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Plasmonic Resonances and Their Application to Thin-Film Solar Cell

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Abstract

This chapter furnishes the plasmonic properties of metal nanostructure and its application to thin-film solar cell. Plasmonics is an emerging branch of nanooptics where light metal interaction in subwavelength domain is studied. Metal supports surface plasmon resonance that has tunable signature, which depends on the morphology as well as surrounding media. These plasmonic resonances can be tuned in a broader range of solar spectra by changing several parameters such as size, shape and medium. Moreover, metals show scattering properties that could be utilized to enhance optical path length of photon inside the thin film of solar device. The chapter mainly focusses on the study of plasmonic resonance of smaller- and larger-sized metal nanoparticle using semi-analytical as well as numerical approach. For the estimation of optical properties like extinction spectrum and field profile of larger-sized nanoparticle, finite-difference time-domain (FDTD) method is used. The field distribution in both silver and gold nanoparticle cases has been plotted in 'on' resonance condition, which has a broader range of applications.

Keywords: plasmonics, metal nanoparticle, surface plasmon resonance, extinction cross section, thin film

1. Introduction

Plasmonics is an emerging branch wherein the interaction of electromagnetic waves to the conduction electron of metal nanoparticles is studied. Plasmonic properties of metal nanoparticles have generated a great interest among the material researchers in the recent years and have attracted them to understand the physics behind it for applying the same

in various fields. The optical properties of metal nanoparticles are highly dependent on its morphology and the surrounding medium [1–4]. These optical properties include scattering, absorption and extinction cross section which are obtained by solving the Maxwell's equation after the interaction of light with the nanogeometries. The optical cross sections are generally greater than the geometrical cross section. When the light interacts with the metals, two fundamental excitations are observed. These excitations are either propagating known as surface plasmon polaritons (SPP) or non-propagating known as surface plasmon resonance (SPR). These fundamental excitations have a wide range of applications. The candidates used as plasmonic elements are metals and few semiconductors, and they have their own optical features in different regimes of electromagnetic spectrum. These metals exhibit surface plasmon resonance (SPR) properties on interaction with the incident field. The SPR depends on several parameters such as size and shape of metal and choice of the surrounding media. The influence of surrounding media on the SPR peak positions has a great interest in material research society. One can tune these SPR peak positions by choosing different surrounding media. The tunable behaviors of SPR with size shape and surrounding environments would cover a wide range of applications such as biosensor, Raman spectroscopic, waveguide and thin-film photovoltaic device [5–7].

The occurrence of the SPR resonances is due to the interaction of incident light frequency and its match with the frequency of collective oscillation of electrons inside the metal. Under such matching condition, a giant electric field is observed near the metal nanosurface, which could be used for various applications. The physics of SPR could be utilized in different fields of science and technology wherein the light metal interaction is taken into account. It could be utilized in biosensor field, thin-film plasmonic photovoltaic devices, surface-enhanced Raman scattering field and communication field also [6, 7].

The work furnishes the plasmonic properties isolated in metal nanosphere and its interaction to the silica environment. This work explores the optical properties of isolated spherical-shaped medium and small-sized metal nanoparticle. The analysis of small-sized nanoparticle has been done using dipolar model, but the restriction with this model is that it can be applied for larger-sized nanoparticle. Therefore, we have to use numerical technique in full-wave analysis that needs to be taken into account. The purpose of selecting the silica environment is due to its frequent use in the photovoltaic devices. Silica is used as a spacer layer in thin-film device fabrication, and it is also used as a core or coating material whose thickness plays an important role to tune the plasmonic resonance. Therefore, the aim of this work is to present systematic review of medium- and small-sized metal nanoparticle under the influence of silica environment.

2. Optical properties of metal nanoparticles

The optical properties of metal nanosphere embedded in semiconductor environment have been discussed under the quasi-static approximation, where we have assumed that the size of metal nanosphere is much smaller than the wavelength of incident light. In this approximation, we have taken metal nanosphere which is embedded in a semiconductor medium having

constant electric field. The Laplace equation $\nabla^2 \Phi = 0$ with appropriate boundary condition was solved for finding out the potential, electric field, scattering and absorption and extinction cross section [8]. The schematics of modeled structure is shown in **Figure 1**, wherein the incident field interacts with the nanosphere of radius a and dielectric $\epsilon(\omega)$ constant embedded in surrounding environment having dielectric constant ϵ_m .

The potential inside and outside the sphere that are obtained after solving the Laplace equation under appropriate boundary conditions are expressed as

$$\Phi_{in} = -\frac{3\epsilon_m}{\epsilon + 2\epsilon_m} E_0 r \cos\theta \text{ and} \quad (1)$$

$$\Phi_{out} = -E_0 r \cos\theta + \frac{r \cos\theta}{r^3} a^3 E_0 \left(\frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right) \quad (2)$$

After solving the potential profile, one can easily obtain the electric field expression as

$$E = -\nabla\Phi \quad (3)$$

The polarization of metal sphere under the influence of constant electric field is expressed as

$$P = 4\pi\epsilon_0 \epsilon_m a^3 E_0 \left(\frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right) \quad (4)$$

and polarizability of nanosphere is

$$\alpha = 4\pi a^3 \left(\frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \right) \quad (5)$$

where ϵ, ϵ_m are the dielectric constant of sphere and medium, a is the radius of sphere and α , is the dipolar polarizability.

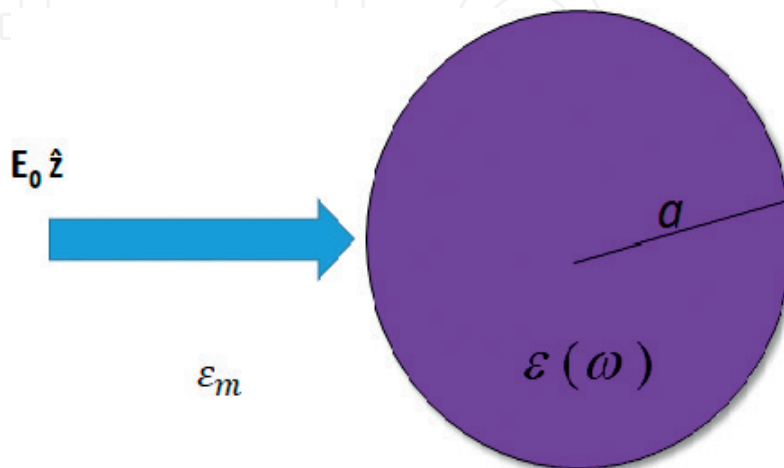


Figure 1. Optical properties of metal nanosphere placed in a uniform static electric field E_0 .

The optical properties are expressed in terms of optical cross sections such as scattering and absorption, and it can be calculated by deriving the Poynting vector from the reference [8]:

$$\langle C_{scat} \rangle = \frac{k^4}{6\pi} |\alpha|^2 = \frac{8\pi}{3} k^4 a^6 \left| \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right|^2 \quad (6)$$

$$\langle C_{abs} \rangle = k \operatorname{Im}\{\alpha\} = 4\pi k a^3 \operatorname{Im} \left[\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right] \quad (7)$$

The sum of these two cross sections will give rise to the extinction cross section:

$$C_{ext} = C_{scat} + C_{abs} \quad (8)$$

If the cross sections are normalized by their geometrical cross section, then it is called by a new name known as Q-extinction. For spherical geometry, geometrical cross section is πa^2 ; therefore, Q-extinction for sphere is

$$Q_{extn} = \frac{C_{ext}}{\pi a^2} \quad (9)$$

There are several parameters involved in the study of optical signature of plasmonic geometry. Out of these parameters, optical constant of metal is one of most important parameters. Therefore, we have given a special attention to the same. This optical constant has a dual character: one at the bulk level and the other at the nanolevel. The nanolevel character comes via the size of the geometry, which has been derived from Drude-Lorentz model, which can be expressed as [8, 9]

$$\varepsilon(\omega) = \varepsilon_{bulk}(\omega) + \frac{\omega_p^2}{\omega^2 + j\gamma_{bulk}\omega} - \frac{\omega_p^2}{\omega^2 - j\gamma\omega} \quad (10)$$

$$\gamma = \gamma_{bulk} + A \frac{v_f}{a}$$

where ω_p is the bulk plasmon frequency, ω is the frequency of incident light photon and $\tau_{bulk} = 1/\gamma_{bulk}$ is the damping constant of bulk silver metal. Where γ is the effective relaxation time, $v_f = 1.39 \times 10^6$ m/s is the Fermi velocity of electron in silver, A is geometrical parameter and its value lies between 2 to 1 (in our case we have chosen $A = 1$) [10] and a is the radius nanoparticle. Using the optical constant of metal at the nanolevel, extinction spectrum is studied.

3. Extinction cross section of silver and gold nanosphere: semi-analytical approach

The optical property of silver and gold nanosphere has been discussed in terms of extinction efficiency which is the ratio of extinction cross section to geometrical cross section. Wavelength-dependent extinction efficiency of silver and gold nanosphere for three

different radii ranging from 5 to 7 nm has been plotted as shown in **Figure 2**. It can be observed from the spectrum that the choice of two different metals would cover two different parts of electromagnetic spectrum. For silver, SPR resonance was observed at wavelength 410 nm, while for gold, it was around 560 nm. The magnitude of extinction is a function of nanosphere radii, while its SPR peak positions are almost independent of the chosen radii. The nanoplasmonic coupling to the silica ($N = 1.54$) has been studied in terms of extinction efficiency and SPR resonances. The two different metals exhibit their SPR resonances in two different regimes of solar spectrum due to different optical constant and Frohlich conditions.

The simulated extinction spectra as shown in the above figures of silver and gold nanosphere clearly give the idea of extinction magnitude and SPR wavelength which can be used to compute the electric field distribution near the surface of metal nanosphere. **Figure 3a** shows the electric field profile of silver nanosphere embedded in silica environment at SPR wavelength 410 nm. The legend in the figure shows the normalized field (E/E_0) magnitude in y-z plane. The computation of electric field has been done by using COMSOL Multiphysics software with triangular fine grid. The red region shows the high-intensity zone which can be utilized for various applications [11–15].

Further, we have also done the analysis to visualize the electric field distribution of gold nanosphere of radius 50 nm embedded in silica medium as shown in **Figure 3b**. The near field has been computed at SPR wavelength 560 nm. From the field distribution, it was observed that the magnitude of field is different for silver and gold due to different SPR wavelengths. These different magnitudes of fields can be used to increase the electron hole or exciton generation rate inside the thin film of solar device.

The above semi-analytical model has certain restrictions that it is valid only for the smaller-sized metal nanoparticle. Therefore, for the analysis of optical properties of larger-sized metal nanoparticle, we required some numerical approach like discrete dipole approximation (DDA), finite-difference time-domain (FDTD), finite element method (FEM) and surface integral equation (SIE). In this chapter, we have used the FDTD technique to simulate the optical properties

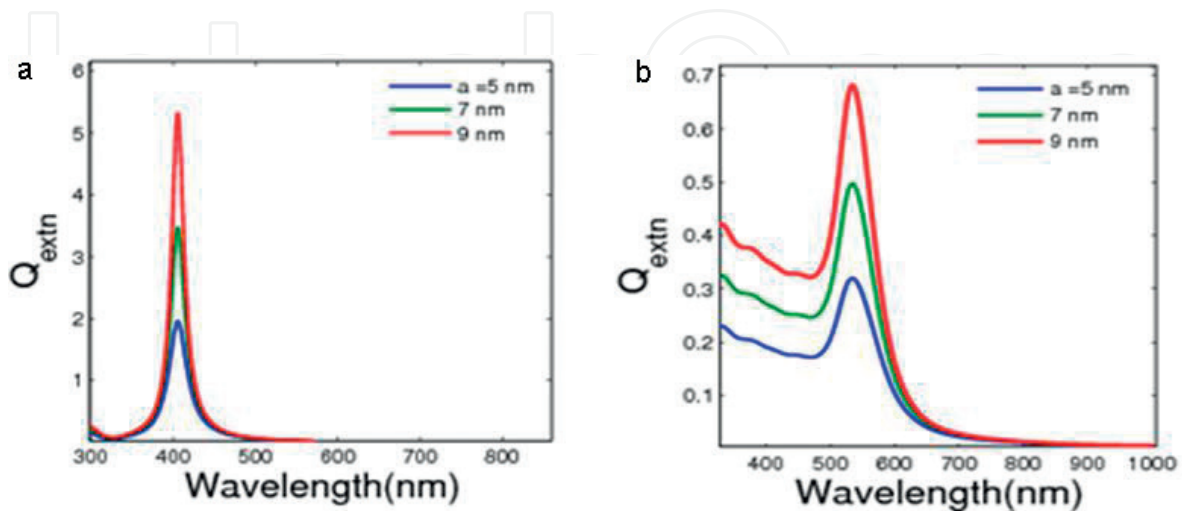


Figure 2. Wavelength-dependent extinction spectra of (a) silver and (b) gold metal nanosphere embedded in medium having refractive index $N = 1.54$.

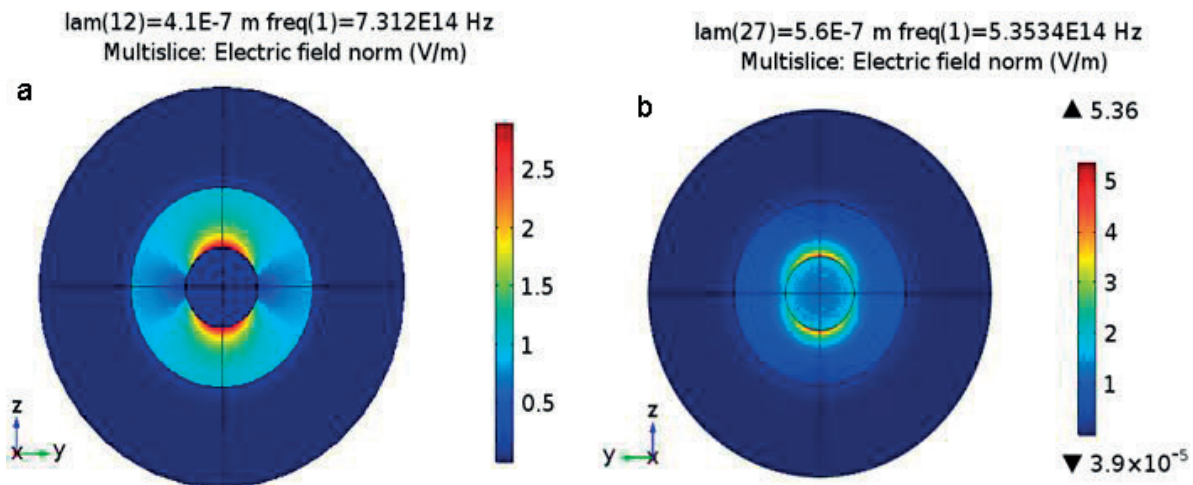


Figure 3. Electric field distribution of (a) silver and (b) gold nanosphere of radius 7 nm surrounded by silica matrix having $N = 1.54$.

of spherical-shaped metal nanoparticle [16]. We have used the Lumerical-based finite-difference time-domain technique to study the optical properties of noble metals. The metals are silver and gold whose optical constants are taken from the literature [8, 9]. These metals are surrounded by silica environment having constant dielectric constant. The objective of the work is to analyze the distribution of electric field near the metal surface in a resonance condition.

4. Scattering cross section of noble metal nanosphere: FDTD technique

We have plotted the scattering cross section of silver nanosphere of radius 50 nm surrounded by silica matrix as shown in **Figure 4**. In the previous study, we have chosen the smaller-sized nanoparticle whose optical properties have been studied in quasi-static domain. In quasi-static domain, we have chosen the static behavior of charge instead of oscillating behavior because the particle size is much smaller than the wavelength of light. When the particle size is smaller than the wavelength of light, in such a case, the particle feels the oscillating field because the electric field is no more static throughout the particle volume. Therefore, we have used the FDTD technique to study the plasmonic signature of larger-sized silver metal nanosphere. This shows the surface plasmon resonance at wavelength 564 nm, as shown in **Figure 4a**. We have also plotted the near-field distribution of 50 nm silver nanosphere at its SPR wavelength as shown in **Figure 4b**. The computed electric field gives the normalized field intensity magnitude 70 unit.

Further, we have also studied the optical properties of larger-sized gold nanoparticle embedded in silica matrix as shown in **Figure 5**. The scattering cross section of 50 nm gold nanosphere has been plotted using FDTD technique. Here, we have solved Maxwell's equation to obtain the cross-sectional profile, which has the dimension of area. The scattering is the reradiation of electromagnetic field which is absorbed by the surrounding media. The higher the scattering from the nanoparticle, the higher the photon absorption into the active medium. For 50 nm gold nanosphere, SPR wavelength was observed at 625 nm (**Figure 5a**), and we believe that

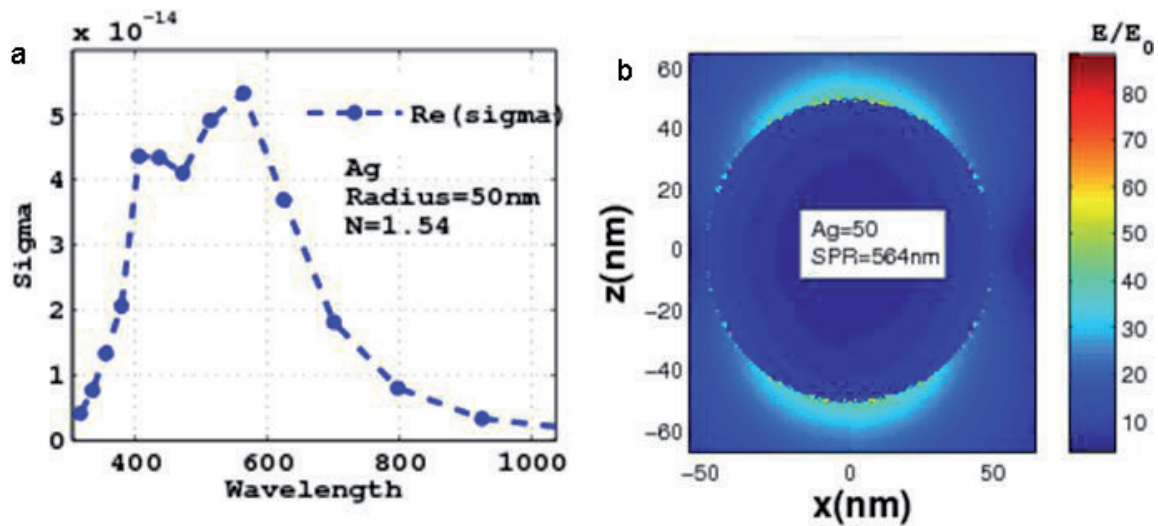


Figure 4. (a) Wavelength-dependent extinction spectra and (b) electric field distribution silver metal nanoparticle of radius 50 nm embedded in silica matrix.

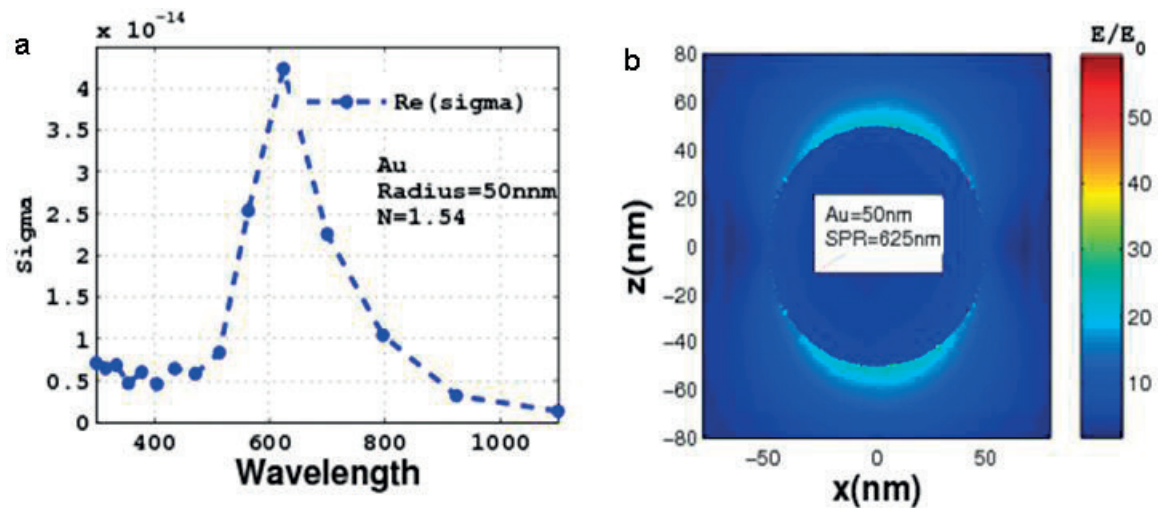


Figure 5. (a) Wavelength-dependent extinction spectra. (b) Electric field distribution of gold metal nanoparticle of radius 50 nm embedded in silica matrix.

under the SPR, maximum sun light can be harvested to produce electricity. The electric field distribution near the metal surface has also been done at SPR wavelength 625 nm as shown in **Figure 5b**. The magnitude of normalized field is indicated in scale bar. In nutshell, optical properties of two different types of metal such as silver and gold are studied in silica environment.

5. Conclusions

Here, we have analyzed the optical properties of noble metal nanoparticle in different regime electromagnetic spectra. The special emphasis has been given on the semi-analytical as well as numerical model. Two different types of numerical techniques such as FDTD and COMSOL Multiphysics are used to study the plasmonic resonances which cover a broader range of

applications. The computed electric field magnitude at SPR wavelengths corresponding to smaller- and larger-sized metal nanoparticle would clearly suggest experimentalist to fabricate various sizes of nanoparticle whose SPRs are preknown.

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Conflict of interest

The authors do not have any conflict of interest.

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