a physical conductive medium. As the conductivity increases, the bonding dimer plasmon (BDP) which is due to the inherent plasmon mode of the individual particles blue-shifts and broadens due to screening at the junction forming screened bonding dimer plasmon (SBDP). For large conductance, a low energy charge transfer plasmon (CTP) also appears in the spectra with a line width that decreases with increasing conductance. This is due to the newly enabled plasmon mode via charge transfer through the conductive junction [181, 182]. Among the experimental studies on CTP, conductive junctions are either realized by thin metal nanowires of the same material as coupling particles [97, 185], close proximity causing quantum tunneling effects [186, 187] or by direct contact of the particles [184]. In general, most of the analysis and observations on CTP are carried using base particles as nanospheres, nanodisks and nanorods.

We herein report a study on CTP by realizing conductive junctions via polydiacetylene which is a conductive polymer. Initially we verified the theory on spherical particles (AuNP) using FEM modeling and spectroscopy. Then we proceeded to analyze the effect on nanoprisms (AuNPr), an anisotropic shape. In the process we also achieved a relatively simple method to form dimers and higher order coupled systems.

4.2 Conductive Coupling of Gold Nanospheres

4.2.1 Theoretical Analysis

To theoretically compute the absorption and scattering of coupled AuNPs, we have considered two AuNPs each of radius 25 nm. Two cases were compared where in one, the coupled system consisted of two AuNPs were kept closely with a gap of 4 nm gap in between them in water medium and in another, the above coupled system were coated with thin layer of polydiacetylene which bridged the particles making a conductive connection between the AuNPs. For simulation, the optical parameters of Au at room temperature 293 K were taken from the fitted value (Appendix B.2) as explained in chapter 1. The optical parameters of polydiacetylene were taken from previously reported calculations and experimental data [188] which is also similar to that of polyacetylene [189] (Appendix B.5). Absorption power (P_{abs}) is calculated as the heat dissipated in the structure as $Q_r = \int \vec{J} \cdot \vec{E} dV$, where $\vec{J}$ is current density and $\vec{E}$ is the electric field inside the nanoparticle. Scattered power (P_{sca}) is calculated as the relative power ($relP$) of electric field in the far field integrated over a circular domain containing the nanoparticle (Equation Eq. 4.1). Extinct power (P_{ext}) is then the sum of the above two powers. In COMSOL, these terms

are calculated by the following relations:

$$\begin{aligned}
 relP &= \frac{1}{2} Re \left\{ \begin{bmatrix} relH_z^* & -relH_y^* & 0 \\ 0 & relH_x^* & -relH_z^* \\ -relH_x^* & 0 & relH_y^* \end{bmatrix} \begin{bmatrix} relE_y \\ relE_z \\ relE_x \end{bmatrix} \right\} \\
 P_{sca} &= \oiint sum(relP) \\
 P_{ext} &= P_{abs} + P_{sca}
 \end{aligned} \tag{Eq. 4.1}$$

where '*rel*' stands for relative status for which COMSOL solves the electromagnetic field giving the scattered components in the far field:

$$relE = E_{total} - E_{background} \tag{Eq. 4.2}$$

Here $E_{background}$ is the background field in which the scatterer is placed and E_{total} is the total field in the presence of scatterer. All the y-axis magnitudes correspond to an input excitation intensity of 10^{10} W/m^2 . Using these analytical expressions and FEM simulation, the extinction and absorption of the coupled gold nanoparticle system is calculated and is shown in Figure 4.1. It can be seen that the conductive coupling via conductive polydiacetylene interface mediates a charge transfer path between the systems forming a new peak (CTP) at around 940-960 nm. The expected blue-shift of the peak at 570 nm to form SBDP could not be further calculated due to the limitations of FEM method to converge for low wavelength in thin areas between the nanoparticles. Here Finite Differential Time Domain (FDTD) method is the preferred tool to successfully converge to a solution.

Figure 4.1: Calculated absorption and extinction spectra of the coupled AuNPs comparing the capacitive coupling and conductive coupling.

4.2.2 Experimental Analysis

The thiolated diacetylene monomer obtained from our collaborators at Division of Chemistry and Biological Chemistry (CBC), School of Physics and Mathematical Sciences (SPMS), Nanyang Technological University, Singapore has been utilized as such without further purification. Gold nanoparticles (radius ca.25 nm) were purchased from Sigma-Aldrich and used without further purification. AuNP solution (0.5 mL, 0.5 mg/mL solution) was concentrated by centrifugation at 6000 rpm for 20 min. The concentrated AuNPs were then dispersed in 1.5 mg/mL diluted diacetylene solution (0.25 mL). The diacetylene was diluted in a solution of ethanol, phosphate buffered saline (PBS) and distilled water. The formed mixture was kept for incubation by stirring for 20 hrs. This allows the thiol

Figure 4.2: Schematic representation of diacetylene coated AuNPs getting bound to form plasmonic coupling. The coupling is realized by the photopolymerization of diacetylene monomer upon UV irradiation.

exchange to occur for the diacetylene to get coated over the nanoparticle surface forming a 1-2 nm thin layer. Following this, the mixture was centrifuged at 6000 rpm for 20 min to remove excess diacetylene. The final stage involves inducing the binding of the coated nanoparticles by polymerizing the diacetylene monomer to form polydiacetylene. The stimulus for polymerization is UV light. The solution is exposed to UV for varying irradiation time under constant stirring. Figure 4.3 shows the Transmission electron microscope (TEM) images taken. We were successful in preparing conductive interface mediated coupled system of gold nanoparticles. A thin lining is visible around the nanoparticles which is the polymer coating. However, since the stirring and photopolymerization time was not optimized, the number of particles in a coupling was not controlled and thus higher order systems than expected (dimer) were formed. The corresponding UV-Vis absorption spectra is measured (Figure 4.4). A new peak is formed in NIR region at 1185 nm which can be attributed to the contribution from CTP. It is reported that the CTP blueshifts with increas-

Figure 4.3: Transmission electron microscope (TEM) images of polydiacetylene mediated conductive coupled AuNPs.

ing junction conductance [97, 98, 181–183], increasing junction radius or by reducing coupling particle size. Hence in our case, the red-shifted CTP than the calculated value can be due to the reduced conductance of polymer junction by poor binding or overestimation of polymer conductivity during simulation approximations. Additionally, a screened peak (SBDP) at 540 nm blueshifted from 570 (found from simulation) is visible.

We also measured the UV-Vis absorption of a thin layer of polydiacetylene coated on a glass slide (Figure 4.5). The polydiacetylene was observed to change colour to blue by the UV exposure. The prolonged exposure of more than 500-600 s however made the transition of the polymer from this blue phase to red phase as shown in inset of Figure 4.5. This monomer-to-blue-red chromatic phase transitions were explained in previous studies [190]. The blue form of the polymer usually gives absorption

Figure 4.4: Measured absorption spectra of AuNP solution (black solid line) and polydiacetylene assisted conductive coupled AuNP system (red solid line) formed by 300 s of UV exposure. Black dotted lines shows the simulated extinction spectrum of the conductive coupled AuNPs. Red dotted lines shows the simulated extinction spectrum of two capacitive coupled AuNPs (from Figure 4.1) which hints towards the expected blueshift arising from the screened plasmon resonance.

band at around 650 nm while the red form at around 550 nm [191]. In our experiment, our UV irradiation time to form conductive binding between the nanoparticles were 300 s or less. Hence, we assumed the polymer interface will be in blue phase in the coupled AuNPs. The blue phase with absorption at 650 nm is similar to the absorption spectrum of the trans-isomer whose absorption can be obtained from previous literatures [192]. Hence, we used the optical constants of trans form of the polymer (see Appendix B.5) for our calculations.

Figure 4.5: Measured absorption spectra of polydiacetylene layer in the blue phase and red phase. The inset shows the simulated absorption cross-section for cis- and trans-polyacetylene.

4.3 Conductive Coupling of Gold Nanoprisms

4.3.1 Theoretical Analysis

4.3.1.1 Single Gold Nanoprism

To theoretically compute the absorption and scattering of single AuNPrs, we relied on 2D simulation (for simplicity) in COMSOL Multiphysics. We considered a 100 nm side length AuNPr. All calculations were conducted as per explained in section 4.2.1. Single nanoprisms are expected to exhibit 3 peaks namely longitudinal dipole resonance which is the dominant [129], longitudinal quadrupole and lateral quadrupole resonance. Longitudinal dipole is excited by in plane excitation and lateral

Figure 4.6: (a) and (b) shows the in plane excitations to trigger the dominant longitudinal dipole resonance with two orthogonal cases of electric field component. (c) and (d) shows the FEM simulated electric field enhancement factor for the cases in (a) and (b) respectively. (e) is the simulated spectra.

Figure 4.7: (a) and (b) shows the in plane excitations to trigger intermediate longitudinal quadrupolar resonance with two orthogonal cases of electric field component. (c) and (d) shows the FEM simulated electric field enhancement factor for the cases in (a) and (b) respectively. (e) is the simulated spectra.

by out of plane excitation which is the weakest [193]. Hence for our simulation, we used all these excitation directions. Figure 4.6 (a, b) shows the dominant in plane excitation, their corresponding field enhancement map at 730 nm (Figure 4.6 (c, d)) and their simulated absorption-extinction spectra (Figure 4.6 (e)). Similarly, Figure 4.7 and 4.8 shows the intermediate in plane excitation and out of plane excitation respectively. However, in each case orthogonal pair of excitations produced similar spectra for both

Figure 4.8: (a) and (b) shows the out of plane excitations to trigger the weak lateral quadrupolar resonance with two orthogonal cases of electric field component. (c) and (d) shows the FEM simulated electric field enhancement factor for the cases in (a) and (b) respectively. (e) is the simulated spectra.

Figure 4.9: Average (a) absorption and (b) extinction spectrum.

extinction and absorption. Figure 4.6 represents the dominant longitudinal dipole resonance and Figure 4.7 represents the intermediate longitudinal quadrupolar resonance. In Figure 4.8, since the assumption of large thickness (dimension in 3rd direction) in 2D is made by COMSOL, simulation fails to produce the expected weak resonance from lateral quadrupole. Therefore, we omit contribution from out of plane excitation. Additionally, a blue-shift in spectrum is expected due to the large thickness [180, 194]. The average spectrum of an AuNPr can thus be averaged as shown in Figure 4.9 where we obtained two peaks as expected.

4.3.1.2 Coupled Gold Nanoprism

Similar to the calculations done for single AuNPrs, FEM simulations were conducted for coupled AuNPrs. The coupled particles were separated by 4 nm. Here, due to the anisotropy of the triangular shape, formation of CTP and SBDP can be individually observed from different excitation modes. Figure 4.10 (a, b) shows the absorption and extinction spectrum respectively, corresponding to the dominant in-plane excitation (longitudinal dipole) where a CTP is present around 750-940 nm. Figure 4.10 (c, d) shows the absorption and extinction spectrum respectively, corresponding to the intermediate in-plane excitation (longitudinal quadrupolar) where CTPs is present above 1000 nm and an SBDP is present at 470 nm blue-shifted from 490 nm. Figure 4.10 (e, f) is the averaged absorption and extinction of all the above modes.

4.3.2 Experimental Analysis

The ligand exchange and grafting of AuNPrs with diacetylene following polymerization were done as explained in section 4.2.2. Initially, we used diacetylene solution in a proportion as used for AuNPs. Figure 4.11 shows the corresponding TEM images characterizing the formed coupled nanoprisms. In order to analyze coupled systems of higher number of particles, we varied the diacetylene proportion by doubling the quantity to 0.5 mL while preparing the mixture. Figure 4.12 shows the corresponding TEM image where similar results corresponding to coupling were obtained but with excess polymer. However, with reduced stirring speed while exposing to UV light for polymerization, different structures like chain systems as shown in Figure 4.13 were also formed. However, a single/multiple clear distinct peak in the absorption was difficult to be observed due to uncontrolled nature of orientation and number of particles

Figure 4.10: Calculated absorption and extinction spectra of the coupled AuNPs comparing the capacitive coupling and conductive coupling.

Figure 4.11: Transmission electron microscope (TEM) images of polydiacetylene mediated conductive coupled AuNPs (prepared using 0.25 mL 1.5 mg/mL diacetylene solution).

Figure 4.12: Transmission electron microscope (TEM) images of polydiacetylene mediated conductive coupled AuNPs (prepared using 0.5 mL 1.5 mg/mL diacetylene solution).

Figure 4.13: Transmission electron microscope (TEM) images of polydiacetylene mediated conductive coupled AuNPs (prepared using 0.25 mL 1.5 mg/mL diacetylene solution and reduced stirring speed while photopolymerization).

Figure 4.14: Measured absorption spectra of AuNPr solution (black solid line) and polydiacetylene assisted conductive coupled AuNPr system (red solid line) formed by 300 s of UV exposure. A small bump is visible near 1200 nm marked by a green dotted box.

in the bound coupled systems (Figure 4.14). Proper optimization such as incubation conditions while grafting diacetylene monomer on nanoprism, UV exposure conditions, diacetylene concentration, etc. needs to be further explored. Appropriate proportion of nanoparticle-diacetylene mixture and stirring speed while incubation is anticipated to control the diacetylene grafting over the nanoparticle and hence focus the polymer coating on corners only. Hence, the binding can be restricted forming corner to corner coupled nanosystems. Suitable UV exposure conditions needs to be studied for controlling the extend of polymerization.

Irradiation time (s)	AuNP (with 0.25 mL diacetylene solution)	AuNPr (with 0.25 mL diacetylene solution)	AuNPr (with 0.5 mL diacetylene solution)	AuNPr (with 0.25 mL diacetylene solution, reduced stirring speed)
300	Dimers > 60%	Dimers < 30%	Dimers < 30%	Dimers < 10%
600	Dimers < 40%	Dimers < 20%	Dimers < 20%	No dimers
900	Dimers < 5%	No dimers	No dimers	No dimers

Table 4.1: Irradiation time vs percentage of dimers for AuNP and AuNPr system from TEM grid analysis. Diacetylene solution used in every experiments is of concentration 1.5 mg/mL.

4.4 Conclusion

In conclusion, we have demonstrated an easy procedure for stimulus responsive formation of coupled structures using UV light exposure and photopolymerization of diacetylene monomer to polydiacetylene. The formation was confirmed on spherical gold nanoparticles as well as on anisotropic triangular gold nanoprisms. Using appropriate conditions, nature of structures can be controlled from dimers and trimers to long chains. UV exposure time and stirring speed was found to affect the type of coupled structures formed in the ensemble sample solution and thus needs further optimization to control the number of nanoparticles per coupled system. Table 4.1 summarizes the effect of the two above mentioned parameters in forming dimers, which was estimated from the TEM grid while imaging. In the process of achieving bound structures, the medium of binding used was a conductive polymer (polydiacetylene). The presence of conductive coupling was theoretically analyzed and further characterized using TEM and UV-Vis spectra.

Chapter 5

Conclusions and Future Work

In this chapter, we provide a summary of the work conducted for the project highlighting significant contributions. This chapter of thesis will conclude with potential future works that arises from these findings.

5.1 Conclusions

In this thesis, we commenced with a discussion of possible effects of plasmonic interaction with nanoparticles. Electromagnetic interaction can be used for both disruptive as well as constructive effects. Silica is a widely used coating agent on plasmonic materials for biomedical applications. Damage caused by laser interaction on silica is also widely known and has been studied extensively, but the damage happens under extremely high laser intensity. However, since the silica coating in nanomaterials is in close contact with the plasmonically active nanoparticles, the disruptive effect can be induced with low intensity. This is due to the plasmonic enhancement of various phenomena which can potentially destabilize the silica structure. To explore more on this, we initially mod-

eled and analyzed laser interaction on silica coated gold nanostructures with further characterization and imaging. A rupture was observed which was attributed to differential thermal expansion of the core-shell structure. Following, we studied triangular shape, an asymmetric shape with corners. Modeling and experiments on silica coated silver nanoprisms revealed field enhancement at the corners. With appropriate duration of irradiation, we were able to induce a controlled damage on the silica coating. Finally, electromagnetic interaction was also used to construct structures as well by photopolymerization of diacetylene to bind gold nanoparticles and nanoprisms. In the process, we achieved a conductive interface mediated binding to show charge transfer plasmon which is highly tunable at NIR region. Overall, the main contribution of the thesis are as follows:

- (i) We modeled a more realistic analytical lattice temperature profile for the Gaussian pulse excitation which is valid as a one-temperature model (OTM) in nanosecond pulse regime. Previous, estimations for the lattice temperature were either only an approximate peak value for the temperature or a temporal profile for temperature derived using approximation of an ideal rectangular pulse irradiation. We combined several possible temperature dependent parameters and iteration for convergence purpose.
- (ii) We explored two damage mechanisms in hetero-nanostructures, where shape of the nanoparticle was found to be a major deciding factor for the cause of instability. For a spherical core-shell structure, differential thermal expansion was the only primary cause possible under working conditions of lower temperatures. The temperature could be made sufficient enough to form stress and induce crack in the coating. At the same time, for a nanoprism based core-shell structure, the corners favoured field enhancement and thus dielec-

tric breakdown of silica in close contact.

- (iii) We modeled the conditions upon plasmonic interaction with nanostructures. We propose that these conditions can be used to design and actuate or prevent damage of nanostructures depending on the purpose. For conventional usage like imaging and sensing, photothermal therapy, etc, the nanostructures must be preserved as such. Meanwhile, the coating can be used as a carrier for suitable agent. In this case, controlled damage of the carrier coating is desirable to make drug delivery possible.
- (iv) We achieved preliminary results in constructing nanostructures and obtaining coupled nanoparticles and chains via an easy procedure in solution phase. Using UV as stimulus agent, thiolated diacetylene monomer on the nanoparticles were photopolymerized to form higher order structures.
- (v) By forming coupled structures, we also achieved a conductive interface mediated coupling using a conductive polymer polydiacetylene as binding medium. This enables a bridged path between structures for the charge transfer. Due to the new path of charge flow, a new peak (CTP-charge transfer plasmon) forms at NIR region. The CTP is highly sensitive to the shape of the coupling particles and conductivity of the interface and hence highly tunable.

5.2 Future Work

- (i) Dielectric breakdown damage of silica from nanoscale:

It was observed in our study with silica coated nanoprisms that the silica dielectric can be damaged using electric field using low fluence of the order 10 J/cm^2 . Most of the reported studies and model-

Figure 5.1: Schematic of drug release upon laser excitation.

ing were based on damage at microscale which required even high fluence of the order 2000 J/cm^2 . More insight into the root cause of dielectric breakdown by accurate modeling of avalanche and multiphoton ionization can be developed using plasmonic interaction breakdown of silica.

(ii) Drug delivery and imaging:

After testing cytotoxicity along with *in vivo* and *in vitro* biocompatibility, a significant potential of nanoprisms that can be proposed is in drug delivery. Initial experiments can be planned for drug loading and delivery in tissue phantoms *in vivo* and *in vitro*. Using a drug loaded destructible or optically unstable coating helps to release the drugs by remotely controlled destruction triggered by optical excitation. Figure 5.1 illustrates the anticipated mechanism.

The mesoporous dielectric coating will be loaded with suitable drugs to be delivered. This drug loaded nanostructure can be destabilized by optical excitation rupturing the drug carrying coating releasing the drug. The optical excitation can be done remotely when the carriers reaches the target or when required giving a control over the deliv-

Figure 5.2: Schematic summary of dielectric/polymer coated plasmonic nanostructures in controlled drug delivery and other applications (imaging and photothermal therapy).

ery of the drug. The nanostructures can be stabilized by graphene oxide wrapping and the same can be tested on this modified structure. The size of the coating and amount wrapping can affect the stability and the nanostructure can be designed accordingly. Finally

the graphene oxide also enables the targeted drug delivery due to its ability to attach to a targeting ligand. Along with drug delivery using mesoporous silica coating, deep tissue imaging is possible by constructing and tuning the nanostructures absorbance/extinction. Apart from silica coating, polymer coating is another promising contribution to the hetero-nanostructure for imaging. The coated polymer can be attached with targeting ligands to enable photothermal therapy as well. Figure 5.2 briefly presents the research phases proposed study. This concludes the primary aim of the study to explore the possibilities of drug deliverable plasmonic nanostructures including controlled drug delivery by optical excitation.

Appendix A

Laser Irradiation Setup and Fluence Calculation

A.1 Laser Setup

Figure A.1: Schematic of laser irradiation setup.

Figure A.1 shows the schematic setup used for our experiment. Following a laser source to excite a nanosecond pulsed laser of appro-

appropriate wavelength, a biconvex lens was used to collimate the Gaussian laser beam. For NIR irradiation in Chapter 2, a long-pass filter of cut off 710 nm was used to remove any other harmonics generated by the laser source. A neutral density filter is used to control the fluence falling on the sample. A planar mirror adjusted at 45° guides the collimated Gaussian beam towards the focusing lens which is then focused into the sample.

A.2 Fluence Calculation

The laser fluence upon irradiation on the sample was estimated by considering factors like propagation of Gaussian beam, reflection at interfaces, depth-resolved optical fluence distribution within sample columns [116], etc. Using the Gaussian beam propagation, the beam profile was estimated inside the sample. The profile thus provides the beam spot size to estimate the fluence at each point. Additionally, the fluence propagating through the sample suffers loss due to the optical density (OD). Thus, the fluence vary at each point inside the sample due to Gaussian profile as well as the depth dependent loss due to the OD. Finally, taking into account the above factors, the average fluence (F_{av}) inside the sample under analysis is determined.

A.2.1 Gaussian Beam Propagation

Figure A.2 illustrates the propagation of Gaussian beam through the focusing lens which is guided into the sample. A Gaussian beam propagating through z-axis with amplitude $U(r)$ can be expressed as:

$$U(r) = A_0 \frac{W_0}{W(z)} \exp\left[-\frac{\rho^2}{W^2(z)}\right] \exp\left[-jkz - jk\frac{\rho^2}{2R(z)} + j\zeta(z)\right] \quad (\text{Eq. A.1})$$

where $W(z) = W_0 \sqrt{1 + (z/z_0)^2}$ is the beam radius at location z , $W_0 = \sqrt{\lambda z_0 / \pi}$ is the beam waist (smallest beam radius or beam radius at location $z = 0$), λ is the excitation wavelength ($\lambda = 526$ nm for exciting AuNP@SiO₂ in Chapter 1 and $\lambda = 900$ nm for exciting AgNPr@SiO₂ in Chapter 2), ζ is the phase shift, A_0 is a constant, z_0 is the Rayleigh range, $R(z) = z[1 + (z_0/z)^2]$ is the radius of curvature of wavefront and $\rho^2 = x^2 + y^2$. All this information can also be contained using the representation of q -parameter where:

$$q(z) = z + jz_0 \quad (\text{Eq. A.2})$$

or equivalently

$$\frac{1}{q(z)} = \frac{1}{R(z)} - j \frac{\lambda}{\pi W^2(z)} \quad (\text{Eq. A.3})$$

Starting at the interface of focusing lens, the q -parameter of the beam inside the sample can be estimated using the transmission matrix (ABCD matrix) for Gaussian beam.

$$M = M_{sample} \times M_{free} \times M_{lens} = \begin{bmatrix} A & B \\ C & D \end{bmatrix} \quad (\text{Eq. A.4})$$

where M is the total transmission matrix, M_{lens} is the matrix for transmission through a thin lens, M_{free} is the matrix for free space propagation after the lens and before entering the sample and M_{sample} is the matrix for refraction at the planar boundary between air and sample.

Figure A.2: An illustration to estimate fluence on the sample.

$$\begin{aligned}
 M_{lens} &= \begin{bmatrix} 1 & 0 \\ -\frac{1}{f} & 1 \end{bmatrix} \\
 M_{free} &= \begin{bmatrix} 1 & z \\ 0 & 1 \end{bmatrix} \\
 M_{free} &= \begin{bmatrix} 1 & 0 \\ 0 & \frac{n_{air}}{n_{sample}} \end{bmatrix}
 \end{aligned} \tag{Eq. A.5}$$

where $f = 40$ mm is the focal length of the focusing lens, $n_{air} = 1$, and $n_{sample} = 1.33 (= n_{water})$ are the respective refractive indices. The samples are diluted with water and hence, the sample refractive index is approximated to that of water. Then total transmission matrix M is calculated by substituting Equation Eq. A.5 in Equation Eq. A.4.

Now for input q -parameter q_I , since the beam is considered colli-

Figure A.3: Comparison of Gaussian beam in air for 526 nm and 900 nm and their change when propagating through AuNP@SiO₂ and AgNPr@SiO₂ sample columns respectively.

mated, radius of curvature of wavefront $R(z) = \infty$ and waist radius $W(z)$ was found to be ~ 2 mm. Using Equation Eq. A.3, we get

$$\frac{1}{q_I(z)} = \frac{1}{\infty} - j \frac{526, 900 \text{ nm}}{\pi(2 \text{ mm})^2} \quad (\text{Eq. A.6})$$

$$q_I = j8.1604, j13.9626$$

Output beam has a q -parameter q_T , in the sample as

$$q_T = \frac{Aq_I + B}{Cq_I + D} \quad (\text{Eq. A.7})$$

Now $W(z)$ profile inside the sample can be found using imaginary part of q_T^{-1} (from Equations Eq. A.3 and Eq. A.7). Once the $W(z)$

is estimated, the cross-sectional area and thus the fluence $F(z)$ at each height inside the sample can be estimated. Then the average fluence the sample receives is calculated as

$$F_{av} = \frac{1}{h} \int F(z) dz \quad (\text{Eq. A.8})$$

where $h = 10$ mm is the height of the sample. Figure A.3 shows the difference in Gaussian beam profiles at different excitation wavelengths used for our study and corresponding change when passed through samples.

A.2.2 Depth Resolved Fluence

Since there is an absorbance μ_a for the solution, fluence reaching into depths reduces and the depth-resolved optical fluence can be found by modifying Equation Eq. A.8 to the following [116]

$$F_{av} = \frac{1}{h} \int_0^h F(z) e^{-\mu_a(\lambda)z} dz \quad (\text{Eq. A.9})$$

where ' h ' is the height of the sample column through which the Gaussian laser beam propagates, $F(z)$ is the expected fluence for Gaussian beam propagation at each height ' z ' inside the sample, $\mu_a(\lambda)$ is the absorbance or optical density (OD) of the solution during selected wavelength (λ) of irradiation ($\mu_a(526) = 10 \text{ cm}^{-1}$ for AuNP@SiO₂ solution in Chapter 1 and $\mu_a(900) = 4.6734 \text{ cm}^{-1}$ for AgNPr@SiO₂ solution in Chapter 2). The above Equation Eq. A.9 gives us the average fluence (F_{av}) inside the sample under analysis. The sample height was adjusted accordingly to get required fluence. Figure A.4 shows the region where Gaussian beam through samples and the corresponding fluence profile whose average was used for further calculations.

Figure A.4: Region of propagation through which Gaussian beam propagates through AuNP@SiO₂ solution (marked in black) and AgNP@SiO₂ solution (marked in red). The insets show their corresponding fluence profile through the samples.

A.2.3 Transmission Coefficient

Finally, the ambient electric field E_0 is calculated using Poynting vector relation $I_{av} = (E \times H^*)/2$, i.e., $I = (E^2 n c \epsilon_0)/2$ and including a small correction factor of transmission coefficient τ to account of reflection and transmission of light when traveling from air to water. The corrected electric field inside the sample will be $E' = \tau E$, where

$$\tau = \frac{2n_{air}}{n_{sample} + n_{air}}$$

giving a value of $\sim 86\%$ transmission ($\tau = \sim 0.86$).

Appendix B

Optical Parameters of the Materials Used for the Study

B.1 Silica

Figure B.1: Refractive index of fused silica measured at 20°C [106].

B.2 Gold

Figure B.2: Plots showing measured data (solid line), derived from $2nk$ and $k^2 - n^2$ by Otter [31] and fitted data (dotted line) at different temperatures. Top row shows the real and imaginary parts of refractive indices. Bottom row shows the real and imaginary parts of dielectric constants.

B.3 Silver

Figure B.3: Dielectric constant of silver thin film measured by spectroscopic ellipsometry at 300 K. [29].

B.4 Graphene Oxide

Figure B.4: Dielectric constant of single/multiple layers of graphene oxide determined by imaging ellipsometry [150].

B.5 Polyacetylene

The reported dielectric permittivity was found by applying the Kramers-Kronig relations on measured transmittance, reflectance and absorption. The values for trans- isomer (parallel) of polyacetylene were

used for our simulation study as it is similar to the optical response of polydiacetylene.

Figure B.5: Dielectric constant of polyacetylene [189].

Publication

Journal Papers

- (i) Thomas, R., Sreejith, S., Joshi, H., Pedireddy, S., Stuparu, M.C., Zhao, Y. and Soh, C. B., 2016. "Optically Induced Structural Instability in Gold-Silica Nanostructures: A Case Study", *The Journal of Physical Chemistry C*, 120 (20), pp.11230-11236.

DOI: 10.1021/acs.jpcc.6b01662

- (ii) Thomas, R., Phua, S. Z. F., Sreejith, S., Zhao, Y. and Soh, C. B., 2017. "Light Intensity Field Enhancement (LIFE) Induced Localized Edge Abrasion of Silica-Coated Silver Nanoprisms", *Nanoscale*, 9 (40), pp.15356-15361.

DOI: 10.1039/C7NR03171H

- (iii) Thomas, R., Anivind, K., Vishal, K. J., Sreejith, S., Min, L. J., Zhao, Y., Soh, C. B. and Lim, C. T. "Conductive Plasmonic Coupling and Charge Transfer Plasmons in Gold Nanoparticles", (in preparation).

Bibliography

- [1] Helmuth Horvath. Gustav mie and the scattering and absorption of light by particles: Historic developments and basics. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 110(11):787–799, 2009.
- [2] J Alan Creighton and Desmond G Eadon. Ultraviolet–visible absorption spectra of the colloidal metallic elements. *Journal of the Chemical Society, Faraday Transactions*, 87(24):3881–3891, 1991.
- [3] U Kreibig and L Genzel. Optical absorption of small metallic particles. *Surface Science*, 156:678–700, 1985.
- [4] Emilie Ringe, Jeffrey M. McMahon, Kwonnam Sohn, Claire Cobley, Younan Xia, Jiaxing Huang, George C. Schatz, Laurence D. Marks, and Richard P. Van Duyne. Unraveling the effects of size, composition, and substrate on the localized surface plasmon resonance frequencies of gold and silver nanocubes: A systematic single-particle approach. *The Journal of Physical Chemistry C*, 114(29):12511–12516, 2010.
- [5] Titus Sandu. Shape effects on localized surface plasmon resonances in metallic nanoparticles. *Journal of Nanoparticle Research*, 14(6):905, 2012.
- [6] William L Barnes, Alain Dereux, and Thomas W Ebbesen. Surface plasmon subwavelength optics. *Nature*, 424(6950):824–830, 2003.

- [7] John M Ziman. *Principles of the Theory of Solids*. Cambridge university press, 1972.
- [8] Eduardo A Coronado and George C Schatz. Surface plasmon broadening for arbitrary shape nanoparticles: A geometrical probability approach. *The Journal of chemical physics*, 119(7):3926–3934, 2003.
- [9] Gregory V Hartland. Optical studies of dynamics in noble metal nanostructures. *Chemical reviews*, 111(6):3858–3887, 2011.
- [10] Kenji Setoura, Daniel Werner, and Shuichi Hashimoto. Optical scattering spectral thermometry and refractometry of a single gold nanoparticle under cw laser excitation. *The Journal of Physical Chemistry C*, 116(29):15458–15466, 2012.
- [11] F Hache, D Ricard, and Christopher Flytzanis. Optical nonlinearities of small metal particles: surface-mediated resonance and quantum size effects. *JOSA B*, 3(12):1647–1655, 1986.
- [12] WA Kraus and George C Schatz. Plasmon resonance broadening in small metal particles. *The Journal of chemical physics*, 79(12):6130–6139, 1983.
- [13] L Genzel, TP Martin, and U Kreibig. Dielectric function and plasma resonances of small metal particles. *Zeitschrift für Physik B Condensed Matter*, 21(4):339–346, 1975.
- [14] U Kreibig. Electronic properties of small silver particles: the optical constants and their temperature dependence. *Journal of Physics F: Metal Physics*, 4(7):999, 1974.
- [15] Pierre Grua and Herve Bercegol. Dynamics of electrons in metallic nanoinclusions interacting with an intense laser beam. In *Laser-Induced Damage in Optical Materials: 2000*, pages 579–587. International Society for Optics and Photonics, 2001.
- [16] J-Y Bigot, J-Y Merle, O Cregut, and A Daunois. Electron dynamics

- in copper metallic nanoparticles probed with femtosecond optical pulses. *Physical review letters*, 75(25):4702, 1995.
- [17] H Ehrenreich and HR Philipp. Optical properties of ag and cu. *Physical Review*, 128(4):1622, 1962.
- [18] Peter B Johnson and R-W_ Christy. Optical constants of the noble metals. *Physical review B*, 6(12):4370, 1972.
- [19] Pablo G Etchegoin, EC Le Ru, and M Meyer. An analytic model for the optical properties of gold. *The Journal of chemical physics*, 125(16):164705, 2006.
- [20] Aleksandar D Rakić, Aleksandra B Djurišić, Jovan M Elazar, and Marian L Majewski. Optical properties of metallic films for vertical-cavity optoelectronic devices. *Applied optics*, 37(22):5271–5283, 1998.
- [21] Alessandro Alabastri, Salvatore Tuccio, Andrea Giugni, Andrea Toma, Carlo Liberale, Gobind Das, Francesco De Angelis, Enzo Di Fabrizio, and Remo Proietti Zaccaria. Molding of plasmonic resonances in metallic nanostructures: Dependence of the non-linear electric permittivity on system size and temperature. *Materials*, 6(11):4879–4910, 2013.
- [22] Roberto Rojas and F Claro. Theory of surface enhanced raman scattering in colloids. *The Journal of chemical physics*, 98(2):998–1006, 1993.
- [23] DC Marinica, AK Kazansky, P Nordlander, J Aizpurua, and AG Borisov. Quantum plasmonics: nonlinear effects in the field enhancement of a plasmonic nanoparticle dimer. *Nano letters*, 12(3):1333–1339, 2012.
- [24] Allan D Boardman. *Electromagnetic surface modes*. John Wiley & Sons, 1982.
- [25] Yu Luo, AI Fernandez-Dominguez, Aeneas Wiener, Stefan A Maier,

- and JB Pendry. Surface plasmons and nonlocality: a simple model. *Physical review letters*, 111(9):093901, 2013.
- [26] O Ekici, RK Harrison, NJ Durr, DS Eversole, M Lee, and A Ben-Yakar. Thermal analysis of gold nanorods heated with femtosecond laser pulses. *Journal of physics D: Applied physics*, 41(18):185501, 2008.
- [27] Meindert Alexander van Dijk et al. *Nonlinear optical studies of single gold nanoparticles*. Doctoral thesis, Leiden University, 2007.
- [28] Pieter Winsemius, FF Van Kampen, HP Lengkeek, and CG Van Went. Temperature dependence of the optical properties of au, ag and cu. *Journal of Physics F: Metal Physics*, 6(8):1583, 1976.
- [29] S Tripura Sundari, Sharat Chandra, and AK Tyagi. Temperature dependent optical properties of silver from spectroscopic ellipsometry and density functional theory calculations. *Journal of Applied Physics*, 114(3):033515, 2013.
- [30] Philippe Nozières and David Pines. *The theory of quantum liquids*. Perseus, 1999.
- [31] M Otter. Temperaturabhängigkeit der optischen konstanten massiver metalle. *Zeitschrift für Physik A Hadrons and Nuclei*, 161(5):539–549, 1961.
- [32] Rijil Thomas, Sivaramapanicker Sreejith, Hrishikesh Joshi, Srikanth Pedireddy, Mihaela Corina Stuparu, Yanli Zhao, and Soh Cheong Boon. Optically induced structural instability in gold–silica nanostructures: A case study. *The Journal of Physical Chemistry C*, 120(20):11230–11236, 2016.
- [33] SI Anisimov, BL Kapeliovich, and TL Perelman. Electron emission from metal surfaces exposed to ultrashort laser pulses. *Zh. Eksp. Teor. Fiz*, 66(776):375–377, 1974.

- [34] CL Tien and TQ Qiu. Heat transfer mechanism during short pulse laser heating of metals. *American Society of Mechanical Engineers Journal of Heat Transfer*, 115:835–841, 1993.
- [35] JK Chen and JE Beraun. Numerical study of ultrashort laser pulse interactions with metal films. *Numerical Heat Transfer: Part A: Applications*, 40(1):1–20, 2001.
- [36] Renat R Letfullin, Thomas F George, Galen C Duree, and Brett M Bollinger. Ultrashort laser pulse heating of nanoparticles: comparison of theoretical approaches. *Advances in Optical Technologies*, 2008, 2008.
- [37] Michael I Mishchenko, Joachim W Hovenier, and Larry D Travis. *Light scattering by nonspherical particles: theory, measurements, and applications*. Academic press, 1999.
- [38] Viktor Myroshnychenko, Jessica Rodríguez-Fernández, Isabel Pastoriza-Santos, Alison M Funston, Carolina Novo, Paul Mulvaney, Luis M Liz-Marzán, and F Javier Garcia de Abajo. Modelling the optical response of gold nanoparticles. *Chemical Society Reviews*, 37(9):1792–1805, 2008.
- [39] Nathan Ida. *Numerical modeling for electromagnetic non-destructive evaluation*, volume 1. Springer Science & Business Media, 1994.
- [40] Allen Taflove and Susan C Hagness. *Computational electrodynamics*. Artech house, 2005.
- [41] Christian Hafner. Post-modern electromagnetics. *John Wihley*, 1999.
- [42] Michael I Mishchenko, Larry D Travis, and Andrew A Lacis. *Scattering, absorption, and emission of light by small particles*. Cambridge university press, 2002.
- [43] Amit Kumar, Sungi Kim, and Jwa-Min Nam. Plasmonically en-

- gineered nanoprobes for biomedical applications. *Journal of the American Chemical Society*, 138(44):14509–14525, 2016.
- [44] Shuming Nie and Steven R Emory. Probing single molecules and single nanoparticles by surface-enhanced raman scattering. *science*, 275(5303):1102–1106, 1997.
- [45] Yi Fu, Jian Zhang, and Joseph R Lakowicz. Plasmon-enhanced fluorescence from single fluorophores end-linked to gold nanorods. *Journal of the American Chemical Society*, 132(16):5540–5541, 2010.
- [46] Jon A Dieringer, Adam D McFarland, Nilam C Shah, Douglas A Stuart, Alyson V Whitney, Chanda R Yonzon, Matthew A Young, Xiaoyu Zhang, and Richard P Van Duyne. Introductory lecture surface enhanced raman spectroscopy: new materials, concepts, characterization tools, and applications. *Faraday discussions*, 132:9–26, 2006.
- [47] Pm Andrew and WL Barnes. Energy transfer across a metal film mediated by surface plasmon polaritons. *Science*, 306(5698):1002–1005, 2004.
- [48] David J Bergman and Mark I Stockman. Surface plasmon amplification by stimulated emission of radiation: quantum generation of coherent surface plasmons in nanosystems. *Physical review letters*, 90(2):027402, 2003.
- [49] Katherine A Willets and Richard P Van Duyne. Localized surface plasmon resonance spectroscopy and sensing. *Annu. Rev. Phys. Chem.*, 58:267–297, 2007.
- [50] Jeffrey N Anker, W Paige Hall, Olga Lyandres, Nilam C Shah, Jing Zhao, and Richard P Van Duyne. Biosensing with plasmonic nanosensors. *Nature materials*, 7(6):442–453, 2008.
- [51] Martin A Green and Supriya Pillai. Harnessing plasmonics for solar

- cells. *Nature Photonics*, 6(3):130–132, 2012.
- [52] Jing Zhao, Xiaoyu Zhang, Chanda Ranjit Yonzon, Amanda J Haes, and Richard P Van Duyne. Localized surface plasmon resonance biosensors. *Nanomedicine*, 1(2):219–228, 2006.
- [53] Xiaofeng Fan, Weitao Zheng, and David J Singh. Light scattering and surface plasmons on small spherical particles. *Light: Science & Applications*, 3(6):e179, 2014.
- [54] Mary-Margaret Seale-Goldsmith and James F Leary. Nanobiosystems. *Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology*, 1(5):553–567, 2009.
- [55] Georgios A Sotiriou. Biomedical applications of multifunctional plasmonic nanoparticles. *Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology*, 5(1):19–30, 2013.
- [56] Alessandro Feis, Cristina Gellini, Pier Remigio Salvi, and Maurizio Becucci. Photoacoustic excitation profiles of gold nanoparticles. *Photoacoustics*, 2(1):47–53, 2014.
- [57] Mohammad E Khosroshahi and Andreas Mandelis. Combined photoacoustic ultrasound and beam deflection signal monitoring of gold nanoparticle agglomerate concentrations in tissue phantoms using a pulsed nd: Yag laser. *International Journal of Thermophysics*, 36(5-6):880–890, 2015.
- [58] Sivaramapanicker Sreejith, Tran Thi Mai Huong, Parijat Borah, and Yanli Zhao. Organic–inorganic nanohybrids for fluorescence, photoacoustic and raman bioimaging. *Science Bulletin*, 60(7):665–678, 2015.
- [59] Aneta J Mieszawska, Willem JM Mulder, Zahi A Fayad, and David P Cormode. Multifunctional gold nanoparticles for diagnosis and therapy of disease. *Molecular pharmaceuticals*, 10(3):831, 2013.
- [60] Jun Xia, Chulhong Kim, and Jonathan F Lovell. Opportuni-

- ties for photoacoustic-guided drug delivery. *Current drug targets*, 16(6):571–581, 2015.
- [61] Swarup Kumar Maji, Sivaramapanicker Sreejith, James Joseph, Manjing Lin, Tingchao He, Yan Tong, Handong Sun, Sidney Wing-Kwong Yu, and Yanli Zhao. Upconversion nanoparticles as a contrast agent for photoacoustic imaging in live mice. *Advanced Materials*, 26(32):5633–5638, 2014.
- [62] Alexander O Govorov and Hugh H Richardson. Generating heat with metal nanoparticles. *Nano today*, 2(1):30–38, 2007.
- [63] Chakkooth Vijayakumar, Bijitha Balan, Akinori Saeki, Tetsuya Tsuda, Susumu Kuwabata, and Shu Seki. Gold nanoparticle assisted self-assembly and enhancement of charge carrier mobilities of a conjugated polymer. *The Journal of Physical Chemistry C*, 116(33):17343–17350, 2012.
- [64] Aniruddha Ray, Ananya Mukundan, Zhixing Xie, Leshern Karamchand, Xueding Wang, and Raoul Kopelman. Highly stable polymer coated nano-clustered silver plates: a multimodal optical contrast agent for biomedical imaging. *Nanotechnology*, 25(44):445104, 2014.
- [65] Geoffrey P Luke, Ashvin Bashyam, Kimberly A Homan, Suraj Makhija, Yun-Sheng Chen, and Stanislav Y Emelianov. Silica-coated gold nanoplates as stable photoacoustic contrast agents for sentinel lymph node imaging. *Nanotechnology*, 24(45):455101, 2013.
- [66] Lakshmi V Nair, Shaiju S Nazeer, Ramapurath S Jayasree, and Ayyappanpillai Ajayaghosh. Fluorescence imaging assisted photodynamic therapy using photosensitizer-linked gold quantum clusters. *ACS nano*, 9(6):5825–5832, 2015.
- [67] Xinjian Yang, Yuqian Ren, and Zhiqiang Gao. Silver/gold core–

- shell nanoprism-based plasmonic nanoprobe for highly sensitive and selective detection of hydrogen sulfide. *Chemistry—A European Journal*, 21(3):988–992, 2015.
- [68] Alexandre Garreau, Mohammadali Tabatabaei, Renjie Hou, Gregory Q Wallace, Peter R Norton, and François Lagugné-Labarthet. Probing the plasmonic properties of heterometallic nanoprisms with near-field fluorescence microscopy. *The Journal of Physical Chemistry C*, 120(36):20267–20276, 2016.
- [69] Mohammad M Shahjamali, Yong Zhou, Negin Zaree, Can Xue, Jinsong Wu, Nicolas Large, C Michael McGuirk, Freddy Boey, Vinayak Dravid, Zhifeng Cui, George C Schatz, and Chad A Mirkin. Ag-ag₂s hybrid nanoprisms: Structural versus plasmonic evolution. *ACS nano*, 10(5):5362–5373, 2016.
- [70] Jatish Kumar, Xingzhan Wei, Steven Barrow, Alison M Funston, K George Thomas, and Paul Mulvaney. Surface plasmon coupling in end-to-end linked gold nanorod dimers and trimers. *Physical Chemistry Chemical Physics*, 15(12):4258–4264, 2013.
- [71] Steven J Barrow, Xingzhan Wei, Julia S Baldauf, Alison M Funston, and Paul Mulvaney. The surface plasmon modes of self-assembled gold nanocrystals. *Nature communications*, 3:1275, 2012.
- [72] Padmanabhan Pramod and K George Thomas. Plasmon coupling in dimers of au nanorods. *Advanced Materials*, 20(22):4300–4305, 2008.
- [73] Carsten Sönnichsen, Björn M Reinhard, Jan Liphardt, and A Paul Alivisatos. A molecular ruler based on plasmon coupling of single gold and silver nanoparticles. *Nature biotechnology*, 23(6):741–745, 2005.
- [74] Tamitake Itoh, Vasudevanpillai Biju, Mitsuru Ishikawa, Yasuo Kikkawa, Kazuhiro Hashimoto, Akifumi Ikehata, and Yukihiro Ozaki.

- Surface-enhanced resonance raman scattering and background light emission coupled with plasmon of single ag nanoaggregates. *The Journal of chemical physics*, 124(13):134708, 2006.
- [75] Athiyannathil Sujith, Tamitake Itoh, Hiroko Abe, Abdul Aziz Anas, Kenichi Yoshida, Vasudevanpillai Biju, and Mitsuru Ishikawa. Surface enhanced raman scattering analyses of individual silver nanoaggregates on living single yeast cell wall. *Applied Physics Letters*, 92(10):103901, 2008.
- [76] Robert Williams Wood. On a remarkable case of uneven distribution of light in a diffraction grating spectrum. *Proceedings of the Physical Society of London*, 18(1):269, 1902.
- [77] Erwin Kretschmann and Heinz Raether. Notizen: radiative decay of non radiative surface plasmons excited by light. *Zeitschrift für Naturforschung A*, 23(12):2135–2136, 1968.
- [78] Andreas Otto. Excitation of nonradiative surface plasma waves in silver by the method of frustrated total reflection. *Zeitschrift für Physik*, 216(4):398–410, 1968.
- [79] Alyson V Whitney, Jeffrey W Elam, Shengli Zou, Alex V Zinovev, Peter C Stair, George C Schatz, and Richard P Van Duyne. Localized surface plasmon resonance nanosensor: a high-resolution distance-dependence study using atomic layer deposition. *The Journal of Physical Chemistry B*, 109(43):20522–20528, 2005.
- [80] Amanda J Haes, Shengli Zou, George C Schatz, and Richard P Van Duyne. A nanoscale optical biosensor: the long range distance dependence of the localized surface plasmon resonance of noble metal nanoparticles. *The Journal of Physical Chemistry B*, 108(1):109–116, 2004.
- [81] Andrew C Tam. Applications of photoacoustic sensing techniques. *Reviews of Modern Physics*, 58(2):381, 1986.

- [82] Hideaki Kurita, Akinori Takami, and Seiichiro Koda. Size reduction of gold particles in aqueous solution by pulsed laser irradiation. *Applied Physics Letters*, 72(7):789–791, 1998.
- [83] Daniel Werner and Shuichi Hashimoto. Controlling the pulsed-laser-induced size reduction of au and ag nanoparticles via changes in the external pressure, laser intensity, and excitation wavelength. *Langmuir*, 29(4):1295–1302, 2013.
- [84] Michael Strasser, Kenji Setoura, Uwe Langbein, and Shuichi Hashimoto. Computational modeling of pulsed laser-induced heating and evaporation of gold nanoparticles. *The Journal of Physical Chemistry C*, 118(44):25748–25755, 2014.
- [85] Stephan Link, Clemens Burda, B Nikoobakht, and Mostafa A El-Sayed. Laser-induced shape changes of colloidal gold nanorods using femtosecond and nanosecond laser pulses. *The Journal of Physical Chemistry B*, 104(26):6152–6163, 2000.
- [86] Daniel Werner and Shuichi Hashimoto. Improved working model for interpreting the excitation wavelength-and fluence-dependent response in pulsed laser-induced size reduction of aqueous gold nanoparticles. *The Journal of Physical Chemistry C*, 115(12):5063–5072, 2010.
- [87] Zhanliang Sun. *Pulsed laser induced breakdown in solid state materials and air*. PhD thesis, 2015.
- [88] Arlee V Smith and Binh T Do. Bulk and surface laser damage of silica by picosecond and nanosecond pulses at 1064 nm. *Applied optics*, 47(26):4812–4832, 2008.
- [89] Luke A Emmert and Wolfgang Rudolph. *Laser-Induced Damage in Optical Materials*, chapter Femtodecond Laser-Induced Damage in Dielectric Materials, pages 127–151. CRC Press, 2015.
- [90] Zhilin Xia, Dawei Li, Yuan'an Zhao, and Yuting Wu. New damage

- behavior induced by nanosecond laser pulses on the surface of silica films. *Optics & Laser Technology*, 46:77–80, 2013.
- [91] Hervé Bercegol, Florian Bonneau, Philippe Bouchut, Patrick Combis, J Donohue, Laurent Gallais, Laurent Lamaignère, Carol Le Diraison, Marc Loiseau, Jean-Yves Natoli, et al. Laser ablation of fused silica induced by gold nanoparticles: comparison of simulations and experiments at $\lambda = 351$ nm. In *International Symposium on High-Power Laser Ablation 2002*, pages 1055–1066. International Society for Optics and Photonics, 2002.
- [92] Florian Bonneau, Patrick Combis, Jean-Luc Rullier, J Vierne, M Pellin, M Savina, M Broyer, E Cottancin, J Tuillon, M Pellarin, et al. Study of uv laser interaction with gold nanoparticles embedded in silica. *Applied Physics B: Lasers and Optics*, 75(8):803–815, 2002.
- [93] Michael D Feit and Alexander M Rubenchik. Influence of subsurface cracks on laser-induced surface damage. In *XXXV Annual Symposium on Optical Materials for High Power Lasers: Boulder Damage Symposium*, pages 264–272. International Society for Optics and Photonics, 2004.
- [94] Xiang Gao, Guoying Feng, Jinghua Han, and Lingling Zhai. Investigation of laser-induced damage by various initiators on the subsurface of fused silica. *Optics express*, 20(20):22095–22101, 2012.
- [95] Runni Tian, Rong Qiu, Yong Jiang, and Junbo Wang. Study on laser intensity modulation by spherical inclusion in silica subsurface. In *The International Conference on Photonics and Optical Engineering and the Annual West China Photonics Conference (icPOE 2014)*, pages 94493U–94493U. International Society for Optics and Photonics, 2015.
- [96] Hiroyuki Yoshikawa, Togo Matsui, and Hiroshi Masuhara. Re-

- versible assembly of gold nanoparticles confined in an optical microcage. *Physical Review E*, 70(6):061406, 2004.
- [97] Fangfang Wen, Yue Zhang, Samuel Gottheim, Nicholas S King, Yu Zhang, Peter Nordlander, and Naomi J Halas. Charge transfer plasmons: Optical frequency conductances and tunable infrared resonances. *ACS Nano*, 9(6):6428–6435, 2015.
- [98] Alemayehu Nana Koya and Jingquan Lin. Charge transfer plasmons: Recent theoretical and experimental developments. *Applied Physics Reviews*, 4(2):021104, 2017.
- [99] Yun-Sheng Chen, Wolfgang Frey, Seungsoo Kim, Pieter Kruizinga, Kimberly Homan, and Stanislav Emelianov. Silica-coated gold nanorods as photoacoustic signal nano-amplifiers. *Nano letters*, 11(2):348, 2011.
- [100] Yun-Sheng Chen, Wolfgang Frey, Seungsoo Kim, Kimberly Homan, Pieter Kruizinga, Konstantin Sokolov, and Stanislav Emelianov. Enhanced thermal stability of silica-coated gold nanorods for photoacoustic imaging and image-guided therapy. *Optics express*, 18(9):8867–8878, 2010.
- [101] A Soltan Monem, Nihal Elbialy, and Noha Mohamed. Mesoporous silica coated gold nanorods loaded doxorubicin for combined chemo–photothermal therapy. *International journal of pharmaceuticals*, 470(1):1–7, 2014.
- [102] Shun Shen, Hongyan Tang, Xiaotong Zhang, Jinfeng Ren, Zhiqing Pang, Dangge Wang, Huile Gao, Yong Qian, Xinguo Jiang, and Wuli Yang. Targeting mesoporous silica-encapsulated gold nanorods for chemo-photothermal therapy with near-infrared radiation. *Biomaterials*, 34(12):3150–3158, 2013.
- [103] Sivaramapanicker Sreejith, James Joseph, Kim Truc Nguyen, Vadakke Matham Murukeshan, Sun Woh Lye, and Yanli Zhao.

- Graphene oxide wrapping of gold–silica core–shell nanohybrids for photoacoustic signal generation and bimodal imaging. *Chem-NanoMat*, 1(1):39–45, 2015.
- [104] Douglas B Leviton and Bradley J Frey. Temperature-dependent absolute refractive index measurements of synthetic fused silica. In *SPIE Astronomical Telescopes+ Instrumentation*, pages 62732K–62732K. International Society for Optics and Photonics, 2006.
- [105] Yong Guo, Zhi-Yong Wang, Qi Qiu, Jun Su, Yunxiang Wang, Shuangjin Shi, and Zhenfang Yu. Theoretical and experimental investigations on the temperature dependence of the refractive index of amorphous silica. *Journal of Non-Crystalline Solids*, 429:198–201, 2015.
- [106] IH Malitson. Interspecimen comparison of the refractive index of fused silica*. *Josa*, 55(10):1205–1209, 1965.
- [107] OA Yeshchenko, IS Bondarchuk, VS Gurin, IM Dmitruk, and AV Kotko. Temperature dependence of the surface plasmon resonance in gold nanoparticles. *Surface Science*, 608:275–281, 2013.
- [108] Viktor K Pustovalov. Theoretical study of heating of spherical nanoparticle in media by short laser pulses. *Chemical Physics*, 308(1):103–108, 2005.
- [109] Daniel Werner, Shuichi Hashimoto, Takayuki Uwada, et al. Remarkable photothermal effect of interband excitation on nanosecond laser-induced reshaping and size reduction of pseudospherical gold nanoparticles in aqueous solution. *Langmuir*, 26(12):9956–9963, 2010.
- [110] Ali Hatef, Behafarid Darvish, Adrien Dagallier, Yevgeniy R Davletshin, William Johnston, J Carl Kumaradas, David Rioux, and Michel Meunier. Analysis of photoacoustic response from gold–silver alloy nanoparticles irradiated by short pulsed laser in water. *The Journal*

of *Physical Chemistry C*, 119(42):24075–24080, 2015.

- [111] Jacob Lubliner. *Plasticity theory*. Courier Corporation, 2008.
- [112] Samy Merabia, Sergei Shenogin, Laurent Joly, Pawel Koblinski, and Jean-Louis Barrat. Heat transfer from nanoparticles: A corresponding state analysis. *Proceedings of the National Academy of Sciences*, 106(36):15113–15118, 2009.
- [113] Kun Zheng, Chengcai Wang, Yong-Qiang Cheng, Yonghai Yue, Xiaodong Han, Ze Zhang, Zhiwei Shan, Scott X Mao, Miaomiao Ye, Yadong Yin, et al. Electron-beam-assisted superplastic shaping of nanoscale amorphous silica. *Nature communications*, 1:24, 2010.
- [114] Yonghai Yue and Kun Zheng. Strong strain rate effect on the plasticity of amorphous silica nanowires. *Applied Physics Letters*, 104(23):231906, 2014.
- [115] Lihong V Wang. Tutorial on photoacoustic microscopy and computed tomography. *IEEE Journal of Selected Topics in Quantum Electronics*, 14(1):171–179, 2008.
- [116] Jing Wang, Tan Liu, Shuliang Jiao, Ruimin Chen, Qifa Zhou, K Kirk Shung, Lihong V Wang, and Hao F Zhang. Saturation effect in functional photoacoustic imaging. *Journal of biomedical optics*, 15(2):021317–021317, 2010.
- [117] Junjie Yao and Lihong V Wang. Sensitivity of photoacoustic microscopy. *Photoacoustics*, 2(2):87–101, 2014.
- [118] Carolyn L Bayer, Seung Yun Nam, Yun-Sheng Chen, and Stanislav Y Emelianov. Photoacoustic signal amplification through plasmonic nanoparticle aggregation. *Journal of biomedical optics*, 18(1):016001–016001, 2013.
- [119] Salavat Aglyamov, Suhyun Park, Jignesh Shah, and Stanislav Emelianov. Role of photoacoustic and ultrasound imaging in photothermal therapy. In *Photoacoustic Imaging and Spectroscopy*,

pages 481–491. CRC Press, 2009.

- [120] Gerald J Diebold, Andrew C Beveridge, and Theron J Hamilton. The photoacoustic effect generated by an incompressible sphere. *The Journal of the Acoustical Society of America*, 112(5):1780–1786, 2002.
- [121] Yun-Sheng Chen, Wolfgang Frey, Salavat Aglyamov, and Stanislav Emelianov. Environment-dependent generation of photoacoustic waves from plasmonic nanoparticles. *Small*, 8(1):47–52, 2012.
- [122] Alexander Kuhlicke, Stefan Schietinger, Christian Matyssek, Kurt Busch, and Oliver Benson. In situ observation of plasmon tuning in a single gold nanoparticle during controlled melting. *Nano letters*, 13(5):2041–2046, 2013.
- [123] Eshel Faraggi, Shijun Wang, and Bernard Gerstman. Stress confinement, shock wave formation, and laser-induced damage. In *Bio-medical Optics 2005*, pages 209–215. International Society for Optics and Photonics, 2005.
- [124] Werner Stöber, Arthur Fink, and Ernst Bohn. Controlled growth of monodisperse silica spheres in the micron size range. *Journal of colloid and interface science*, 26(1):62–69, 1968.
- [125] Bruno Palpant, Yannick Guillet, Majid Rashidi-Huyeh, and Dominique Prot. Gold nanoparticle assemblies: Thermal behaviour under optical excitation. *Gold Bulletin*, 41(2):105–115, 2008.
- [126] Christy L. Haynes and Richard P. Van Duyne. Nanosphere lithography: A versatile nanofabrication tool for studies of size-dependent nanoparticle optics. *The Journal of Physical Chemistry B*, 105(24):5599–5611, 2001.
- [127] Michelle Duval Malinsky, K Lance Kelly, George C Schatz, and Richard P Van Duyne. Chain length dependence and sensing capabilities of the localized surface plasmon resonance of

- silver nanoparticles chemically modified with alkanethiol self-assembled monolayers. *Journal of the American Chemical Society*, 123(7):1471–1482, 2001.
- [128] Amanda J Haes and Richard P Van Duyne. A nanoscale optical biosensor: sensitivity and selectivity of an approach based on the localized surface plasmon resonance spectroscopy of triangular silver nanoparticles. *Journal of the American Chemical Society*, 124(35):10596–10604, 2002.
- [129] Leif J Sherry, Rongchao Jin, Chad A Mirkin, George C Schatz, and Richard P Van Duyne. Localized surface plasmon resonance spectroscopy of single silver triangular nanoprisms. *Nano letters*, 6(9):2060–2065, 2006.
- [130] Isabel Pastoriza-Santos and Luis M Liz-Marzán. Colloidal silver nanoplates. state of the art and future challenges. *Journal of Materials Chemistry*, 18(15):1724–1737, 2008.
- [131] Jonathan C Riboh, Amanda J Haes, Adam D McFarland, C Ranjit Yonzon, and Richard P Van Duyne. A nanoscale optical biosensor: real-time immunoassay in physiological buffer enabled by improved nanoparticle adhesion. *Journal of Physical Chemistry B*, 107(8):1772–1780, 2003.
- [132] Amanda J. Haes, W. Paige Hall, Lei Chang, William L. Klein, and Richard P. Van Duyne. A localized surface plasmon resonance biosensor: First steps toward an assay for alzheimer’s disease. *Nano Letters*, 4(6):1029–1034, 2004.
- [133] Denise E Charles, Damian Aherne, Matthew Gara, Deirdre M Ledwith, Yurii K Gun’ko, John M Kelly, Werner J Blau, and Margaret E Brennan-Fournet. Versatile solution phase triangular silver nanoplates for highly sensitive plasmon resonance sensing. *Acs Nano*, 4(1):55–64, 2009.

- [134] Ignác Capek. *DNA Engineered Noble Metal Nanoparticles: Fundamentals and State-of-the-art-of Nanobiotechnology*. John Wiley & Sons, Inc., Hoboken, NJ, USA, 2015.
- [135] Kimberly A Homan, Michael Souza, Ryan Truby, Geoffrey P Luke, Christopher Green, Erika Vreeland, and Stanislav Emelianov. Silver nanoplate contrast agents for in vivo molecular photoacoustic imaging. *ACS nano*, 6(1):641, 2012.
- [136] Min Hu, Carolina Novo, Alison Funston, Haining Wang, Hristina Staleva, Shengli Zou, Paul Mulvaney, Younan Xia, and Gregory V Hartland. Dark-field microscopy studies of single metal nanoparticles: understanding the factors that influence the linewidth of the localized surface plasmon resonance. *Journal of materials chemistry*, 18(17):1949–1960, 2008.
- [137] Yu Kyung Tak, Sukdeb Pal, Pravin K Naoghare, Sabarinathan Ranganasamy, and Joon Myong Song. Shape-dependent skin penetration of silver nanoparticles: does it really matter? *Scientific reports*, 5, 2015.
- [138] D Patrick O’Neal, Leon R Hirsch, Naomi J Halas, J Donald Payne, and Jennifer L West. Photo-thermal tumor ablation in mice using near infrared-absorbing nanoparticles. *Cancer letters*, 209(2):171–176, 2004.
- [139] J Jayabalan, Asha Singh, and Rama Chari. Effect of edge smoothening on the extinction spectra of metal nanoparticles. *Applied Physics Letters*, 97(4):041904, 2010.
- [140] Bartłomiej Grzeńkiewicz, Krzysztof Ptaszyński, and Michał Kotkowiak. Near and far-field properties of nanoprisms with rounded edges. *Plasmonics*, 9(3):607–614, 2014.
- [141] Tomohiro Mori, Kenzo Yamaguchi, Yasuhiro Tanaka, Yoshifumi Suzuki, and Masanobu Haraguchi. Optical characteristics of

- rounded silver nanoprisms. *Optical Review*, 23(2):260–264, 2016.
- [142] Dinggeng He, Xiaoxiao He, Kemin Wang, Zhen Zou, Xue Yang, and Xuecai Li. Remote-controlled drug release from graphene oxide-capped mesoporous silica to cancer cells by photoinduced ph-jump activation. *Langmuir*, 30(24):7182–7189, 2014.
- [143] Xing Ma, Qiuyu Qu, Yun Zhao, Zhong Luo, Yang Zhao, Kee Woei Ng, and Yanli Zhao. Graphene oxide wrapped gold nanoparticles for intracellular raman imaging and drug delivery. *Journal of Materials Chemistry B*, 1(47):6495–6500, 2013.
- [144] Sung Myung, Aniruddh Solanki, Cheoljin Kim, Jaesung Park, Kwang S Kim, and Ki-Bum Lee. Graphene-encapsulated nanoparticle-based biosensor for the selective detection of cancer biomarkers. *Advanced Materials*, 23(19):2221–2225, 2011.
- [145] Sivaramapanicker Sreejith, Xing Ma, and Yanli Zhao. Graphene oxide wrapping on squaraine-loaded mesoporous silica nanoparticles for bioimaging. *Journal of the American Chemical Society*, 134(42):17346–17349, 2012.
- [146] Sungjin Kim, Sook Hee Ku, Seong Yoon Lim, Jae Hong Kim, and Chan Beum Park. Graphene–biomineral hybrid materials. *Advanced Materials*, 23(17):2009–2014, 2011.
- [147] Qing Wang, Qing Li, Xiaohai Yang, Kemin Wang, Shasha Du, Hua Zhang, and Yajie Nie. Graphene oxide–gold nanoparticles hybrids-based surface plasmon resonance for sensitive detection of microRNA. *Biosensors and Bioelectronics*, 77:1001–1007, 2016.
- [148] Sivaramapanicker Sreejith, Hrishikesh Joshi, and Yanli Zhao. *Graphene-Based Materials in Biosensing, Bioimaging, and Therapeutics*, pages 35–61. Springer International Publishing, Cham, 2016.
- [149] Eden Morales-Narváez, Livia Florio Sgobbi, Sergio Antonio Spinola

- Machado, and Arben Merkoçi. Graphene-encapsulated materials: Synthesis, applications and trends. *Progress in Materials Science*, 86:1 – 24, 2017.
- [150] Inhwa Jung, Matthias Vaupel, Matthew Pelton, Richard Piner, Dmitriy A Dikin, Sasha Stankovich, Jinho An, and Rodney S Ruoff. Characterization of thermally reduced graphene oxide by imaging ellipsometry. *The Journal of Physical Chemistry C*, 112(23):8499–8506, 2008.
- [151] CM Osburn and EJ Weitzman. Electrical conduction and dielectric breakdown in silicon dioxide films on silicon. *Journal of the Electrochemical Society*, 119(5):603–609, 1972.
- [152] BC Stuart, MD Feit, S Herman, AM Rubenchik, BW Shore, and MD Perry. Nanosecond-to-femtosecond laser-induced breakdown in dielectrics. *Physical review B*, 53(4):1749, 1996.
- [153] Guido Mann, Simone Pentzien, and Jörg Krüger. Beam diameter dependence of surface damage threshold of fused silica fibers and preforms for nanosecond laser treatment at 1064nm wavelength. *Applied Surface Science*, 276:312–316, 2013.
- [154] Jinghua Han, Yaguo Li, Changtao He, Qiuhui Zhang, Ruihua Niu, Liming Yang, and Guoying Feng. Effects of laser plasma on damage in optical glass induced by pulsed lasers. *Optical Engineering*, 51(12):121809–1, 2012.
- [155] Stavros G Demos, Raluca A Negres, Rajesh N Raman, Alexander M Rubenchik, and Michael D Feit. Material response during nanosecond laser induced breakdown inside of the exit surface of fused silica. *Laser & Photonics Reviews*, 7(3):444–452, 2013.
- [156] Wolfgang Rudolph, Luke Emmert, Zhanliang Sun, Dinesh Patel, and Carmen Menoni. Laser damage in dielectric films: What we know and what we don't. In *SPIE Laser Damage*, pages 888516–

888516. International Society for Optics and Photonics, 2013.
- [157] Rafael R Gattass and Eric Mazur. Femtosecond laser micromachining in transparent materials. *Nature photonics*, 2(4):219, 2008.
 - [158] Nicolaas Bloembergen. Laser-induced electric breakdown in solids. *IEEE Journal of Quantum Electronics*, 10(3):375–386, 1974.
 - [159] William S Hummers Jr and Richard E Offeman. Preparation of graphitic oxide. *Journal of the American Chemical Society*, 80(6):1339–1339, 1958.
 - [160] Liguang Xu, Maozhong Sun, Wei Ma, Hua Kuang, and Chuanlai Xu. Self-assembled nanoparticle dimers with contemporarily relevant properties and emerging applications. *Materials Today*, 19(10):595–606, 2016.
 - [161] Ming-Qiang Zhu, Li-Qiong Wang, Gregory J Exarhos, and Alexander DQ Li. Thermosensitive gold nanoparticles. *Journal of the American Chemical Society*, 126(9):2656–2657, 2004.
 - [162] Christopher J Orendorff, Patrick L Hankins, and Catherine J Murphy. pH-triggered assembly of gold nanorods. *Langmuir*, 21(5):2022–2026, 2005.
 - [163] Yi Shen, Min Kuang, Zhong Shen, Jörg Nieberle, Hongwei Duan, and Holger Frey. Gold nanoparticles coated with a thermosensitive hyperbranched polyelectrolyte: towards smart temperature and pH nanosensors. *Angewandte Chemie International Edition*, 47(12):2227–2230, 2008.
 - [164] Ximei Qian, Jun Li, and Shuming Nie. Stimuli-responsive sensors nanoparticles: conformational control of plasmonic coupling and surface raman enhancement. *Journal of the American Chemical Society*, 131(22):7540–7541, 2009.
 - [165] Saide Z Nergiz and Srikanth Singamaneni. Reversible tuning of plasmon coupling in gold nanoparticle chains using ultrathin

- responsive polymer film. *ACS applied materials & interfaces*, 3(4):945–951, 2011.
- [166] Malte S Strozyk, Munish Chanana, Isabel Pastoriza-Santos, Jorge Pérez-Juste, and Luis M Liz-Marzán. Protein/polymer-based dual-responsive gold nanoparticles with ph-dependent thermal sensitivity. *Advanced Functional Materials*, 22(7):1436–1444, 2012.
- [167] Ke Zhang, Xiao Zhu, Fei Jia, Evelyn Auyeung, and Chad A Mirkin. Temperature-activated nucleic acid nanostructures. *Journal of the American Chemical Society*, 135(38):14102–14105, 2013.
- [168] Fei Han, Alexander H Soeriyadi, SRC Vivekchand, and J Justin Gooding. Simple method for tuning the optical properties of thermoresponsive plasmonic nanogels. *ACS Macro Letters*, 5(5):626–630, 2016.
- [169] KK Caswell, James N Wilson, Uwe HF Bunz, and Catherine J Murphy. Preferential end-to-end assembly of gold nanorods by biotin-streptavidin connectors. *Journal of the American Chemical Society*, 125(46):13914–13915, 2003.
- [170] K George Thomas, Said Barazzouk, Binil Itty Ipe, ST Shibu Joseph, and Prashant V Kamat. Uniaxial plasmon coupling through longitudinal self-assembly of gold nanorods. *The Journal of Physical Chemistry B*, 108(35):13066–13068, 2004.
- [171] PK Sudeep, ST Shibu Joseph, and K George Thomas. Selective detection of cysteine and glutathione using gold nanorods. *Journal of the American Chemical Society*, 127(18):6516–6517, 2005.
- [172] Shan Lin, Mei Li, Erik Dujardin, Christian Girard, and Stephen Mann. One-dimensional plasmon coupling by facile self-assembly of gold nanoparticles into branched chain networks. *Advanced Materials*, 17(21):2553–2559, 2005.
- [173] Anand Gole and Catherine J Murphy. Biotin- streptavidin-induced

- aggregation of gold nanorods: Tuning rod-rod orientation. *Langmuir*, 21(23):10756–10762, 2005.
- [174] ST Shibu Joseph, Binil Itty Ipe, P Pramod, and K George Thomas. Gold nanorods to nanochains: mechanistic investigations on their longitudinal assembly using α , ω -alkanedithiols and interplasmon coupling. *The Journal of Physical Chemistry B*, 110(1):150–157, 2006.
- [175] Gretchen A DeVries, Markus Brunnbauer, Ying Hu, Alicia M Jackson, Brenda Long, Brian T Neltner, Oktay Uzun, Benjamin H Wunsch, and Francesco Stellacci. Divalent metal nanoparticles. *Science*, 315(5810):358–361, 2007.
- [176] Jonathan A Fan, Chihhui Wu, Kui Bao, Jiming Bao, Rizia Bardhan, Naomi J Halas, Vinothan N Manoharan, Peter Nordlander, Genady Shvets, and Federico Capasso. Self-assembled plasmonic nanoparticle clusters. *science*, 328(5982):1135–1138, 2010.
- [177] Nicolas Pazos-Perez, Claudia Simone Wagner, Jose M Romo-Herrera, Luis M Liz-Marzán, F Javier García de Abajo, Alexander Wittemann, Andreas Fery, and Ramón A Alvarez-Puebla. Organized plasmonic clusters with high coordination number and extraordinary enhancement in surface-enhanced raman scattering (sers). *Angewandte Chemie International Edition*, 51(51):12688–12693, 2012.
- [178] Wei Ma, Hua Kuang, Libing Wang, Liguang Xu, Wei-Shun Chang, Huanan Zhang, Maozhong Sun, Yinyue Zhu, Yuan Zhao, Liqiang Liu, et al. Chiral plasmonics of self-assembled nanorod dimers. *Scientific reports*, 3, 2013.
- [179] Bo Gao, Yahya Alvi, David Rosen, Marvin Lav, and Andrea R Tao. Designer nanojunctions: orienting shaped nanoparticles within polymer thin-film nanocomposites. *Chemical Communications*,

49(39):4382–4384, 2013.

- [180] David A Rosen and Andrea R Tao. Modeling the optical properties of bowtie antenna generated by self-assembled ag triangular nanoprisms. *ACS applied materials & interfaces*, 6(6):4134–4142, 2014.
- [181] O Pérez-González, N Zabala, AG Borisov, NJ Halas, P Nordlander, and J Aizpurua. Optical spectroscopy of conductive junctions in plasmonic cavities. *Nano Letters*, 10(8):3090–3095, 2010.
- [182] Jake Fontana and Banahalli R Ratna. Highly tunable gold nanorod dimer resonances mediated through conductive junctions. *Applied Physics Letters*, 105(1):011107, 2014.
- [183] Alemayehu Nana Koya and Jingquan Lin. Bonding and charge transfer plasmons of conductively bridged nanoparticles: The effects of junction conductance and nanoparticle morphology. *Journal of Applied Physics*, 120(9):093105, sep 2016.
- [184] Jake Fontana, Nicholas Charipar, Steven R Flom, Jawad Naciri, Alberto Piqué, and Banahalli R Ratna. Rise of the charge transfer plasmon: Programmable concatenation of conductively linked gold nanorod dimers. *ACS Photonics*, 3(5):904–911, may 2016.
- [185] M Schnell, A Garcia-Etxarri, AJ Huber, K Crozier, J Aizpurua, and R Hillenbrand. Controlling the near-field oscillations of loaded plasmonic nanoantennas. *Nature Photonics*, 3(5):287–291, 2009.
- [186] Yugang Sun, Jonathan J Foley, Sheng Peng, Zheng Li, and Stephen K Gray. Interfaced metal heterodimers in the quantum size regime. *Nano Letters*, 13(8):3958–3964, 2013.
- [187] Lin Wu, Shu Fen Tan, Michel Bosman, Joel KW Yang, Christian A Nijhuis, and Ping Bai. Charge transfer plasmon resonances across silver-molecule-silver junctions: estimating the terahertz conductance of molecules at near-infrared frequencies. *RSC Adv.*,

6(75):70884–70894, 2016.

- [188] B Reimer, H Bässler, J Hesse, and G Weiser. Optical properties of a polydiacetylene single crystal evidence for van hove singularities. *physica status solidi (b)*, 73(2):709–716, 1976.
- [189] Günther Leising. Anisotropy of the optical constants of pure and metallic polyacetylene. *Physical Review B*, 38(15):10313, 1988.
- [190] Yevgeniy Lifshitz, Yuval Golan, Oleg Konovalov, and Amir Berman. Structural transitions in polydiacetylene langmuir films. *Langmuir*, 25(8):4469–4477, 2009.
- [191] Luisa Ariza-Carmona, María T Martín-Romero, Juan J Giner-Casares, Marta Pérez-Morales, and Luis Camacho. Elastic nanocomposite structures formed by polyacetylene–hemicyanine mixed films at the air–water interface. *The Journal of Physical Chemistry C*, 117(42):21838–21848, 2013.
- [192] H Eckhardt. On the optical properties of trans-polyacetylene. *The Journal of chemical physics*, 79(4):2085–2086, 1983.
- [193] S Requena, H Doan, S Raut, A DÁchille, Z Gryczynski, I Gryczynski, and YM Strzhemechny. Linear dichroism and optical anisotropy of silver nanoprisms in polymer films. *Nanotechnology*, 27(32):325704, 2016.
- [194] Gabriella S Métraux and Chad A Mirkin. Rapid thermal synthesis of silver nanoprisms with chemically tailorable thickness. *Advanced Materials*, 17(4):412–415, 2005.