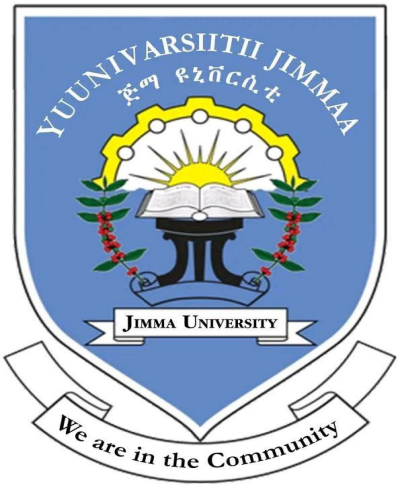

SIZE DEPENDENT LOCAL FIELD ENHANCEMENT FACTOR OF CdSe BASED CORE TRIPLE LAYER SPHERICAL NANO PARTICLES

By:

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Abbreviation and Acronym

Ag: Silver

CdSe: Cadmium selenide

EM: Electromagnetic

IR: Ifra-red

LFEF: Local Field Enhancement Factor

LSPRs: Localized Surface Plasmon Resonances

LSPs: Localized Surface Plasmons

NCs: Nanocomposites

NPs: Nanoparticles

PSPs: Propagating Surface Plasmons

SiO_2: Silica or Silicon dioxide

SPPs: Surface Plasmon Polaritons

SPRs: Surface Plasmon Resonances

ZnSe: Zinc selenide

Abstract

Nanoparticle is a general term in which nano refers to size and denotes a billionth of a unit. Since nanoparticles have been in use, they have become the cornerstones of nanoscience and nanotechnology. Their applications in the real world require specific sizes, shapes, compositions, and structures. Hence, this dissertation is devoted to the theoretical and numerical investigations of the effects of size, shape, surface plasmons, and host medium on the optical properties of core-shell nanocomposites (NCs). We reviewed on the size-dependent local field enhancement factor (LFEF) of CdSe@ZnSe@Ag core/spacer/shell spherical nanoparticles within the framework of quasi-static approximation was numerically and theoretically investigated. From the potential distributions in the core, shell(s), and host medium, and using the modified Drude-Sommerfeld model, we separately obtained the expressions for LFEF of core/spacer/shell nanocomposites. By changing the sizes of each of the components of the nanocomposites in these expressions, we understand that the LFEF of CdSe@ZnSe@Ag increases with a decrease in the size of the core. At the same time, the resonance peaks are red shifted in the inner interface and blue shifted in the outer interface of the shell. The result also reveals that whether the shell radius is kept constant or decreased, increasing the core size produces a lower field enhancement factor showing that the core size is a crucial parameter to change the field enhancement factor of the dielectric core and metal shell nanoparticle (NP). In general the sizes of the core, the spacer and the shell have vigorous effects on the local field enhancement factor of core-shell nanoparticles. The feature direction of this study likely involves experimental characterization and theoretical modeling to explore how the size variations of CdSe@ZnSe@Ag core triple-layer spherical nanoparticles influence their local field enhancement factor, which is crucial importance for their application in nanotechnology and photonics.

1

Introduction

1.1 General Back Ground of the Study

1.1.1 Nanoparticles and plasmonics

Nanoparticles and plasmonics are fascinating areas of study at the intersection of nanotechnology and photonics, with profound implications across various fields including physics, chemistry, biology, and engineering.Nanoparticles are tiny particles with dimensions typically between 1 and 100 nanometers.They can be made from various materials such as metals (e.g. gold, silver), semiconductors (e.g. quantum dots), or oxides. What makes nanoparticles unique is their size, which often leads to novel optical, electronic, and magnetic properties that differ significantly from bulk materials.These properties are heavily influenced by quantum mechanics and the surface effects that dominate at the nanoscale.Plasmonics refers to the study and application of plasmons[LongDash]collective oscillations of electrons in a metal or semiconductor nanoparticle when stimulated by light. Plasmons are highly sensitive to the nanoparticle' s size, shape, and the surrounding medium, allowing for precise control over their optical properties. This sensitivity makes plasmonic nanoparticles invaluable in sensing applications, where they can detect minute changes in their environment, such as the presence of specific molecules or biomarkers.The field of plasmonics enables the manipulation of light at nanoscale dimensions, far smaller than the wavelength of light itself, leading to advancements in technologies such as nanoscale imaging, ultra-sensitive biosensors, and enhanced solar cells. Moreover, plasmonic nanoparticles can concentrate light into extremely small volumes, known as "hot spots," which are exploited in techniques like surface - enhanced Ra-

man spectroscopy (SERS) for detecting trace amounts of chemicals[1].

1.1.2 Semiconductor nanoparticles : CdSe

Semiconductor nanoparticles, particularly those made of cadmium selenide (CdSe), are a prominent class of nanomaterials with intriguing optical and electronic properties. Here's an introduction to CdSe nanoparticles

Composition and Structure Chemical Composition : CdSe nanoparticles are composed of cadmium (Cd) and selenium (Se) atoms arranged in a crystal lattice structure. Size : These nanoparticles typically range from 1 to 10 nanometers in diameter, making them suitable for various applications due to their quantum size effects.

Optical Properties Quantum Confinement : At such small sizes, CdSe nanoparticles exhibit quantum confinement effects. This means that the band gap of the material increases as the size decreases, leading to tunable absorption and emission wavelengths across the visible spectrum.

Fluorescence : CdSe nanoparticles are known for their strong and size-dependent fluorescence properties. They emit light when excited by photons of higher energy than their band gap, making them useful in applications such as biological imaging and optoelectronics.

Synthesis and Functionalization Synthesis Methods : CdSe nanoparticles can be synthesized using various techniques, including colloidal methods where precursors are reacted in solution under controlled conditions to nucleate and grow nanoparticles.

Surface Functionalization To stabilize and modify their surface properties, CdSe nanoparticles are often coated with organic ligands or polymers, which can also facilitate their dispersion in different solvents or matrices.

Applications Biomedical Imaging : Due to their fluorescence properties, CdSe nanoparticles are used extensively in bioimaging applications, such as labeling and tracking biological molecules and cells.

Optoelectronic Devices They are utilized in LEDs (light-emitting diodes), solar cells, and displays due to their efficient light emission and absorption properties.

Sensors : CdSe nanoparticles can be used as sensitive probes in sensors for detecting

various analytes, leveraging their optical and electrical characteristics.

Environmental Considerations : Toxicity Concerns : CdSe nanoparticles contain cadmium, which is toxic. Efforts are ongoing to mitigate environmental and health risks associated with their use through encapsulation, surface modification, or alternative materials

1.1.3 Core-shell and multilayer nanoparticles

Core-shell nanoparticles consist of a core material surrounded by a shell of a different material or materials. The core and shell materials can be chosen to combine different properties or functionalities, offering synergistic benefits.

Structure : Core : The central part of the nanoparticle, typically consisting of one material (e.g., a metal, semiconductor, or magnetic material). The core' s properties, such as its optical, magnetic, or electronic behavior, can be tuned based on its composition and size.

Shell : The outer layer surrounding the core, made of a different material. The shell can modify the core's properties, provide stability, enhance biocompatibility, or impart additional functionalities like improved dispersibility or protection against environmental factors.

Multilayer nanoparticles consist of multiple layers of different materials stacked around a central core. Each layer serves a specific purpose, such as controlling properties, providing functionality, or protecting the core. Structure :

Core Similar to core-shell nanoparticles, multilayer nanoparticles have a core material, which may be a single component or a composite structure.

Multiple Layers : Successive layers of different materials are deposited around the core, offering precise control over the nanoparticle' s properties and functionalities. These layers can vary in thickness and composition.

1.1.4 Size dependent in local field enhancement

Local field enhancement occurs due to the excitation of localized surface plasmon resonances (LSPRs) in metallic nanoparticles (e.g., gold, silver) when illuminated with light.This phenomenon leads to the formation of intense electromagnetic fields near the nanoparticle surface, significantly enhancing the interaction between inci-

dent light and nearby molecules (such as analytes in SERS). Size Dependence in Local Field Enhancement Resonance Condition :
Plasmon Resonance Frequency : The resonance frequency of plasmons in nanoparticles is highly dependent on their size, shape, and composition. For spherical nanoparticles, the LSPR wavelength λ, LSPR is primarily influenced by the nanoparticle diameter (d). It follows approximately the Mie theory predictions, where larger nanoparticles exhibit LSPRs at longer wavelengths. [2] **Size-Dependent Effects** Quantum Size Effects : In nanocrystals, quantum size effects become prominent, altering the electronic structure and influencing the plasmonic properties is can lead to size-tunable plasmon resonances and localized field enhancements.
Field Localization Smaller nanoparticles typically exhibit more pronounced field localization in "hot spots" near their surfaces. This Localization results in higher local electromagnetic field intensities, enhancing the SERS signal strength for molecules in proximity to these hot spots. Experimental Observations Experimental Verification : Studies have demonstrated that smaller nanoparticles generally exhibit higher SERS enhancement factors compared to larger nanoparticles. This size-dependent enhancement is critical for achieving high sensitivity in SERS-based detection of trace analytes.

1.1.5 Application

CdSe-based triple layer spherical nanoparticles exhibit size-dependent local field enhancement factors, influencing their applications in various fields, including optics, photonics and sensing. Here is an exploration of their applications based on size-dependent local field enhancement

1. **Tunable Optical Properties**

    - **The size of CdSe nanoparticles affects their band gap and thus their absorption and emission spectra. Triple-layered CdSe nanoparticles can be engineered to have precise optical properties by controlling the size of each layer. This tunability is crucial for applications in LEDs, displays, and photovoltaics where specific emission wavelengths are required.**

2. **Sensing and Detection Applications**

    - **Surface-Enhanced Raman Scattering (SERS) : CdSe nanoparticles, especially those with triple-layer structures, can enhance local electromagnetic fields when excited near their plasmonic resonances. This enhancement is size-dependent and can be optimized for sensitive detection of molecules in SERS applications. The triple-layer design allows for precise control over the local field enhancement factors, maximizing the SERS signal intensity and detection sensitivity.**

3. **Catalysis and Energy Applications**

    - **Photocatalysis : CdSe nanoparticles can serve as photocatalysts for various chemical reactions under light irradiation. Size-dependent local field enhancement can enhance the efficiency of charge separation and catalytic activity, making them suitable for applications in water splitting, pollutant degradation, and CO_2 reduction.**
    - **Energy Conversion : In solar cells and photodetectors, CdSe nanoparticles with optimized sizes can enhance light absorption and charge carrier generation. The size-dependent local field enhancement factors contribute to improving the overall efficiency and performance of these devices.**

4. **Nanomedicine and Imaging**

    - **Biomedical Imaging : CdSe nanoparticles are used as contrast agents in imaging techniques such as fluorescence imaging and photoacoustic imaging. Their size-dependent optical properties and local field enhancement can improve imaging sensitivity and resolution, facilitating applications in disease diagnosis and monitoring**
    - **Drug Delivery : Triple-layer CdSe nanoparticles can be designed to encapsulate drugs within their core and provide controlled release through their shell layers. Size-dependent local field enhancement can enhance**

the targeting efficiency and therapeutic efficacy of drug delivery systems in cancer therapy and personalized medicine.

1.2 Statement of the problem

The interest of studying core-shell nanoparticles has been driven by the need in developing nanomaterials and nanostructures with desired properties. These properties mainly involve optical, electronic or magnetic phenomena of the nanoparticles. Coreshell particles have been known since the 1920's [3]. However, it was only in 1951 that the first theoretical studies were reported by Aden and Kerker [4], who extended Mie theory for the optical properties of a sphere coated with a concentric spherical shell particles. The first experiments on core-shell metal particles only appeared later in 1964 when Morriss and Collins [5]applied the theory of Aden and Kerker to silver coated gold. As metal nanoparticles gained increasing attention more detailed investigations began in the late 1980's, encompassing various types and aspects of coated particles. Since then, through the fine-tuning of cores and shells of nanoparticles, various types of functional materials with modified properties have been achieved [6]-[7]. These tailored properties are increasingly important in the development of smaller, cheaper, faster, and more efficient optoelectronic devices. In structure In structure of core-shell materials, the shell is used to passivate the surface of nonradioactive recombination sites of the core with the goal to improve its optical properties and reduce chemical attack. Furthermore, it separates physically the optically active core from its surrounding medium. Overcoating also prevents the leakage of core materials thereby reducing the toxicity of quantum dots [8]. Finally,this encapsulation can lead to the strengthening of quantum confinement effect which enables quantum dots reach their higher emission intensity or shift the maximum in the emission spectrum toward longer wavelengths. For instance, cadmium selenide (CdSe) nanocrystals can emit fluorescence at different wavelengths depending on their size, being feasible to synthesize in all UV-V is spectra and use them as emitters in optoelectronics or in (bio) chemical sensing as labels [9]. To further improve the photoluminescence efficiency of such nanocrystals, overcoating them using inorganic shell materials having similar lattice parameters and higher band gap energy is found to be suc-

cessful. In case of CdSe, preferred shell materials include zinc sulphide (ZnS), zinc selenide (ZnSe), and cadmium sulphide (CdS) [10]-[13]. Among these, the combination of CdSe and ZnSe into a core-shell structure is highly desirable to prevent the evolution of interfacial misfit dislocations that also act as trapsfor electrons and holes [14]. However in this study we investigated, using CdSe as a core and silver metal as a plasmonic shell, size dependent local field enhancement factor (LFEF) in the presence ZnSe as spacer.

1.3 Basic research questions

In this Thesis, the following questions will be expected to be answered:

1. What is the value of LFEF with increasing core and shell at fixed spacer thickness?

2. What is the value of LFEF with spacer size is increasing at fixed core and shell sizes?

3. What is the value of LFEF with shell size is increasing at fixed sizes of the core and spacer?

4. What is the value of LFEF with core size is increasing and spacer thickness is decreasing at fixed NP size?

5. What is the value of LFEF with core size is decreasing and spacer thickness is increasing at fixed size of NP?

6. What is the value of LFEF with spacer and shell thicknesses are increasing at fixed core size?

1.4 Objectives of the study

1.4.1 General objective

The general objective is, to investigate the Size Dependent of LFEF Cdse@ZnSe@Ag core shell spherical Nanoparticles embedded in host matrix Sio_2.

1.4.2 Specific objectives

The study will try to address the following specific objectives. These are:

- **Investigate how variations in core and shell sizes, coupled with a decrease in spacer thickness, affect the LFEF of the nanoparticles.**
- **Investigate the dependency of LFEF on spacer thickness**
- **Determine the impact of increasing shell size on LFEF under conditions where core and spacer sizes remain constant**
- **Investigate the correlation between core size reduction and LFEF.**
- **Investigate effects of core size on LFEF of CdSe@ZnSe@Ag spherical core-shell NPs.**
- **Investigate the effect of size on LFEF.**

1.5 Significance of the study

Optical Properties : Quantum Confinement Effects : In semiconductor nanoparticles (e.g., quantum dots), size determines the band gap and optical properties due to quantum confinement. Smaller nanoparticles have larger band gaps and emit light at shorter wavelengths, enabling tunable emission spectra crucial for applications in LEDs, displays, and biomedical imaging.
Plasmonic Resonances : Metallic nanoparticles exhibit size-dependent plasmonic resonances, influencing their interaction with light and the resulting local field enhancement. This size dependency is exploited in surface-enhanced spectroscopies (e.g., SERS) for sensitive detection and imaging applications.
Electrical and Magnetic Properties : Quantum Transport : In nanowires and nanotubes, size affects electron transport properties such as conductivity and mobility.Quantum confinement modifies electronic band structures, leading to unique electrical behavior essential for nanoelectronics and sensors.
Magnetic Behavior : Magnetic nanoparticles exhibit size-dependent magnetic properties, including coercivity and magnetic susceptibility. These properties are

crucial for applications in magnetic storage, biomedical applications (e.g., magnetic hyperthermia), and spintronics. Size and layer thickness dependency Size and layer thickness dependency in nanomaterials and thin films offer unparalleled opportunities for tailoring material properties and functionalities across diverse applications. Understanding and controlling these dependencies are essential for advancing nanotechnology, enabling innovations in optics, electronics, energy, biomedical devices, and beyond. Continued research and development in nanoscale materials design promise to unlock new capabilities and address emerging challenges in various technological and industrial sectors.

1.6 Scope of the study

The scope of this study is calculations of local field enhancement factor CdSe@ZnSe@Ag using Quasi-static Approximation. All LFEF calculations will be performed using mathematica. The study limited to for core CdSe(5nm-9nm),(fixed at 9nm),(fixed at 10nm),(2nm-10nm),(10nm-6nm)and (fixed at 9nm) for spacer ZnSe (fixed at 10nm),(10nm-10.8nm),(fixed at 14nm),(18nm-14nm)(11.2nm-12nm)and(10nm-14nm) for Shell Ag (12nm-16nm),(fixed at 18nm),(20nm-24nm),(fixed at 20nm),(fixed at 20nm)and(16nm-24nm).

1.7 The Out line of the Study

This Thesis contains four chapters and organized as follows:- Chapter 1, is Introduction to the problem, Chapter 2 deals with the theoretical background on nano particles in general and the concepts of size dependent local field enhancement Cdse based core and single shell nano particles Chapter 3 about Materials and Methodology of the study. chapters 4 is about Result and Discussion and, Finally Chapter 5 is the conclusion and Bibliography is attached at the end of the thesis.

2

Review of Related Literature

2.1 Introduction

This studies show that core-shell nanocomposites have attracted increasing research interest due to their outstanding properties such as versatility, tunability, and stability [15].[16]. A core-shell nanocomposite consists an inner core and outer shell(s) that is composed of different materials. The combination of different material properties in core-shell system leads to several novel properties for potential applications in various fields such as electronics, optics, biomedicine, envi- ronmental science, materials, energy, magnetism, and catalysis [17]-[18]. Moreover, the properties of these core-shell materials can be easily tuned by varying the size, shape, morphology as well as the type of the core, shell and embeding medium [19]-[21]. Among the widely studied core- shell nanocomposites is the CdSe-based quantum dots (QDs). In particular, the emission intensity of CdSe QDs can be increased several times when it is capped with a ZnS shell to form a CdSe-ZnS core-shell structure [22]. In addition, CdSe nanocrystals are considered as the most promising emitting materials in the visible spectral region because their emission color can dramatically be adjusted from blue to red. Wide band gap semiconductors such as ZnS, CdS, and ZnSe can be used as the shell material [23] to cap a CdSe core. But among these semiconductors, ZnSe over coated CdSe nanoparticles have shown advantages that not only the bandgap of ZnSe low toxicity as compared to CdS and ZnS [24]. Moreover, its lattice parameter and binding energy are 5.67 A^o and 20 meV respectively, while the band gap alignment is of type I, where both electrons and holes are confined in the CdSe core [25]-[27].The lattice parameter mismatch of ZnSe relative to the CdSe core (6.3 commonly used

ZnS shell (10.6 material parameters make ZnSe an excellent shell material to cap a CdSe core in a core-shell nanocomposite. In support of this, experimental studies show that when CdSe is covered with ZnSe, the optical properties of the combination is enhanced [30]. It was also reported that CdSe@ZnSe core-shell quantum dot are novel materials incorporating CdSe core in a ZnSe shell .For instance, the photoluminescence intensity of a CdSe@ZnSe coreshell nanocomposites can be significantly enhanced by coating (capping) the CdSe core with a few layers of ZnSe shell [31]. But to the best of our knowledge, few or no theoretical and numerical studies were carried out to support those many experimental works. Moreover, as the heterostructures formed with metal and semiconductor composite nanostructures provide another efficient opportunity for tuning the unique optical properties of nanoparticles[32],the plasmonic effects are also found to be interesting.For CdSe based core- shell nanocomposites, the effect of the sizes of the core,the shell (metal), and the spacer (semiconductor) on the local field enhancement factor (LFEF) were not further studied yet. Hence, this study focuses on the theoretical and numerical investigations of the size dependent LFEF of CdSe@Ag and CdSe@ZnSe@Ag core-shell spherical nanoparticle embedded in the host matrix,SiO_2.

2.2 Definition

Nano is used as a prefix for a unit of time or length, it means one billionth of that unit. The prefix “nano” originates from the Greek word “dwarf” that means something small. In conventional view, nano material means among the three dimensions at least one dimension should be less than 100 nm. But when ever all three dimensions are less than 100 nm, it is called nano particle. Nano particles are of great scientific interest as they are effectively a bridge between bulk materials and atomic and molecular structures. A bulk material should have constant physical properties regardless of its size, but where as in nano-scale this is often not the case. Size dependent properties are observed such as quantum confinement in semiconductor particles surface plasmon resonance in some metal particles and super para-magnetism in magnetic nanoparticle. There fore, in recent

year nanoparticle synthesis is an interesting research topic

2.3 Local field enhancement

The local field, originally introduced by Lorentz as the field at an atom is now assumed to act on the particle as a whole. It is the field produced at an atomic site by all other atoms acting on the reference atom [33]. Nanoshells exhibit local field enhancement effects similar to pure metal clusters[34]. The excitation of LSPs is accompanied by a local field enhancement, which is exploited in many and extremely different applications such as, surface-enhanced Raman spectroscopy, surface-enhanced fluorescence, and confocal microscopy, as well as to enhance the efficiency of solar cells, or to structure surfaces [35]. The field enhancement effect strongly depends on the polarization properties of the exciting radiation. In particular, the extinction spectra of noble metal nanoparticles are dominated by pronounced surface plasmons. These resonances are attributed to a coherent excitation of the conduction band electrons, excited by means of an electro- magnetic field. One of the unique features of metal nanoparticles is their strong field enhancement in the vicinity of their surface. In the quasi-static regime, let us consider a small metal sphere illuminated with a plane monochromatic wave

$$E = E_o exp[i(kz - \omega t)] \tag{2.1}$$

where E is the incident electromagnetic field, E_o the field amplitude, z is the coordinate along a main axis of the spherical nanoparticle, and k is the wave vector. The field outside the sphere is the sum of the incident field and the field scattered by the particle. In the quasistatic regime, the latter field is equal to the field of a point dipole, located in the center of the sphere, and oscillating with the same frequency as the incident field. The amplitude of the near field of the oscillating dipole may be derived from the dependence of its potential φ(r, θ) on the distance r from the center of the sphere and on the polar angle θ with respect to the polarization direction of the incident field[36].

$$\varphi(r,\theta) = R^3 \frac{\varepsilon M - \varepsilon d}{\varepsilon M + 2\varepsilon d} E_o \frac{cos\theta}{r^2} \tag{2.2}$$

where R, ε M , and ε d are the same as defined for Eqn.(2.2) Differentiation with respect to r and θ gives the normal E_r and tangential E_θ components of the electric

field as

$$E_r = 2R^3 \frac{\varepsilon M - \varepsilon d}{\varepsilon M + 2\varepsilon d} E_o \frac{cos\theta}{r^2} \tag{2.3}$$

$$E_\theta = R^3 \frac{\varepsilon M - \varepsilon d}{\varepsilon M + 2\varepsilon d} E_o \frac{sin\theta}{r^2} \tag{2.4}$$

Eqns. (2.3) and (2.4) provide the basis for application of metal nanoparticles based on the field enhanced. The square of the modulus of the electric field serves as a driving force for all surface-enhanced spectroscopies. This value may be written as

$$|E|^2 = R^6 |\frac{\varepsilon M - \varepsilon d}{\varepsilon M + 2\varepsilon d}|^2 E_o^2 \frac{1 + 3cos^2\theta}{r^6} \tag{2.5}$$

and defines the field outside the sphere for $r \geq R$. As might be easily seen, the field on the nanoparticle surface(r=R) does not depend on the nanoparticle size.This is due to the restriction to the quasistatic regime. On the other hand, Eqn.(2.5) reveals that outside the nanoparticle, the field drops off rapidly with increasing distance from the surface. Hence, the highest field enhancements are achieved on, or in close vicinity of the nanoparticle surface The field amplitudes are largely enhanced at this resonance wavelength provided that the imaginary part of the permittivity $Im[\varepsilon M]$, i.e. the damping is small. From Eqn(2.5), the local field enhancement factor, $|F|^2$ by definition is given by If the angular dependence is neglected the local field enhancement F is given by[37]

$$F = \frac{\varepsilon M - \varepsilon d}{\varepsilon M + 2\varepsilon d} \frac{R^6}{r^3} \tag{2.6}$$

Neglecting the angular dependence is justified since the physical relevant square of the modulus of the electric field falls off rapidly as $|E|^2 \, \alpha 1/r^6$

2.4 Core-shell nanocomposites

There are large varieties of core-shell nanoparticles available so far with a wide range of applications. As a result, the classification of all the avail- able core-shell nanoparticles, which depends on their industrial applications or is based on some other property is a challanging task. In this section we attempt to review the

core-shell nanoparticles depending on their material properties. In a broad sense clearly the core or shell materials in a core-shell particle are either made of inorganic or organic materials

2.5 Classification of Core Shell Nanoparticle

Depending on their material properties, the core-shell nanoparticles can be classified into four main different groups:

2.5.1 Inorganic-inorganic

Inorganic-inorganic types of particles are widely used for the improvement of semiconductor efficiency, information storage, optoelectronics, catalysis, quantum dots, optical bioimaging, biological labeling, etc. Furthermore, of the different types of inorganic-inorganic nanoparticles, it can be seen that, in general, both the cores and shells are made of metal, metal oxide, other inorganic compounds, or silica. Depenping on the nature of the shell material, core-shell particles can be broadly classified into two categories: either silica-containing ones or those comprised of any other inorganic material. Some of the examples include CdSe- CdS, $Au - SiO_2$ **, CdSe-ZnS, CdTe-CdSe, CdSe-ZnSe-ZnS, and** $CdSe - SiO_2$**.**

2.5.2 Inorganic-organic

Inorganic-organic core-shell nanoparticles are made of metal, a metallic compound, metal oxide or a silica core with a polymer shell or a shell of any other high density organic material. Some examples of this type of core-shell NCs include Au-PSMA, Fe_3O_4**-PEG,Fe-PIB,** SiO_2**-PS, where PSMA, PEG, PIB and PS denote polystyrene methacrylate, polyethylene glycol, polyisobutylene, and polystyrene, respectively. The advantages of the organic coating on the inorganic material are many fold. One example is the fact that the oxidation stability of the metal core is increased when otherwise the surface atoms of the metal core can be oxidized to the metal oxide in a normal environment [38]. In addition, they exhibit enhanced biocompatibility for bioapplications [39][40].**

2.5.3 Organic-inorganic

organic-inorganic type which are structurally just the reverse of inorganic-organic core-shell type explained above. These types of particles, in general, have the dual properties of both the inorganic and organic materials [41]. The inorganic material, especially a metal oxide coating on an organic material is beneficial in several respects, such as increased strength of the overall material [42], resistance to oxidation, thermal and colloidal stability [43], and and abrasion resistance [44]. At the same time, these particles also show polymeric properties such as excellent optical properties, flexibility and toughness and in addition they can improve the brittleness of the inorganic particles [45]. Recently this type of nanoparticle proved of great research interest because of their extensive applications in different fields of material science including paints, magnetic fluids, catalysis, microelectronics

2.5.4 Organic-organic

Organic-organic[47]core-shell NCs where both the core and shell particles are made of a polymer or another organic material. They are known as "smart particles" and have a wide range of applications in different fields, such as drug delivery,biosensing, chemical separation ,biomaterials and catalysis [48] [54].The advantages of having a polymer coating on another polymer is to modify the physical properties of the overall material, such as toughness [53].Few examples of this class of core-shell NCs are polyphenylene-PEO and PTBA-PS where, PEO and PTBA are polyethylene oxide and poly-tert-butyl acrylate, respectively.

2.6 Lorentz model for band electron

He develop a classical theory of optical properties in which the electrons and ions of matter were treted in a simple harmonic oscillators subject to the driving force of applied EM field to understand this model let us consider an atom with electron bound to the nucleus in much the same way as small mass bound to large mass by a spring . Then, for an electron of charge -e and mass m, the equation of motion of bound electron for displacement $r = r_o exp(-i\omega t)$

$$m\frac{\partial d^2 r}{\partial dt^2} + m\gamma\frac{\partial dr}{\partial dt} + kr = -eE_O e^{-i\omega t} \tag{2.7}$$

Where, γ is a damping factor and k is the spring constant.For a time harmonic optical electromagnetic field $E = E_o exp(-i\omega t)$, the dipole moment of the electron -e and the positive nucleus +e is given by

$$p = -er = -\frac{e^2/m}{\omega_o 2 - \omega^2 + i\gamma\omega} E \tag{2.8}$$

Where$\omega_o = \sqrt{k/m}$ is the a resonant frequency. The polarization P due to n atoms or electron-nucleus pairs per unit volume is

$$P = np = \frac{ne^2/m}{\omega_o^2 - \omega^2 - i\gamma\omega} E \tag{2.9}$$

To include the interband contribution to the polarization can be extended and the displacement vector D can written as

$$D = \varepsilon_o E + P_{IB} + P \tag{2.10}$$

Where $P_{IB} = \varepsilon_o X_{IB} E$ is polarization due to the interband contribution.Then ,the displacement vector D can be written further as

$$D = \varepsilon_o (1 + X_{IB} + X_{DS}) E \tag{2.11}$$

Where

$$X_{IB} = \frac{\omega_p^2}{\omega_o^2 - \omega^2 - i\gamma\omega} \tag{2.12}$$

Then the contribution of bound electrons to the dielectric function can be given by

$$\varepsilon_{IB} = 1 + \frac{\omega_p^2}{\omega_o^2 - \omega^2 - i\gamma\omega} \tag{2.13}$$

with real and imaginary part of

$$\varepsilon'_{IB} = 1 + \frac{\omega_p^2(\omega_o^2 - \omega^2)}{(\omega_o^2 - \omega^2)^2 + \gamma^2\omega^2}, \varepsilon"_{IB} = \frac{\omega_p^2\gamma\omega}{(\omega_o^2 - \omega^2)^2 + \gamma^2\omega^2}. \tag{2.14}$$

From Eqn.(2.10),the complex dielectric function incorporating all optical material properties around the visible region is given by

$$\varepsilon(\omega) = (1 + X_{IB} + X_{DS}). \tag{2.15}$$

Substituting for X_{DS} this equivalent to

$$\varepsilon(\omega) = 1 + \frac{\omega_p^2}{\omega_o^2 - \omega^2 - i\gamma\omega} - \frac{\omega_{p^2}}{\omega^2 + i\gamma\omega} \tag{2.16}$$

considering effective parameters ω_p and γ, and by introducing ε_∞ as contribution of interband transition to polarizability the dielectric function is given by

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \tag{2.17}$$

The dimensional dependence of the dielectric function was introduce within the framework of the model of the mean free path of conduction electrons. Decreasing the size of nanoparticle will eventually cause the thickness to become less than the bulk mean free path ,and electron scattering from the surface of the particle will have decreasing effect thus broadening its plasmon resonance peaks . If the electron mean free path depends on size of the nanoparticle, a correction is available for the nanoshells and in this case ,γcan be modified to

$$\gamma(r) = \gamma_o + A\frac{VF}{r_{eff}} \tag{2.18}$$

Where γ_o is the damping constant of the bulk material VF is the electron velocity at the Fermi surface, A is an empirical parameter used for matching the calculated damping with the experimental result .for a core-shell spherical NCs of core-radius r_1 and shell radius r_2, r_{eff} is the effective mean free path of collision and can be calculated from

$$r_{eff} = \frac{1}{2}[(r_2 - r_1)(r_2^2 - r_1^2)]^{\frac{1}{3}} \tag{2.19}$$

2.7 QUANTUM DOT

A quantum dot consists of a semiconductor core which is responsible for the fundamental optical properties (i.e., light absorption and emission). The luminescence of quantum dots is caused by the quantum confinement effect and defects in the crystalline structure of quantum dots. From this perspective, quantum dots can be tuned like metal nanoparticles to absorb and/or scatter different colors Quantum confinement effect refers to electrons and holes being spatially restricted in a material whose dimensions are on the order of or smaller than the exciton Bohr radius 40of that material. The bulk exciton Bohr radius is the natural physical separation in a crystal between the electron in the conduction band and the hole it leaves behind in the valence band. Under quantum confinement conditions, energy levels may be treated as discrete and the band gap becomes size dependent, increasing as the nanocrystal size decreases. On the other hand, the defects on the surface of the nanocrystal can reduce luminescence of the dots because atoms on the quantum dot surface have dangling bonds which trap electrons after absorbing a quantum of energy. Relaxation of the electron-hole system occurs in this case by nonradiative way and as a result the luminescence quantumyield of quantum dots is significantly reduced. For these reasons it is important tocontrol the quality of a quantum dot surface by overcoating it with the second semiconductor layer or shell

2.8 Calculation and Models

2.8.1 Quasi-Static Approximation

If the size "a" of a given particle is much smaller than the wavelength, λ, of the incident driving field, the variation of the phase of this field across the particle is negligible, so an incident plane wave can be approximated by a constant field. This is known as the quasi-static approximation, A quasi-static system means a system for which

- **The sources and fields change slowly;**
- **one or more of the terms in the field equations can be neglected.**

2.8.2 Mie Theory

For spherical nanoparticles,Mie theory provides a framework to calculate scattering,absorption,and the LFEF.The theory accounts for the core and shell sizes,and the dielectric functions of the materials involved.
Numerical Simulations: Computational methods like finite-difference time-domain (FDTD) or finite element method (FEM) simulations are often used to model the electromagnetic fields around complex nanostructures. These simulations can predict the LFEF for various sizes and configurations.
Empirical and Analytical Models: Simplified models can also be employed,especially for approximating trends. These might involve fitting experimental data to theoretical predictions. Example Trends Smaller Core Size: Leads to stronger quantum confinement,potentially increasing the LFEF due to higher energy states being more susceptible to plasmonic interactions from the shell.
Optimal Shell Thickness: There exists an optimal shell thickness for maximum LFEF. Too thin a shell may not support strong plasmon resonance, while too thick a shell may dampen the field enhancement due to increased scattering.
Experimental Observations: Experimental studies often involve measuring the optical properties (e.g.,absorption,scattering spectra) and using these to infer the LFEF. Techniques like surface-enhanced Raman scattering (SERS) can directly measure the enhancement factors.
Practical Applications Sensing: Enhanced LFEF improves the sensitivity of sensors based on CdSe-core/shell nanoparticles, useful in detecting low concentrations of analytes.Photovoltaics:Improved light absorption due to enhanced local fields can lead to more efficient solar cells.Biomedical Imaging:Increased LFEF can improve the contrast and resolution of imaging techniques using these nanoparticles.In general,the size-dependent LFEF of CdSe-based core and single-shell nanoparticles is a complex interplay of quantum mechanical effects and plasmonic phenomena. Understanding and optimizing these factors require both theoretical models and experimental validation.

2.9 Approaches of synthesis

For synthesis of nano material there are two approaches, "Top Down" and "Bottom Up". The "Top Down" approach often uses the traditional workshop or micro fabrication methods where externally controlled tools are used to cut, mill and shape materials into the desired shape and order. For example like lithographic techniques (e.g., UV, electron or ion beam, scanning probe, optical near field), film deposition and growth, laser-beam processing and mechanical techniques (e.g., machining, grinding, and polishing). Where as "Bottom-up" approaches, in contrast, use the chemical properties of single molecules to cause single-molecule components to automatically arrange themselves into some useful conformation, like chemical synthesis, laser induced assembly (i.e., laser tapping), self assembly, colloidal aggregation and 2-photon confocal processing. These approaches utilize the concepts of molecular self assembly. The trick with bottom-up manufacturing is the understanding of chemical and physical properties of nanoparticle and manipulating them to self-assemble. Neither the top-down nor bottom-up approach is superior at the moment each has its advantages and disadvantages. However, the bottom-up approach has an inherent size limit much smaller than top down approach. And also bottom up approach have the potential to be more cost-effective in the future because for this approach there are absolute precision, complete control on the process and minimum energy loss compare to top down approach.

2.10 Triple layer spherical nanoparticles

First consider a concentric n-layer nanocomposite that consists of multiple nanoscale layers of controllable thickness. The electrostatic potential for each of the regions (layers) satisfy the Laplace's equation which is given by is the electric potential associated with the electric field induced inside and outside the nanocomposite, i is the region where electric potential is to be determined. Let, the dielectric function of the ith region can be represented by e_i. The potential distribution in the different regions of the n-layered nanocomposite is obtained by solving the Laplace's

equation. Accordingly, the potential ϕ_i in each region is given by

$$\phi_i(r,\theta) = (A_i r + \frac{B_i}{r^2})cos\theta \tag{2.20}$$

where A_i and B_i are the coefficients correspond to the electric monopole and dipole terms, respectively. These coefficients, A_i and B_i are to be determined by employing the appropriate boundary conditions for the continuities of the tangential and normal components of the electric field and the displacement vector, respectively. In our case, the spherical coordinates (r;θ) are used, where r is the radial distance and θ is the polar angle, while the direction of the applied field E_o is chosen along the z-axis. Then, the electric field E_i in the i^{th} region for the concentric spherical n-layered nanocomposite is obtained using the equation E_i = -$\bigtriangledown\phi$(r;θ), where ϕ(r;θ) is given by Eqn. (2.20). Hence, the field takes the following form:

$$\vec{E_i} = A_1(-cos\theta\hat{e}r + sin\theta\hat{e}\theta) + B_i\hat{r}{-}3(2cos\theta\hat{e}r + sin\theta\hat{e}\theta) \tag{2.21}$$

where i = 1,2,..., n with n being the number of layers and $\hat{e}$r and $\hat{e}\theta$ are the unit vectors in the r and q directions, respectively. Next, we consider a triple layered (n = 3) core-shell nanostructure in which region one with i = 1 is a semiconductor core (CdSe) of dielectric function ε1, while the outer region is the embedding medium (SiO_2) with real dielectric constant ε_n+1 = ε_4. The dielectric functions of the spacer (ZnSe) and the metallic shell (Ag) are ε_2 and ε_3, respectively. Similarly, the radii of the dielectric core, the spacer, and the metallic shell are denoted by r_1, r_2, and r_3, respectively. For triple layered nanocomposite, there are four regions. Thus, by extending Eqn. (2.11) to spherical nanocomposite, the expressions for the electric fields in each region are as follows:

$$\vec{E_1} = A_1(-cos\theta\hat{e}_r + sin\theta\hat{e}_\theta) + B_1 r^{-3}(2cos\theta\hat{e}_r + sin\theta\hat{e}_\theta) \tag{2.22}$$

$$\vec{E_2} = A_2(-cos\theta\hat{e}_r + sin\theta\hat{e}_\theta) + B_2 r^{-3}(2cos\theta\hat{e}_r + sin\theta\hat{e}_\theta) \tag{2.23}$$

$$\vec{E_3} = A_3(-cos\theta\hat{e}_r + sin\theta\hat{e}_\theta) + B_3 r^{-3}(2cos\theta\hat{e}_r + sin\theta\hat{e}_\theta) \tag{2.24}$$

$$\vec{E}_4 = A_4(-cos\theta\hat{e}_r + sin\theta\hat{e}_\theta) + B_4 r^{-3}(2cos\theta\hat{e}_r + sin\theta\hat{e}_\theta) \tag{2.25}$$

Where A_4=E_o and A_1, A_2, A_3, B_2, B_3 and B_4 are unknowns to be determined by imposing the appropriate boundary conditions. In particular, the coefficient B_1 = 0, since the magnitude of the electric field in the dielectric core is constant. To investigate the LFEF inside the concentric sphere, it is suffice to determine the electric field induced inside the dielectric core. This means that (since B1 = 0), we only need to determine the coefficient A_1 found in Eqn. (2.22). Hence, employing the relevant boundary conditions at the interfaces, this coefficient can be shown to have the following form

$$A_1 = \frac{27}{2}\frac{\varepsilon_2\varepsilon_3\varepsilon_4}{f_2 M}E_o = F \tag{2.26}$$

Where

$$M = y_1\varepsilon_3^2 + y_2\varepsilon_3 + y_3 \tag{2.27}$$

$$f_2 = 1 - (\frac{r_2}{r_3})^3 y_1 = f_1(\varepsilon_1 - \varepsilon_2) + 3\varepsilon_3 \tag{2.28}$$

$$y_2 = (\frac{3}{f_2} - 1)[3(\frac{\varepsilon_1}{2} + v\frac{2\varepsilon_4}{3})\varepsilon_2 + f_1(\varepsilon_1 - \varepsilon_2)(\varepsilon_4 - \varepsilon_2)] + \varepsilon_2(f_1(\varepsilon_1 - \varepsilon_2) - \varepsilon_4 - \frac{3}{2}\varepsilon_2) \tag{2.29}$$

$$y_3 = \varepsilon_2\varepsilon_4(3\varepsilon_1 + 2f_1(\varepsilon_2 - \varepsilon_1)) \tag{2.30}$$

Where

$$f_1 = 1 - (\frac{r1}{r_2})^3 \tag{2.31}$$

Substituting Eqn.(2.26) into Eqn(2.22) the magnitude of induced field inside the dielectric core is found to be

$$E_1 = E = \frac{27}{2}\frac{\varepsilon_2\varepsilon_3\varepsilon_4}{f_2 M}E_o \tag{2.32}$$

The coefficient of E_o in Eqn.(2.26) is the local field enhancement factor (F).That is

$$F = \frac{E}{E_o} = \frac{27}{2}\frac{\varepsilon_2\varepsilon_3\varepsilon_4}{f_2 M}. \tag{2.33}$$

and the modulus square of the LFEF becomes:

$$|F|^2 = |\frac{27}{2}\frac{\varepsilon_2\varepsilon_3\varepsilon_4}{f_2 M}|^2. \tag{2.34}$$

2.11 Triple-Layer Spherical Nanostructure within Host Matrix

This structure typically comprises three concentric layers surrounding a central core, each with distinct materials and properties. The diagram likely highlights the following key components:

- **core1. The innermost layer, which serves as the foundation of the nanostructure. The core material can be chosen based on desired properties such as magnetic, optical, or catalytic functions.**
- **Inner shellEncasing the core, the inner shell layer modifies and enhances the core's properties. This shell can be tailored to improve stability, prevent core oxidation, or provide a controlled release mechanism if used in drug delivery applications**
- **Outer shellThe outermost layer, which interacts directly with the host matrix. This shell can be engineered to provide biocompatibility, additional stability, or functional interfaces with the surrounding environment**
- **host matrixThe medium in which the triple-layer nanostructure is embedded. This matrix supports and stabilizes the nanostructure, influencing its overall behavior and effectiveness**

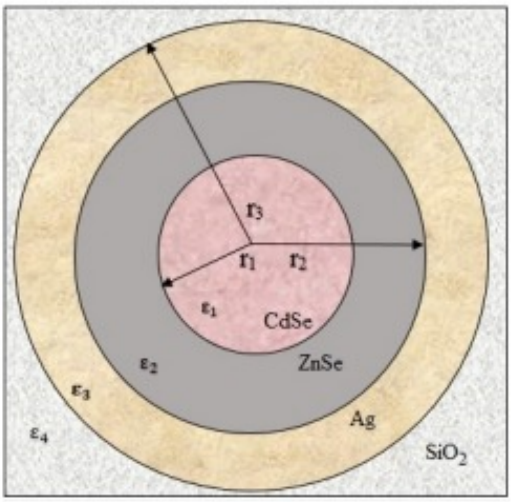

Figure 2.1: Triple layer spherical nanostructure embedded in host matrix

3

Materials and Methodology

3.1 Methodology

For numerical calculations, Mathematic Software used to determine the size dependent local field enhancement factor of CdSe@ZnSe@Ag based triple layer spherical nanoparticles.

3.2 Computational

Under the quasi-static approach, we calculated LFEF, in spherical core-shell NP. The particle may be represented by an oscillating dipole. Oscillating dipoles are often analyzed using the quasi-static approximation.This approximation is important for a qualitative understanding of the interaction of light with nanoparticles as it considerably simplifies the mathematical analysis

4

Results and Discussion

In this study,ZnSe was placed as a spacer between the CdSe core and Ag shell and the local electric field enhancement was analyzed usin eqn (2.34).

4.1 When core and the shell sizes are increasing and fixed spacer thickness

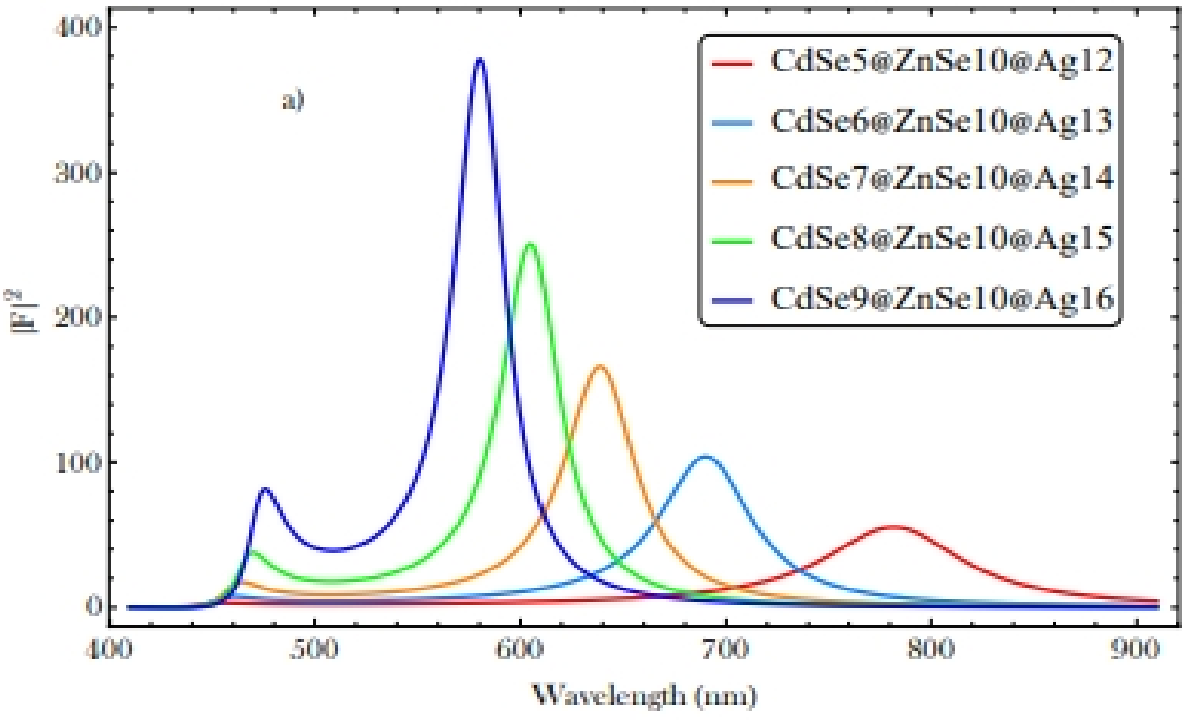

Figure 4.1: LFEF of CdSe@ZnSe@Ag: (a) when core and the shell sizes are increasing and fixed spacer thickness

This figure show, as the core and shell sizes increase, the overall size of the nanoparticle also increases.With a thicker spacer, the distance between the core

- shell interface and the outer Ag shell also decreases.As a result, the plasmon resonance shifts to higher energies (shorter wavelengths) due to the increased confinement of the electrons within the nanoparticle structure.This shift is depicted by the increasing LFEF values as the core and shell sizes increase and the spacer thickness decreases.

4.2 When spacer size is increasing at fixed core and shell size

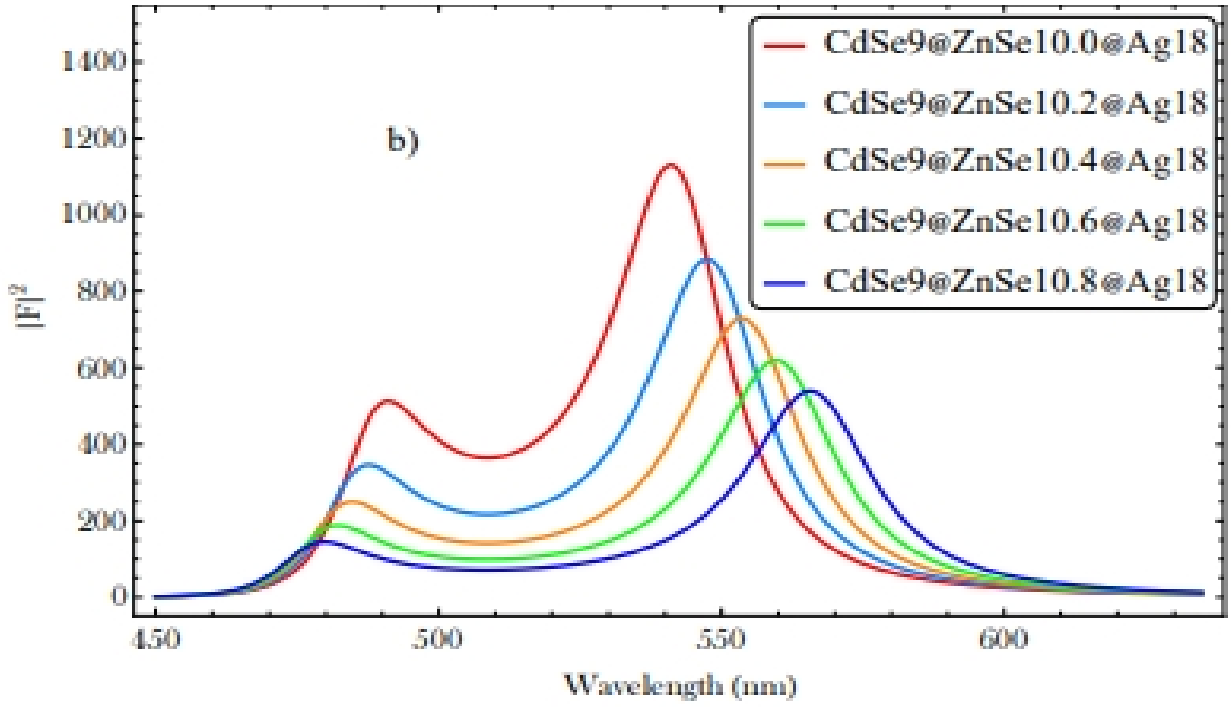

Figure 4.2: LFEF of CdSe@ZnSe@Ag: when spacer size is increasing at fixed core and shell sizes.

For Figure 4.2 When spacer size is increasing at fixed core and shell sizes : Here, the core and shell sizes remain constant while the spacer thickness increases.As the spacer size increases, the distance between the core-shell interface and the outer Ag shell also increases.This leads to a decrease in the confinement of the electrons within the nanoparticle structure, causing the plasmon resonance to shift to lower energies (longer wavelengths).Hence, the LFEF values decrease as

the spacer size increases at fixed core and shell sizes.

4.3 When shell size is increasing at fixed sizes of the core and spacer

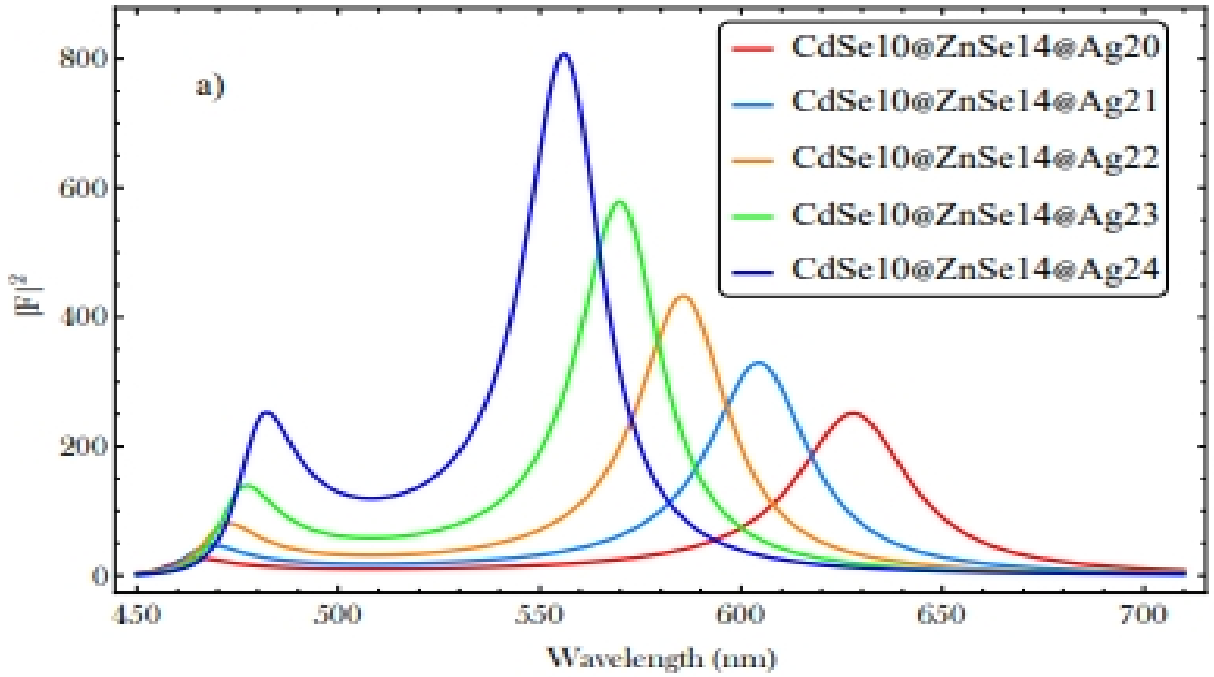

Figure 4.3: LFEF of CdSe@ZnSe@Ag: when shell size is increasing at fixed sizes of the core and spacer

for fig 4.3

In this case, the core and spacer sizes remain constant while the shell size is increasing.As the shell size increases, there is more Ag material surrounding the CdSe core.This results in a greater confinement of the electrons within the nanoparticle structure, leading to a higher plasmon resonance energy.Therefore, the LFEF values will increase as the shell size increases at fixed core and spacer sizes.This is depicted by the increasing LFEF values in the graph as the Ag shell thickness increases

4.4 When core size is increasing and spacer thickness is decreasing at fixed NP size

for fig 4.4 The NP (nanoparticle) size remains fixed, but the core size increases

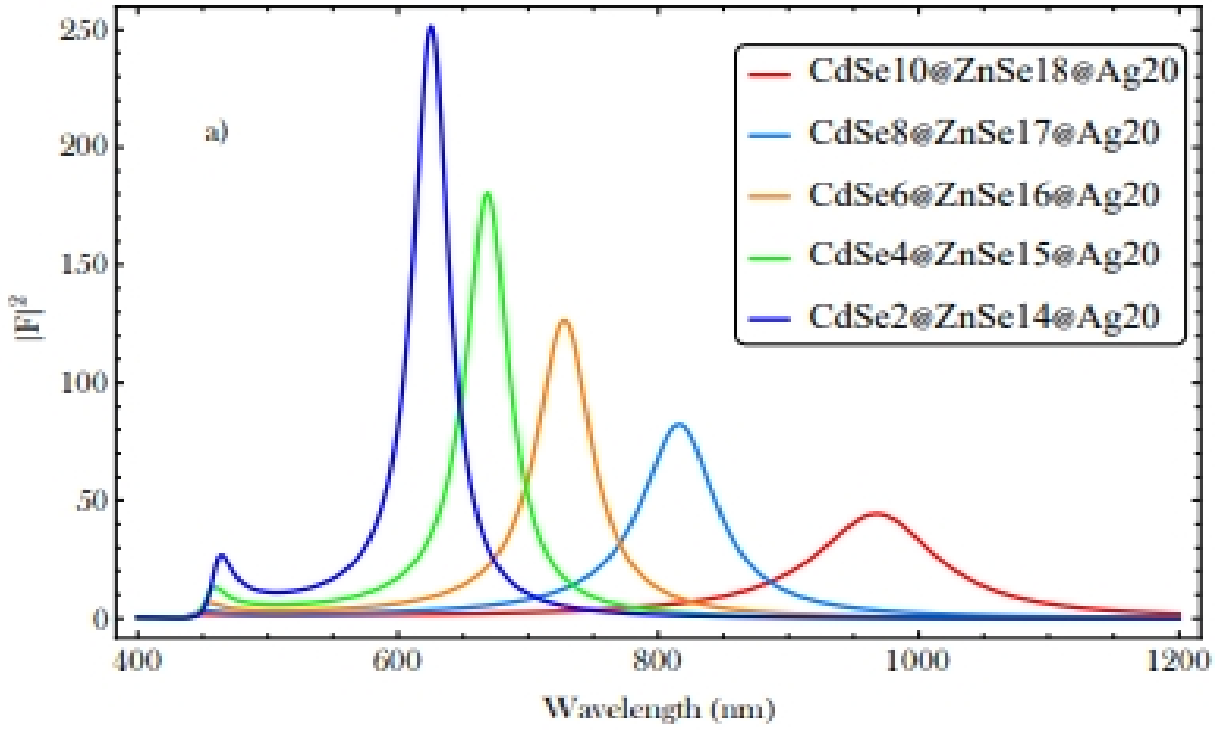

Figure 4.4: LFEF of CdSe@ZnSe@Ag: when core size is increasing and spacer thickness is decreasing at fixed NP size

while the spacer thickness decreases.As the core size increases, more CdSe material is present, which affects the electron density and thus alters the plasmon resonance characteristics.Additionally, as the spacer thickness decreases, the distance between the core - shell interface and the outer Ag shell reduces, leading to stronger interactions between the components and a higher confinement of electrons.These factors collectively result in a shift of the plasmon resonance to higher energies, indicating an increase in LFEF values as the core size increases and spacer thickness decreases at a fixed NP size.

4.5 When core size is decreasing and spacer thickness is increasing at fixed size of NP

for fig 4.5 When core size is decreasing and spacer thickness is increasing at a fixed size of the nanoparticle (NP) :

In this case, the size of the CdSe core decreases while the thickness of the ZnSe spacer increases, maintaining the overall size of the NP.As the core size decreases,

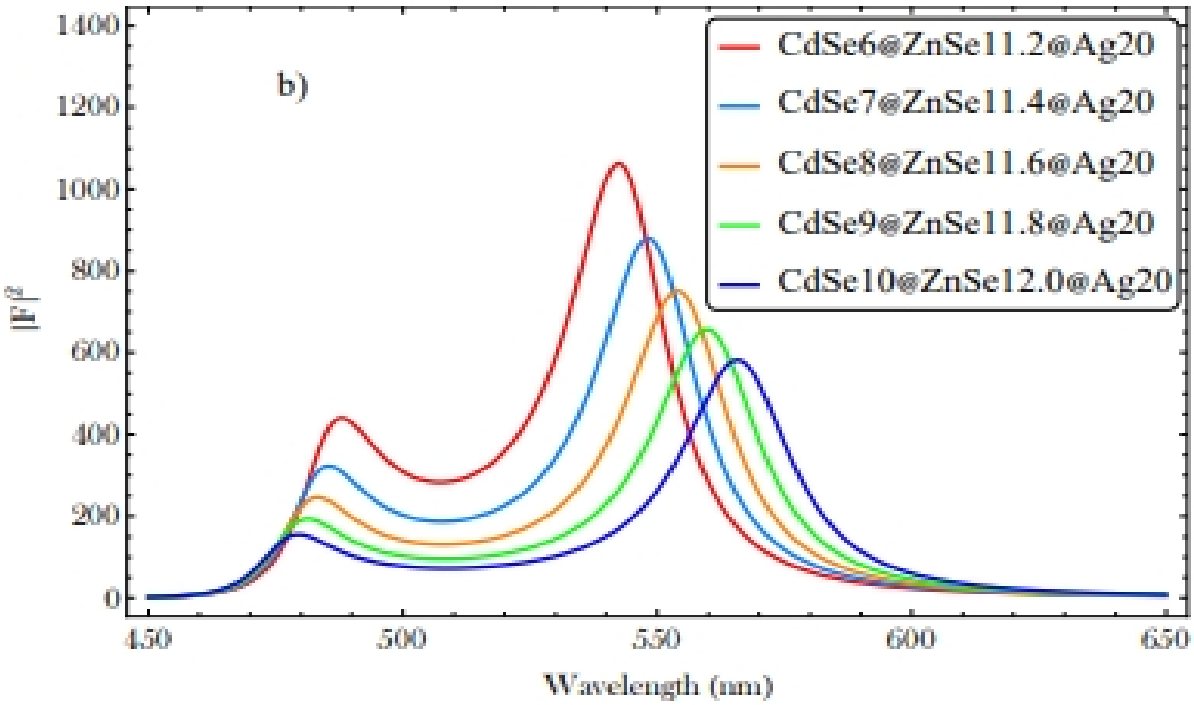

Figure 4.5: LFEF of CdSe@ZnSe@Ag: when core size is decreasing and spacer thickness is increasing at fixed size of NP

there is less CdSe material available, leading to fewer electrons participating in the plasmonic resonance.Simultaneously, as the spacer thickness increases, there is a greater distance between the CdSe core and the outer Ag shell, resulting in weaker interactions between these components and lower confinement electrons.These factors collectively lead to a decrease in the LFEF values as the core size decreases and spacer thickness increases at a fixed NP size

4.6 When spacer and shell thicknesses are increasing at fixed core size

For fig 4.6 When spacer and shell thicknesses are increasing at a fixed core size. In this graph, the core size remains constant while both the ZnSe spacer and Ag shell thicknesses increase.As the spacer and shell thicknesses increase, there is more ZnSe and Ag material surrounding the CdSe core, respectively.This results in stronger interactions between the components and a higher confinement of electrons within the NP structure.Consequently, the plasmon resonance shifts to

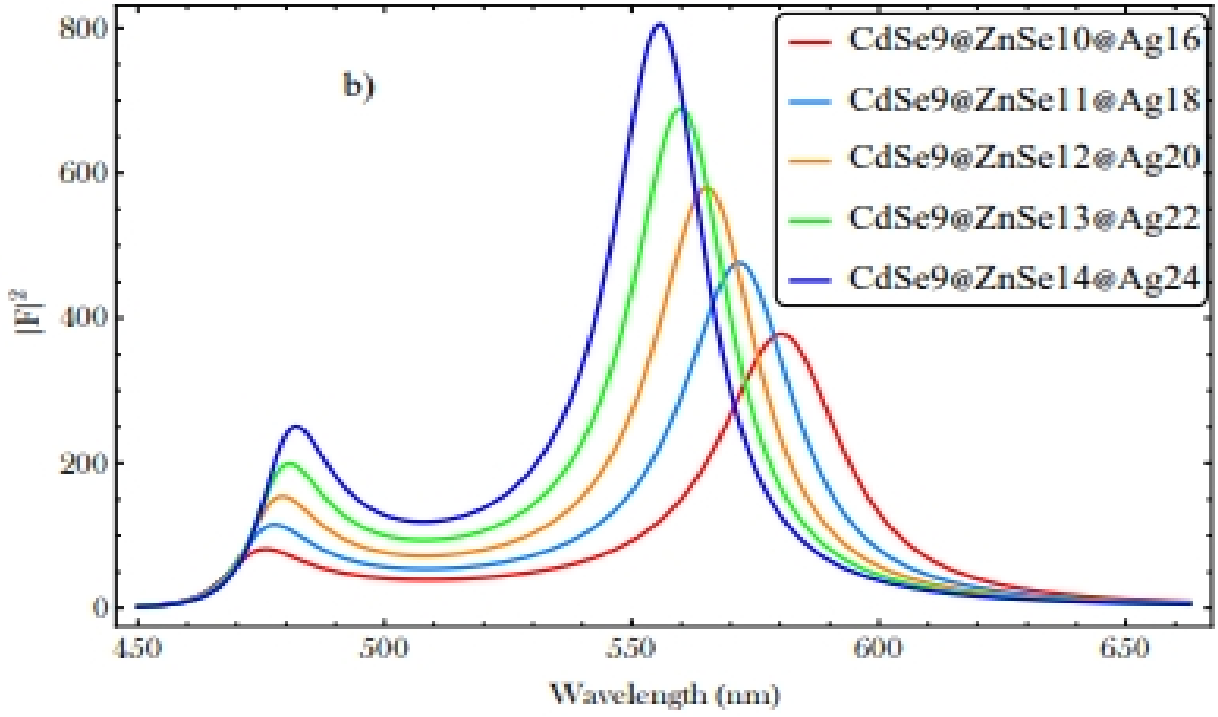

Figure 4.6: LFEF of CdSe@ZnSe@Ag: when spacer and shell thicknesses are increasing at fixed core size.

higher energies, leading to an increase in the LFEF values as the spacer and shell thicknesses increase at a fixed core size

5

conclusion

In triple layered core-shell spherical nanoparticle, an increase in the size of the spacer led to a decrease in the field enhancement factor of the nanocomposite. For fixed sizes of the core and the NP, the lower the size of the spacer produces the higher the field enhancement factor. On the other hand increasing the thickness of the shell size increases the magnitude of the resonance peaks. Similarly, increasing the thicknesses of both the spacer and the shell sizes also increased the field enhancement factor. In conclusion the sizes of the core, the spacer and the shell have vigorous effects on the local field enhancement factor of core-shell nanoparticles. The possibility of obtaining size dependent LFEF by adjusting the sizes of nanoparticles make these nanocomposites attractive for applications in optoelectronics and nonlinear optics.

The feature direction of this study likely involves experimental characterization and theoretical modeling to explore how the size variations of CdSe@ZnSe@Ag core triple-layer spherical nanoparticles influence their local field enhancement factor, which is pivotal for their application in nanotechnology and photonics.

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COLLAGE OF NATURAL SCIENCES

PERFORMANNCE CERTIFICATE FOR MASTER'S DEGREE

Name of Student: **Berhanu Kasaye A/Bulgu**

Graduate Program: **MSc Regular**

ID No.: **RM0716/15-0**

1. Course Work Performance Excellent, Very Good, Good, Satisfactory, Fail.

Course Code	Course Title	Cr.hr	Score(100)	Grade	Rank	Remark
Phys 799	Graduate Thesis	6		A^-	Very Good	

Thesis Title: SIZE DEPENDENT LOCAL FIELD ENHANCEMENT FACTOR OF CdSe BASED CORE TRIPLE LAYER SPHERICAL NANO PARTICLES

2. Board of Examiners decision Mark X in one of the boxes. Pass □ Failed □

If failed, give reasons and indicate plans for re-examination.

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3. Approved by:

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