Chapter 2

# A Perspective on Plasmonics within and beyond the Electrostatic Approximation

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**Abstract**

Plasmonic is an emerging branch of nanophotonics wherein the electromagnetic properties of nanoparticles are studied for variety of applications. The optics of nanoparticles is studied in terms of surface plasmon resonances and optical cross section. Initially the first principle approach has been used to study the plasmonic fundamentals known as electrostatic approach. Under this approach, various parameters are taken into account to observe the electromagnetic properties of plasmonic nanogeometries. This electrostatic model is only used to analyze the optical signature of smaller size plasmonic geometries. Therefore, for the estimation of optical properties of larger size nanoparticle numerical model (Discrete Dipole Approximation) has been used. The observed surface plasmon resonances could be useful in sensing field, SERS signal detection and thin film solar cell application.

**Keywords:** plasmonics, nanoparticle, surface plasmon resonance, optical cross section

## 1. Introduction

Plasmonics is the emerging branch of nanophotonics which deals the coupling of light to the collective oscillation of electrons inside the metal nanoparticles. The coupling of light to the metal nanoparticles produces resonances under specific condition known as surface plasmon resonance (SPR) that has tremendous applications [1–5]. The resonant interaction between them will localize the electromagnetic field near the meal surface and drastically enhances the optical scattering phenomenon. When the light interacts with the metallic nanostructures two fundamental excitations are observed. These two fundamental excitations are surface plasmon polaritons (SPP) and localized surface plasmon resonance (LSPR). The surface plasmon polaritons is propagating, dispersive electromagnetic waves coupled to the electron plasma of a metal at a dielectric interface. The other excitation is localized surface plasmons which are non-propagating excitations of the conduction electrons of metallic nanostructures coupled to the electromagnetic field. Such modes arise due to the scattering of a sub-wavelength conductive nanoparticle in an oscillating electromagnetic field. An effective restoring force on the driven electrons is induced by the curved surface of the particle leading to resonance and field amplification both inside and in the near-field zone outside the particle. This resonance is called the localized surface plasmon or short localized plasmon resonance [6–11]. Plasmon resonances can be excited by direct light illumination which do not require any phase-matching. In addition to solid particles, other nanostructures that support localized plasmons are dielectric inclusions in metal bodies or surfaces, and nanoshells [6, 12–15]. For gold and silver nanoparticles, the resonance lies in the visible region of the electromagnetic spectrum leading to bright colors exhibited by particles both in transmitted and reflected light. This is direct consequence of resonantly enhanced absorption and scattering of light from these particles. From the viewpoint of electromagnetic and optics, a major consequence of the resonantly enhanced polarization is associated enhancement in the efficiency with which a metal nanoparticle scatters and absorbs light [6, 8, 16–19].

An important properties exhibit by plasmonic elements like silver, gold, copper and aluminum is surface plasmons which concentrate the optical energy in nanoscale [20–24]. The existence plasmonic properties (like surface plasmon mode) in materials is entirely depends on their dielectric constants. Surface plasmon mode is an important property by which one can concentrate the optical energy in nanoscale domain [15, 25–28]. As the dielectric constants are the complex quantities in which real part is the reflection and imaginary part represent the absorption or loss. Therefore, on the basis of dielectric constant value one can define the definition good and bad plasmonic materials and also decides the weather the material having plasmonic properties or not. Those materials are the plasmonic materials for which dielectric constant $\varepsilon_m$ has a negative real part, Re $\varepsilon_m < 0$ and imaginary part of dielectric constant is much less than the real part of dielectric constant (Im $\varepsilon_m \ll$ Re $\varepsilon_m$). Under these two conditions surface plasmon resonances are most effective due to minimum losses in metals. Silver and gold shows plasmon properties in visible range because it satisfies above two properties in visible range [11, 29–31]. The real and imaginary part of dielectric constant of gold metal shows their variation with wavelength in **Figure 1a** and **b**.

The work furnishes the study of plasmonic properties of metal nanostructures within and beyond the electrostatic approximation. In the electrostatic approximation we have analyze the interaction of electromagnetic field to metal nanoparticle whose size is much smaller than the wavelength of incident light. In such situation particle experienced only constant or static field throughout the particle volume. Since this model is restricted to smaller size nanoparticles in which only dipolar analysis is taken into account. The dipolar analysis means, we have truncated the potential series upto two terms and apply Laplace equation to obtain the field, polarizability expression and resonance condition. As the size of nanoparticle increases it starts to experience the oscillation behavior of field and electrostatic approximation completely fails. Therefore we need to require techniques which describe the full wave analysis.

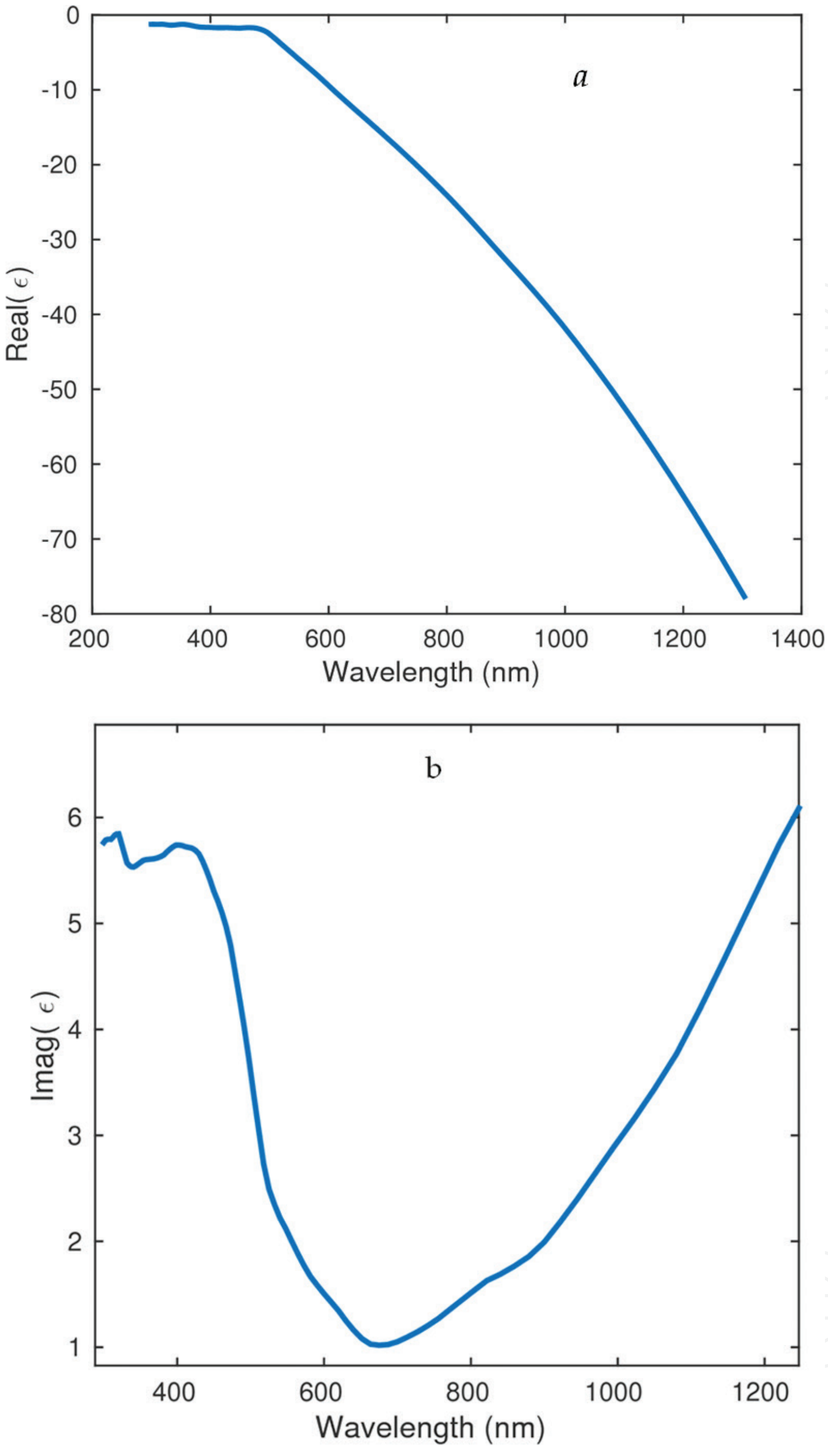


**Figure 1.** Wavelength dependent (a) real and (b) part of dielectric constant of gold.

Discrete Dipole Approximation (DDA) technique is one of them which is based on the dipole discretization concept and frequently used to simulate the plasmonic properties of arbitrary size, shape nanostructure. We have used this simulation technique to study the plasmonic properties of larger size metal nanostructure.

## 2. Theoretical model: scattering by small size metal nanosphere

Theoretical model discuss the plasmonic properties of metal nanoparticle within electrostatic approximation wherein particle size is smaller than the wavelength of light. Under such assumption Laplace equation has been solved with suitable boundary condition to find out the optical parameters [13, 32]. The Laplace equation is expressed as

$$\nabla^2 V = 0 \tag{1}$$

and its solution in spherical polar coordinate is

$$\mathrm{V(r)} = \sum_{l,\mathrm{m}} \mathrm{A}_{l,\mathrm{m}}\, r^{-l-1}\, Y_l^m(\theta, \varphi) + \sum_{l,\mathrm{m}} B_{l,\mathrm{m}}\, r^{l}\, Y_l^m(\theta, \varphi) \tag{2}$$

Truncating the potential series only for dipolar term which correspond to $l = 1$ one can find the value of potential inside and outside the spherical surface as

$$V_{in} = -\frac{3\,\varepsilon_m}{\varepsilon + 2\,\varepsilon_m} E_0\, r \cos\theta, \tag{2a}$$

$$V_{out} = -E_o\, r \cos\theta + \frac{r\cos\theta}{r^3} a^3\, E_0\left(\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\,\varepsilon_m}\right) \tag{2b}$$

Once we have potential profile, the calculation of field and polarizability can be easily obtained by $E = -\nabla V$ expression.

The applied field polarizes the metal nanostructure and its polarization is in the same direction of applied electric field. If the size of nanoparticle is small enough then polarization is in the direction of applied field while for larger size nanoparticle the oscillation of electron is no longer symmetric and the polarization mechanism is split into component form such as transverse and longitudinal. Here the study reveals the optical properties of smaller size nanoparticle therefore, polarization of particle is in the same direction of applied field. The polarization is simply the dipole moment per unit volume which is expressed as

$$p = \varepsilon_m\, \alpha E_0 \tag{2c}$$

where $E_0$ is the applied electric field and $\alpha$ is the polarizability of nanosphere expressed as

$$\alpha = 4\pi a^3\left(\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\,\varepsilon_m}\right) \tag{3}$$

The symbol $a$ is the radius of metal nanosphere, $\varepsilon, \varepsilon_m$ are the dielectric constant of metal sphere and surrounding environment. The expression of polarizability is an important parameter in the discussion of resonance physics. The concept of resonance brought into the picture from the denominator part of polarizability expression. The polarizability gets resonantly enhanced when $|\varepsilon + 2\,\varepsilon_m| = 0$ which is known as Fröhlich condition.

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As we know when the incident electromagnetic field interacts with metallic nanostructure, some fraction of light gets absorbed and some of them gets scattered. The magnitude of the these absorbed and scattered light can be expressed in terms of scattering and absorption cross section as

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

$$Q_{scat} = \frac{\langle C_{scat} \rangle}{\pi a^2} \tag{5}$$

where symbol $k$ is the incident light wave vector, $\varepsilon, \varepsilon_m$ are the dielectric constant of metal and surrounding medium.

A spherical shape metal nanoparticle is taken into account to observe the optical properties like scattering cross section and surface plasmon resonances. **Figure 2** represent the wavelength dependent normalized cross section of three different radii of spherical shape silver metal nanoparticle. We observed that as the size of nanoparticle increases corresponding magnitude of scattering cross section increases. But the position of SPR peak position is same for all radii which is at 364 nm.

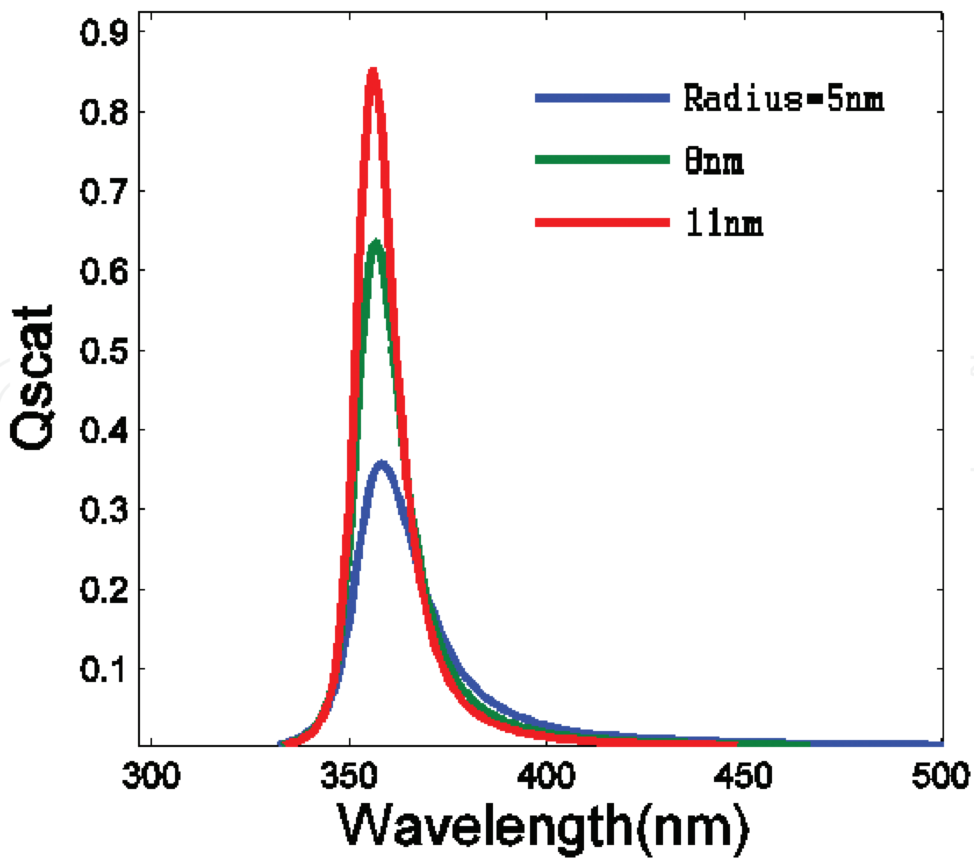


**Figure 2.** Wavelength dependent scattering cross section of silver metal nanoparticle of three different radii.

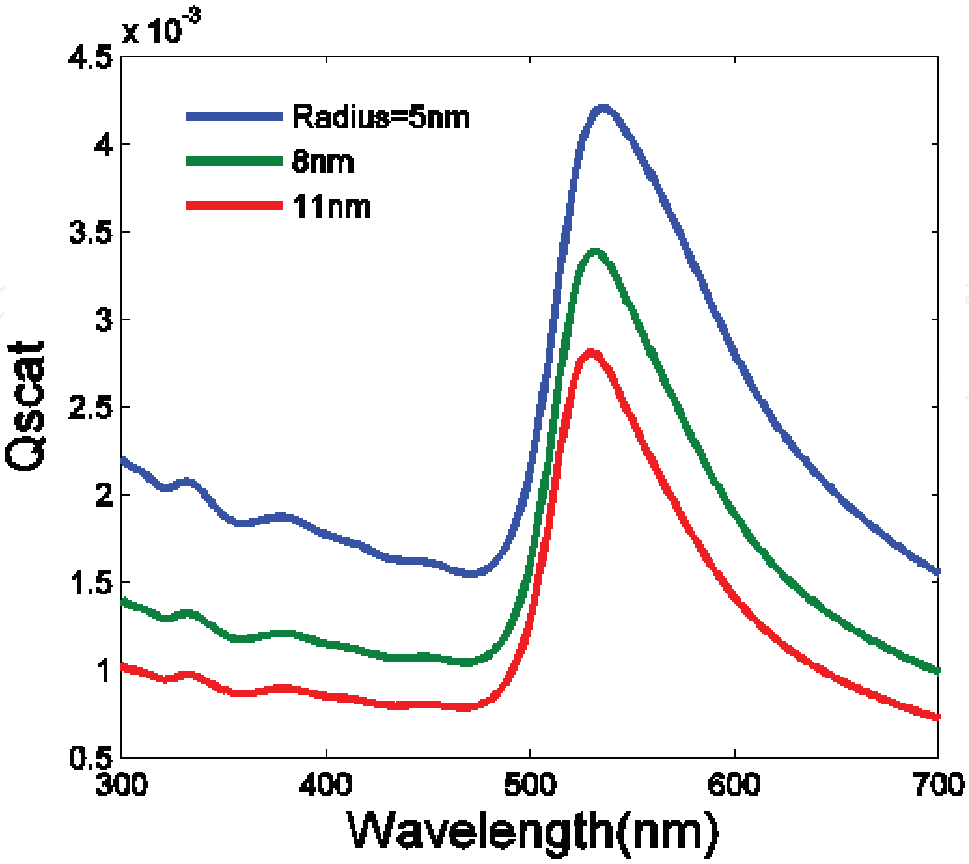


**Figure 3.** Wavelength dependent scattering cross section of gold metal nanoparticle of three different radii.

In **Figure 3**, we have discussed the wavelength dependent scattering cross section of gold metal nanoparticle for three different radii. Here we observed that, as the radii of gold nanoparticle increases corresponding cross section magnitude increases with red shifted SPR resonance. In case of silver the SPR peak position is fixed at one wavelength while for gold the peak positions are red shifted with the radii. The SPR peak position for gold nanosphere surrounded by air (N = 1) is at 554 nm for radius 5 nm. The additional advantages of gold nanoparticle over the silver are analyzed in terms of SPR peak positions and corresponding spectral width known as full width at half maxima (FWHM).

These two different types of metal nanoparticle are described within the electrostatic approximation which is only valid for smaller size. Therefore, for the description of lager size nanoparticle we have used the numerical method discrete dipole approximation (DDA) which is valid within and beyond the electrostatic approximation.

## 3. Numerical approach: scattering by large size metal nanosphere

The numerical technique that we have used to simulate the optical properties of large size nanoparticle is discrete dipole approximation method. In this method, target is discretized into large number of polarizable dipoles [33]. Each dipole situated at the corner of a cubic lattice and the relation between them i.e., separation or distance of one dipole to other are managed by the lattice parameter. The chosen target in this technique is expressed in terms of volume as $V = Nd^3$, where N is the number of discretized dipole and d is the lattice spacing and the size of target is also expressed in term of effective radius as $a_{eff} = (3V/4\pi)^{1/3}$. The technique is applicable only when the following criteria is satisfied

$$|m|kd < 1,$$

where k is wave vector, lattice parameter and m is the complex refractive index of chosen target material. The main input parameter in DDA technique is the dielectric constant of target and surrounding media in which target is embedded. The complex dielectric function of composite system is provided by input file which can be expressed as

$$\varepsilon_{relative} = \frac{\varepsilon_{target}}{\varepsilon_{medium}} \tag{6}$$

Here, the target is assumed as a point dipole situated at the each corner of cube. Further, placement position $\vec{r}_i$ and polarizability $\vec{\alpha}_i$ of the point dipoles need to be flexible for DDA calculation. Each entity is represented by a dipole moment as

$$\vec{p}_i = \alpha_i.\vec{E}_{i,loc} \tag{7}$$

$$\vec{E}_{i,loc} = \vec{E}_{i,app} + \vec{E}_{i,ind} \tag{8}$$

where $\vec{E}_{i,app}$ and $\vec{E}_{i,ind}$ is the applied and induced field respectively acting on the i[th] individual because of the radiation of all the others (N – 1) dipoles that set up the NPs. The field $\vec{E}_{i,app}$ and $\vec{E}_{i,ind}$ is given by the following relation

$$\vec{E}_{i,app} = E_0 e^{i(\vec{k}.\vec{r}-\omega t)} \tag{9}$$

$$\vec{E}_{i,ind} = -\sum_{j=1}^{N} \vec{A}_{ij}.p_j \tag{10}$$

$$\vec{A}_{ij}.\vec{p}_j = \frac{e^{ikr_{ij}}}{r_{ij}^3}\left\{k^2\,\vec{r}_{ij}\left(\vec{r}_{ij}\times\vec{p}_j\right) + \frac{(1-ikr_{ij})}{r_{ij}^2}\left[r_{ij}^2\,\vec{p}_j - 3\,\vec{r}_{ij}\left(\vec{r}_{ij}.\vec{p}_j\right)\right]\right\} \tag{11}$$

$$\vec{p}_i = \alpha_i.\left(\vec{\mathrm{E}}_{i,app} - \sum_{j=1}^{N}\vec{A}_{ij}.p_j\right) \tag{12}$$

where k = |*k*| represents the incident wave vector.

Dipole moment symbolizes the optical behavior of the target geometry. Therefore, the extinction and absorption cross section can be achieved after calculating the set of dipole moments as given by

$$C_{ext} = \frac{4\pi k}{\left|\vec{E}_0\right|^2} \sum_{i=1}^{N} \text{Im}\left\{\vec{E}^{*}_{i,inc}.\vec{p}_i\right\} \tag{13}$$

$$C_{abs} = \frac{4\pi k}{\left|\vec{E}_0\right|^2} \sum_{i=1}^{N} \left\{\text{Im}\left[\vec{p}_i.(\alpha_i^{-1})^* \vec{p}_i^{\,*}\right] - \frac{2}{3} k^3 \left|\vec{p}_i\right|^2\right\} \tag{14}$$

$$\begin{aligned} C_{sca} &= C_{ext} - C_{abs} \\ Q_i &= \frac{C_i}{\pi a_{eff}^2} \end{aligned} \tag{15}$$

where $C_i$ signifies the optical cross section, $i$ represents the running index includes extinction, absorption and scattering, $Q_i$ represents the normalized optical cross section and $a_{eff}$ effective radius of target.

The simulation effects could be visualized in terms of scattering cross section as shown in **Figure 4**. A 50 nm radius gold metal sphere is discretized into 4224 number of dipole to see the plasmonic properties like scattering cross section and surface plasmon resonance. The SRP wavelength of 50 nm gold nanosphere was observed at wavelength 560 nm.

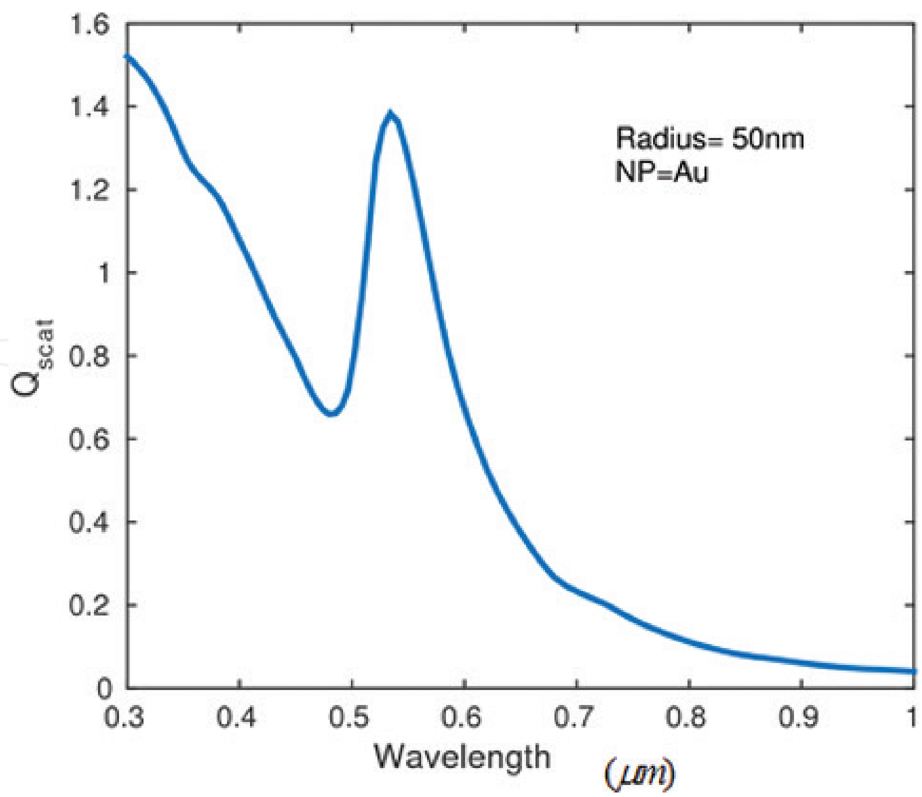


**Figure 4.** Wavelength dependent scattering cross section of 50 nm gold nanosphere surrounded by air.

## 4. Conclusion

The work described the optical properties of plasmonic nanogeometries in terms of optical cross section and surface plasmon resonance. Two different types of metals like silver and gold are taken into account to see the optical properties. The surface plasmon resonance corresponding to these metals lies in visible range of electromagnetic spectrum wherein most of the applications exist. Therefore, the work guides to plamonic community to simulate various types of metal nanostructure which exhibit SPR in different part of electromagnetic spectrum. These tunable nature of surface plasmon resonances can be used in many purposes such as sensing, photovoltaic and Raman spectroscopy.

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## Conflict of interest

The authors do not have any conflict of interest.

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