INVESTIGATION OF THE OPTICAL PROPERTIES OF DIELECTRIC METAL CORE/SHELL SPHERICAL NANOSTRUCTURES BY EMPLOYING THE MIE THEORY

BY

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The undersigned hereby certify that they have read and recommended to School of Graduate programs for acceptance a graduate project entitled "**Investigation of Optical Properties of Dielectric Metal/Core Shell Spherical Nanostructures by Employing the Mie Theory**", by **Yohannes Ayele Alaro** in partial fulfillment of the requirement for the Degree of **Master of Science in Physics.**

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DEDICATION

This work is dedicated to:

My Father: Who doesn't see any other ways of success but education and encourage us to pursue it.

My Mother: Who’s help; encouragement, wise advice and providing everything necessary at home become an inspiration up to the finishing line.

To those students or graduates of physics who endure the difficulties of studying the subject for the pursuit of knowledge and/or any qualification.

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Abstract

In this project, we present the investigation of the optical properties of dielectric/metal core/shell spherical nanostructures by employing the Mie theory. In this work, the nanomaterials, historical background, definition, synthesis, characterization, classification, its special type are covered especially metal core/shell which is the focus of this project is given a special attention. In addition to this one of the physicochemical properties of metal nanostructures and their application, the effects of size, shape and structure on the nanomaterials properties are presented and the question why we use nanoparticles is answered. The other most important point, complex dielectric function of nanomaterials or nanostructures and its relation with the bulk or parent material and plasmon and local surface plasmon resonance of nanostructures are discussed. Topic which leads us to the final goal of this project Mie scattering theory is explained. In addition, the relevant formulas used for the study such as scattering coefficients and absorption, scattering and extinction cross-sections are presented from Mie theory and the extended Mie theory. Finally, using the Mie theory calculator for the silica (SiO_2) core, silver (Ag) shell nanostructure and silica (SiO_2) core with silver (Ag), gold (Ag) and copper (Cu) shell nanostructures, the cross-sections are calculated and we found that keeping the SiO_2 core diameter (50 nm) constant and changing the shell thickness (3-12 nm) and shell type between Ag, Au and Cu cause the spectra to shift towards the longer or shorter wavelength side and also change the absorption, scattering and extinction cross-sections peak, the amount of absorption and scattering cross-sections, whether absorption or scattering cross-sections contributes more for extinction spectra, the wavelength at which these cross-sections occur and the possible application of the nanoshells.

CHAPTER ONE: INTRODUCTION

1.1 Background of the Study

Owen Chamberlain says, “The development of physics, like the development of any science, is a continuous one”. This is a fact. We found at a time were there exist different fields of physics and it is obvious that they are evolved or come in to being at different time. Among these fields, nanoscience or nanophysics, which caught the attention of many scientists, institutions, countries and universities, and which give amazing result and expected to give much more in the future is the one that can be mentioned. Nanoscience is the science of the study of matter at the nanoscale ranges that deals with understanding their size and structure dependent properties and compare the emergence individual atom or molecule or bulk material related differences. When the size of a material is reduced to the nanoscale usually from 1-100 nm they show completely different optical, electrical, magnetic, mechanical and thermal properties from parent material. This implies that nanomaterials have different or in some case better optical and magnetic behavior, electrical and thermal conductivity and mechanical strength. These behavior which are applied in technological product such as a bullet proof jacket made up of carbon nanotube, transistor very small in size, sanitizer which protect object from virus for a week, water purifying device, cancer therapy in medicine are some of the sciences fruit. Recently in our country Ethiopia we witness the advertisement and sell of a very strong and unbreakable mobile nanoscreen.

Putting aside the introduction about nanoscience, the topic of this project is investigation of optical property of dielectric/metal core/shell spherical nanostructure by employing Mie theory. This theory is the exact solution to Maxwell equation of electromagnetic plane wave interacting with homogeneous, isotropic sphere of radius R having the same dielectric constant as the bulk material and it explain about optical properties of spherical nanoparticles. These optical properties are absorption, scattering, extinction cross-sections and efficiencies and the relationship between them. The above optical properties for nanoshell can also be investigated through the powerful extended Mie theory.

Through implementing the Mie theory a group of researchers was undertaken a study on the trends in the optical resonance wavelength, the extinction cross section and the relative contribution of scattering to extinction with change in the nanoparticle dimension for three classes of nanoparticles Si-Au nanoshell, gold nanosphere and Gold nanoroads and the

calculated results of the spectra shows that the optical properties of the nanoparticles were highly dependent on the nanoparticles size, shape and core-shell composition .

1.2 Statement of the Problem

The above relationships mentioned in the result of the research between size, shape and core shell composition and optical property and other physicochemical properties of nanomaterials and the applications which emerge from it, is the base of the nanoscience. Unfortunately, I was introduced to the world of nanoscience from the discussion held at end of the final year semester and from the project research title presented by the advisor. The root cause of not knowing a lot about nanoscience in advance could be divers but unable to answer questions raised during lecture, unable to explain the uses, properties, side effects of new technological products example nanoscreen mobile coverer shows the presence of the problem. Therefore, for those of us who does not have enough knowledge about the science in advance in University one of the method that can be used to fill the gap is assigning project like this.

Besides fulfilling the main theme of the project which is the calculation of optical properties of nanoshell large part of this work is dedicated for the understanding of nanoscience basics and Mie theory. Subsequently the major outcome are calculated results of absorption, scattering and extinction cross-sections and the relationship between them, obtaining clear graphs and their interpretation, indicating room for improvement in previous and new scientific knowledge, inspiration, paving a way for the pursuit of new scientific knowledge.

1.3 Objectives of the Project

The project's investigation of the amazing optical properties of dielectric metal core shell spherical nanostructures through employing the Mie theory and my own drawbacks lead to the conduction of this study. So,

- The general objective of this project is investigation of optical properties of dielectric metal core shell spherical nanostructure using Mie theory.
- The specific objectives are gaining an understanding on the definition, concept, laws, principles, theories of nanoscience and the different application of nanoshell under the umbrella of the project title and the initiation of the pursuit of new scientific knowledge.

1.4 Organization of the Project

In Chapter 1, the background of nanoscience, its technological products and Mie theory are briefly introduced. Then the result of a study conducted by Mostafa A. El-Sayed and his colleague and the main cause of the research and its objective are shortly reviewed.

In Chapter 2, the beginning of the history of nanomaterial and nanotechnology from the Egyptian period up to the recent year is briefly reviewed. In addition to this the nanomaterials definition, synthesis through top-down and bottom-up approach, its characterization through different techniques, it's classification based on different criteria and one of its special type core-shell with its synthesis and application are presented. Besides to these the optical property of nanomaterial and its dependence on size, shape and structure and the reason why nanomaterials become a highly sought after material are explained. Then, the change in the classical theory of optical property of bulk material from nanomaterial, the definitions of plasmon and local surface plasmon resonance (LSPR) and the factors affecting LSPR are discussed. Finally, the statement of Mie theory and the definition of the optical properties it explain are briefly reviewed.

In Chapter 3, the model and the method used to conduct the project are explained. Then the parameters used in the study and the Mie theory calculator implemented for the simulations of cross-sections are presented.

In Chapter 4, the result and discussion of the graph obtained from the Mie theory calculator is presented.

In Chapter 5, the research work undertaken in this project is concluded.

CHAPTER 2: LITERATURE REVIEW

2. Nanomaterials

2.1 History and the Development of Nanomaterial and Nanotechnology

The history of nanomaterials begun in the ancient civilization of human being and continues up to the recent centuries without knowing that they are using what we call it now nanomaterial and nanotechnology. By the time humans already exploited the reinforcement of ceramic matrixes by including natural asbestos nanofiber more than 4500 years ago. The ancient Egyptians were also used hair dye made from ≈ 5 nm diameter PbS nanoparticles more than 4000 years ago. Similarly "Egyptian blue" was the first synthetic pigment which was prepared and used by Egyptian using a sintered mixture nanometer size glass and quartz around 3rd century B.C. Egyptian blue represent a multifaceted mixture of $CaCuSi_4O_{10}$ and SiO_2 (both glass and quartz). In ancient geographical regions of the Roman Empire, including countries such as Egypt, Mesopotamia and Greece, the extensive use of Egyptian blue for decorative purpose has been observed during archeological explorations. The synthesis of metallic nanoparticles (NPs) via chemical method date back to the 14th and 13th century B.C when Egyptians & Mesopotamians started making glass using metals, which can be cited as the beginning of the metallic nanoparticle era. These materials may be the earliest example of synthetic nanomatrials in physical application. Similarly, the Celtic red enamels originating from the 400-100 B.C period have been reported to contain (Cu) nanoparticles and cuprous oxide (cuprite Cu_2O). Until the Middle Ages, the reputation of soluble gold was based mostly on its fabulous curative powers of various diseases, for examples, heart and venereal diseases, dysentery, epilepsy, and tumors; it was also used in the diagnosis of syphilis [1].

Optical characteristics

Optical characteristics of nanomaterials from the late bronze age (1200-1000 B.C) red glass has been found in Frattesina di Rovigo (Italy) that is colored by surface Plasmon excitation of Cu nanoparticles. Beyond this, the optical characteristics of nanoparticles have been used for time immemorial in sculpture and paintings even before the 4th century A.D. The most famous example is the Lycurgus cup (fourth century AD) illustrated in figure 2.1 and this extraordinary cup is the only complete historic example of a very special type of glass that changes color when held up to the light. The opaque green light cup turns in to glowing

translucent red when light is shone through it internally (i.e., light incident on the cup at 90^0 to the viewing direction). Analysis of the glass revealed that it contains a very small quantity of tiny (~70 nm) metal crystals of Ag and Au in an approximate ratio of 14:1 which give it, these unusual optical properties. It is the presence of these nanocrystals that gives the Lycurgus cup its special color display.

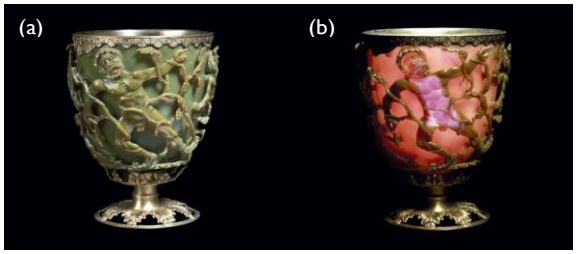
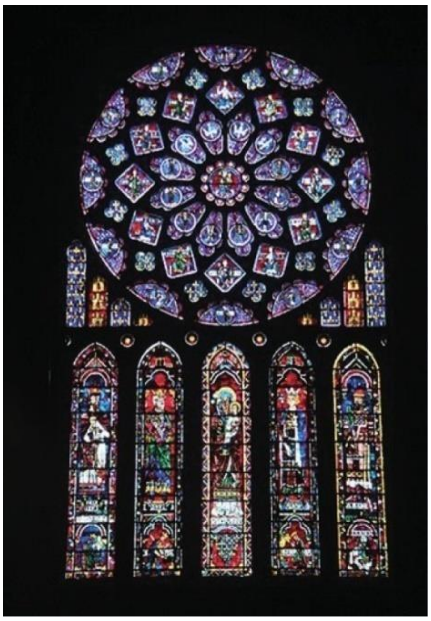


Figure 2.1: Photographs of the famous Lycurgus cup which displays a different color depending on whether it is illuminated externally (a) or internally (b). [1]

In 1807 in a well-known publication Michael Faraday reported the formation of deep red solutions of colloidal gold by reduction of an aqueous solution of chloroaurates ($AuCl_4^-$) by phosphorus in CS_2 a two phase system. He also investigated the optical properties of thin films prepared from dried colloidal solution and observed reversible color changes of the film up on mechanical compression from bluish-purple to green. Since that pioneering work, thousands of scientific papers have been published on the synthesis, modification, properties of metal nanoparticles, using a wide variety of solvents and other substrates [1].

In 1908 the German physicist Gustav Mie published a paper on the optics of turbid media, particularly colloidal metal solution, which uses Maxwell's equation of electromagnetic plane wave interacting with a homogeneous, isotropic sphere to explain the optical properties of the metal nanoparticles. Unfortunately since the publication of the paper from 1908-1945 G.C Mie's articles on colloidal metal solution belongs to the so called sleeping beauties and wall flowers i.e., paper received much delayed appreciation. It was after 1945 that his investigation received a broad appreciation and application. The development of computer engineering especially advanced the usefulness of Mie theory [2]. Nowadays this theory is the most cited and used to explain similar optical phenomenon by nanoparticles. In addition to the above mentioned studies nanotechnology is easily evident in various old churches. A well known application of early nanotechnology is the ruby red color that was used for

stained glass windows during the middle Ages. Beautiful examples of these applications can be found in glass windows of many Gothic European cathedrals among which the Leon Cathedral (Spain) and another example that is seen at world heritage cathedral Notre-Dame de Chartres in France Figure 2.2: can be mentioned of course the medieval artisans were unaware that they were using nanotechnology. They just knew that a particular process produced a beautiful effect. Later the development of analytical instrument in the science clarified the reasons behind the generation of color. These vivid colors were generated or controlled by the size and form (or shape) of the nanoparticles of gold and silver.



Red

Ag (~100 nm, Triangle)

Yellow:

A u (~100 nm, Spheres)

Green:

Au (~50 nm, Spheres)

Light blue:

Ag (~90 nm, Spheres)

Blue:

Ag (~40 nm, Spheres)

Figure 2.2: Rosace nord stained glass in the Cathédrale Notre-Dame de Chartres (France), color changes depend on the size and shape of gold and silver nanoparticle. [1]

Nanotechnology

The conceptual underpinnings of nanotechnologies were first laid out in 1959 by the physicist Richard Feynman, in his lecture "There is plenty of room at the bottom'' Feynman 1959. Feynman explored the possibility of manipulating material at the scale of individual atoms and molecules, imagining the whole of encyclopedia Britannica written on the head of a pin and foreseeing ability to examine and control matter at the nanoscale. In addition the term "nanotechnology" was not used until 1974, Norio Taniguchi, a researcher at university of Tokyo, Japan used it to refer to the ability to engineer materials precisely at the nanometer level. The primary driving force for miniaturization at that time comes from the electronics industry which aimed to develop tools to create smaller (and therefore faster and more

complex) electronic devices on silicon chips. Therefore from the historical background mentioned above it is clear that human being have been using nanomaterial and nano-technology for centuries. Therefore explaining or defining nanomaterial, nanotechnology and the related terms is very important for common understanding of the science behind and for its future application.

2.2 Definition of Nanomaterial and Related Terms

The prefix "nano" is derived from the Greek word for dwarf.

Table 2.1: Definition of nanoparticles and nanomaterials by various organizations; International organization for standardization (ISO), American society of testing and materials (AS TM), National institute of occupational safety and health (NIOSH), scientific committee on consumer products (SCCP), British Standard Institution (BSI) and Bundesantalt fur Arbeitsmedizin (BAUA).

	Nanoparticle	Nanomaterial
ISO	A particle spanning 1–100 nm diameter	-
ASTM	An ultrafine particle whose length in 2 or 3 places is 1-100 nm	-
NIOSH	A particle with diameter b/n 1 and 100 nm or a fiber spanning range 1 – 100 nm	-
SCCP	At least one side is in the nanoscale range	Material for which at least one side or internal structure is in the nanoscale.
BSI	All the fields or diameters are in the nanoscale range	Material for which at least one side or internal structure is in the nanoscale
BAUA	All the fields or diameters are in the nanoscale range	Material consisting of a nano-structure or a nanosubstance

The use of various definitions across different jurisdictions act as major hurdle to regulatory efforts as it leads to legal hesitation in applying regulatory approaches for identical nano-materials. Therefore the need to satisfy diverging considerations is a major challenge in developing a single interaction definition for nanomaterials.

Recently the British Standards Institution proposed the following definitions for the scientific terms that have been used [3].

- **Nanoscale:** Approximately 1 to 100 nm size range.
- **Nanoscience:** the science and study of matter at the nanoscale that deals with understanding their size and structure dependent properties and compares the emergence of individual atoms or molecules or bulk materials related difference.
- **Nanotechnology:** Manipulation and control of matter on the nanoscale dimension by using scientific knowledge of various industrial and biomedical applications.
- **Nanomaterial:** Material with any internal or external structures on the nanoscale dimensions.
- **Nanoobject:** Material that possesses one or more peripherial nanoscale dimensions.
- **Nanoparticle:** Nanoobject with three external nanoscale dimensions. The term nanorod or nanoplate is employed, instead of nanopartcle (NP) when the longest and shortest axes length of nanoobjects are different.
- **Nanofiber:** When two similar exterior nanoscale dimensions and a third larger dimension are present in a nanomaterial it is referred to as nanofiber.
- **Nanocomposite:** Multiphase structure with at least one phase on the nanoscale dimension.
- **Nanostructure:** Composition of interconnected constituent parts in the nanoscale region.
- **Nanostructured material:** Materials containing internal or surface nanostructure.

Despite the existence of different definitions of the nanomaterials and the related terms, with a very few deviation from each other countries institutions, individual scientists and companies continue to use the application of the nanomaterial produced by different synthesizing method.

2.3 Synthesis of Nanomaterial

The drive for finding novel routs for the synthesis of nanomaterials has gained considerable momentum in recent years owing to the ever increasing demand for smaller particle size. Prior to the synthesis of a nanophase material, the size and dimensional feature of the material to be prepared have to be defined. Accordingly a suitable preparative method can be adopted. Controlling the microstructure at the atomic level has been of great multidisciplinary interest to the fields such as physics, chemistry, biology, and material science. As the particle size scale down to a few nanometers, the constituting atom exhibit highly defective coordination environment. In short microstructural features such as small grain size, large number of interfaces and grain boundary junctions, pores and various lattice defects that result from the chosen routs for synthesis contribute significantly to the unique physical and chemical properties of nanomaterial. Various methods can be employed for the synthesis of nanoparticles (NPs) but these methods are broadly divided in to two main class. These are:

A. **Top-down synthesis:** In this method larger molecules are decomposed in to smaller units and then this unites are converted in to suitable NPs. Examples of this method are; mechanical milling, chemical etching, sputtering, laser ablation, electro-explosion etc.

B. **Bottom–up synthesis:** This approach employed in reverse way from top- down and NPs are formed from relatively simpler substances, therefore this approach is also called building up approach. Example of this method are spinning, template support synthesis, plasma or flame spraying synthesis, laser pyrolysis, chemical vapor deposition, physical vapor deposition, atomic molecular condensation, biological synthesis via bacteria, yeast, fungi, algae, plants etc. Some synthesis methods are explained below [4].

2.3.1 Sol- gel (colloidal) processing

Sol-gel (colloidal) processing is a popular processing route for the synthesis of a wide variety of materials in desired shapes (particles, fibers or films). The formation of a sol by dissolving the metal alkoxide, metal organic or metal inorganic salt precursors in a suitable solvent is the primary step. In sol-gel process up on drying the sol, Polymetric network is formed in which the solvent molecules are trapped inside (gel). Subsequently, drying of the gel followed by the calcinations and sintering leads to the final ceramic product.

2.3.2 Laser ablation methods

This technique involves the vaporization of a target using pulsed laser, which is then followed by the controlled condensation in a diffusion cloud chamber under well-defined conditions of temperature and pressure. A wide variety of metal oxides, carbides, nitrides can be synthesized in nanoscale dimensions using this method.

2.3.3. Physical vapor deposition

PVD involves condensation from the vapor phase. The PVD process is composed of three main steps, (a) generating a vapor phase by evaporation or sublimation of the material (b) transporting the material from the sources to substrate, and (c) formation of the particle and/or film by nucleation and growth. Different techniques have been used to evaporate the source such as electron beam, thermal energy sputtering, cathodic arc plasma, and pulsed laser. Different nanowires, nanobelt and nanosheet, nanoribbon, nanotube etc. have been synthesized using PVD.

2.3.4. Lithography

Lithography involves the patterning of a surface through exposure to light, ions or electrons and then subsequent etching and/or deposition of material on to that surface to produce desired device.

Self-assembly is a bottom-up production technique in which atoms or molecules arrange themselves into ordered nanoscales structures by physical or chemical interactions between the units.

Positional assembly the final bottom up technique, where by atoms, molecules or clusters are deliberately manipulated and positioned one by one.

Chemical synthesis is a method of producing raw materials, such as molecules or particles, which can then be used either directly in their bulk disordered form, as the building blocks of more advanced ordered materials produced using the self-assembly and positional assembly.

Nanomaterials are synthesized in different morphologies depending on the required properties for the desired application. But the major issues for the synthesis of nanoparticles are:-1) the control of particle size and composition, and 2) the control of the interfaces and

the distribution of the nano-building block within the fully formed nanostructured materials.

Nowadays, many more types of nanomaterials are synthesized than only a decade ago, and in higher amount than before. But the facts mentioned above are not the end goal. This means understanding the inter-relationship between structures and properties of nanomaterials are important and NPs need to be characterized on both atomic and nanometer scale. The characteristics of the above involve determining the shape and size of the nanoparticles and understanding of inter-particle interactions. This information is important both from the scientific and the industrial application point of view. Therefore, a number of characterization techniques have been employed to produce structural and other information. Among many characterization techniques of nanomaterials few of them are explained in the next subtopic.

2.4 Characterization Techniques for Nanoparticles

Nanostructure has attracted huge interest as a rapidly growing class of materials for many applications. Several techniques have been used to characterize the size, crystal structure, elemental composition and variety of other physical properties of nanoparticles [5]. In several cases there are physical properties that can be evaluated by more than one technique. Different strength and limitation of each technique complicate the choice of the most suitable method while often a combinational characterization approach is needed. Here the present recent knowledge only on the use of a few numbers of experimental techniques that are available for the characterizations of nanoparticles is discussed. It is important to notice that these different characterization techniques are classified according to the concept or group of the technique used, the information they can provide or the materials that they are distend for. These techniques are sometimes exclusive for the study of a particular property, while in other cases they are combined. For instance there is microscopy-based technique which provides information on size, morphology and crystal structure of the nanomaterials. Magnetic techniques are specialized for certain groups of materials. Technique such as x-ray spectroscopy and scattering provides further information on the structure, elemental composition, optical properties and other common and more specific physical properties of the nanoparticle samples.

Two of the main parameters studied in the characterization of NPs, are size and shape. It is also possible to measure size distribution, degree of aggregation, surface area and to some extent evaluate the surface-chemistry. Size, size distribution and organic ligands present on the

surface of the particle may affect other properties and possible applications of the NPs. In addition the crystal structure of the NPs and their chemical composition are thoroughly investigated as a first step after nanoparticle synthesis.

2.4.1 X-ray based techniques

X-ray diffraction (XRD) is one of the most extensively used techniques for the characterization of NPs. Typically XRD provides information regarding the crystalline structure, nature of phase, plastic parameters and crystalline grain size. An advantage of the XRD technique commonly performed in samples of powder from usually after drying their corresponding colloidal solutions is that it results in statistically representative volume-averaged values.

2.4.2. Additional techniques for the characterization of the structure, composition, and other main NPs properties

1. UV-Vis spectroscopy is another relatively facile and low cost characterization method that is often used for the study of nanoscale materials. It measures the intensity of light reflected from a reference material. NPs have optical properties that are sensitive to size, shape, concentration, agglomeration state and refractive index near the NP surface, which makes UV-Vis spectroscopy an important tool to identify, characterize and investigate these materials and evaluate the stability of NP colloidal solution.

2. Dynamic light scattering (DLS) is a widely employed technique to find the size of NPs in colloidal suspensions in the nano and sub micrometer range.

2.4.3 Microscopy techniques for NP characterization

1. Transmission electron microscopy (TEM) is the most common technique to analyze nanoparticle size and shape since it provides not only direct images of the sample but also the most accurate estimation of the nanoparticle homogeneity.

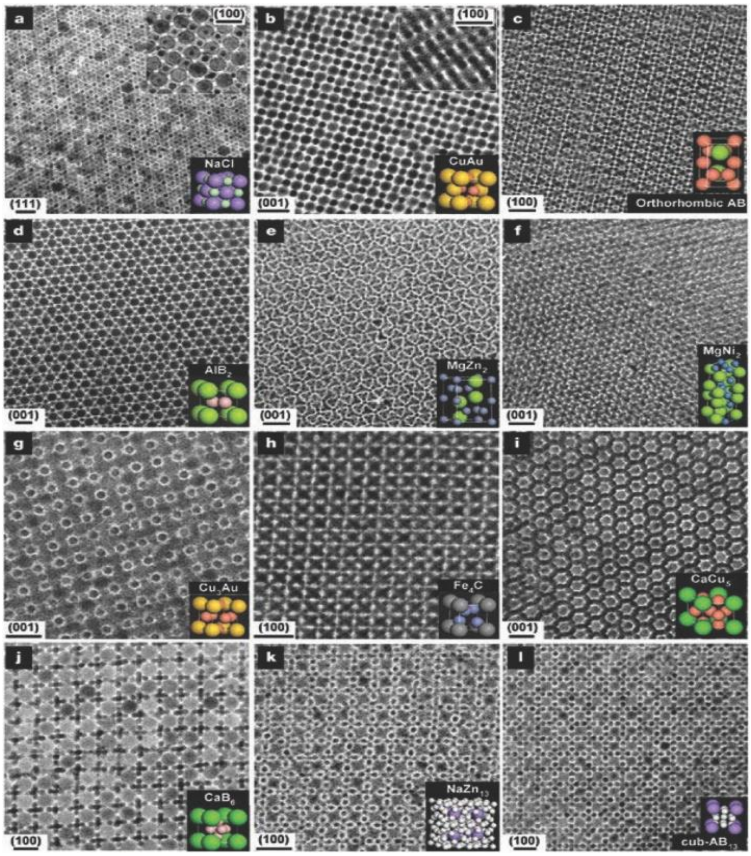


Figure 2.3: Image from the transmission electron microscopy (TEM) of different nanosized supperlattice nanoparticles. [5]

2. High resolution transmission electron microscopy (HRTEM) - provides important information on the nanoparticle internal structure. HRTEM is an imaging mode of transmission electron microscopy that uses phase-contrast imaging where both transmitted and scattered electrons are combined to produce the image. Phase-contrasting imaging is the technique with the highest resolution ever developed and allows the detection of the array of atoms in acrystalline structures.

The characterization techniques mentioned above and others help to determine the shape, size, distribution, mechanical, chemical and optical properties. This is an important part of scientific study and industrial process. It serves two broad purposes as quality control and as part of research and development of new processes, materials and products. The information taken during characterization can also be helpful for the classification of nanoparticles. Based on the above mentioned facts and others the following subtopics categorize nanoparticles in to different groups depending on various criteria.

2.5 Classification of Nanomaterials

Many types of nanomaterials and nanoparticles have been reported and many other varieties are predicted to appear in the future. Therefore the need for classification has become necessary. The first idea for nanomaterial classification was given by Gleiter. Here nano-materials are classified depending on their crystalline forms and chemical compositions. However Gleiter's scheme was not fully complete because the dimensionality of the NPs and NMs was not considered. In 2007 Pokoropivny and Skorokhod made a new scheme of classification for nanomaterials which include the recently developed composite nanostructure such as 0D, 1D, 2D and 3D. Generally nanomaterials can be classified based on their composition, dimension and origin [3].

2.5.1 Classification of nanomaterials based on composition

Most currently nanomaterials (NMs) can be organized in to four material based categories. These are;

1) **Carbon-based nanomaterials:** Generally these nanomaterials contain carbon, and are found in morphologies such as hollow tubes, ellipsoids, spheres. Fullerenes (C_{60}), Carbon nanotubes, Carbon nanofibers, Carbon black graphene (Gr) and carbon onions are included under the carbon based nanomaterials category.

2) **Inorganic-based nanomaterial:** These nanomaterials include metal and metal oxide nanoparticles and nanomaterials. These nanomaterials can be synthesized in to metal such as Au or Ag nanoparticles metal oxides such as TiO and ZnO nanoparticles and semiconductors silicon and ceramics.

3) **Organic-based nanomaterials:** These include nanomaterials made mostly from organic matter, excluding carbon based or inorganic based nanomaterials. The utilization of nanocovalent (weak bond) interactions for the self-assembly and design of molecules helps to transform the organic nanomaterials in to desired structures such as dendrimers, micelles, Li-posomes and polymers nanoparticles.

4) **Composite-based nanomaterials:** Composite nanomaterials are multiphase NPs and NMs with one phase on the nanoscale dimension that can either combine NPs with other NPs or NP combined with large or with bulk type materials or more complicated structures such as a metal-organic frame works. The composites may be any

combinations of carbon based, metal based or organic based NMs, with any form of metal ceramic, or polymer bulk materials.

2.5.2 Classification of nanomaterial based on their dimensions

This classification is highly dependent on the electron movement along the dimensions in the nanomaterial.

Zero dimension or Quantum dot nanomaterials: Nanomaterials in which electrons are confined in all spatial dimensions.

One dimensional (1D) or Quantum wire nanomaterials: Nanomaterials with one dimension in the nanometer scale and the electron move along only one direction.

Two dimensional (2D) or Quantum well nanomaterials: Nanomaterials that have two dimensions in the nanometer scale and the electron in it moves along two axes.

Three dimentional (3D) nanomaterials: Nanomaterials that are at nanoscale in all three dimensions and the electrons move along the three dimensions

2.5.3 Classification of materials based on their origin

Apart from dimension and material based classifications, NPs and NSMs can also be classified as natural or synthetic based on their origin.

1) **Natural nanomaterials:** are produced in nature either by biological species or through anthropogenic activities. Naturally occurring NMs are present through the Earth's sphere such as atmosphere which includes the whole troposphere, the hydrosphere, which includes oceans, lakes, rivers, ground water and hydrothermal vents, the lithosphere which is comprised of rocks, soils, magma or lava at particular stages of evolution and the biosphere, which covers micro-organisms and higher organisms including humans.

2) **Synthetic (engineered) nanomaterials:** are produced by mechanical grinding, engine exhaust and smoke or are synthesized by physical, chemical, biological or hybrid methods.

Classifying nanomaterials based on different criteria is important, but identifying one that has unique physicochemical properties and applications in technology is far superior tasks than

classifying. Thanks to the advanced technology and the rigorous work of scientists, researchers, countries like USA, England, Japan, Germany etc within the above class of nanomaterials it is managed to identify special type with very small dimensions, novel characteristics, diverse functionality and application in technology. These special types of nanomaterials are fullerene, carbon nanotube, nanoporous, materials, dandrimers, aerogels, zeolites, core-shell structure etc. The next subtopic provides a brief discussion on core shell nanostructures.

2.6 Special Type of Nanomaterial

2.6.1 Core shell composite structure

Core-shell nanoparticle composite structures are an ordered assembly of nanoscale structures. This new structure is formed by using a particular nanomaterial to coat another kind of nanomaterials through chemical bonds or other interactions. It is a higher level of composite nanostructure. This structure provides many new properties beyond the reach of single nanoparticles, which are widely appreciated for a wider application prospects than single nanoparticles. The design and controllable synthesis of composite nanomaterial with core-shell structures has been an increasingly important forefront of materials science in recent years. As functional material with a new structure, such materials are favored by researchers because they have many unique properties, such as single dispersion, core-shell operability, stability, control, self-assembly, and capabilities involved in light, electricity, magnetic, catalytic, chemical and biological reasons, and regulation can be largely achieved for many properties of composite nanomaterials [6].

Core-shell nanomaterials can be divided into different categories by applying different criteria. Depending on whether a chemical reaction may occur between core-shell particles, it can be divided in to physical coating and chemical coating type. Depending on the different core-shell components, it can be divided in to three categories; organic- inorganic, inorganic-organic and inorganic-inorganic types. These core-shell structures are designed for specific purpose. The relatively stable nature of the shell is used to protect the core particles from the occurrence of physical and chemical change, another potential objective of the shell is to imp- rove the surface activities of the core particles as well as stability, dispersion, and so on. Through surface coating, core particles can have magnetic, optical, catalytic properties that are unique to shell particles.

Nanoshell nanostructure

A nanoshell is composed of a spherical dielectric or semiconductor core homogenously coated with a concentric nanoscale metallic shell. By tailoring the geometric parameters of nanoshells one can fine-tune the particles light absorption and scattering properties all the way across the visible and near infrared (NIR) spectral regions, enabling wide spread applications .

Because nanoshells are spherically symmetric, there local surface Plasmon resonances (LSPRs) can be analytically described by Mie scattering theory. In 1951, Aden and Kerker first proposed the model for simulating the absorption and scattering of electromagnetic waves from a spherical particles consisting of a dielectric core and a metallic shall based on Mie scattering theory. Neeves and Birnbo proposed in 1989 that such core-shell geometry could give rise to LSPRs modes with their wavelengths tunable over a broad spectral range. The LSPRs of a nanoshell are extraordinarily sensitive to the inner and outer dimensions of metallic shell layer [7]. One study shows the optical extinction spectra of Au nanoshells calculated using Mie scattering theory. In this set of calculations, the radius of the silica core was fixed at 60 nm, and the shell thickness was varied from 5 nm to 20 nm. Since the overall sizes of the Au nanoshells are beyond the quasi-static limit, both the dipole and the quadrapole LSPR bands show up in the extinction spectra and progressively red-shift as the shell thickness ratio is varied between 3 nm and 12 nm, the predicted resonance of the nanoshell spans a range of 300 nm in wavelength. In contrast, if the order of these layers were inverted, that is a Au core and a dielectric silica shell, less than a 20 nm optical resonance shift would be expected.

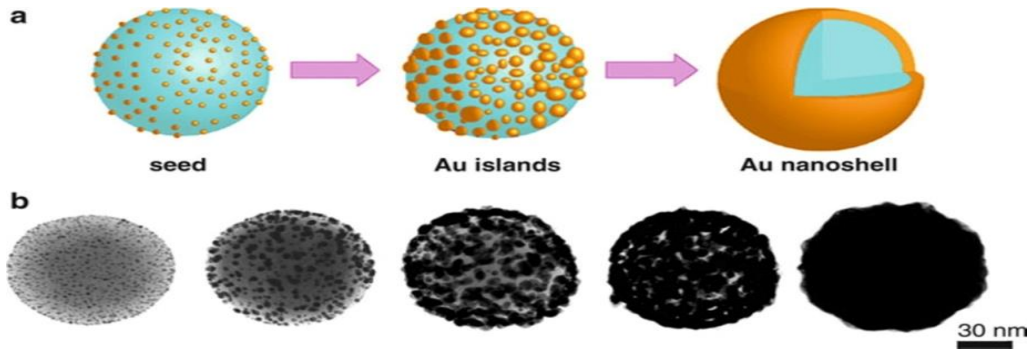


Figure 2.4: (a) Scheme of seed mediated electroless plating of Au nanoshell surrounding silica cores. (b) TEM images that reveal the whole process of Au nanoshell growth on the surface of silica cores. [7]

Example of nanoshell synthesis

Halas and coworkers have done pioneering work on the fabrication of metal nanoshells through a multistep; seed mediated electro-less plating approach. In 1998 they controllably fabricated silica- Au core-shell nanoparticles, which overcome many of the limitations of the Au_2 S-Au nanoshells. The whole procedure for the fabrication of the silica-Au nanoshells can be schematically illustrated in figure 2.4: a. The procedures of the synthesis can be explained as follows:

1. highly monodispersed silica cores with precisely controlled diameters ranging from 50 nm to 800 nm are fabricated using the Stober method-a chemical process used to prepare Silica (SiO_2) particles of controllable and uniform size.
2. the surface of the silica core particles are then functionalized with amine groups.
3. small Au colloidal (1 nm-2 nm) are subsequently absorbed on to the silica surfaces through Au amine interactions.
4. the immobilized Au colloids act as nucleation sites catalyze the electroless planting of Au to form Au islands on the surface of silica.
5. as an increasing amount of Au is plated the Au islands gradually grow larger and eventually coalesce to form a complete nanoshell. Figure. 2.4: b shows a set of TEM image that reveals the whole process of Au nanoshell growth on the surface of the silica cores.

The final thickness of the Au nanoshells, which is typically in the range from 5 nm to 100 nm, can be precisely controlled by adjusting the amount ratio between silica and Gold tetrachloride ($HAuCl_4$) added. By using these seed mediated electroless plating method, continuous Au, Ag, Cu, and bimetallic nanoshells with controllable core and shell dimensions have been successfully fabricated using silica, polymer or cuprous oxide beads as core materials.

Application of nanoshells

Most of the limitations of those first nanoshells were overcome by a new type of gold nanoshells, synthesized by Halas and coworkers after that the application of nanoshells flourished. From application of nanoshell surface enhanced Raman scattering (SERS),

medicine such as cancer therapy, thermal ablation of tumors, photothermal modulated drug delivery, tissue welding and biosensing and imaging fano-resonances in metal-dielectric-metal (MDM) nanoshells and photonics can be mentioned.

The enhanced properties of nanomaterials or nanoparticles compared to their parent or bulk material draw a lot of attention in the scientific community during the last few decades. And the ever increasing demand for the novel properties compelled countries, institutions, researchers to invest resources in order to understand the properties, applications, large scale production and the possible side effects of the nanomaterial. Due to the commitment of the stake-holders nowadays, especially the physicochemical properties like electrical, optical, mechanical, thermal, magnetic properties, from which one of them is explained latter, are well studied understood and the results are applied in nanotechnology example in nanodevice biomedicine etc.

2.7 Optical Properties

The optical properties of NPs are different among nanomaterials to a greater extent. For instance, noble metal NPs have size dependent optical properties and exhibit a strong UV-visible extinction band that is not present in the spectrum of the bulk metal. This extinction band results when the incident photon frequency is consistent with the collective excitation of the conduction electrons and is known as local surface plasmon resonance (LSPR). LSPR excitation results in the wavelength selection absorption with extremely larger molar excitation coefficient resonance, Rayleigh scattering with efficiency equivalent to that of ten fluorophores and enhanced local electromagnetic field near the surface of NPs that enhanced spectroscopies. It is well established that the pick wave length of the LSPR spectrum is dependent up on the size, shape and inter-particle spacing of the NPs as well as its own dielectric properties and those of its local environment including the substrate, solvents and absorbent. Gold colloidal NPs are accountable for the rusty colors seen in blemished glass door or windows while, Ag NPs are typically yellow. Actually, the free electrons on the surface in these NPs (d electrons in Ag and Au) are freely transportable through the nanomaterial. The mean free path for Ag and Au is 50 nm, which is more than the NPs size of these materials. Thus, no scattering is expected from the bulk, up on light interaction, instead they set in to standing resonance conditions, which is responsible for SPR in these NPs.

The above topic explain the fascinating optical property of metal nanoparticle that is completely different from those of either the corresponding bulk material or the atoms or molecules. The difference in the properties of the nanomaterials from the bulk counterpart are observed due to size, shape, structure and other changes occur in the material below a certain critical size and for most material it is below 100 nm. Nanoparticles of noble metals, such as Au, Ag and Cu have attracted tremendous attention due to their interesting geometry dependent optical properties. The effect of the change in size, shape and structure of materials are presented in the next subtopic.

2.8 Effects of Size, Shape, and Structure

2.8.1 Size control of nanoparticles

The physical and chemical properties of nanomaterials depend not only on their composition but also on the particle size and shape and structure. Accordingly, a high quality synthesis protocol must first of all provide control over particle size and shape and it is important to fabricate nanoparticles with a single target size in mind. For example if the diameter of an Au nanosphere is made to increase the SPR will be gradually shifted from 530 nm to the longer wavelength side. Then if nanoparticles differ in size their optical characteristics will also change significantly.

It is important to realize that the physical properties of a nanoparticle can change with the aggregation ratio; eventhough the colloidal solution may contain nanoparticles of identical size.

2.8.2 Shape control of nanoparticle

The shape of nanoparticle is an important factor that determines the nature of the surface Plasmon resonance band just as size of the nanoparticles did. Absorption spectra in the visible spectral region of various Au rod shaped nanoparticles, i.e., nanorods with change in aspect ratio (the ratio of length of longer side to shorter side) are shown in figure 2.5: The diameters of the Au nanorods espousing a pillar form and used in ranged from 5 - 20 nm and the lengths from 20 - 150 nm. It is worth nothing that the change in the ratio of a nanorod is related to the size ratio of a crystal face. An increase in the size ratio (aspect ratio) shifts the maximal absorption band to the longer wavelength. Therefore the physical composition of the nanorods can easily change their spectroscopic features.

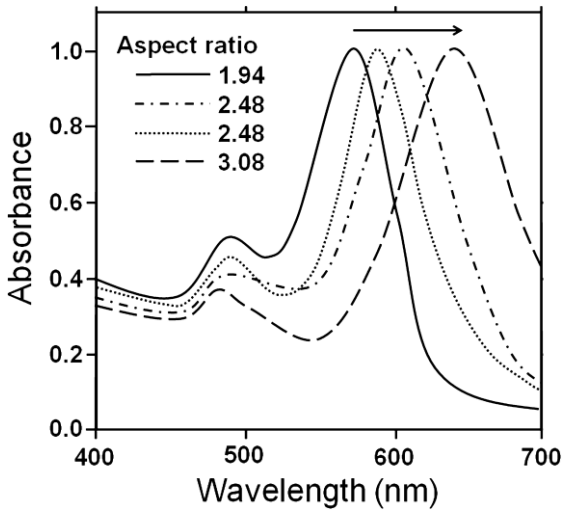


Figure 2.5: Visible-light spectra of Au rod-shaped nanoparticles with various aspect ratios of rod-shaped nanoparticle. [1]

2.8.3 Structure control of nanoparticles

Nanoparticles that are composed of two or more metal differ in their catalytic, magnetic and optical characteristics from nanoparticles that consist of a single metal. The core-shell structure in which the metal at the center differs from the peripheral metal (figure 2.6) for instance, although the color of a Silver (Au) nanoparticle liquid dispersion is purplish red and that of a Gold (Ag) nanoparticle liquid dispersion appears yellow, whenever Au forms the core and Ag the shell the structure then takes an orange color. This change in color directly indicate the effects of structure on the optical properties of nanomaterials .

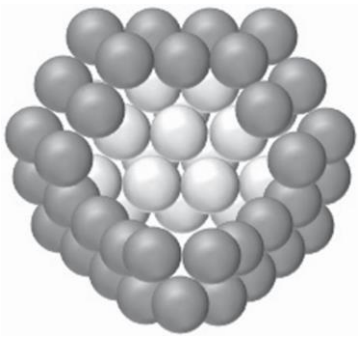


Figure 2.6: Schematic images of bimetallic nanoparticles: coreshell structure. [1]

Many scientists, researchers, engineers, Science fiction authors imagined, thought, designed ideas that are not yet become reality due to absence of material for their specific goal. But

most of them believe that one day their idea become reality because of the abundance use of nanomaterials. Why these groups of people put their trust on nanomaterial?

2.9 Why Nanoparticles?

Nanoparticles, crystal and nanolayer manufacturing processes aim to take advantage of these four kinds of effects [8].

1. New physical, chemical or biological properties.
2. Interaction length scale of physical, chemical and biological phenomena become comparable to the size of the particle, crystal or respective microstructure grain.
3. Generation of new atomic, molecular and macromolecular structures of materials by using various synthesis routs:
4. Significant increase of the degree of complexity and speed of processes in particulate systems.

Time scale change because of smaller distances and the increase spectrum of forces (electro-static, magnetic, electrophoresis radiation pressures other) with intrinsically short time scales.

For instance for nanoparticles smaller than the electron mean free path (a few tenth for nanometers for bulk metal), scattering electrons with the particles boundaries (surface) become important. This process reduces the electron mean free path which intern leads to in-crease in the imaginary part of the dielectric function. To account for this fact, a size dependent dumping constant which is the average total time τ between collisions of free electrons with other electrons, lattice vibrations and imperfections must be introduced in the real and imaginary parts of the nanomaterial dielectric function.

2.10 Dielectric Function of Nanomaterial

2.10.1. Lorentz-Drude model of dielectric function

The expression of the dielectric function for a nanoscopic particle is not trivial. However, if suitable and physically meaningful corrections are made the classical concept of dielectric function can be extended down to nanometer sizes. This classical model of dielectric function is Lorentz model. According to this model matter is composed of electrons and ions as a collection of independent, identical, isotopic and dumped charged harmonic oscillator.

Therefore optical properties are consequence of the way in which these oscillators respond to electromagnetic fields. According to this model, the dielectric function is given by [7]

$$\varepsilon = 1 + \frac{\omega_p^2}{\omega_o^2 - \omega^2 - i\omega\gamma} \qquad (2.1)$$

2.10.2. Free electron contribution

According to Drude model electrons in bulk metals are considered essentially free since they can be promoted to higher empty energy level (from top of the energy distribution near the Fermi level) with very small photon energies. In this sense it is considered that they are not bound to the ion core, so their resonant frequency may be set equal to zero in the Lorentz model. Therefore, the expression for dielectric function of a free electron metal can be obtained according to the Drude model by putting $\omega_o = 0$ in equation (2.1) and it becomes

$$\varepsilon_{free}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \qquad (2.2)$$

In general this complex dielectric function for bulk metals can be decomposed in to the terms, a complex free electron term and a complex inter-band or bound electron term. Since the dielectric function is additive it can be written as,

$$\varepsilon(\omega) = \varepsilon_{\text{free - electron}}(\omega) + \varepsilon_{\text{bound – electron}}(\omega) \qquad (2.3)$$

$$\varepsilon(\omega) = \varepsilon'(\omega) + \varepsilon''(\omega)$$

So the real and imaginary parts of dielectric function have contributions from both complex free and bound electrons and the real and imaginary parts of the free electron is given by,

$$\varepsilon'_{free}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \gamma_{free}^2} \qquad (2.4)$$

$$\varepsilon''_{free}(\omega) = \frac{\omega_p^2 \gamma_{free}}{\omega(\omega^2 + \gamma_{free}^2)} \qquad (2.5)$$

The dielectric constant for nanoparticles or nanometeric system is not only a function of wavelength (frequency) of the incident radiation but also is sensitive to the size and shape of the particle. To account for this fact, it is necessary to include a size-dependent damping constant to the expression of bulk dielectric constant as written in equation (2.7) below. In a bulk metal the damping constant γ_{free} is the average total time τ between collisions of the

free electrons with other electrons (electron- electron) scattering, lattice vibration (electron-photon) scattering, and imperfections. It can be expressed as

$$\gamma_{free}^{bulk} = \frac{1}{\tau} = \frac{1}{\tau_{el-el}} + \frac{1}{\tau_{el-ph}} + \frac{1}{\tau_{imp}} \quad (2.6)$$

$$\gamma_{free}^{size} = \gamma_{free}^{bulk} + C\frac{V_F}{r} \quad (2.7)$$

where V_F is the velocity of the electron at Fermi level and "r" is the radius of the particle, C is proportionally constant for the details of the electron scattering process at the boundary. When γ_{free} is replaced by the size-dependent expression the equations (2.4) and (2.5) takes the form

$$\varepsilon_{free}^{'}(\omega r) = 1 - \frac{\omega_p^2}{\omega^2 + (\gamma_{free}^{size})^2} \quad (2.8)$$

$$\varepsilon_{free}^{''}(\omega r) = \frac{\omega_p^2 \gamma_{free}^{size}}{\omega(\omega^2 + \gamma_{free}^{size})^2} \quad (2.9)$$

2.10.3. Bound electron contribution

In the above equation $\varepsilon_{free}(\omega)$ become size dependent and a complete expression for dielectric function is made up by a free electron component and a bound electron component.

$$\varepsilon(\omega) = \varepsilon_{free}(\omega) + \varepsilon_{bound}(\omega) \quad (2.10)$$

$$\varepsilon(\omega) = \varepsilon'(\omega) + \varepsilon''(\omega)$$

If the bound contribution is considered size independent its value may be determined by subtracting $\varepsilon_{free}(\omega)$ from bulk experimental data $\varepsilon(\omega)$ taken from Palik or Johnson and Charisty [7]. That means

$$\varepsilon''(\omega) = \varepsilon(\omega) - \varepsilon'(\omega) \quad (2.11)$$

The Drude model described above takes in to account only electrons in the outer atomic orbital. For example 5s, 6s, and 4s states for silver, gold and copper respectively. But the single and multiple interband electron transition for example transitions from 5d band to the 6sp band in gold which cannot be ignored when the incident light frequency fall in the visible region add its contribution to the dielectric function of the material. This effect can be taken

in to account through different formula of bound electron contribution. Electronic interband transitions are transitions when the energy of the incoming photon is large enough to overcome the band gap and promote valance or bound electrons to conduction band of the material.

Optical properties of materials is alternatively described by the real and imaginary parts of the complex refractive index N = n + ik for non magnetic media, the relation N = $\sqrt{\varepsilon}$ holds so that the real and imaginary parts of both refractive index and dielectric functions are related by,

$$\varepsilon' = n^2 - k^2 \qquad (2.12)$$

$$\varepsilon'' = 2nk \qquad (2.13)$$

The change in the dielectric constant of nanoparticles is one of the factors that can change surface plasma vibration and thereby local surface plasmon resonance (LSPR). This LSPR which is the most important factor in the study of nanoparticle is highly dependent on the kind of metal size shape and other factors of nanoparticle. Then what is Plasmon? What is LSPR?

2.11 Plasmon and LSPR

Metallic nanostructures possess size, shape and geometry dependent localized surface plasmon resonance. Plasmon represents the collective oscillation of a free charge in a metal, and considered as a kind of plasma wave. The positive electrical charge in the metal is fixed and the free electron is free to move around it, an applied external field, as from a light source, causes the free electrons at the surface of the metal to vibrate collectively, giving rise to surface Plasmon. Since electrons are also particles with an electric charge, when they vibrate they also generate an electric field, and when the electric field from the vibration of free electrons and applied external electric field (e.g., electromagnetic waves) resonate the resulting phenomenon is referred to as a surface plasmon resonance that takes place at the surface of the metal. However, if light irradiates a solution that contains dispersed metal nanoparticles smaller than the wavelength of light, then depending on the electric field of light, the deviation produces a free electron at the surface of the metal. As a result the weak or thick portions of the electric field appear on the nanoparticles surface (figure 2.7: a, b) and can be considered as a kind polarization. Such localized Plasmon resonance is called

localized surface plasmon resonance (LSPR). Or in metallic nanoparticle systems, the collective oscillations of free electrons are confined to a finite volume defined by the particle dimension. Since the Plasmon of nanoparticles are localized rather than propagating that is why they are known as localized surface Plasmon resonance.

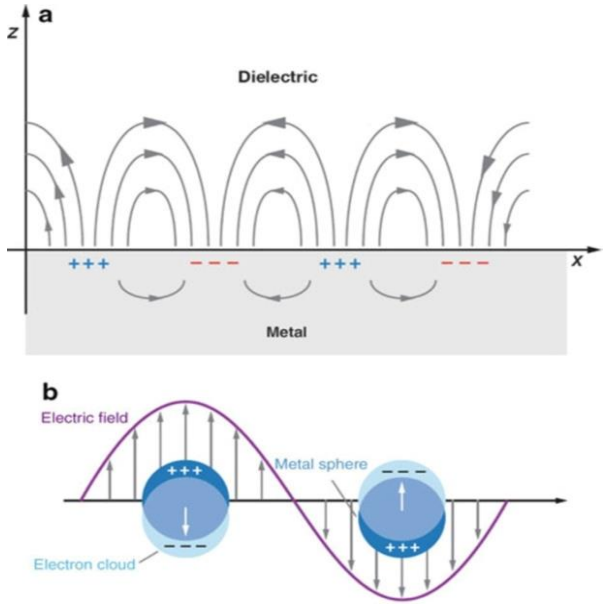


Figure 2.7: Schematic illustrations of (a) a propagating Plasmon at metal-dielectric interface and (b) a LSPR of a metal nanosphere. [7]

LSPR is typically concentrated in a very narrow region on the surface of a nanoparticle. The wavelength corresponding to the LSPR depends on the kind of metal, the shape of the metal nanoparticle, and the extent of aggregation of the metallic nanoparticles. Moreover the surface plasma vibration also changes with the dielectric constant and the quality of the carried fluid. Usually LSPR, manifest themselves on a combined effect of scattering and absorption in the optical extension spectra, as depicted in figure 2.7: b, the free electrons of Au nanosphere oscillate coherently in response to the electric field of incident light .

It is a historical fact that Micheal Faraday was the first person to observe the spectacular color change of spherical solid Au nanoparticles and about a century ago Gustav Mie applied Maxwell's equation to explain the strong absorption of green light by Au nanosphere under plane wave illumination, which establishes for the first time the rigorous scientific foundation for our understanding of this interesting phenomenon. Despite the presence of published papers on the same topic by other scientists we still refer Mie theory to explain similar phenomenon. What is Mie theory? What kind of optical properties does it explains?

2.12 Mie Scattering Theory

The optical characteristics of metal colloids have been known and used for centuries; our scientific understanding on the origin of these properties has immerged far more recently, beginning with the development of classical electromagnetic theory. It was realized almost a century ago that classical electromagnetic theory (i.e., solving Maxwell's equations for light interacting with a particle) based on Mie scattering theory can provides a quantitative description of the scattering and absorption spectra of spherical nanoparticles, even though Mie's work is incapable of addressing shape effect.

This Mie scattering theory is the exact solution to Maxwell's electromagnetic field equation for a plane wave interacting with a homogeneous, isotopic sphere of radius R with the same dielectric constant as bulk metal. Therefore, Mie's scattering theory is effective way of explaining absorption, scattering, and extinction cross-sections and absorption, scattering, and extinction efficiencies of spherical particle size ranging from 1-100 nm.

2.12.1. Definition of optical properties of nanomaterial

2.12.1.1. Absorption and scattering

Absorption is a phenomenon which occurs when the free electrons in metallic nanostructure are driven by the incident electric field to collectively oscillate at a certain resonate frequency and the incident light is absorbed by the nanoparticles and when some of these photons is converted in to phonon or vibration of the lattice.

Scattering is a phenomenon which occurs when the free electron in a metallic nanoparticle are driven by the incident electric field to collectively oscillate at a certain resonant frequency and the incident light is absorbed by the nanoparticles and when some of these photons is released with the same frequency and energy in all direction.

2.12.1.2. Absorption, scattering and extinction cross-sections

Absorption cross-section (C_{abs}) − is defined as the fraction of the electromagnetic power absorbed (W_{abs}) by the nanoparticle, with respect to the intensity I_o of the incident plane sinusoidal wave.

$$C_{abs} = \frac{W_{abs}}{I_O}$$

Scattering crass-section (C_{sca}) − is defined as the fraction of the electromagnetic power scattered (W_{sca}) by the nanoparticles with respect to the intensity Io of the incident plane sinusoidal wave.

$$C_{sca} = \frac{W_{sca}}{I_o}$$

Extinction cross-section (C_{ext}) is defined as the sum of C_{abs} and C_{sca}

$$C_{ext} = C_{abs} + C_{sca}$$

Both C_{abs} and C_{sca} have the dimension of area and depends on the wavelength and the direction and polarization state of the incident beam and the particle orientation.

2.12.1.3. Absorption, Scattering and Extinction Efficiencies

Extinction efficiency (Q_{ext}) − is defined as the ratio of the energy scattered or absorbed by the particle to the energy incident on its physical cross-section.

$$Q_{ext} = \frac{C_{ext}}{area}$$

Absorption efficiency (Q_{abs}) − is defined as the ratio of the energy absorbed by the particle to the energy incident on its physical cross-section.

$$Q_{abs} = \frac{C_{abs}}{area}$$

Scattering efficiency (Q_{sca}) − is defined as the ratio of the energy scattered by the particle to the energy incident on its physical cross-section.

$$Q_{sca} = \frac{C_{sca}}{area}$$

CHAPTER THREE: MODEL AND METHOD

3.1 Core-Shell Model

In this core shell model it is assumed that the shell or coating is homogeneously coated on to the core. As it will be explained latter there refractive index (RI) and diameter of the core and the surrounding medium RI and its type are similar throughout the calculation. In addition to this the refractive index (RI) and type of the core, coating and surrounding medium materials the wavelength or spectral range which are used as an input for core-shell Mie calculation are all encoded within the Mie theory calculator from different sources and it is this calculator which is used for the simulation of cross sections of the model .

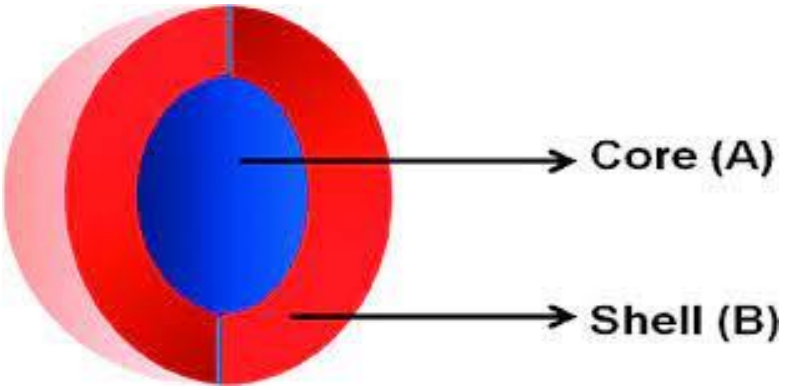


Figure 3.1: Schematic illustration of the core shell nanoparticle .

The expression of absorption, scattering and extinction cross sections for a coated sphere is the same as that of a single homogeneous sphere except that the form of scattering coefficients $a_n \; and \; b_n$ depends on the radial variation of $\varepsilon \; and \; \mu$ [9]. Therefore, the extinction cross section C_{ext} and scattering cross-section C_{sca} can be expressed as

$$C_{ext} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)Re(a_n + b_n) \qquad (3.1)$$

$$c_{sca} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)Re(|a_n|^2 + |b_n|^2) \qquad (3.2)$$

And the absorption cross section C_{abs} is simply

$$C_{abs} = C_{ext} - C_{sca} \qquad (3.3)$$

From the expression k is the wave number and can be expressed as $k = \frac{2\pi N}{\lambda}$, where N is the refractive index of medium and λ is the wavelength of the incident wave.

The Mie coefficients or scattering coefficient can be expressed as

$$a_n = \frac{\psi_n(x)\psi_n'(mx) - \psi_n'(x)\psi_n(mx)}{\xi(x)\psi_n'(mx) - \xi'(x)\psi_n(mx)} \quad (3.4)$$

$$b_n = \frac{m\psi_n(x)\psi_n'(mx) - \psi_n'(x)\psi_n(mx)}{m\xi(x)\psi_n'(mx) - \xi'(x)\psi_n(mx)} \quad (3.5)$$

In equation (3.4) and (3.5) $m = {N_p}/{N_m}$ stands for relative refractive index of the particle

$\psi_n(x) = xj_n(x)$ and $\xi_n(x) = xh_n^{(1)}(x)$ are the Ricciati-Bessel, Ricciati Hankel functions respectively. The prime (') denotes derivation with respect to its arguments [9].

Mie's formula extension to a coated sphere

Above it is expressed that the cross-sections of a single sphere and coated sphere are similar in form as described by equation (3.1), (3.2), (3.3) except the change in scattering coefficients a_n and b_n. Therefore the scattering coefficients for coated sphere is given by

$$a_n = \frac{\psi_n(y)[\psi_n'(m_2y) - A_nX_n'(m_2y)] - m_2\psi_n'(y)[\psi_n(m_2y) - A_nX_n(m_2y)]}{\xi_n(y)[\psi_n'(m_2y) - A_nX_n'(m_2y)] - m_2\xi'(y)[\psi_n(m_2y) - A_nX_n(m_2y)]} \quad (3.6)$$

$$b_n = \frac{m_2\psi_n(y)[\psi_n'(m_2y) - B_nX_n'(m_2y)] - \psi_n'(y)[\psi_n(m_2y) - B_nX_n(m_2y)]}{m_2\xi_n(y)[\psi_n'(m_2y) - B_nX_n^1(m_2y)] - \xi_n'(y)[\psi_n(m_2y) - B_nX_n(m_2y)]} \quad (3.7)$$

$$A_n = \frac{m_2\psi_n(m_2x)\psi_n'(m_1x) - m_1\psi_n'(m_2x)\psi_n(m_1x)}{m_2X_n(m_2x)\psi_n'(m_1x) - m_1X_n'(m_2x)\psi_n(m_1x)} \quad (3.8)$$

$$B_n = \frac{m_2\psi_n(m_1x)\psi_n'(m_2x) - m_1\psi_n(m_2x)\psi_n'(m_1x)}{m_2X_n'(m_2x)\psi_n(m_1x) - m_1\psi_n'(m_1x)X_n(m_2x)} \quad (3.9)$$

where m_1 and m_2 are refractive indices of the core and coating relative to the surrounding medium x=ka, y=kb x and y are size parameters of the core and shell "k" is the wave number a and b are radius of the core and shell respectively [10].

3.2 The Mie Theory Methodology

Research method is a very important step to explain a study in terms quantitative or qualitative dimensions and give a considerable detail of techniques to be used for obtaining, analyzing and interpreting the data. In this project we use the Mie theory methodology in order to calculate the cross sections of dielectric/metal core shell spherical nanostructure and to conduct the study core diameter and type, shell thickness and type, surrounding type, the corresponding refractive index of each material and the wavelength range are used as a parameter for silica (SiO_2) core and silver (Ag), gold (Au), and copper (Cu) shell to calculate the absorption, scattering and extinction cross sections. First the cross sections of silica core silver shell nanostructure at a fixed core diameter (50 nm), various shell thickness (3, 6, 9, and 12 nm), at the same surrounding medium of water and at the same wavelength range of (300-800 nm) are investigated. In addition to this the effects of different coating materials Ag, Au and Cu on cross-section at the same silica core size diameter 50 nm, at the same shell thickness (15 nm), at the same surrounding medium (water) and at same spectral range (300 -800 nm) are investigated. The refractive index of silica and water are the same throughout the calculation.

In this project the Mie calculation is undertaken using the Mie theory calculator which is developed by Dr. Steve Oldenburg. The calculator is a very powerful tool in providing information about cross-sections and to undergo the calculation the parameters which are mentioned in the Mie theory like refractive index or dielectric constant type of material and others are all included within it from different sources. The calculator for instance, in the case of core shell nanostructure placed in a medium, provide options of choosing the core type and diameter, shell type and thickness, surrounding medium type and refractive index and spectral range or wavelength interval and it gives the plot of cross-sections versus wavelength of any given data or value. In addition to this on the graph of the calculator absorption, scattering and extinction cross-sections can be indicated at any given wavelength and the data can also be downloaded.

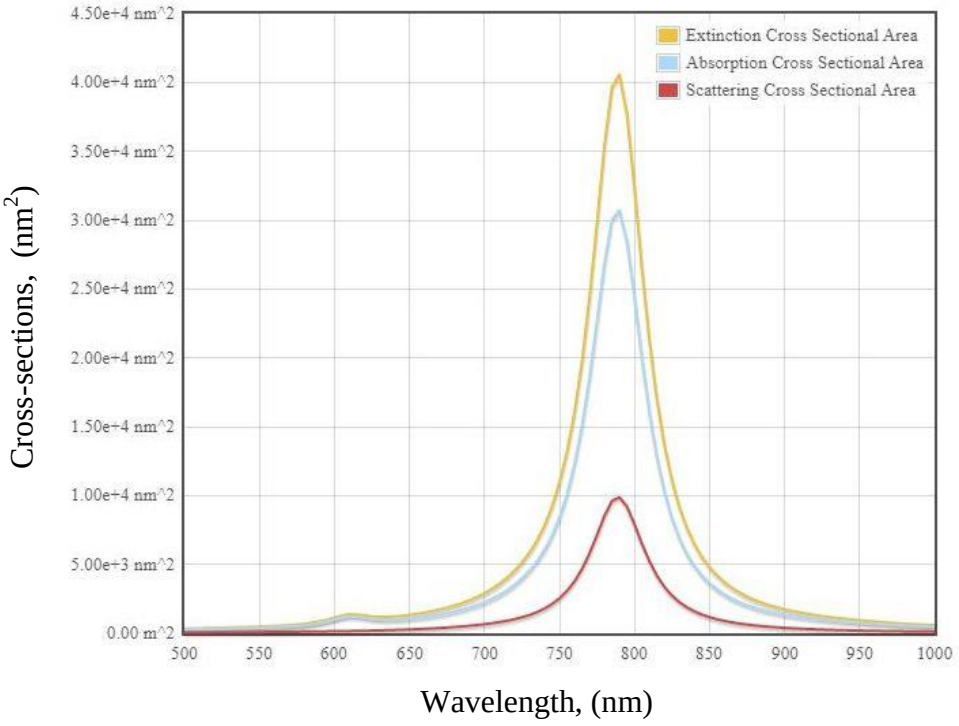
CHAPTER FOUR: RESULTS AND DISCUSSION

This part deals about the result and discussion of data or information obtained from Mie theory calculator.

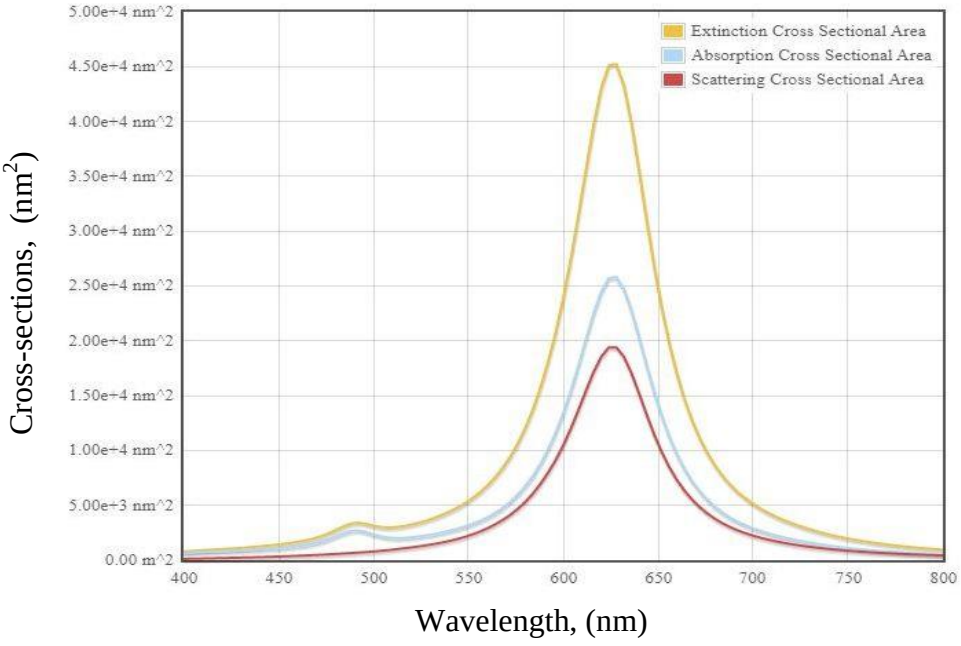
4.1 Effects of Different Shell Thickness on Cross-sections

The effect of different shell thickness on the absorption, scattering, and extinction cross-sections is studied and the results are shown in Figures 4.1 (a) - (d).

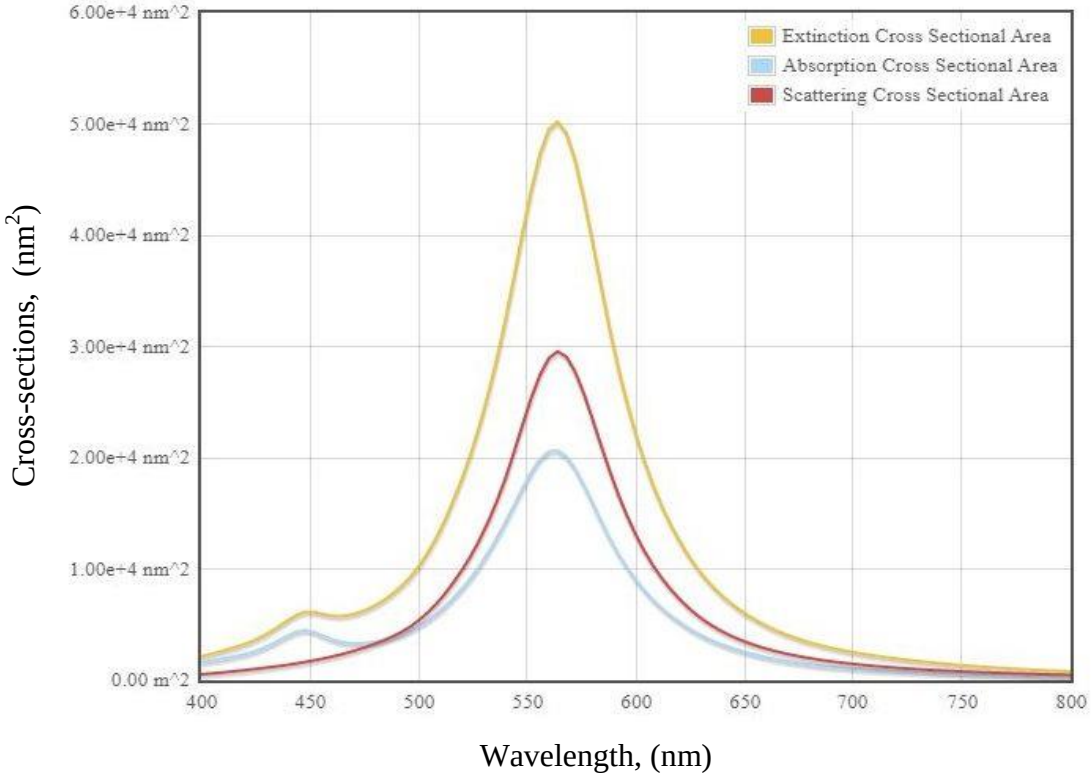
a) Graph of 50 nm diameter Silica (SiO_2) Core 3 nm thick Silver (Ag) Shell nanostructure.



b) Graph of 50 nm diameter Silica (SiO_2) Core 6 nm thick Silver (Ag) Shell nanostructure.



C) *Graph of 50 nm diameter Silica (SiO_2) Core 9 nm thick Silver (Ag) Shell nanostructure.*



d) *Graph of 50 nm diameter Silica (SiO_2) Core 12 nm thick Silver (Ag) Shell nanostructure.*

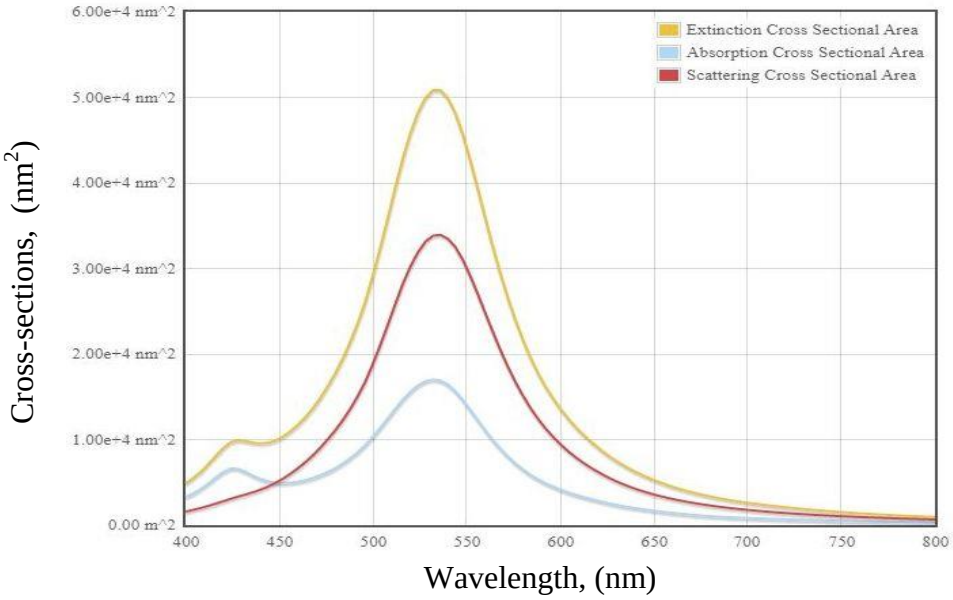


Figure 4.1: Graphs of cross-sections versus wavelength for different shell thickness and same Silica core diameter and surrounding medium (water).

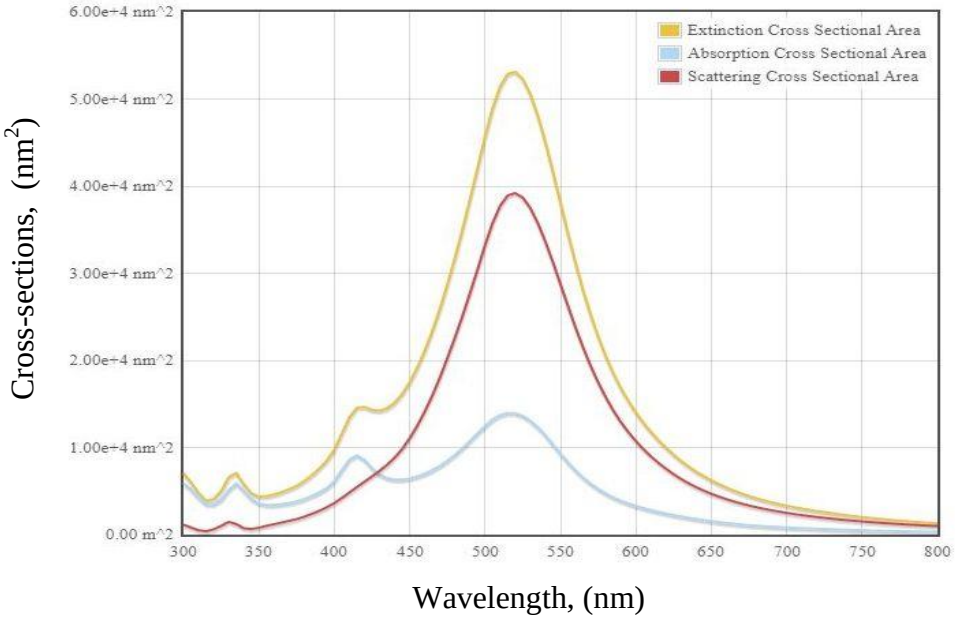
In Figure 4.1: (a) and (b) the absorption, scattering, and extinction cross-sections tends to go towards the longer wavelength side, i.e., a red-shift occur. In addition, the absorption cross-section dominates the scattering cross-section and absorption cross-section contributes more to the extinction spectra of the nanoshell. In Figure 4.1 (c) and (d) the scattering cross-section dominates absorption cross-section and scattering cross-section contribute more to the extinction spectra. The other most important point noticed is that when the shell thickness increases from 3-12 nm, all the three cross-sections, i.e., the absorption, extinction, and scattering cross-sections shift from the longer wavelength to the shorter wavelength side, i.e., blue shift occur. Also, the cross-section resonance peaks of the scattering and extinction cross-sections increase while the peaks of the absorption cross-section decrease and the wavelength at which the first big peaks occur at almost the same wavelength value. Near the ultraviolet region, for all shell thickness 3 nm-12 nm, the scattering cross-section is almost close to zero and it is dominated by absorption cross-section and the contribution for extinction spectra almost only obtained from absorption cross-section. In the second small peaks for all shell thickness of 3 nm-12 nm the absorption cross-section is dominant than scattering and thereby its contribution more to extinction spectra. The results demonstrate

that a variation in shell thickness changes or affects the absorption and scattering cross-sections and their respective contribution to the spectra of the extinction cross-section.

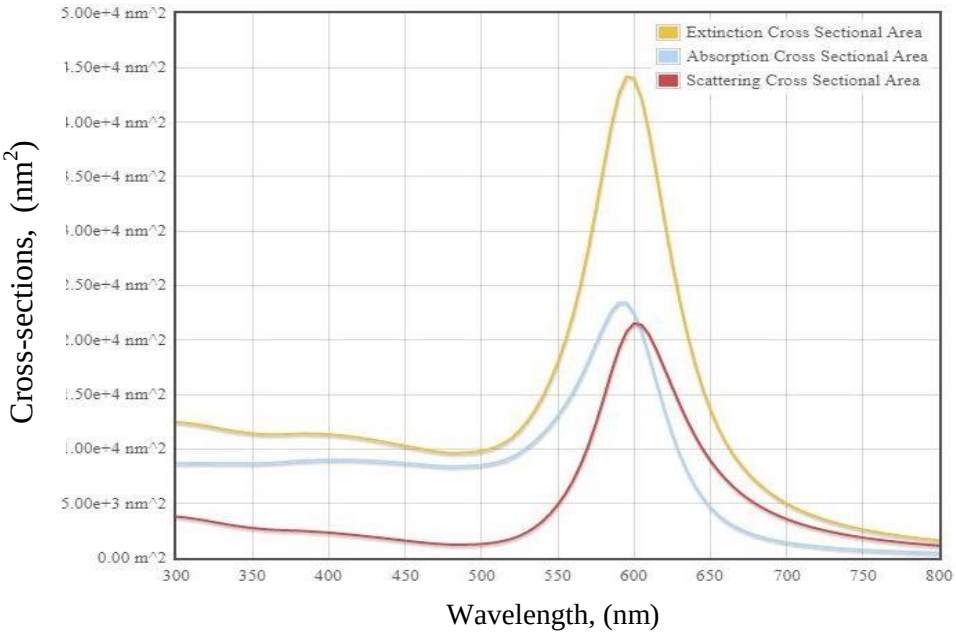
4.2 Effect of Different Shell Type on Cross-sections

The effect of different types (Ag, Au, and Cu) of the shell (coat) material on the absorption, scattering and extinction cross-sections is studied and the results are shown in Figure 4.2 (a) - (c).

a) Graph of 50 nm diameter Silica (SiO_2) Core 15 nm Silver (Ag) Shell type nanostructure.



b) Graph of 50 nm diameter Silica (SiO_2) Core 15 nm Gold (Au) Shell type nanostructure.



C) Graph of 50 nm diameter Silica (SiO_2) Core 15 nm Copper (Cu) Shell type nanostructure.

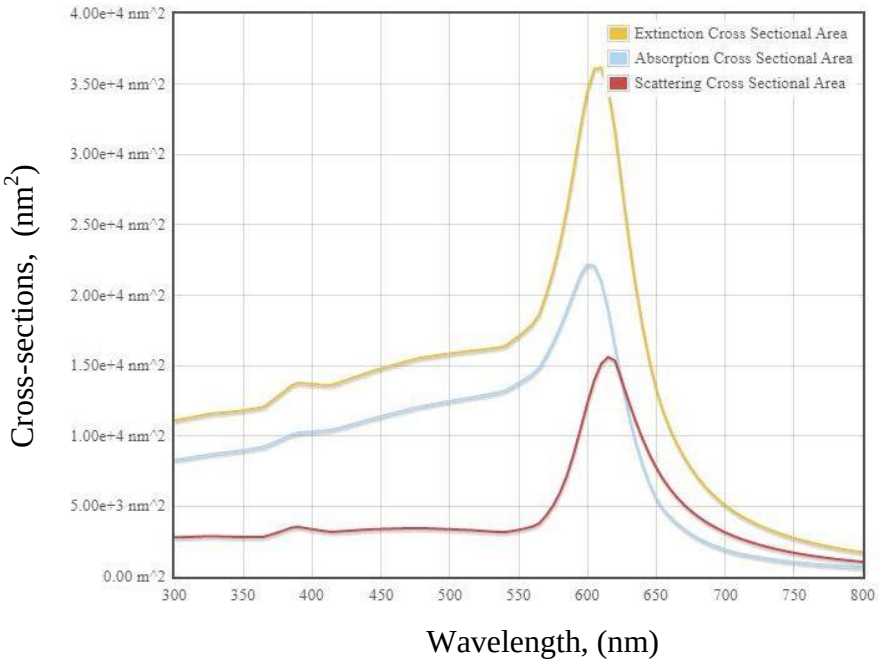


Figure 4.2: Graphs of the three cross-sections versus wavelength for different coating materials with same Silica core diameter and surrounding medium (water).

In Figure 4.2 (a) for the nanoshell silver thickness of 15 nm the scattering cross-section dominates the absorption cross-section. In Figure 4.2 (b) and (c) for gold and copper nanoshell thickness of 15 nm the absorption cross-section dominates the scattering cross-section. In addition, the absorption cross-section of the copper nanoshell is a bit greater than that of a gold nanoshell. This means that for the scattering cross-section of copper and gold to be dominant their shell thickness must be increased beyond 15 nm. The other point noticed hear is that the wavelength at which the peak of these cross-sections occur are slightly different for Au and Cu. These results demonstrate that the kind of material from which the shell of the nanostructure is made, keeping the other parameters same, can change or affect the absorption and scattering cross-sections as well as their potential applications. The results of this project are in agreement with research results conducted and presented by El-sayed and his team and the research results written in Ref. [7].

CHAPTER FIVE: CONCLUSIONS

In this project we implement the Mie method in order to investigate the dielectric/metal core-shell spherical nanostructures cross-sections and their relationships and thereby to identify the optical behavior of the nanoshell. On the other hand the most important point taken into account is that the understanding of the different application of nanoshell. In addition to these before directly tackling the above objectives grasping a better understanding of the history, definitions, concept, law of nanoscience or nanophysics under the umbrella of the project title was important. Finally accomplishing all these step by step initiate the pursuit or the quest for new scientific knowledge and gaining a confidence and way of experience and idea sharing.

Beside the above summary there were scientists that discover different methods for studying optical properties of material. But due to certain criteria they cannot be used equally for all types of materials. Therefore, the optical properties of dielectric/metal core-shell nano-structure can be studied through different means but in this work only Mie theory is used.

The other fascinating fact encountered is that research force one to realize different situations and opportunities. Through preparing for the study we found that currently nanoscience is one of the science that have been studied by researchers, institutions, universities due to its current amazing results and what is anticipated in the future.

In order to get the benefits nanoscience stakeholders must work very hard. In this project the Mie theory calculator is implemented to simulate optical properties of dielectric/metal core-shell spherical nanostructure specifically silica core silver shell nanostructure. In this case when the thickness of a silica core silver shell nanostructure is increased from (3-12 nm) by keeping the core diameter (50 nm), medium water (n = 1.3) and wavelength interval (300-800 nm) constant we investigate and found a change in absorption, scattering and extinction cross-sections. In addition to this for very small shell thickness of 3 nm silver the absorption, scattering and extinction cross sections tends to go towards the longer wavelength side this confirms the occurrence red shift and the absorption cross-section dominate the scattering cross-section. When shell thickness increase above 6 nm the cross-sections tends to go towards the shorter wavelength side this confirms the occurrence of blue shift and scattering cross-section dominate the absorption cross-section and it contribute more for the extinction cross-section. In addition to this near the ultraviolet region for shell thickness of 3-12 nm the scattering cross-section is almost close to zero and also absorption cross-section dominate

scattering cross-sections and for the second small peaks for all shell thickness of 3-12 nm the absorption cross-section is dominant than scattering and it contribute more for the extinction spectra.

In the other investigation keeping the silica core diameter (50 nm), silver shell thickness (15 nm), surrounding medium water (n = 1.3) and wavelength range (300-800 nm) constant changing the type of shell material between silver, gold and copper we found for silica core silver shell scattering cross-section dominate absorption cross-section and for gold and copper absorption cross-section dominate scattering cross section. In addition to this, the wave length at which the peaks of absorption, scattering and extinction cross sections occurs at slightly different wavelength value for Gold and Copper.

Generally, from the results it is possible to conclude that changing the shell thickness and shell type of a nanoshell structures change the absorption, scattering and extinction cross-sections and affect whether absorption or scattering cross-sections contribute more for the extinction cross-sections and also the extinction peak and the amount of absorption and scattering cross-sections. These in turn affects the possible application of the nanoshell structure (this means, for example the nanostructures can be used for either photo-thermal therapy or scattering based imaging and other applications based on whether absorption or scattering dominates). Precisely controlling shell thickness and shell type of nanomaterial affects the possible application of the nanostructured material, in other word we can fine tune or arrange the nanostructure for the required purpose through adjusting the shell thickness and shell.

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DECLARATION

I hereby declare that this Master of Science project is my original work and it has not presented for a degree in any other university and that all sources of material used for the project have been dully acknowledged.

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Signature: _____

This project has been submitted for examination with my approval as a University advisor.

Name: Dr. Belayneh Mesfin

Signature: _____

Place and time of submission:

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January 2022