Computational Modeling of Nanoscale Interaction of Plasmonic Materials with 2D Materials for Sensing Applications

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COMPUTATIONAL MODELING OF NANOSCALE INTERACTION OF PLASMONIC MATERIALS WITH 2D MATERIALS FOR SENSING APPLICATIONS

A Thesis
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
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in
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Abstract

Plasmonics is a new and exciting field that has the potential to advance many different types of technology, from information processing and energy harvesting to sensing and imaging. The broad field of plasmonic materials and their potential to improve the functionality of cutting-edge technologies are examined in this thesis.

The thesis explores the synthesis, characterization, and manipulation of plasmonic materials after providing an overview of the basic ideas behind plasmonics. Their distinct plasmonic properties and possible uses are clarified by a thorough investigation of a variety of materials, including noble metals, two-dimensional materials, metal oxides and hybrid structures.

A thorough analysis of the Finite-Difference Time-Domain (FDTD) simulations used with different plasmonic materials is presented in this thesis. The theoretical foundation for FDTD simulations and their use in the investigation of plasmonic phenomena is established at the onset of the study. It then goes on to examine the properties of various plasmonic materials, such as noble metals, 2D materials and hybrid structures. The optical response, near-field enhancements, and dispersion properties of these materials are examined and contrasted using thorough simulations. This understanding of these plasmonic behaviors is utilized to control and manipulate a material's performance and functionality in a particular technology. Using FDTD simulations, the thesis explores how material parameters, including size, shape, and dielectric constant, affect the plasmonic properties. Through the systematic variation of these parameters, valuable insights can be obtained regarding the optimization of plasmonic devices and systems' performance.
The thesis also discusses new developments and avenues for future research in plasmonics, including the creation of novel materials, the investigation of hybrid plasmonic systems. It also addresses the difficulties and restrictions associated with using FDTD simulations to model plasmonic materials, including issues with accuracy and computational complexity.

All things considered; this thesis offers an in-depth overview of how FDTD simulations are used to study different plasmonic materials. Through clarifying the optical characteristics, investigating dependence between parameters, and assessing new materials, it advances the field of plasmonics research and makes the creation of creative plasmonic systems and devices easier.
Chapter 1. Introduction

Plasmonics, a fast-growing multidisciplinary field at the interface of photonics, nanotechnology, and materials science, has garnered a lot of attention lately due to its potential to control light at the nanoscale. By employing surface plasmons—metallic nanostructures that display collective oscillations of free electrons—plasmonics offers previously unheard-of opportunities to control light-matter interactions that exceed the diffraction limit of conventional optics [1, 2].

Surface plasmon resonance (SPR) is a method used in plasmonics to explore the properties and functions of the interaction between light and matter [3, 4]. At the interface between materials with positive and negative permittivities—typically a dielectric and a metal—collective oscillation of charge carriers is responsible for surface plasmon resonance (SPR) [4]. These oscillations, manifested as surface plasmon polaritons (SPP) or localized surface plasmon resonance (LSPR), can confine electromagnetic fields at a deep subwavelength scale, enhancing local fields and enabling light manipulation below the diffraction limit. This capability has driven significant interest in plasmonic materials across disciplines such as photonics, chemistry, energy, and life sciences, leading to numerous potential applications [5-7]. Because of this, over the past 30 years, plasmonic materials and surface plasmon resonance (SPR) have drawn increasing scientific attention.

Plasmonic devices are made using sophisticated nanofabrication techniques, but production limitations result in unknowns that impact device performance. Accurately predicting system responses depends heavily on mathematical modelling and numerical
simulation, underscoring their significance in the design process. Several numerical methods like domain-discretization or boundary-discretization methods are used to model plasmonic devices. Domain-discretization methods (Finite Element Method (FEM) and Finite Difference Time Domain (FDTD)) achieve high accuracy with increased discretization, feasible in 2D simulations with modern hardware [8]. Boundary-discretization techniques (Multiple Multipole Program (MMP), Method of Auxiliary Sources (MAS), and Mesh-less Boundary Integral Equation (BIE)) offer speed and accuracy advantages in 2D, but these benefits may diminish in complex 3D analyses due to denser or ill-conditioned matrices [8, 9]. The optimal method depends on problem dimensions and complexity. In our research, we employed FDTD simulations. The Finite Difference Time Domain (FDTD) method is extensively used and advanced for modeling the optical characteristics of metal nanoparticles within a Yee grid. Researchers employ FDTD to predict nanoparticles' extinction spectra by varying their size, shape, and concentrations [10].

Plasmonic response of materials vary depending on their compositions, size, shape, surrounding media etc. In our research using FDTD simulations we showed how we can vary the plasmonic properties of different materials (metals, 2D materials, metal oxides) based on the desired application of those materials.

1.1. Plasmonics

Plasmonics is the study of electron oscillations in metallic nanostructures and nanoparticles (NPs), particularly focusing on surface plasmons with unique optical properties. These surface plasmons can confine light at the nanoscale and are highly sensitive to the surrounding medium and material properties. Researchers can control
surface plasmon resonances by adjusting parameters like size, shape, periodicity, and materials [11-14]. Advances in technology have enabled the production of new plasmonic systems with precise control over these parameters. Theoretical and computational tools have also improved, aiding in the understanding of plasmonic optical properties.

Surface plasmons are waves that propagate along a conductor's surface. Modifying the structure of metal surfaces enables customization of these waves, especially in their interaction with light. Surface plasmons (SPs) are employed to concentrate light in structures smaller than the wavelength of light by exploiting the differences in permittivity between metals and the surrounding non-conducting media. This light concentration leads to heightened electric fields, allowing for the manipulation of interactions between light and matter, as well as enhancing non-linear effects. For example, in techniques like surface-enhanced Raman spectroscopy (SERS), the presence of tiny metallic structures, smaller than the wavelength of light, is critical for achieving significant signal amplification, enabling the detection of individual molecules. Additionally, the augmented field associated with SPs renders them useful for sensing applications, including the detection of biomolecules, with commercial systems already developed for this purpose. Plasmon resonance is defined by surface plasmon resonance (SPR) and localized surface plasmon resonance (LSPR).

Surface Plasmon Resonance (SPR) is the resonant oscillation of conduction electrons stimulated by incident light at the interface between materials with positive and negative permittivity. It is an essential component of color-based biosensors, lab-on-a-chip sensors, diatom photosynthesis, and other instruments that measure material adsorption onto a planar metal surface or metal nanoparticles.
LSPR refers to the collective oscillations of electron charges within metallic nanoparticles when stimulated by light, resulting in heightened near-field intensity at the resonance wavelength. Although this intensity is concentrated around the nanoparticle and diminishes quickly into the surrounding dielectric material, resonance also enhances scattering of light in the far-field through the particle. The phenomenon of Localized Surface Plasmon (LSP) emerges from confining a surface plasmon within a nanoparticle, with dimensions like the wavelength of the incident light.

Figure 1. Schematic representation of surface plasmon resonance (SPR) excitation. (a) SPR wave or surface plasmon polariton (SPP). (b) Localized SPR (LSPR) in a spherical nanoparticle and the associated absorbance spectrum [15].

Localised surface plasmon resonances (LSPRs), which are collective electron oscillations seen in nanoparticles, are shown in Figure 1. These oscillations are contained within the boundaries of the nanoparticles. Similar excitations are known as surface plasmon polaritons (SPPs) in continuous films, and they signify propagating oscillations. In LSPR, a plasmon is thought of as a quasiparticle that is contained inside the nanoparticle volume [3].
There are multiple factors that influence how plasmonic nanoparticles, like gold nanoparticles (AuNPs), react to electromagnetic radiation. These comprise the size, form, morphology, arrangement, and closeness of the nanoparticles to each other as well as the medium's composition. [16]. Each of these factors plays a crucial role in shaping the optical properties and behavior of the nanoparticles when interacting with electromagnetic waves.

To understand the LSPR frequency or plasmonic resonance frequency, we need to understand the relationship between the dielectric displacement (D) of the electron gas in relation to the incident electric field (E),

\[ D = \varepsilon_0 E + P \]

where \( \varepsilon_0 \) is the permittivity of the free space and \( P \) is the polarization density. \( P \) is defined by

\[ P = \frac{-n e^2}{m (\omega^2 + i \gamma \omega) E} \]

where 'n' represents the number density of particles, 'e' is the elementary charge, 'm' is the effective mass of the particle, '\( \omega \) ' is the angular frequency of the electric field, and '\( \gamma \)' is the damping coefficient. This formula describes how the polarization of the medium responds to the applied electric field, considering the properties of the particles and the frequency of the field.

So now, \[ D = \varepsilon_0 \left( 1 - \frac{\omega_p^2}{\omega^2 + i \gamma \omega} \right) E \]
wherein \( \omega_p = \sqrt{\frac{e^2 n}{\epsilon_0 m}} \) is the plasma or natural frequency of the material at which collective oscillations of electrons in the material become significant, and it depends on the density of charge carriers and their effective mass. And \( \varepsilon_r(\omega) = \left(1 - \frac{\omega_p^2}{\omega^2 + i\gamma \omega}\right) \) is the relative permittivity of the material. Under the approximation of no damping, relative permittivity becomes,

\[
\varepsilon_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2}
\]

If we consider plasmon resonance conditions, \( \varepsilon_r < -\varepsilon_m \), \( \varepsilon_m \) is the dielectric permittivity of the surrounding medium, we get the LSPR frequency,

\[
\omega_{max} = \frac{\omega_p}{\sqrt{1 + 2\varepsilon_m}}
\]

The localised surface plasmon resonance (LSPR) frequency of a plasmonic nanoparticle is closely related to its morphology, or size, shape, and structure. The density of free electrons inside the nanoparticle and the dielectric constant of the surrounding medium are two important parameters that are intimately related to the LSPR frequency [15]. These parameters essentially define the shape, position, and width of the plasmonic absorption in the electromagnetic spectrum. As will be covered in more detail in the sections that follow, comprehending and managing these variables is essential for developing and enhancing the functionality of plasmonic nanoparticles in a variety of applications.

The collective electron oscillation in nanoparticles results in a significant optical extinction cross section \( (\sigma_{ext}) \), encompassing both scattering and absorption contributions. When
light interacts with nanoparticles, induced dipole oscillators emit light at the same frequency, scattering it in all directions. The effective area for scattering is termed the scattering cross section \( \sigma_{\text{sca}} \) [17]. Additionally, the nanoparticles' electric resistance leads to absorption of incident light, with the oscillating electrons losing energy as heat. This absorption, represented by the absorption cross section \( \sigma_{\text{abs}} \), can be utilized for localized heating applications such as hyperthermia in cancer therapy. In essence, the extinction cross section encompasses both scattering and absorption phenomena in nanoparticles [18].

The extinction cross-section is, \( \sigma_{\text{ext}} = \sigma_{\text{sca}} + \sigma_{\text{abs}} \)

1.2. Effect of Material Compositions

1.2.1. Metals

Because of their optical characteristics, metals—in particular, gold (Au) and silver (Ag)—are preferred for plasmonic applications. Ag's low optical loss in the visible and near-infrared spectra makes it desirable, but oxidation is a problem. Conversely, Au exhibits good optical properties and superior chemical stability. Although they are thought to be less expensive options, aluminium (Al) and copper (Cu) are unstable chemically in air. Because of their reactivity with water and air, alkali metals have potential but need special storage conditions.

Alkali metals see limited use in plasmonics due to their reactivity, while Pd and Pt, favored for catalysis, aren't suitable for plasmonic applications due to their strong absorption of visible light. Only few noble metals like Au, Ag, and Cu fulfill the requirements of plasmonic resonance condition of \( \varepsilon_r = -2\varepsilon_m \). Alloyed metals are extensively researched, allowing
manipulation of surface plasmon resonance (SPR) wavelengths through combinations of noble metals. For instance, Au$_x$Ag$_{(1-x)}$ alloy nanoparticles exhibit SPR across the UV–vis spectrum, with a redshift as particle size increases. Varying silver mole fractions in Au$_x$Ag$_{(1-x)}$ alloys yield a single plasmon absorption, comparable in strength to composite Gold and Silver, displaying a linear increase in the blue shift of the plasmon band [19, 20]. By changing geometric shapes and structures of metallic nanoparticles and nanostructures, we can shape and control their plasmonic properties [21]. Only a few noble metals like Au, Ag, and Cu fulfill the requirements of plasmonic resonance condition of $\varepsilon_r = -2\varepsilon_m$.

### 1.2.2. 2D Materials

Recent progress in nanofabrication and characterization has led to a surge in research interest in ultra-thin two-dimensional (2D) nanomaterials, known for their impressive plasmonic properties. These materials, consisting of atomic-thin layers, exhibit distinct light-matter interaction behaviors owing to the quantum confinement effect. Consequently, their electronic structures and optical properties deviate significantly from those of bulk materials. Leveraging these advanced electronic and optical traits, the plasmonic properties of 2D nanomaterials offer highly desirable attributes. Potential 2D plasmonic materials include graphene, black phosphorene, hexagonal boron nitride (hBN), metal oxides, metal carbides and nitrides (MXenes), metal halides, pnictogens, and non-metals [22]. These two-dimensional materials exhibit a wide variety of plasmonic and electronic characteristics, such as surface state behaviour, low dangling bonds, high surface area, spin-orbit coupling, and the quantum spin Hall effect [23, 24].
Because of their thin structures and strong quantum confinement effects, 2D materials exhibit enhanced electronic and optical properties and strong radiation-matter interactions [25]. Promising results have been obtained from research on the plasmonic properties of two-dimensional materials, specifically graphene and hexagonal boron nitride (hBN). Graphene is highly effective for plasmonic applications because of its single-atom thickness, environmental sensitivity, and tunability with external magnetic and electric fields, especially when heavily doped [26, 27]. Efficiency is increased by combining graphene with other 2D materials [28]. As a substrate for graphene-based plasmonic applications, hBN exhibits promise due to its unique crystal structure that matches graphene and its capacity to maintain bandgap across a wide range of thicknesses [29, 30]. This allows for enhanced plasmon lifetime and a wide range of plasmonic properties [31]. MXenes are a new class of 2D materials that contain nitrides and carbides. They are metallically conductive, have high stability, and can be combined with other materials to customise their properties for a range of uses [32]. They can be used as plasmonic materials equivalent to graphene.

### 1.2.3. Metal Oxides

Plasmonic properties can indeed be observed in metal oxides under specific conditions. LSPR has also been found in significantly doped semiconductor nanocrystals, such as tin oxide [33, 34], copper chalcogenides [35], and zinc oxide [36]. Because the stoichiometry or doping can be changed to tune the LSPR energy, heavily doped semiconductors have LSPRs that are not found in metals. This additional method of tuning the optical properties makes heavily doped semiconductors unique. [37]. Agrawal et al. [38] demonstrated that similar to degenerately doped semiconductors, conductive metal oxide (CMO) materials
offer a strong substitute for traditional metals, especially in the infrared (IR) range. The controllable plasmonic responses of nanoparticles, such as localized surface plasmon resonance (LSPR), are determined by their chemical composition and characteristics. CMOs and metals have similar characteristics, such as high conductivity and polarizability, but they come from different sources of free charge carriers. Since CMOs are semiconductors, they depend on doping to produce free carriers, unlike intrinsically conducting metals.

In photonic systems, scattering losses can be harmful because they lower light propagation efficiency, weaken local electric fields, and broaden LSPR peaks, all of which lower sensor sensitivity. Although Ag shows minimal interband scattering because of its little overlap with the LSPR frequency, some losses, such as the d-d transition interband scattering in Au, are intrinsic [39]. Metal oxides exhibit low levels of interband scattering due to their wide bandgaps and low-energy LSPRs. While electron-electron scattering is negligible at low temperatures, temperature-dependent electron-phonon scattering is more noticeable at high temperatures [40]. However, metal oxides may suffer significant defects scattering from dopants and crystal defects, impacting damping [41]. The dielectric constant, absorption coefficient, refractive index, and other parameters are influenced by the type of dopant, carrier concentration, and scattering in metal oxides such as In2O3, ZnO, and CdO [38].

1.3. Effect of size

The optical and electronic properties of metal nanoparticles are significantly influenced by the confinement of conduction electrons, resulting in the surface plasmon resonance (SPR) band's position and width modulation [42, 43]. Two distinct effects contribute to
size effects: external (electrodynamics) and internal. External size effects, driven by electromagnetic wave retardation, are explained by Mie theory, while internal size effects stem from electron scattering on the nanoparticle’s surface [44]. The SPR band broadens with decreasing nanoparticle size due to electron scattering, then broadens further with increasing size due to radiation damping. The SPR red shifts as the size of the nanoparticles gets smaller. This change takes place due to the scattering rate of free electrons in nanoparticles being size dependent. [45].

Figure 2. Absorption and scattering cross sections, \( \sigma_{\text{abs}} \) and \( \sigma_{\text{scat}} \), of a-i) AuNPs and b-i) AgNPs in water with diameter of 40, 60, 80, and 100 nm, and (a-ii,b-ii) show their electric field enhancement (\( E/E_0 \)) at the wavelength of scattering resonance, respectively [18].

Figure 2, a-ii,b-ii shows the electric field distribution of Au and Ag nanosphere (40–100 nm in diameter) at resonance frequency with a field amplification \( E/E_0 \) reaching close to \( \approx 7 \) for Au and \( \approx 14 \) for Ag.
1.4. Applications

Plasmonics is extremely valuable in many fields, including information sciences, chemistry, biology, and energy [46, 47]. Based on the special properties of plasmonics, typical applications in bioimaging, sensing, surface-enhanced Raman scattering (SERS), chemical reactions, and metasurface have been reported [4, 19, 48].

1.4.1. Health

Plasmonic nanomaterials have revolutionized biomedical applications, particularly in diagnosis and therapy [49]. They are now integral to theragnostic, combining multiple functions within one nanostructure, offering new possibilities in medicine. In diagnosis, plasmonic nanoparticles serve as contrast agents for various imaging techniques, providing high-contrast images of cancer cells. They are also utilized as sensors for detecting biomolecules with remarkable sensitivity. Moreover, plasmonic nanoparticles are employed in therapeutic applications such as phototherapy and photodynamic therapy, leveraging light-induced heat generation and controlled drug release for efficient treatment, especially in combating cancer. This integration of plasmonic nanoparticles with light-based therapies represents a significant advancement in medical treatment methodologies.

1.4.1.1. Point of Care Applications

Plasmonics technologies facilitate the detection and analysis of an array of biomolecules critical for diagnosis and therapeutic monitoring. Among these biomolecules are disease biomarkers, proteins, and enzymes, whose detection is pivotal for understanding disease states and designing targeted treatments [50, 51]. Additionally, plasmonics technologies have revolutionized the detection of DNA sequences, providing researchers and clinicians
with unprecedented insights into genetic predispositions and diseases [52]. Furthermore, the rapid and sensitive detection of drugs using plasmonic techniques underscores their potential in pharmacological research and personalized medicine. One of those techniques is SERS.

In our paper [51], we mentioned SERS-LFA has many advantages over traditional LFA, including a much lower LOD and the ability to detect a wide range of analytes quantitatively and in multiplex. However, the need for lavish equipment and long signal possession time limits its use as a universal immunological technique for point-of-care testing. Recent developments in compact SERS readers for LFA strips show promise in solving these issues. Further developments could include creating a lateral flow strip with low Raman background and modifying SERS tags to eliminate nonspecific adsorption. Combining SERS-LFA with biochips could lead to a portable and ultrasensitive detection platform for point-of-care diagnostics.

For point of care applications, different types of readout systems like photoacoustic reader, thermal contrast reader, colorimetric and UCNP reader all are usually designed based on the plasmonic properties of nanoparticles [51].

1.4.1.2. Photothermal Therapy

Photothermal therapy, an increasingly popular cancer treatment, relies on locally increasing temperature in tumors through laser irradiation, converting light into heat [46]. Plasmonic nanoparticles serve as highly efficient photo-absorbing agents, enhancing light absorption and ensuring photostability. This therapy offers simplicity, rapid patient recovery, and minimal hospital stays. Plasmonic nanoparticles act as new generation
photothermal contrast agents, selectively targeting tumor cells, thereby minimizing damage to healthy tissue [53].

1.4.2. Plasmons in Solar Applications
Plasmonics, with its remarkable ability to manipulate light, emerges as a compelling avenue for solar energy harvesting. Within metal-semiconductor heterojunctions, plasmons facilitate enhanced photoconversion through multiple mechanisms [46]. Firstly, they trap light efficiently, maximizing its interaction with the semiconductor material. Additionally, plasmons facilitate the transfer of hot electrons and holes, augmenting the photogenerated charge carriers' mobility. Moreover, plasmon-induced resonance energy transfer (PIRET) further boosts the efficiency of energy conversion processes [54]. These synergistic effects underscore the potential of plasmonics to revolutionize solar energy technologies, offering a pathway towards more efficient and sustainable energy production. These technologies are used in Plasmon-Enhanced Thin-Film Silicon Solar Cells, Plasmon-Enhanced OPVs, Plasmon-Enhanced Dye-Sensitized Solar Cells, solar heaters etc.
Chapter 2. Computational modeling of plasmonic structures

2.1. Electromagnetic Simulation

Electromagnetic simulation refers to the use of computational techniques to model and analyze the behavior of electromagnetic fields in various structures, devices, or environments. These simulations are based on mathematical models and numerical methods to solve Maxwell's equations, which describe how electric and magnetic fields interact and propagate.

The classical Curl (Maxwell) equations and Constitutive relations provide a comprehensive framework for understanding the interaction of metals with electromagnetic fields.

Curl equations describe how the fields are produced:

\[ \nabla \times E = -\frac{\partial B}{\partial t} \]

\[ \nabla \times H(r, t) = \frac{\partial D(r, t)}{\partial t} + J \]

Constitutive relations explain how fields interact with materials:

\[ D(t) = [\varepsilon(t)] \ast E(t) \]

\[ B = [\mu(t)] \ast H(t) \]

In these above equations, \( E = \) Electric Field Intensity (V/m), \( B = \) Magnetic Flux Density (Wb/m\(^2\)), \( H = \) Magnetic Field Intensity (A/m), \( D = \) Electric Flux Density (C/m\(^2\)), \( J = \) Electric Current Density (A/m\(^2\)), \( \varepsilon = \) Permittivity (F/m) and \( \mu = \) Permeability (H/m).
For electromagnetism at nanoscale, one needs to understand quantum Maxwell’s equations. Now, every field quantity in the original Maxwell's equations is raised to the level of a field operator, which is comparable to an infinite-dimensional matrix operator. Additionally, as demonstrated by classical electromagnetics, macroscopic electromagnetic theory can be applied when the wavelength of the electromagnetic field is significantly longer than the size of the atom or the lattice spacing.

A Hamiltonian, \( \hat{H} \) associated with the aforementioned Maxwell’s equations and the corresponding quantum state equation has to be satisfied:

\[
\hat{H}|\psi\rangle = \hbar \frac{\partial}{\partial t}|\psi\rangle
\]

To completely characterise the quantum system, we must solve this above equation for the time evolution of the quantum state \( |\psi\rangle \) in addition to solving the quantum Maxwell's equations. The source of this quantum system's extensive data content is the connection between a quantum Hamiltonian and a quantum state and the quantum Maxwell's equations.

In computational electromagnetics, numerical techniques such as Finite Element Analysis (FEA), Rigorous Coupled Wave Analysis (RCWA), Discrete Dipole Approximation (DDA), and Finite-Difference Time-Domain (FDTD) are employed to address a range of wave propagation, scattering, and diffraction-related problems. They all have similar functions, but they differ in their underlying ideas, advantages, and disadvantages.

- Finite Element Analysis (FEA):

FEA discretizes the problem domain into smaller elements and solves the governing equations (such as Maxwell's equations for electromagnetics) within each element. It is
widely used in structural analysis, heat transfer, and electromagnetics. It is suitable for complex geometry, material properties, and boundary conditions and can handle multiphysics problems. However, this method is computationally expensive for large-scale problems. Accuracy can be limited by mesh quality and element shape.

- Rigorous Coupled Wave Analysis (RCWA):

RCWA solves Maxwell's equations for periodic structures by decomposing the fields into Fourier components and applying boundary conditions. It is particularly useful for analyzing periodic structures like gratings, photonic crystals, and metamaterials. This method is efficient for these types of structures and provides detailed information on diffraction efficiencies, band structures, etc. On the contrary, it is limited to periodic structures. Convergence can be slow for certain configurations.

- Discrete Dipole Approximation (DDA):

DDA represents scatterers as a collection of discrete dipoles and solves for their interactions with incident fields. It is a general method to simulate light scattering by arbitrarily shaped particles. It is suitable for irregularly shaped and heterogeneous scatterers. This method is versatile for a wide range of scatterer geometries and materials and can handle large-scale problems. However, it is computationally intensive, especially for large numbers of dipoles. Accuracy depends on the distribution of dipoles.

- Finite-Difference Time-Domain (FDTD):

The Finite-Difference Time-Domain (FDTD) method is a commonly used technique to solve electromagnetic problems. It is useful in a variety of fields, such as the study of dielectrics, antennas, metal object scattering, microstrip circuits, and the effects of
electromagnetic radiation on the human body. FDTD is particularly useful as a reliable and accurate way to model nano-scale optical devices. FDTD provides rigorous solutions to Maxwell’s equations directly, without the need for physical approximations; the computational scope is limited only by computing power.

2.2. The FDTD Method

By solving Maxwell's equations on a mesh, the FDTD method computes E and H at grid points that are separated by $\Delta x$, $\Delta y$, and $\Delta z$, with E and H intertwined in all three spatial dimensions. The effects of transmission, absorption, reflection, and scattering are all included in FDTD. While FDTD is a time-domain solution, frequency analysis can also be done with the FFT and DFT, or Fast Fourier Transforms.

In FDTD method, while solving any problem, the following flow of Maxwell’s equations are followed:

![Figure 3. Maxwell’s equations in the FDTD method.](image-url)
For linear, isotropic, and non-dispersive materials, \([\mu(t)] = \mu, [\varepsilon(t)] = \varepsilon\)

So, the flow of the Maxwell’s equation becomes:

\[
\nabla \times E(t) = -\mu \frac{\partial H(t)}{\partial t}
\]

A circulating \(E\) field induces a change in the \(H\) field at the center of circulation in proportion to the permeability.

\[
\nabla \times H(t) = \varepsilon \frac{\partial E(t)}{\partial t}
\]

A circulating \(H\) field induces a change in the \(E\) field at the center of circulation in proportion to the permittivity.

Figure 4. Electric field and magnetic field in the FDTD method.

After considering Finite-Difference Approximations of Time Derivative (\(\Delta t\)), we get Update Equations:

\[
H(t + \frac{\Delta t}{2}) = H(t - \frac{\Delta t}{2}) - \frac{\Delta t}{\mu} \nabla \times E(t)
\]

\[
E(t + \Delta t) = E(t) + \frac{\Delta t}{\varepsilon} \nabla \times H(t + \frac{\Delta t}{2})
\]

These update equations are used in computer codes or the FDTD problem solver software-s.
The Maxwell equations in three dimensions describe six electromagnetic field components: \( E_x, E_y, E_z \) and \( H_x, H_y, \) and \( H_z \). Assuming an infinite structure in the \( z \) dimension and field independence in \( z \), characterized by

\[
\varepsilon_r(\omega, x, y, z) = \varepsilon_r(\omega, x, y)
\]

\[
\frac{\partial E}{\partial z} = \frac{\partial H}{\partial z} = 0
\]

Where \( \varepsilon_r(\omega) \) is the complex relative dielectric constant \( (\varepsilon_r(\omega) = n^2, \text{where } n \text{ is the refractive index}) \).

Maxwell's equations split into two sets: transverse electric (TE) with \( E_x, E_y, \) and \( E_z \), and transverse magnetic (TM) with \( H_x, H_y, \) and \( H_z \). These sets can only be solved in the \( x\)-\( y \) plane. For example, in TM equations, Maxwell's equations simplify to specific forms:

\[
\frac{\partial D_z}{\partial t} = \frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y}
\]

\[
D_z(\omega) = \varepsilon_0 \varepsilon_r(\omega) E_z(\omega)
\]

\[
\frac{\partial H_x}{\partial t} = -\frac{1}{\mu_0} \frac{\partial E_z}{\partial y}
\]

\[
\frac{\partial H_x}{\partial t} = \frac{1}{\mu_0} \frac{\partial E_x}{\partial x}
\]

The FDTD method solves Maxwell's equations on a discrete spatial and temporal grid, with each field component calculated at different positions within the grid cell, known as the Yee cell.
Our research utilized Ansys Lumerical FDTD software for simulating photonic components. This software allows for the incorporation of dispersive materials with tabulated refractive index data. Different material models like Plasma (Drude), Debye, or Lorentz can be utilized as well. The FDTD solver accommodates several boundary conditions including PML, periodic, and Bloch, along with various source types such as point dipoles, beams, plane waves, total-field scattered-field (TFSF) source, guided-mode source for integrated optical components, and imported source for interfacing with external photonic design software. Our focus was on investigating different plasmonic...
materials and their optical and electromagnetic properties using FDTD simulations. This area of research is relatively new, and the application of computational electromagnetics in plasmonics is still in its early stages.

Nowadays, one of the most significant numerical techniques for the electromagnetic field is the finite-difference time-domain (FDTD) method [55]. Besides, FDTD can simulate the light scattering from metal particles [56, 57]. To further investigate the effect of coupling between nanoparticles and evaluate the impact of local surface plasmon resonance (LSPR), FDTD is employed to simulate the local surface plasmon resonance (LSPR) properties of metallic nanoparticles. The refractive index of the medium can be altered by modifying the parameters influencing the LSPR of metal nanoparticles, emphasising on the LSPR optical characteristics of nanoparticles and occasionally microparticles, and computing the extinction cross-section using the FDTD method [58]. Therefore, FDTD is especially helpful for researching the optical characteristics of different nanoparticles. It has been applied to the study of near-field optical properties of nanoscale materials, near-field probes, plasmonic biosensors based on reflectometry, nanoparticle structures for improving solar cell efficiency, and SERS [47]. It can be used to study how various polarizations and light wavelengths affect various structured or unstructured materials' reflectance, transmission, diffraction, interference, and absorption. It can also be used to record movies that show how light moves through the materials in real time [59].
Chapter 3. Nano-nano Interaction

Plasmonic nanoparticles, which include particles of gold, silver, and platinum, are distinct metallic particles with special optical characteristics because of their size and shape. Plasmonic nanoparticles are used in color-changing sensors, surface-enhanced spectroscopy, lateral flow diagnostics, and labelling because they are incredibly powerful light absorbers and scatterers. The optical response can be tuned from the ultraviolet through the visible to the near-infrared regions of the electromagnetic spectrum by varying the size, shape, and composition of the nanoparticles [60]. The plasmons oscillate at specific resonant frequencies, Surface Plasmon Resonance Frequency, and move with periodic driving forces that can become large amplitude oscillations when they interact.

The dielectric function of the medium and the nanoparticle's wavelength-dependent dielectric function are both necessary for the resonance condition to exist [60, 61]. As such, the size, composition, and media in which the particles are embedded all have a significant impact on the optical properties of nanoparticles [60, 61]. The local refractive index affects the nanoparticle plasmon resonance's peak resonance wavelength as well as its shape. Hence, when we use different materials or a certain material of different sizes, their optical properties such as scattering, absorption and extinction cross-sectional area change. We define a certain material while modelling it by defining its refractive index.

3.1. Gold Nanoparticles (Au NPs)

The interaction between light and matter boosts the electromagnetic field near metallic surfaces, vital for enhancing spectroscopy and detection via plasmonics. Gold
nanoparticles (Au NPs), distinguished among noble metals, offer versatility in synthesis and stability in chemistry. Their strong localized surface plasmon resonance (LSPR) responses in visible and near-infrared wavelengths result from specific factors such as carrier concentration and mobility. Consequently, Au NPs play a crucial role in various nanophotonic devices and biomedical contexts.

The structure was set up, the scattering and absorption cross-section areas, and the electric and magnetic fields of Au NPs were calculated using FDTD simulation. The visible light range, which is set between 300 and 900 nm, is the wavelength range of the simulation. A Total-field scattered-field (TSFT) source was used as the source type; TSFT sources are frequently used to investigate the scattering properties of nanoparticles. In order to determine the absorption cross-section, the perfectly matched later (PMI) boundary was employed. It was a 1 nm by 1 nm grid. The refractive index of Au NPs was defined \( n = 0.27732 \) by Johnson and Christy [62].

Under the above-mentioned parameters, we first set up the simulation for 1 Au NP in Air.
Figure 6. (a) Scattering cross-section and (b) absorption cross-section of a Au NP. (c-d) Electric field distribution of 1 Au NP (d = 20 nm) at λ = 526 nm. The incident wave vector propagation direction and the polarization of the incident electric field is shown. The electric field distribution for the NP is shown in XY (c), XZ (d) and YZ (e) plane.

In Figure 6, the characteristic scattering wavelength is 526 nm, and the characteristic absorption wavelength is 506 nm. The electric field in Figure 6(c-d), was shown at 526 nm. The enhanced electric field is concentrated very close to the surface of the NP (near field with x, y, z = ± 10 nm). This enhanced cross-section area is beneficial for detection.

3.2. Metal Oxide Nanoparticles (HfO$_2$ NPs)

Metal oxides, like metals, demonstrate localized surface plasmon resonance across a range of optical wavelengths. These materials have gained significant traction in research, particularly in biological contexts, over the last decade. Unlike traditional plasmonic materials based on noble metals, these metal oxides offer several advantages including cost-effectiveness, versatile plasmonic properties, and improved biocompatibility, which enhances their appeal for practical applications [48].
Metal oxides (MOs) in their pure form usually possess wide bandgaps, making them either semiconductors or insulators with restricted free charge carriers, hence unable to produce significant localized surface plasmon resonance (LSPR) in the visible and near-infrared (NIR) spectra [63]. Nevertheless, [48] [64]. This occurrence is commonly observed across different types of MOs, such as those composed of Mo, W, In, Ti, V, Zn, Cd, and Re [48]. Previously researchers have worked on mostly plasmonic enhancement of HfO$_2$ as a substrate for metal nanoparticles and their results show that a surrounding medium such as HfO$_2$ substrate with higher refractive index (RI) leads to greater absorption with plasmonic enhancement [65]. In our study, we tried simulating the plasmonic properties of spherical pure hafnium dioxide, HfO$_2$ NPs and compare its characteristics with Au NPs'.

The exact FDTD simulation environment that was set up for Au NPS was also used to set up the structure and calculate the scattering and absorption cross-section areas and electric and magnetic field of HfO$_2$. The refractive index of HfO$_2$ was n = 1.8981 (by Al-kuhaili, 2004) [62].
Figure 7. (a) Variation in scattering cross-sections of AuNP and HfO$_2$ NP with respect to their diameters in vacuum. (b) Variation of scattering cross-sections of AuNP ($d = 15$ nm) and HfO$_2$ NP ($d = 40$ nm) at different wavelengths. Both the nanoparticles were placed on a glass slide. (c, d) Variation of absorbance of AuNP ($d = 15$ nm) and HfO$_2$ NP ($d = 40$ nm) placed on a glass slide at different wavelengths.

In FDTD simulation, Mie theory is used to determine the optical properties. Here, the effective dipole moment can be expressed as

$$P = 4\pi \varepsilon_m R^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}$$

$R$, $\varepsilon_p$ and $\varepsilon_m$ are the radius of particle, dielectric function of the particle and that of the medium, respectively.
The cross-sections for scattering \( (C_{sc}) \) and adsorption \( (C_{abs}) \) are obtained from the scattering field radiated by this dipole, which is induced by the incident plane wave (i.e., the dipole moment \( P \)). The resulting expressions are

\[
C_{sc} = \sigma_{geom} Q_{sc}, \quad Q_{sc} = \frac{8}{3} q^4 \left| \frac{\epsilon_d - 1}{\epsilon_d + 2} \right|^2
\]

\[
C_{abs} = \sigma_{geom} Q_{abs}, \quad Q_{abs} = 4 q I m \left[ \frac{\epsilon_d - 1}{\epsilon_d + 2} \right]
\]

where \( \sigma_{geom} = \pi R^2 \) is the geometrical cross-section. We introduce the dimensionless cross-sections of scattering \( (Q_{sc}) \) and adsorption \( (Q_{abs}) \), the dimensionless size \( q = k R \) and the relative dielectric function \( \epsilon_d = \epsilon_p / \epsilon_m \) for convenience in the discussion that follows. In the formula, \( k \) is the wave vector in medium.

According to the above formula, the efficiency of adsorption will outweigh the efficiency of scattering as the particle size decreases. Light scattering will therefore have difficulty detecting particles that are extremely small in size.

Theoretically, with the increase of the diameter of the nanoparticles, their extinction cross-section \( (= Q_{sc} + Q_{abs}) \) increases. From these equations, we can see that, \( Q_{abs} \propto R \), radius of the nanoparticle and \( Q_{sc} \propto R^4 \). So, as the diameter increases, particle’s absorption cross-section increases more than its scattering cross-section. Hence, the absorption intensity becomes more dominant over the scattering one.

Further, from the above equations, when \( \epsilon_d = \epsilon_p / \epsilon_m = -2 \), the scattering and absorption cross-section will show strong resonance. Only plasmonic materials show negative dielectric constants in the visible wavelength region. Now, our simulation result shows
that scattering cross-section of both nanoparticles increases with the increase of their diameters (Figure 7 (a)). From Figure 7 (a), it is evident that at a particular diameter scattering cross-section of AuNP is always greater than that of a dielectric particle like HfO$_2$. However, when the diameter of the dielectric particle is larger than that of the plasmonic particle, the scattering cross-section of the dielectric particle might exceed that of the plasmonic particle. Figure 7 (b) shows the comparison of scattering cross-section of HfO$_2$NP (d = 40 nm), and AuNP (d = 15 nm) on a glass slide. The HfO$_2$ NP (d = 40 nm) showed higher (~1000 fold) scattering cross-section than AuNP (d = 15 nm).

Moreover, the change in absorption intensity of Au NP and HfO$_2$ NP at different wavelengths is shown in Figures 7(c,d). Each of the particles shows several peaks and dips at different wavelengths. However, the HfO$_2$NP (d = 40 nm) has higher absorbance intensity (~2 fold) than the AuNP (d = 15 nm) at $\lambda = 550$ nm.
Figure 8. Electric field distribution of (a, c, e) HfO$_2$ (d = 40 nm), and (b, d, f) AuNP (d = 15 nm) at l = 526 nm. The incident wave vector propagation direction and the polarization of the incident electric field is shown. The electric field distributions for the NPs are shown in (a, b) XY, (c, d) XZ, and (e, f) YZ plane.

In our simulations, HfO$_2$ NP and AuNP were placed on a glass substrate. The electric field distribution around the NPs obtained from the FDTD simulation are shown in Figure 8. Figures 8a, 8c, and 8e present the cross-sectional distribution of the normalized electric-
field intensity \( (|E|^2/|E_0|^2) \) around the HfO_2 NP at \( l = 526 \text{ nm} \) in the XY, XZ, and YZ planes. The corresponding electric field for the AuNP at \( l = 526 \text{ nm} \) is shown in Figures 8b, 8d, and 8f. For AuNP, the enhanced electric field is concentrated very close to the surface of the NP (near field with \( x, y, z = \pm 10 \text{ nm} \) (See Figures 9b, 9d, 9f). On the contrary, for HfO_2NP, the evanescent electric field is extended over a larger distance (\( x, y, z = \pm 300 \text{ nm} \) (See Figures 9a, 9c, 9e). This would lead to potentially better out of plane coupling and collection of photons using a detector. HfO_2 has higher electric field intensity over the region of \( x = -300 \text{ nm} \) to +300nm. Larger scattering cross-section area is beneficial for detection.
Figure 9. Magnetic field distribution of (a, c, e) HfO$_2$ (d = 40 nm), and (b, d, f) AuNP (d = 15 nm) at $l = 526$ nm. The incident wave vector propagation direction and the polarization of the incident electric field is shown. The electric field distributions for the NPs are shown in (a, b) XY, (c, d) XZ, and (e, f) YZ plane.

Similar to the electric field distribution, HfO$_2$ NP showed better out of plane coupling of magnetic field compared to the Au NP. Figure 7 shows the XY, XZ, and YZ-plane cross-sectional distribution of normalized magnetic field intensity of both HfO$_2$ and Au nanoparticles at $l = 526$ nm.
Chapter 4. Nano-2D material interaction: Self-assembly of 2D HfS$_2$ Nanoplatelets

Liquid interfaces facilitate the organization of nanometer-scale biomaterials with plasmonic properties suitable for molecular diagnostics. Using hierarchical assemblage of 2D hafnium disulfide, HfS$_2$ nanoplatelets and zero-dimensional spherical gold nanoparticles, the design of a multifunctional material is reported. When the target analyte is present, the nanocomposites’ self-assembling pattern changes, altering their plasmonic response. Nanoparticles possess a natural tendency to self-assemble at interfaces, owing to their widespread presence [66]. Additionally, heterostructures composed of 2D nanomaterials offer versatility in various nanoscale optoelectronic applications [67]. Furthermore, incorporating zero-dimensional (0D) plasmonic nanostructures into these 2D materials amplifies their spectral properties [68]. Using 2D and 0D nanomaterials as building blocks can be a way to develop advanced functional materials with improved plasmonic properties.

We did FDTD simulations modelling hierarchical assemblage of 2D hafnium disulfide nanoplatelets and 0D spherical gold nanoparticles to calculate the electromagnetic field enhancement distributions and justify the use of 2D materials as a composite with 0D particles instead of 0D particles alone. The wavelength range of the simulation is set between 300 nm and 900 nm, which is the visible light range. The source type adopted a Total-field scattered-field (TSFT) source, which is often used to study the scattering characteristics of nanoparticles. And perfectly matched later (PMI) boundary was utilized to calculate the absorption cross-section. The grid size was 1 nm x 1 nm. The refractive
The refractive index of HfS\(_2\) is (3.00 - 0.06i) [69].

To model the aggregation of gold nanoparticles in presence of the target DNA, we undertook either a single AuNP or three closely spaced AuNPs. Further to understand the influence of 2D materials, these nanoparticles were either suspended in air or positioned above a substrate mimicking HfS\(_2\) platelet. FDTD results of the gold nanoparticles positioned on the HfS\(_2\) substrate are shown in Figure 10. Figure 10b–d, f–h presents cross-sectional distribution of the normalized EM-field intensity (|E|^2/|E_0|^2) of three and a single gold nanoparticle respectively placed over the HfS\(_2\) substrate in the XY, XZ, and YZ planes. These views were compared to the 3 AuNPs (Figure 10a) and 1 AuNP (Figure 10e) alone in the XY plane. Notably, the maximum EM-field enhancement occurs at the junction of the 3 AuNPs and HfS\(_2\) substrate, which is along the XZ plane (red region in Figure 10c) or YZ plane (red region in Figure 10d). These results offer theoretical demonstration that the agglomerated AuNPs decorated on HfS\(_2\) substrate features superior EM-field enhancement, well consistent with the above experiment data.

The trimeric AuNPs presented on HfS\(_2\) increased the electric field, |E|, by a factor of \(\approx\)10x, compared to single nanoparticle. The increased EM-field also contributed to \(\approx\)10x increase in scattering cross-section, which will lead to scattering of more photons. Increased scattering cross-section is advantageous for colorimetric (UV–vis absorbance based) detection. HfS\(_2\) provides a “nano/micro” substrate for the AuNP to form dimer/trimer/multi-NP (aggregated) structures. This increases the electromagnetic (EM) field at the gap between the AuNPs. The increased EM field or the so-called “hot spots” lead to enhanced light-matter interactions between incident light and the targeted bio
analyte. In addition, HfS2 increased the density of AuNP per unit incident light beam area without aggregation (Figure 11f–h) when compared to the single AuNP in air (Figure 11e). This improves the absorption coefficient. Further in the presence of HfS2, the plasmonic field gets enhanced and extended both in x and z direction. Thus, it may be concluded that this enhanced light-matter interaction, introduced by the 0D+2D composite material than the 0D particles alone, will lead to significant improvement in sensitivity.

To model the aggregation of gold nanoparticles in presence of the target DNA, we undertook either a single AuNP or three closely spaced AuNPs. Further to understand the influence of 2D materials over sensing, these nanoparticles were either suspended in air or positioned above a substrate mimicking HfS2 platelet. Schematic illustration cross section views of the on the HfS2 substrate are shown in Figure 10. Figures 10b-d and 10f-h present cross-sectional distribution of the normalized EM-field intensity (|E|^2/|E_0|^2) of three and a single gold nanoparticle respectively placed over the HfS2 substrate in the XY, XZ and YZ planes. These views were compared to the 3 AuNPs (Figure 10a) and 1 AuNP (Figure 10e) alone in the XY plane. Notably, the maximum EM-field enhancement occurs at the junction of the 3 AuNPs and HfS2 substrate, which is along the XZ plane (red region in Figure 10c) or YZ plane (red region in Figure 10d). These results offer theoretical demonstration that the agglomerated AuNPs decorated on HfS2 substrate features superior EM-field enhancement, well consistent with the above experiment data. The trimeric AuNPs presented on HfS2 increased the electric field, |E|, by a factor of ~10x, compared to single nanoparticle. The increased EM-field also contributed to ~10x increase in scattering cross-section, which will lead to scattering of more photons.
Increased scattering cross-section is advantageous for colorimetric (UV-Visible absorbance based) detection.

Figure 10. Electromagnetic FDTD simulations of the EM-field intensity distribution for representative a–d) three and e–h) one AuNP in different dielectric environment, e.g., HfS2 substrate (b–d and f–h) and air (a and e). Cross-section views for calculating the EM-field enhancement distribution of gold nanoparticles, positioned on the substrate are also shown along XY, XZ, and YZ planes. The region enveloped in white frame represents HfS2 in the simulations. The colors from blue to red represent the EM-field intensity from weak to strong. |E|² and |E₀|² stand for scattered EM-field intensity and incident EM-field intensity respectively. The incident EM-field was polarized in X-direction and propagation vector (k) was in Z-direction.

HfS₂ provides a “nano/micro” substrate for the AuNP to form dimer/trimer/multi-NP (aggregated) structures. This increases the electromagnetic (EM) field at the gap between the AuNPs. The increased EM field or the so called “hot spots” lead to enhanced light-matter interactions between incident light and the targeted bio-analyte. In addition, HfS₂ increased the density of AuNP per unit incident light beam area without aggregation (Figures 10f-h) when compared to the single AuNP in air (Figure 10e). This improves the absorption coefficient. Further in the presence of HfS₂, the plasmonic field gets enhanced and extended both in x and z direction (Figure 11).
Figure 11. Electromagnetic FDTD simulations of the plasmonic magnetic field (H) intensity distribution for an Au NP in different dielectric environment, e.g., HfS2 substrate (bottom) and air (top) along X and Z direction at two different wavelengths, 528 and 607 nm. The colors from blue to red represent the plasmonic magnetic field intensity distribution from negative (weak) to positive (strong).

Thus, it may be concluded that this enhanced light-matter interaction, introduced by the 2D+3D composite material than the 3D particles alone, will lead to significant improvement in sensitivity. The increase in scattering cross-section by order of magnitude was due to the involvement of HfS2 (Figure 12). The improved scattering cross-section may lead to better colorimetric detection. Two separate positioned peaks, 536 nm and 607 nm were also found in the composite absorption spectra predicted theoretically (Figure 12). The red shift of plasmonic resonance with the involvement of HfS2 and appearance of new peak at λ = 607 nm was in corroboration with the experimental data (Figure 12). All these data thus support the involvement of 2D materials than 3D particles alone to obtain better sensitivity towards a selected analyte.
Figure 12. (a) Experimental UV-Visible absorbance of the AuNPs in absence and presence of HfS$_2$ platelets; (b) Peak analysis of the experimentally obtained absorption spectrum for the composite material (AuNP + HfS$_2$); Theoretically predicted (c) scattering cross-section and (d) absorption cross-section of the composite material in comparison to the AuNP system alone.
Chapter 5. Nanometals on microparticles and their interaction: Self-assembly of Janus Particles

In this study, we investigated pH-controlled self-assembly of Janus particles to observe the changes in their Surface-Enhanced Raman Scattering (SERS) and Raman signals. By adjusting the pH of the solution, electrostatic interactions between the Janus particles were manipulated, leading to controlled aggregation and spatial arrangement. At specific pH levels, self-assembly of Janus particles occurs, forming ordered nanostructures that concentrate analyte molecules. This spatial confinement caused significant changes in electromagnetic field intensity and Raman signals. From Raman signals, characteristic peaks were found at Raman Wavenumber, 1002 cm\(^{-1}\). Optimal pH selection enables control over interparticle spacing, plasmonic coupling, and electromagnetic field distribution, leading to remarkable Raman signals. This research also focused on analyzing electromagnetic fields, uncovering how electric and magnetic fields are distributed within Janus particles when exposed to excitation and Raman wavelengths. A decrease in Raman Intensity with the increasing number of Janus particles were observed at the Raman wavenumber. Using Finite-Domain-Time-Difference (FDTD) simulations, a decrease in electromagnetic field intensity with the number of particles were also observed, which validates our experimental finding. Analyzing the structure and optical and electromagnetic properties of Janus particles will further help us understand their behavior and potential applications. Their pH-sensitive responses have potential uses as therapeutic agents and in delivery systems, imaging probes, and biosensors.

The synthesis involved the creation of Janus particles from a blend of Au-PS, resulting in dipolar particles with opposing electric charges. We employed two distinct methods of
PEG functionalization, enabling additional interactions with lysozyme (LYZ). Characterization techniques, including SEM and FIB technology, provided high-resolution images and cross-sectional views, shedding light on the morphology, size distribution, and internal composition of Janus particles. Raman spectroscopy confirmed successful protein conjugation and revealed pH-responsive behavior, with aggregation and disaggregation in response to pH changes. In addition, we utilized various advanced techniques such as TEM, diffraction patterns, EDAX, and elemental mapping to gain structural and elemental insights into assembled Janus particles.

We did FDTD simulations to validate experimental findings. These simulations modeled Janus particles with varying numbers and explained the observed decrease in Raman intensity as a result of plasmonic resonance shifts and plasmonic coupling effects at different wavelengths.

The Raman map of the assembled Janus particles was obtained by acquiring Raman spectra at different points on the sample surface and plotting the intensity or specific Raman band of interest as a function of spatial coordinates is shown in Figure 11. The Raman spectra reveals detailed information about the chemical composition and structural properties, while the map provides a spatial perspective, showing the distribution and organization of the particles within the sample. Raman peaks at \( \sim 1002 \) cm\(^{-1} \) & \( \sim 1032 \) cm\(^{-1} \) are characteristic peaks of polystyrene beads due to the C-C stretching of aromatic ring.
Figure 13. Raman spectra and Raman map of the assembled Janus Particles. The decrease in Raman intensity as the number of spheres increases has been confirmed by utilizing a finite-difference-time-domain (FDTD) approach to validate the experimental results. To prove this, we modeled 3 cases of 1, 2 and 3 Janus particles separately and
after the simulations we calculated the electromagnetic field enhancement distributions at certain wavelength of light source. From the electromagnetic fields for all the cases, we derived the maximum values for each case and plotted them to compare.

Figure 14. Variation of maximum Electric Field with no. of Janus spheres at (a) l = 787 nm and (b) l = 859 nm. (c) Scattering Cross-section with their characteristic peaks of 1, 2 and 3 Janus particles. Electric and Magnetic Fields for (d and g) 1 Janus particle at l = 1982 nm, (e and h) 2 Janus particles at l = 4013 nm and (f and i) 3 particles at l = 5394 nm. Cross-section views for calculating the EM-field enhancement distribution of Janus particles, are shown along XY plane. The colors from blue to red represent the EM-field intensity from weak to strong. The incident electric field was polarized in X-direction and propagation vector (k) was in Z-direction.

Figure 15(a and b) validates our experimental results shown in Figure 14(b). We plotted maximum electric field intensity values with the number of particles at 787 nm and 859 nm. In our experiments, the excitation wavelength was 785 nm, and the characteristic wavenumber was 1002 cm\(^{-1}\) (Figure 14(a)) or ~852 nm. That is why for the simulation
we focused on these two wavelengths. We also compared scattering cross-sections of each case of particles and found out the peaks of their scattering intensity varied over wavelengths ranged from 300 nm to 7000 nm.

In Figure 15(d-i), electric and magnetic fields for 1, 2 and 3 particles are shown at their respective characteristic peaks.

Figure 15. Electric and magnetic Fields for 1 (a and d), 2(b and e) and 3(c and f) Janus particles at l = 787 nm. Electric and magnetic Fields for 1 (g and j), 2(h and k) and 3(i and
I) Janus particles at $l = 859$ nm. Cross-section views for calculating the EM-field enhancement distribution of Janus particles, are shown along XY plane. The colors from blue to red represent the EM-field intensity from weak to strong. The incident electric field was polarized in X-direction and propagation vector ($k$) was in Z-direction.

In Figure 15, for 1, 2 and 3 particles electric and magnetic fields are shown at excitation wavelength i.e., 787 nm and wavelength of characteristic Raman peak i.e., 859 nm.

So, this FDTD simulation study delved into electromagnetic field analysis, revealing the distribution of electric and magnetic fields within Janus particles at excitation and Raman wavelengths.
Chapter 6. Conclusion

In our study, we employed the Finite Difference Time Domain (FDTD) method to comprehensively analyze the plasmonic responses exhibited by a diverse array of materials, each varying in shape and size. We elucidated that these plasmonic behaviors are intrinsically influenced by both the material properties themselves and the characteristics of their surrounding media. Each material possesses its own unique refractive index and dielectric permittivity, resulting in distinct scattering cross-sections that exhibit peaks at specific wavelengths corresponding to their plasmonic characteristics. Importantly, we demonstrated that the manipulation of parameters such as size, shape, and substrates allows for precise control over the observed red or blue shifts in these cross-sections.

Furthermore, these manipulations exert notable effects on the electromagnetic fields surrounding the materials, which have profound implications for numerous applications including disease diagnosis, photothermal therapy, and solar energy conversion. Our findings shed light on the intricate interplay between nanoparticles and their substrates, showcasing how interactions between these entities dynamically influence field enhancements.

We utilized FDTD Method to determine and understand the electric field enhancement due to TMD (transition metal dichalcogenide) platelets, HfS$_2$ and TMO (transition metal oxide) particles, HfO$_2$ to achieve better sensitivity.

Additionally, we explored the behavior of hybrid materials, such as Janus particles featuring a gold-coated polystyrene core, revealing how the presence of a gold coating
enhances the optical and electromagnetic properties of the particles. Although for nanoparticles we get plasmon resonance in visible light wavelength region, for Janus particle we get resonance in far infrared region. To achieve better detection sensibility in FIR region, Janus Particle can be utilized. Through rigorous FDTD simulations, we demonstrated the method's capacity to effectively handle complex structures and materials, thereby enabling us to accurately elucidate plasmonic responses and field enhancements.

In conducting our FDTD simulations, we meticulously selected physical parameters to ensure the validity and reliability of our experimental results. The simulated outcomes generated from our study serve as valuable tools for advancing the understanding of local fields and their intricate interrelations, thereby paving the way for further insights into the fascinating realm of plasmonics.
Chapter 7. Limitations

Although the FDTD method has several benefits to understand plasmonic behavior of materials, there are some disadvantages that hinder the perfect modeling of experimental environments in simulations. Some of these are:

a) The FDTD technique replicates a spatial domain larger than that of the nanoparticles (NPs) and necessitates the simulation of an infinite domain. Simultaneously, it can yield transient outcomes rather than steady-state ones.

b) FDTD encounters difficulties when dealing with specific material properties like dispersion or nonlinearity, and it may face challenges in accurately modeling of irregular shapes.

c) In FDTD, the wave propagation within the discrete grid doesn't adhere precisely to Maxwell's equations' dispersion relations; instead, it follows an approximation of them. The different types of materials that we model in FDTD also have different limitations. For example, metal nanoparticles have larger scattering loss, higher amount of energy dissipation, and poorer tuneability than other plasmonic materials. On the other hand, obtaining consistent device characteristics for 2D nanomaterials on a nanoscale level is difficult because of the intricate nature of fabrication procedures. As a result, the journey toward practical industrial-scale production is prolonged.
Appendix. Letters of Permission

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Vita

Originally from Bangladesh, Maria Iftesum started her academic career at Bangladesh University of Engineering and Technology, where she graduated with a Bachelor of Science in Mechanical Engineering in May 2022. Maria came to the United States to pursue graduate studies in mechanical engineering to learn more and do more research. At the Applied Nanophotonics Lab, Maria had a great time working with Dr. Manas Gartia. Maria successfully completed her final MS-thesis defense exam on March 21, 2024, making her eligible to receive a Master of Science in Mechanical Engineering from Louisiana State University, which will be granted at the institution's commencement in May 2024. Maria is eager to take on new challenges and opportunities as she continues her work as a PhD researcher with the same group.