Calculation of the extinction cross section and lifetime of a gold nanoparticle using FDTD simulations

Archana Radhakrishnan and Dr V. Murugesan

Citation: AIP Conference Proceedings **1620**, 52 (2014); doi: 10.1063/1.4898219
View online: http://dx.doi.org/10.1063/1.4898219
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1620?ver=pdfcov
Published by the AIP Publishing

Calculation of The Extinction Cross Section and Lifetime of A Gold Nanoparticle using FDTD Simulations

Archana Radhakrishnan [1, a)] and Dr V.Murugesan [2, 3, b)]

[1] *B.Tech (Engineering Physics, National Institute Of Technology, Calicut)*
[2] *Assistant Professor (Supercomputer Education and Research Centre, Indian Institute of Science, Bangalore*)

[a)]anju.archana@gmail.com
[b)]murugesh@serc.iisc.in

Abstract. The electromagnetic theory of light explains the behavior of light in most of the domains quite accurately. The problem arises when the exact solution of the Maxwell's equation is not present, in case of objects with arbitrary geometry.
To find the extinction cross-section and lifetime of the gold nanoparticle, the software FDTD solutions 8.6 by Lumerical is employed. The extinction cross-sections and lifetimes of Gold nanospheres of different sizes and arrangements are studied using pulse lengths of the order of femtoseconds. The decay constant and other properties are compared. Further, the lifetimes are calculated using frequency and time domain calculations.

INTRODUCTION

Gold nanostructures are an extensive area of research. Surface Plasmon resonance of gold particles has lead to many interesting studies. In metals the interaction between the electromagnetic radiation and the conduction electrons cause the effect known as SPR. Here the conduction electrons are forced by the incident electric field to jointly oscillate at the resonant frequency relative to the lattice of the positive ions. The absorption of maximum intensity of light takes place at this wavelength. Ideally there should be absorption only at this wavelength but as a result of the line broadening mechanisms the graph of extinction cross section versus wavelength shows a Lorentzian lineshape. The broadening is mainly due to various decay processes. A fraction of it is due to non-radiative decay of plasmons to electron and holes in the conduction band called intraband damping [1]. The excitations between d bands and conduction band are interband damping. With increasing surface to volume ratios many other effects such as interface damping becomes important. With increase in size and coupling with the incident radiation damping leads to plasmons decaying to photons. The lifetime broadening has a characteristic homogeneous linewidth $\Gamma_{hom} = \frac{2\hbar}{T_2}$ which is inversely proportional to the decay time of the coherent polarization of the electronic oscillations.

Some of these photons are later scattered by the nanoparticle in all directions and this is called scattering. While some other photons are transformed to phonons of vibration of the lattice resulting in absorption. The Surface Plasmon Resonance curve peak includes both these cross sections. The size shape and arrangement of the nanostructures have a profound influence on the extinction coefficient. The position of the spectral line depends on the dielectric function of a material. This is why silver has higher energies than gold. The dependence on size is shown in the polaritonic red shift due to electromagnetic retardation, with increase in size for sizes greater than 10 nm [2]. Typically a gold nanoparticle at around 50 nm has a resonance at 520 nm and shows ruby red color. This phenomenon was first noticed by Michael Faraday in 1857 [3].
The resonance peak shifts to red with increase in the dielectric constant of the surrounding medium due to columbic screening effects. The solution of the Maxwell's equation gives the SPR spectra of particles. The solution in the case

Light and Its Interactions with Matter
AIP Conf. Proc. 1620, 52-57 (2014); doi: 10.1063/1.4898219

of nanospheres was first accomplished by Gustav Mie, a German physicist in 1912. [4] The theory was later modified to include many other shapes and simple systems. [5] It was Richard Gans, who modified the theory to include spheroids [6]. Even today we can use the Mie theory to efficiently compute the scattering and absorption coefficients of spheres of any shape and size. Since the exact solution of spheres, spheroids, concentric spherical sells and infinite cylinders have only been identified, we need to assort to approximate methods to solve in the case of other shapes. One of the most common approximate methods is the Finite Difference Time Domain (FDTD) and Discrete Dipole approximation (DDA).

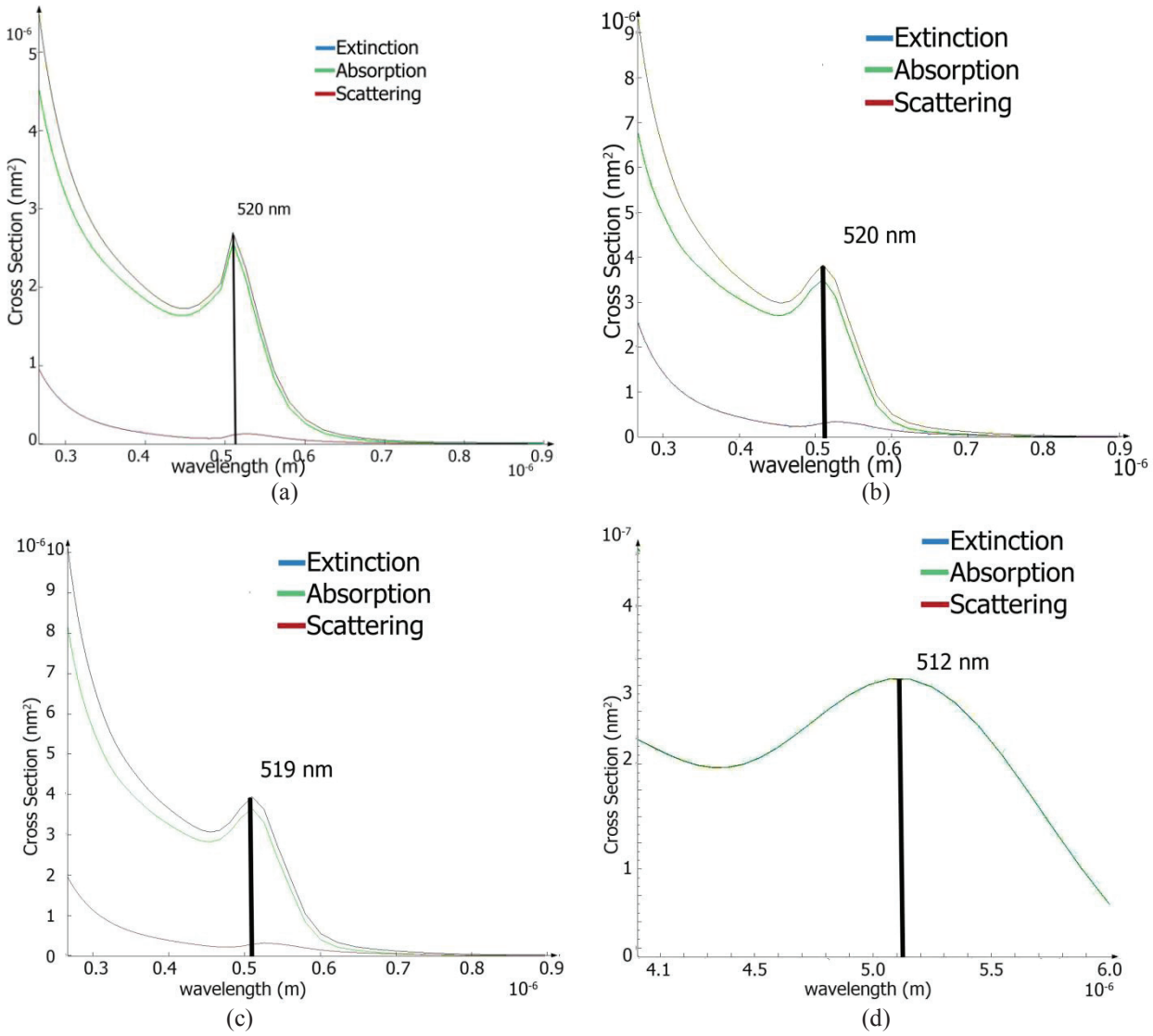

FIGURE 1. The cross-section vs. wavelength (a) 25nm 1 sphere, (b) 25nm 2 spheres, (c) 25nm 2 spheres with light through the center, (d) 5nm 1 sphere.

The two main theories in light scattering are Rayleigh and Mie theory. The former is applicable to small, spherical dielectric substances and the latter applies to all spherical materials (absorbing and non-absorbing). Thus for metallic spheres like gold Mie theory is used. The extinction cross section (C_{ext}) is attained as a series of multipole oscillations if the boundary conditions are specified. This happens when the cluster size is large and as a

result the electric field is non-uniform. When the radius of the particle is very small compared to the wavelength of radiation and thus only dipole oscillations are considered $(2R \ll \lambda)$, According to Mie theory,

$$C_{ext} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2} \tag{1}$$

Here ε_m is the dielectric constant of the medium and $\varepsilon = \varepsilon_1 + i\varepsilon_2$ is the complex dielectric function. At resonance, $\varepsilon_1 = -2\varepsilon_m$

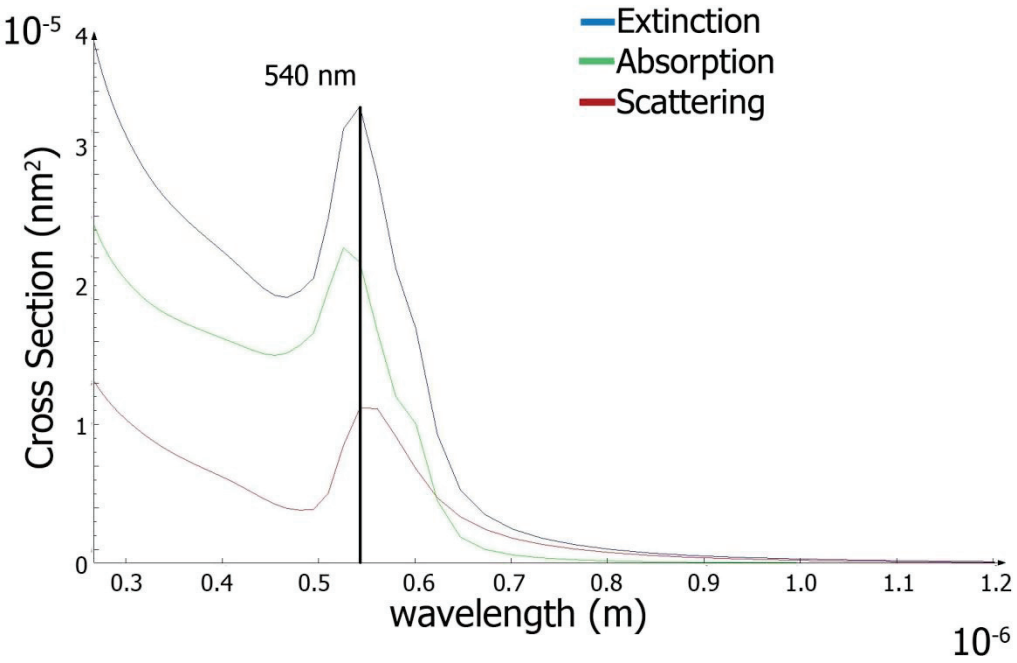

FIGURE 2. The cross-section vs. wavelength for a 2×2×2 array.

Usually the experiments on SPR are performed on cluster ensembles which lead to many inhomogeneous broadening effects that hide the spectral properties of isolated clusters. And make is hard to determine the exact data and compare with theory. This is solved by using numerical techniques and computer simulations. Recently, many experimental techniques like dark field microscopy has been developed to overcome the problem [1].

The SPR properties of gold nanoparticles have been in use for many years to make colored glasses. The Lycugus cup is excellent demonstration of the use of SPR, which scatters green light and transmits red light. Colorimetric sensing which requires highly color sensitive substances and Surface Enhanced Raman Spectroscopy (SERS) also exploit the SPR of gold [7][8]. Recent biomedical applications of SPR has been investigated and seen to be quite effective, like the use in near infrared for soft tissue penetration [9]. In this context here an effort has been made to study the scattering of gold nanospheres using simulations with Finite Difference Time Domain.

PROCEDURE

First of all the structure was constructed that contained a nanosphere using the features in the software FDTD solutions 8.6 by Lumerical. The material was Gold (Johnson and Christy). Then again the various options provided were manipulated and two power monitors, both cubical, were added to calculate the power and thus the absorption and extinction cross-sections. A time monitor was added to calculate the decay of electric field with time. The

source was then modified to introduce a pulse of the order of femtoseconds. The mesh parameters were customized based on the size of the particle and simulation volume was also adjusted accordingly.

Then the simulation was performed. A script was written to calculate the cross sections using the output of the monitors. The decay of electric field was plotted using the feedback of the time-monitor and the data was plotted in a log scale using Origin 8.5.1, the slope of which helps us calculate the lifetime. Both the methods time domain and frequency domain were used to calculate the decay rates because the broadening of the inhomogeneous absorption band had to be taken into account. Additionally the extinction spectra give the frequency corresponding to resonance. The same thing was repeated for different sizes and arrangements which were made possible by using different scripts for different arrangements.

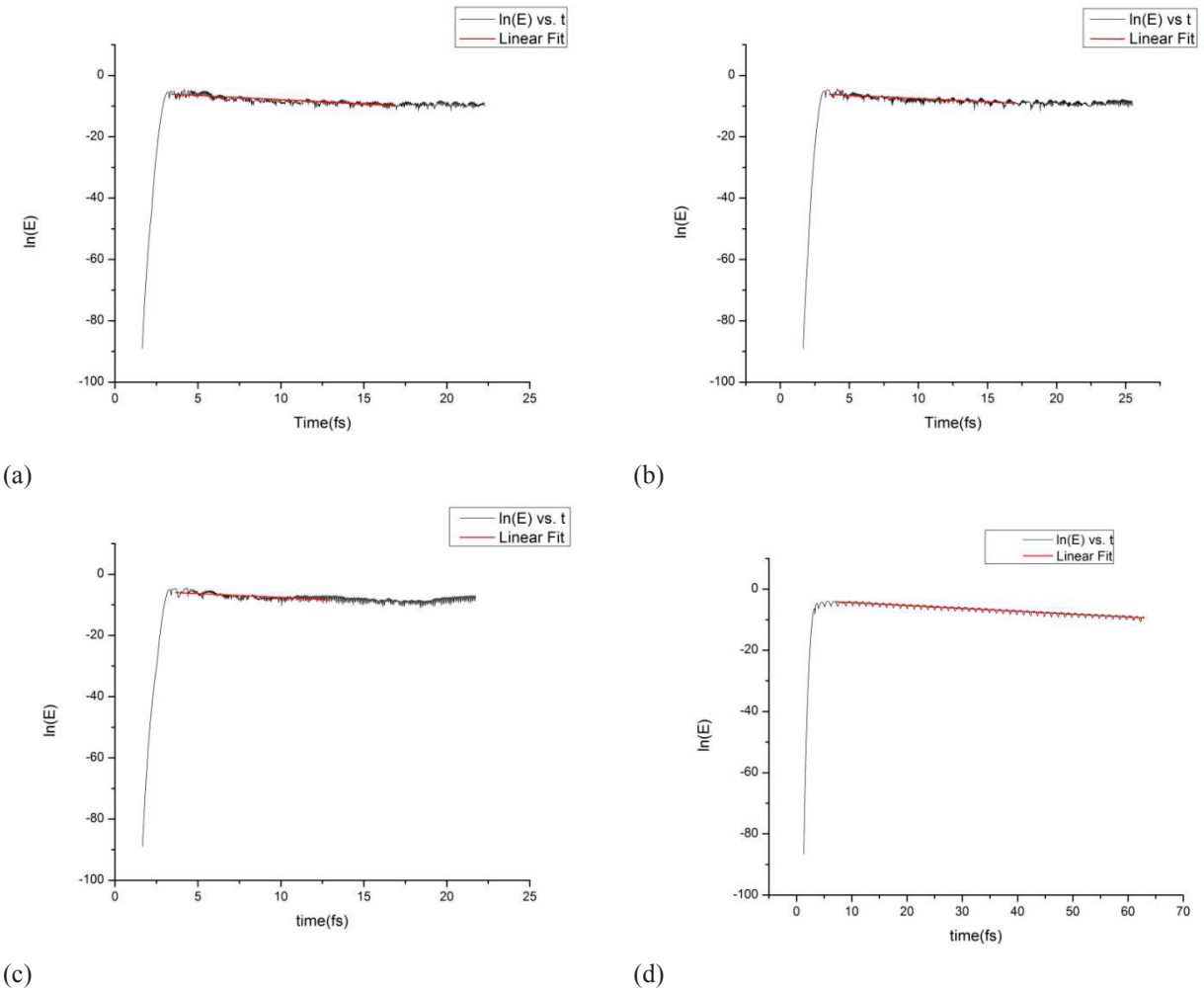

FIGURE 3. ln(E) vs. time. (a) 25nm 1 sphere, (b) 25nm 2 spheres, (c) 25nm 2 spheres with light through the center, (d) 2×2×2 array 25 nm.

RESULTS AND DISCUSSIONS

Particle Plasmon effect for gold nanoparticles is of significance since they absorb wavelengths in visible range and cause local field enhancements. This can be determined by the lifetime that can be calculated from the decay time τ_{sp} in time domain or the bandwidth $\Delta\omega$ in frequency domain. From Fig. 1 when a 25 nm sphere is illuminated by a 1 fs pulse, the resonance wavelength is around 520 nm. This is a good fit with the Mie theory of

scattering and has a Lorentzian lieshape. Any slight variation from the ideal lineshape is due to variations from the pseudo-free electron theory arising from interband transitions above 1.8 eV.

The scattering is very less due to the small size and the absorption is quite high in comparison. The sphere of 5 nm shows scattering that is negligible. Rayleigh theory expects the scattering cross section to drop as the sixth power of the diameter. It very slightly shifts to the red (lower energies) and becomes broader as the number of spheres Increase this is due to enhanced radiation damping as the size and number of particles of the cluster increases. This can be seen by comparing the different diagrams of Fig. 1.

The shift is not very significant and it is observed that the shift of λ_{max} is more profound when the periodicity changes. The dependence on size is due to polaritonic red shift and radiation damping that increase with size. Due to plasmonic coupling among the particles, the aggregation of gold nanospheres produces a color change from red to purple [2]. Thus for single particle the resonance is seen to depend on the shape, size and the dielectric constant of the material and the medium. The variations in the graph for groups of atoms are due to interaction. There are two types of interactions, near field, which is significant for only almost touching particles due to near field electromagnetic waves which are of short range. If the inter-particle distances exceed those allowing near field interaction, interact through dipolar fields which give a collective radiation after interference [10].

TABLE 1. The Lifetime of the simulated spheres by time domain and frequency domain measurements.

Specifications	Source Characteristics	Lifetime by Time Domain Method	Lifetime from resonance width
25nm,1sphere (1 nm gap)	P ploarised	3.57	2.51
25nm,2 spheres(1nm gap)	P ploarised	4.69	2.51
25nm,2 spheres(1nm gap)	S ploarised	3.83	2.51
5nm,2 spheres(1nm gap)	P ploarised	-	2.9

In addition there is a very slight emergence of quadrupolar resonance peak as the number of particles in the array increases. This is common for very large clusters due to the non-uniformity of the optical field across it.
The lifetimes calculated from the time resolved and frequency dependent methods are in agreement with a standard deviation of 0.48 fs, showing that the inhomogeneous extinction band broadening is trivial. This type of broadening is a function of shape which is not present in this case [2]. The directional dependence of the lifetime is quite evident.

CONCLUSIONS

The lifetimes show a dependence on the size. Generally the lifetime decreases with the increase of the radius of the spheres. This is because the radiative damping increases with volume and the lifetime is inversely proportional to the damping. Even though as number of spheres increases the lifetime is supposed to decrease as the effective size increases it is seen that the lifetime increases this might be due to coupling. When the light wave is directed through the centers of the sphere and perpendicular to the line joining the centers of two spheres the lifetime is seen to be more than in the case of radiation parallel to the line joining the centers. This is because of more path length of the radiation in the latter case. Similar relations were observed in the case of arrays.

ACKNOWLEDGMENTS

We express our profound gratitude to Mr. Abhay Tiwari for his timely advice, Prof. Dr. P. Predeep and Mr. Praveen Thappily for reading the manuscript and pointing out corrections and the Indian Academy of Sciences (IAS), Bangalore for making this work possible.

REFERENCES

1. C. Sonnichsen, T. Franzl , T. Wilk, G. von Plessen, J. Feldmann, O. Wilson and P. Mulvaney, Phys. Rev. Lett. 88, 077402/1(2002).

2. U. Kreibig and M. Vollmer, Springer Series in Materials Science 25, 535(1995)
3. P. Mulvaney, Langmuir 12, 788 (1996).
4. G. Mie, Ann. Phys. 25, 377(1908).
5. M. I. Mishchenko, W. J. Wiscombe, J. W. Hovenier and L. D. Travis, ed. M. I. Mishchenko, J. W. Hovenier and L. D. Travis, " Light Scattering by Nonspherical Particles: Theory, Measurements and Applications", Academic Press, San Diego,(2000).
6. R. Gans, Ann. Phys. 37, 881(1912).
7. R. A. Reynolds, C. A. Mirkin and R. L. Letsinger, J. Am. Chem. Soc., 122, 3795(2000).
8. P. M. Tessier, O. D. Velev, A. T. Kalambur, J. F. Rabolt, A. M. Lenhoff and E. W. Kaler, J. Am. Chem. Soc. 122, 9554(2000).
9. J. L. West and N. J. Halas, Annu. Rev. Biomed. Eng. 5, 285 (2003).
10. M. Meier, A. Wokaun, and P. F. Liao, J. Opt. Soc. Am. B**2**, 931 (1985).