doi:10.20944/preprints201811.0364.v1

Localized Surface Plasmons of Gold Nanoparticles

Riyadh D. Mansoor
Engineering College, Al-Muthanna University, Samawa, Iraq.
riyadhdmu@mu.edu.iq

Abstract: **In this paper, the far field and near field optical responses of a gold nanoparticle are studied and simulated numerically. The electromagnetic field was excited by an electric dipole located near one end of the nanorod, which is used to model the emission of a quantum dot. Another excitation method was also simulated in which an incident plane wave is used. The excitation of dark plasmon modes of the gold nanorod is presented. The Poynting equation was solved numerically to study the influence of the gold nanorod on the dipole radiative power. In addition, the extinction cross section of the gold nanoparticle illuminated by the incident plane wave was calculated to estimate the amount of the scattered and absorbed light.**

Keywords— Bio-sensing, Extinction cross-section, Nano-particles, Plasmons, Raman scattering.

I. INTRODUCTION

Surface Plasmons were first observed by Wood in 1902 [1] as unexplained features in the reflection spectra of metallic particles; later, Mie [2] proposed the theory of light scattering by nanoparticles. The theoretical description of the energy loss encountered by electrons travelling in metals, which was given by Pines [3], was considered as the first explanation of the surface plasmons. Pines introduced the term "plasmons" to describe the oscillations of the free electrons in metals that are responsible for the energy loss. After that, Ritchie [4] investigated the electron energy loss in thin metal layers, theoretically, and the term "Surface Plasmons" was introduced. Since then, Surface Plasmons have found enormous applications in different fields such as biosensors, solar cells, and subwavelength imaging [5].

Plasmons in metals are described as coherent oscillations of the electrons in the conduction bands [6]. The plasmon waves either propagate along the surface of the metal (Surface Plasmons) or inside the metal (Bulk Plasmons). Illuminating of metals allows for coupling photon energy to the oscillated electrons and exciting of Surface Plasmons Polaritons SPPs [7]. SPPs can be either propagating waves, which occurs at the interface between metal and dielectric, or a localized SPP, which occur in small size particles (smaller or comparable to the photon wavelengths). The propagating SPPs are confined at the metal-dielectric interface and decays exponentially based on the refractive index of both dielectric and metal. The propagating SPPs can be excited by illuminating the metal-dielectric interface by free space light wave only if the propagation constants of both the SPPs and light wave are coinciding. Different arrangements were proposed to create coupling between light and SP to excite the propagating SPPs [8].

Localized Surface Plasmons LSPs are the most outstanding optical property of small size metallic particles. The electromagnetic field of light will excite the conducting electrons to produce collective oscillations, which are the origin of these optical properties. EM field results in the displacing of conducting electrons from the positive metal lattice. However, the attraction force will act as a restoring force to return the cloud of electrons to its original levels. A resonance behaviour will lead to the excitation of LSP as shown in figure 1 and 2. A comparison between the propagating and localized SPP shows that the electromagnetic field of the propagation SPP is decaying slower than the localized SPP. In addition, the propagating SPPs have a range of frequencies while the localized SPPs are discrete modes. Localized SPPs differ from the propagating SPPs in the excitation process. While the propagating SPPs require a special arrangement for light coupling, localized SPPs excited directly by illuminating nanoparticles with free space light. The similarity between LSPPs and PSPPs is that both are lossy modes. The frequency of LSPPs modes depends on the geometry of the particle and metal type. The shape and size of the particle are of great importance to determine the resonance frequency of the LSPPs modes, the frequency band for spherical NPs is located in the visible band while that of cylindrical NPs is near redshifted. In addition, the quality factor of modes for gold nanorods is higher than that of spherical counterpart due to the lower ohmic loss in the near red band compared to the visible region.

In this paper, LSPPs are studied and modelled numerically to estimate the effect of the excitation of the LSP on the far and near field optical response of spherical and nanorods particles. Spherical nanoparticles are studied first and the absorption cross-section is calculated. Excitation of LSPs in small size spherical particles is of great importance in the fabrication of low-cost solar cells. The effect of particle shape also studied by simulating of nanorods. Excitation of the LSPs in nanorods leads to an enhancement of the electric field results from a dipole in close proximity of nanorods, which can be used in many applications based on the enhanced Raman Scattering.

The rest of this paper is organized as follows: Section 2 is devoted to introducing the theoretical modelling of the localized Surface Plasmons. In section three, the numerical results were introduced and discussed. Finally, the conclusions are in section four.

II. THEORETICAL MODELLING OF LSPPS

A. *Spherical NPs*

Surface Plasmons are excited by the attractive force resulted from the interaction of light and free electrons of metallic nanoparticles. In order to analyse SPP modes, Maxwell's equations need to be solved using the appropriate boundaries. However, the resulted mathematical equations will not describe what the SPPs are. To understand the physical implication of SPPs, consider the particle is illuminated by the electromagnetic field of light as shown in fig. 1. [9]

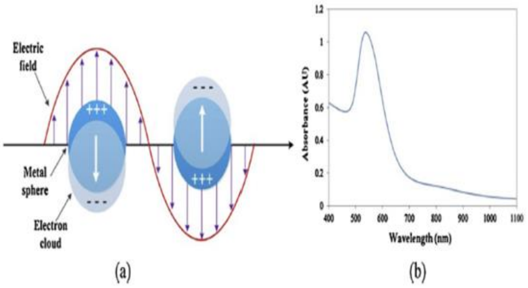


Figure 1. a. representation of electrons oscillations due to the plane wave. b. absorption cross-section [9].

This field will lead to accumulating electrons on one side, leaving the positive charge on the other side in a similar manner of an electric dipole. The electric field inside the particle will be generated due to the dipole effect opposite to that of the light to restore the electrons to its equilibrium position. For the oscillated electrons, the kinetic and electrostatic energies result from the incident light, therefore the excitement of SPP inside the nanoparticle leads to the partial extinguishing of the light due to the conservation of energy. Calculating the optical absorption spectrum provides a good method to notice the excitation of the SPPs. Absorption cross-section of a particle is a measure of the absorption efficiency; if a given nanoparticle absorbs half of the photons hitting its surface, then the absorbing cross section is the half of its geometrical sector. In addition to the absorbing, light also can be scattered in different directions and the scattering cross-section can be calculated. The sum of scattering and absorption cross sections is called the extinction cross-section, which is of great interest for nanoparticles SPPs calculations.

To obtain the scattering cross-section of spherical metallic NPs, the ratio of the total radiated power of the dipole to the intensity of the exciting wave was calculated in [9] as below.

The scattering cross section is

$$\sigma_{scatter} = \frac{8\pi}{3} k^4 a^6 \left| \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \right|^2 \qquad 1$$

Where k is the magnitude of the wave vector of the incident light, ε_m and ε_d are the permittivity of the metal and surrounding respectively, and a is the radius of the spherical NP.

Using Poynting's theorem [10], the absorption cross section is:

$$\sigma_{abs} = 4\pi k a^3 Im\left(\frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d}\right) \qquad 2$$

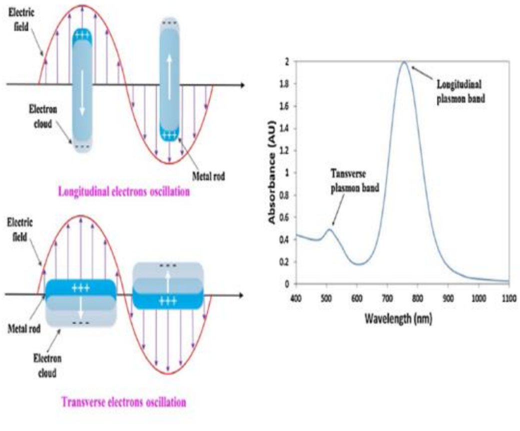
Finally, the extinction cross section is defined as the sum of the absorption and scattering cross sections, as below

$$\sigma_{ext} = \sigma_{abs} + \sigma_{sca} \qquad 3$$

Exploiting SPPs in metallic nanoparticles based solar cells can increase the efficiency of solar panels, the large scattering cross section of NPs allows for high scattering of light at the surface of the panel. As results, the absorption layer will decrease, leading to a big reduction in the fabrication cost [11].

B. *Nanorods*

The surface plasmon is strongly affected by the shape of nanoparticle since the restoring force of the accumulated electrons depends mainly on the particle geometry as shown in fig.2. In this figure, the electrons accumulated along the rod axis generate different plasmons (longitudinal plasmon) from that of perpendicular direction (transversal plasmons) [12].



(a) (b)

Figure 2 a. representation of electrons oscillations due to the plane wave. b. absorption cross-section [12].

For transversal plasmons, the resonant frequency is slightly higher than that for spherical NPs and it is insensitive to the change of aspect ratio, while that of the longitudinal plasmons is lower when the aspect ratio of the nanorod increases. The longitudinal plasmons bands are highly affected by the dielectric properties of the metallic NP as well as the surrounding medium, and the excitation of longitudinal plasmon results in a high absorption of light. The extinction cross-section can be calculated based on the Gan's theory [11] as below:

$$\sigma_{ext} =$$

$$\frac{2\pi V N {\varepsilon_m}^{3/2}}{3\lambda} \sum_j \frac{(\frac{1}{{P_j}^2})\varepsilon_i}{\left(\varepsilon_r + \left(\frac{1-P_j}{P_j}\right)\varepsilon_m\right)^2 + {\varepsilon_i}^2} \qquad 5$$

Where P_j is the depolarization factor and V is the particle volume.

The depolarization factor for nanorods is described as below:

$$P_{length} = \frac{1-e^2}{e^2}\left[\frac{1}{2e}\ln(\frac{1+e}{1-e}\right) - 1] \qquad 6$$

$$P_{width} = \frac{1-P_{length}}{2} \qquad 7$$

Where e is given by

$$e^2 = 1 - (aspect\ ratio)^{-2} \qquad 8$$

Where the aspect ratio is the ratio $\frac{length}{width}$ of the nanorod.

Equation 8 shows that any change in the aspect ratio will lead to a high change in the plasmon band as shown in figure 2.

An important application of the longitudinal plasoms is the enhancement of emitters scattering near the nanorods. It is described as the surface-enhanced Raman scattering (SERS) which called the lightning rod effect. The nanoantenna is another application for optical nanorods where the fluorescence of an emitter placed close to the nanorod can be enhanced. Finally, due to the high sensitivity of the nanorods optical response to the refractive index of the surrounding medium, nanorods are used in biosensing applications.

Section 3 will present a numerical modelling of both a spherical and nanorod made of gold. The scattering and absorption cross-sections for the spherical NP will be calculated numerically and the SERS in the gold nanorod is modelled.

III. CST SIMULATION OF NANOPARTICLES.

A 3D simulation software is used to numerically calculate the optical properties of a nanoparticle exposed to an electromagnetic field. CST is a 3D EM solver that solves Maxwell's equation in both the time domain with Finite integration method FIT and frequency domain with Finite element method FEM. A spherical nanoparticle and cylindrical nanorod were simulated using frequency domain solver as below.

A. Spherical NPs Simulation.

A spherical gold nanoparticle is modelled first using CST with a plane wave source to model the Electromagnetic field of light. The radius of nanoparticle was taken as 20 nm to calculate the absorption cross-section numerically. For Plasmonic applications, two quantities should be calculated. First, the electric field distribution on the outer surface of the spherical NP and the other one is the absorption cross-section. Figure 3 shows the electric field distribution due to the excitation of LSP, while Figure 4 shows the absorption cross-section of the gold nanoparticle. As shown in figure 3, the excitation of the LSP results in an increase of field strength at the NP surface. This Plasmon is called bright plasmon due to the scattering of light. In the other hand, figure 4 shows clearly the increase of light absorption due to the light coupling with the surface Plasmon. Comparison of figures 3 and 4 with Figure 1 shows a good agreement with the published results and allows for using the CST in the modelling of gold nanorods as presented in the next section.

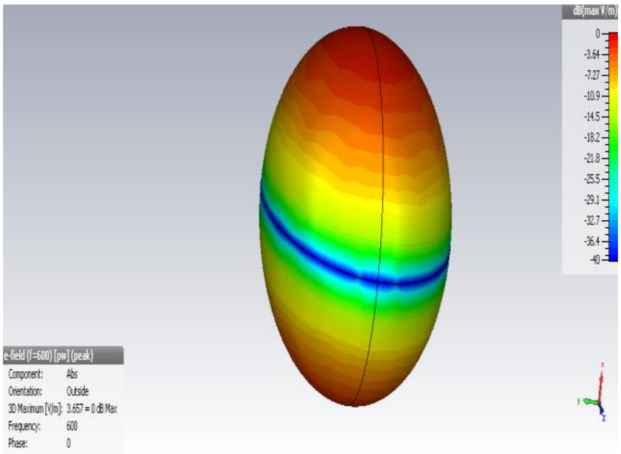


Figure 3. Electric field distribution on the surface of the spherical nanoparticle.

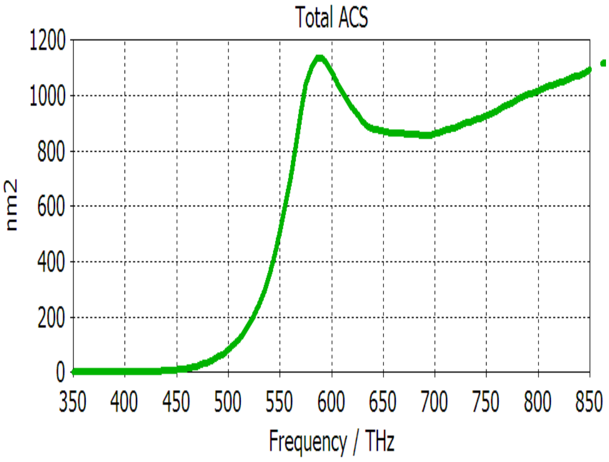


Figure 4. Absorption cross-section of the spherical article.

B. Nanorods Simulation.

In the section above, localized surface plasmon was shown to be excited in a spherical NP by a plane wave. Illuminating nanorod by a plane wave will result in the excitation of the bright plasmons, which is recognized by the light scattering. Other plasmons which will not be coupled to the radiating field are called dark plasmon is simulated in this section. To excite dark plasmons, an emitting source is placed near the nanorod. Gold nanorod is modelled as a circular cylinder, then the upper and lower edges were selected to perform a blend function in the CST to obtain the two hemispherical shape caps. The CST model consists of a gold nanorod of 100 nm long and 5 nm radius which is excited by a small dipole of 3nm length located at a distance of 0.25 nm from the apex of the nanorod. A frequency range of 200-650 THz was used for simulation with a normal background and open boundaries.

The first estimation of the nanorod effect on the electric field distribution is shown in fig.5 where the field pattern was taken at a distance 100.25 nm from the dipole without the presence of nanorod while in fig. 6 shows the enhancement of the electric field at the same point with the nanorod. It can be seen that the excitation of the LSP improves the level of the electric field at the same probe point.

In the presence of the gold NP, two types of powers of the dipole can be calculated, one is the radiative power that is modelled theoretically by the Poynting vector [12] as in equation 9. The other type of power is the non-radiative one, which is also mathematically represented by the Poynting vector as in equation 10.

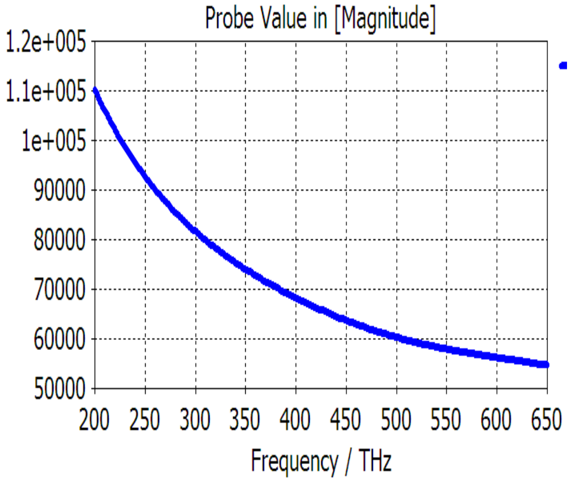


Figure 5. Electric field pattern without nanorod.

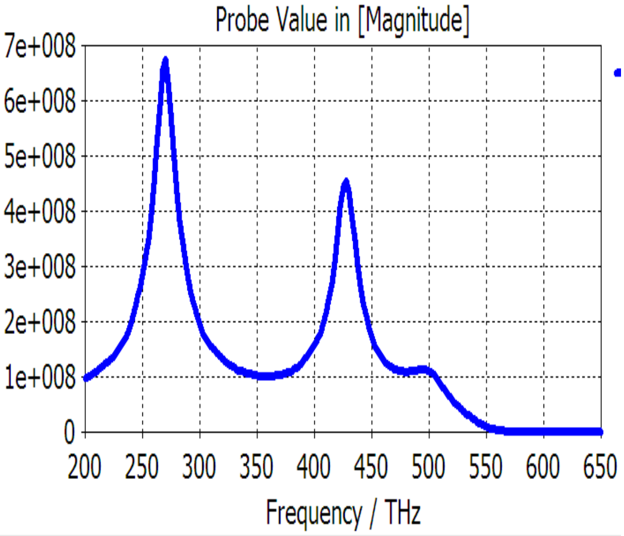


Figure 6. The electric field with the presence of nanorod.

$$P_r = \frac{1}{2} Re \iint (\vec{E} \times \vec{H}).ds \qquad 9$$

$$P_{nr} = -\frac{1}{2} Re \iint (\vec{E} \times \vec{H}).ds \qquad 10$$

S here is the closed surface that encloses both the nanorod and the dipole. To solve equation 9 and 10 numerically using CST, a closed surface is modelled and the radiative and non-radiative powers were calculated. The radiative power of the dipole was simulated numerically by creating a surface containing both the NP and dipole, while the non-radiative power due to the ohmic loss in the gold NP is calculated on the surface of NP only.

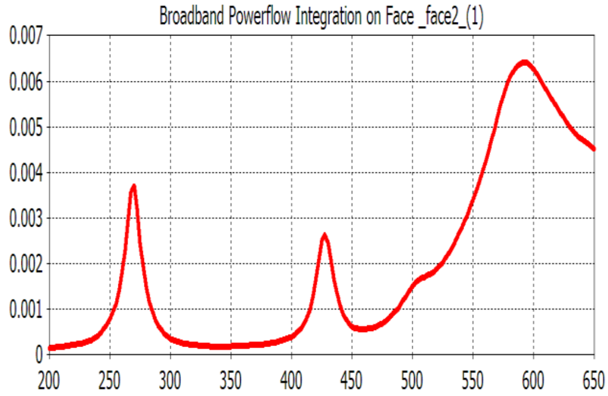


Figure 6. Power leaving the port.

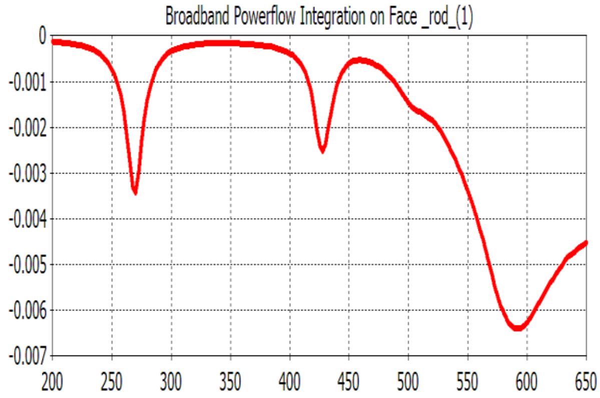


Figure 7. The non-radiative power, which represents the power absorbed by the rod.

Figure 7 shows the numerical solution of equation 9 where the power leaving the port is calculated on the face surface that contains the emitter and the nanorod. While figure 8 shows the non-radiative power due to the nanorod absorption. This figure shows a negative power since the power is calculated as a power flow out to the outer surface. Finally, the radiative power is shown in figure 9 where the far field displays one plasmon that decays due to radiation.

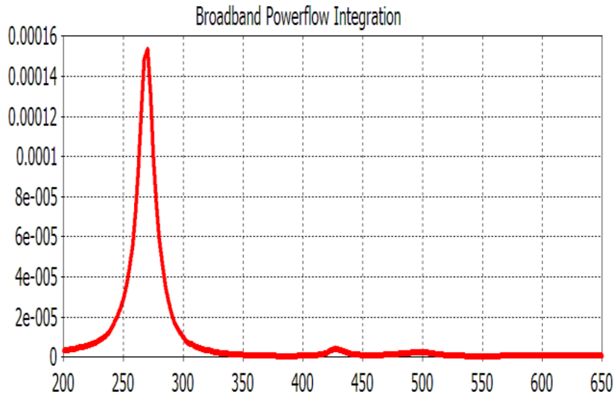


Figure 8. Radiative power from the power flow.

IV. CONCLUSION

Localized surface plasmon was studied and simulated numerically. A spherical and nanorod made of gold were presented in this paper. Surface plasmons are of great interest in many fields of technology ranging from solar cell to optical biosensing. In this work, theoretical and numerical modelling of localized surface plasmon in gold nanoparticles were presented. Absorption cross-section of gold nanoparticles illuminated by a plane wave is calculated. Exciting of the LSP is shown by observing the electric field on the surface of the nanoparticle. Nanorods were also modelled and simulated to estimate the enhancement of near and far field induced by a small dipole close to the nanorod. The enhancement of the electric field was shown due to the excitation of the LSPs.

References

[1] R. W. Wood, “On a Remarkable Case of Uneven Distribution of Light in a Diffraction Spectrum,” Proceedings of the Physical Society of London, vol. 18, p. 269, 1902.

[2] E. Petryayeva, U.J. Krull, Localized surface plasmon resonance: nanostructures,bioassays and biosensing – a review, Analytica Chimica Acta 706 (2011) 8–24.

[3] Barnes, William L., Alain Dereux, and Thomas W. Ebbesen. "Surface plasmon subwavelength optics." nature 424.6950 (2003): 824.

[4] R. H. Ritchie, “Plasma Losses by Fast Electrons in Thin Films,” Physical Review, vol. 106, pp. 874–881, 1957.

[5] S. Kumar, N. J. Wittenberg, and S.-H. Oh, “Nanopore-induced spontaneous concentrationfor optofluidic sensing and particle assembly,” Analytical chemistry, vol. 85, no. 2, pp. 971–977, 2012.

[6] Pattnaik, Priyabrata. "Surface plasmon resonance." Applied biochemistry and biotechnology 126.2 (2005): 79-92.

[7] Mansoor, Riyadh, and Amin Habbeb AL-Khursan. "Numerical modelling of surface plasmonic polaritons." Results in Physics 9 (2018): 1297-1300.

[8] Zayats, Anatoly V., and Igor I. Smolyaninov. "Near-field photonics: surface plasmon polaritons and localized surface plasmons." Journal of Optics A: Pure and Applied Optics 5.4 (2003): S16.

[9] K.A. Willets, R.P. Van Duyne, Localized surface plasmon resonance spectroscopy and sensing, Annual Review of Physical Chemistry, Annual Reviews,Palo Alto 58 (2007) 267–297

[10] Tokman, M. D., E. Westerhof, and M. A. Gavrilova. "Wave power flux and ray-tracing in regions of resonant absorption." Plasma physics and controlled fusion 42.2 (2000): 91.

[11] Catchpole, KR and, and Albert Polman. "Plasmonic solar cells." Optics express 16.26 (2008): 21793-21800.

[12] Billaud, P., et al. "Optical extinction spectroscopy of single silver nanoparticles." The European Physical Journal D 43.1-3 (2007): 271-274.

[13] Cao, J., Sun, T. and Grattan, K. T. V. (2014). Gold nanorod-based localized surface plasmon resonance biosensors: A review. Sensors and Actuators, B: Chemical, 195(May), pp. 332-351. doi:10.1016/j.snb.2014.01.056.

[14] M. Hu, J. Chen, Z.-Y. Li, L. Au, G.V. Hartland, X. Li, M. Marquez, Y. Xia, Gold nanostructures: engineering their plasmonic properties for biomedical applications, Chemical Society Reviews 35 (2006) 1084–1094.

[15] Ungureanu, C., Rayavarapu, R. G., Manohar, S., & Leeuwen, van, T. G. (2009). Discrete dipole approximation simulations of gold nanorod optical properties : choice of input parameters and comparison with experiment. Journal of Applied Physics, 105(10), 102032-1/7. [102032]. DOI: 10.1063/1.3116139.