Investigation of Size Effect in Absorption Spectra of Silver and Gold Nanoparticles

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ABSTRACT— The absorption cross-section of gold and silver nanoparticles has been demonstrated in confined wavelength spectra based on Mie's theory. For this purpose, the numerical study performed with COMSOL for defined particle size to clarify absorption spectra and final results have been compared with experimental data to express the absorption peak occurs in higher wavelength for large particle size which is in around 530 nanometers for gold and 400 nanometer for silver particles. These results show that particle size affects directly on absorption spectra of metallic nanoparticles.

KEYWORDS: Absorption cross section, Au and Ag nanoparticles, Mie theory, plasmonic effects.

INTRODUCTION

For Metal Nano-Particles (MNPs) capturing, manipulating, and concentrating light on a sub-wavelength scale is the cause of being attractive for chemists, physicists, material scientists, and even biologists [1]. All these remarkable properties are attributed to surface plasmon excitations at the interface of a conductor and an insulator as the result of interaction with an electromagnetic wave [2]. The coupling between light and surface plasmons in nanostructures leads to novel phenomena such as transport and storage of the energy [3]. The observation of enhancement in transporting or saving energy on metallic nanoparticle surfaces depends on incident light frequency [4], surrounding medium [5], size, and shape of sub-wavelength nanoparticles [6].

Metal nanoparticles mostly Gold and Silver are structured and characterized on the nanometer scale to introduce MNPs as a prominent candidate for use as part of integrated photonic devices for instance plasmonic lasers [7], optical modulators, sensors [8], and photovoltaic devices [9]. In this regard, the efficiency enhancement of photonic devices depends on the appropriate selection of size and shape of MNPs [10]. The investigation of absorption and transition from MNPs refers to the beginning of the 19century when Mie first developed his classical electrodynamic model for metallic nanospheres; accordingly, the Mie theory analytically solved the problem of interaction between the planar electromagnetic wave and metal nanoparticle classically which leads scattering and absorption cross sections [11].

In recent years, properties of nano-scale particles are being calculated with numerical methods such as time and frequency domain methods. The assumption of frequency domain solutions like finite element method (FEM) and discrete dipole approximation (DDA) is the harmonic time evolution of the electromagnetic field [12], on the contrary, finite difference time domain method (FDTD) time-domain allows to simulate transition of electromagnetic wave [13]. Recent researches allow us to compute the plasmonic effects of spherical nanoparticles in a wide range of size in various models from classical electrodynamic to quantum mechanics methods [14]. One of the most effective semi-classical methods is Random Phase Approximation (RPA), albeit it does not

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support the solution for large particles. RPA as a semi-classical method explains the interactions of light and small metal nanoparticles [15].

In the present paper with the use of the classical Mie approach and FEM calculation employing COMSOL Multiphysics the absorption cross-section spectra of Gold (Au) and Silver (Ag) nanospheres will be demonstrated and compared with experimental results which are obtained with the chemical reduction method.

THEORETICAL MODEL

A. *Numerical modeling*

Mie approach is used to have a survey on plasmon resonance in MNPs, bases on an analytical solution on Maxwell equation for incident planar wave scattered and absorbed by metallic nanoparticles [16]. The weak side of this approach consists of dielectric function which is usually modeled with experimental data, although the same holds to other methods of solution of the Maxwell equation. Commonly used methods are utilizing the finite element solution method of Maxwell equations both in space and time domains, implemented in COMSOL. On the plus side, Mie and numerical FEM approaches provide the possibility of an accurate solution for incident light scattering, reflection, and absorption, closely related to real processes [17].

The numerical study of plasmon excitations in gold and silver nanoparticles have been performed in the framework of COMSOL Multiphysics 5.5 with Wave Optics module. This module allows us to solve the propagation effects of electromagnetic waves in surrounding media like a dielectric. This framework allows us to solve complicated problems without building a model from the ground up. Moreover, the framework of COMSOL was validated by comparison with the Mie Theory. Nevertheless, COMSOL has been employed mostly in simple and complicated models in 3D, 2D, and 1D geometry due to its flexibility versus shape and material set-up. In the way of simulating plasmon resonant effects, the dielectric function is needed so it has been obtained from experimental results of Johnson and Christy [18].

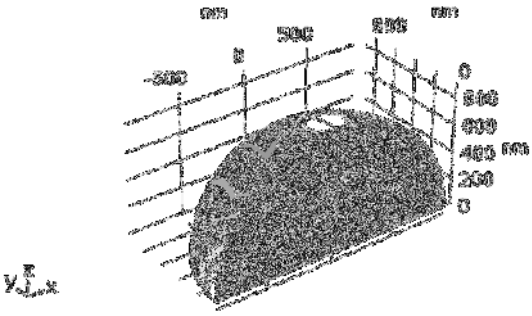

Fig. 1. Schematic of Spherical nanoparticle surrounding by dielectric and PML layers.

The simulation model was built in three domains. Fig. 1 Shows the metallic nanoparticles surrounding with dielectric media and Perfectly Matched Layer (PML), which quenches back-reflections from external surrounding boundaries. Thickness of PML layer was selected suitably to incident wavelength. built-in free meshing COMSOL algorithms help us to discretize our simulation. In this simulation tetrahedral finite elements in the area of the nano-particle and surrounding media, triangular meshing for the boundary of PML, and sweep mesh to divide PML layer into 5 spherical layers. Finally, with the use of parametric sweep, the extinction cross-section was calculated for the wavelength range around the visible area as a sum of absorption and Scattering formula. But numerically the assumption of Quasi-static conditions for particles, much smaller than the wavelength, leads to solving Laplace's equation in the spherical coordinate system. The boundary conditions bring the solution to the end by having a Poynting vector, at the end integration on the surface of nanoparticle the amount of energy will be obtained as below:

$$C_{sca} = \frac{4}{\sqrt{\varepsilon_0 / E_0^{\,2} \mu_0}} \int_V S.\hat{n}\, d\Omega , \tag{1}$$

$$C_{abs} = \frac{4}{\sqrt{\varepsilon_0 / E_0^{\,2} \mu_0}} \int_a U_a dV , \tag{2}$$

$$C_{ext} = C_{abs} + C_{sca} , \tag{3}$$

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where S is the Poynting vector, v is the boundary between PML and the surrounding medium, $\hat{n}$ is the vector normal to the v surface, $E_0$is the amplitude of the electric component of the incident electromagnetic wave, U_a indicates Ohmic heat losses in nanoparticle and V is the nanoparticles volume.

EXPERIMENTAL PROCEDURE

B. *Materials and Preparation*

Hydrogen Tetrachloroauric (III) trihydrate (HAuCl4·3H2O), poly vinylpyrrolidone (PVP), silver nitrate ($AgNO_3$), and Trisodium citrate ($Na_3C_6H_5O_7$) were purchased from Merck and N_2 gas was provided to obtain Stable solutions.

It is well known that there exist different methods for the synthesis of gold nanoparticles, [19] and the citrate reduction is one of the most commonly used ways, where the stable and dispersed gold nanoparticles could be readily obtained and the size of gold nanoparticles could be easily controlled [20].

For preparation Au nanoparticles help of chemical reduction, the Hydrogen Tetrachloroauric dispersed in deionized water with the assistance of ultrasonic methods, the mixed solution was heated and stirred on a hot plate stirrer for 10 min to bring the solution just to boil with stirring subsequently, Pre-prepared solution of (0.5 M) trisodium citrate was added slowly to solution. The remarkable point of adding reduction solution is the more we add, the smaller particles we attain [21]. So different volumes of trisodium citrate were added to the solution and three kinds of gold particles size have been achieved. For the synthesis of Ag nanoparticles, a sustainable amount of (PVP) was dissolved in water at room temperature and then silver nitrate was introduced into the mixture then the sealed bottle heated. With the heating time, the shape and size of Ag nanoparticles could be controlled. And the last step of preparation was bubbling pure nitrogen in solutions for about 20 min to remove oxygen. Characterization Ultraviolet-visible (UV–vis) absorbance spectroscopy measurement The UV spectra of the prepared silver or gold colloids were recorded. Deionized water was used as a reference.

RESULTS AND DISCUSSION

C. *Lab Results*

The addition of different amounts of trisodium citrate on the boiling solution will result from gold nanoparticles in a different range of sizes from 40 to 140 nanometer. Meanwhile, silver nanoparticles were obtained from various heating times. Eventually, the experimental section ends with results of absorption spectra of gold and silver nanoparticles of different sizes to obtain plasmonic absorption peak area in the visible range. Figure 2. provides the area of absorption peak for MNPs.

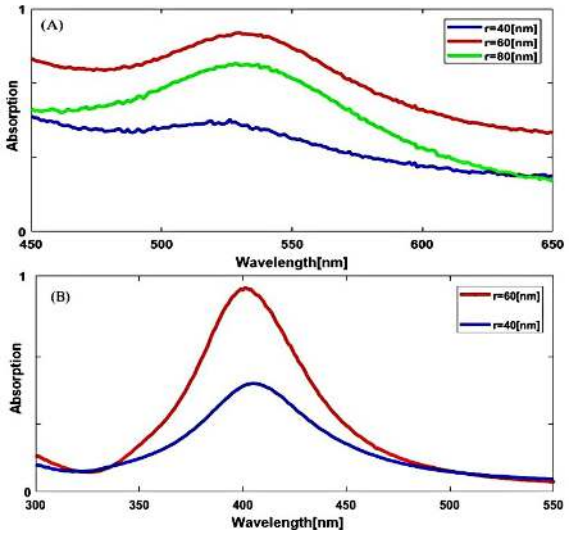

Fig. 2. Absorption spectra for (A) gold and (B) silver nanoparticles was achevied experimentally by UV-visible spectrometer.

D. *Simulation Results*

In our optical simulation, we calculate the absorption spectra of silver and gold nanoparticles to investigate the size effect of nanoparticles in plasmonic resonant. The absorption spectra were calculated for Au and Ag nanospheres surrounded by water (ε=*1.77*). There is a comparison of COMSOL results (points) with Mie theory (lines) for various sizes of nanospheres of these two metals. The size range of Au nanoparticles is from 40nm to 140nm and silver from 20nm to 60nm. The best agreement of Mie theory and COMSOL results corresponds to the same dielectric function

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assumed for both fully equivalent solutions of the Maxwell equation. Figure 3. shows the calculation results of absorption spectra for various sizes of gold and silver nanoparticles which were assumed spherical.

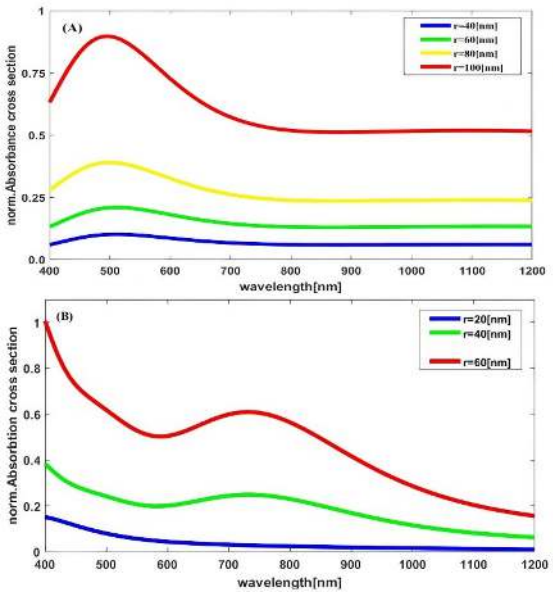

Fig. 3. Normalized absorption cross section is calculated by COMSOL for single (A) gold and (B) silver nanoparticle surrounded by water (same dielectric function assumed) Enhancement of absorption occurred for larger particles.

Moreover, most common simulation models evaluate maximum peak for Au and Ag nanoparticles around 530 and 400 nm Respectively and the shift in absorption spectra for larger nanoparticles had been reported in almost all simulation models furthermore, obtained results in both simulation and experimental section well coincide with other studies results.

CONCLUSION

In this paper, the red shift of plasmon resonance in metallic nanoparticles has been studied to indicate the shift, strongly for larger particles, particularly for gold and silver nanoparticles. Over and above that, both experimental and theoretical studies demonstrated surface plasmon's dependence on the size of MNPs. Fig. 4 provides the absorption peak which rose gradually for larger gold and silver water soluble particles, also these peaks occurred in higher wavelength. Dots express experimental data and lines show the simulation results. The red shift for larger particles is proved by the comparison of experimental and numerical results. In the experimental section, gold and silver nanoparticles are synthesized by chemical reduction method and characterized with UV-Visible spectrometer and absorption spectra obtained in the visible region. Meanwhile, the spectra of absorption of MNPs for various sizes have been achieved numerically by simulating a single particle in dielectric media. Finally, both investigations introduced redshift for larger particles. Accordingly, using larger gold and silver nanoparticles in integrated photonic devices will bring us efficiency enhancement.

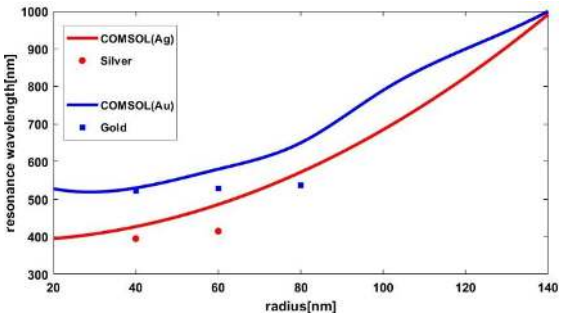

Fig. 4. Comparison of COMSOL (lines) and experimental data(dots) plasmon resonance redshift driven by gold and silver larger nanospheres.

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