

Correlation of Surface Plasmon Resonance Wavelength (SPR) with Size and Concentration of Noble Metal Nanoparticles



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Abstract

Surface plasmon resonance SPR basically refers to collective oscillation of conduction electrons. Having the intrinsic property of sensing the surface properties, SPR have already received tremendous attention in the field of biomedical, Nano sensors, photovoltaics etc. Scientific data have also revealed that it is also highly characterized by the structure, type and dimension of the host nanoparticles, which eventually can lead us to a systematic correlation between different physical attributes of the host nanoparticles and SPR. In this work, we try to make a simplistic approach of correlating size, shape of gold (Au) and silver (Ag) nanoparticles (NPs) with their corresponding peak wavelength. It has also been attempted to bring the concentrations in the same frame. The computed results and the observed results are compared and matching up to a considerable extent has been shown in this work. It is envisioned that this small-scale correlation will help in giving a first insight towards characterization of Au and AgNPs just based only on SPR peak.

Keywords: SPR; Nanoparticles; MATLAB

Introduction

Every property of a material has a characteristic or critical length associated with it; e.g. scattering wavelength for electrical conductivity, plasma frequency (can be converted easily to wavelength) for optical property etc. The fundamental physics and chemistry changes when the dimensions of a solid become comparable to one or more of its characteristic wavelengths, many of which are in the nanometer range. Therefore, in the nano regime, novel physical and chemical properties can be experienced, e.g. yellow shiny bulk gold turn into red when the diameter of it is restricted to 10nm [1-15]. One of the very tempting properties of the nanoparticles is that their properties depend on their size, shape and density. As for instance, in medical applications, the size of the nanoparticles should be less than 100nm. This is because, above this dimension, the nanoparticles become toxic to the living body. So, to implement nanoparticles in different applications, having reliable information about the size, shape and density is indeed imperative. In order to determine the size, shape and density we usually incorporate different techniques. TEM, SEM are used for determining the size and morphology, respectively. Similarly, AFM provides information of shape. These techniques are not in situ, some of them are costly and some processes are time consuming. But with the help of some extraordinary properties of metal nanopar-

ticles called Surface Plasmon Resonance (SPR), the aspects like-size, shape and density of the metal nanoparticles can be feasibly extracted, saving of energy and time.

When total internal reflection occurs in a metal surface, then a wave moves along the surface of incidence which is referred to evanescent wave [2-5]. This wave occurs due to the interaction of electrons in the surface with the electric field of light. In case of metal bulk, the electrons absorb the light and oscillate exactly opposite to that of the incident wave and we perceive this as reflection of light. Therefore, metal appears to be shiny. But in case of metal nanoparticles, if the incident wave is nearly equal to that of the resonance frequency of the NPs, then they oscillate along with the electric field which is called Surface Plasmon Resonance. As such, they absorb a wavelength of light which we call SPR wavelength [1-7]. As the size of the nanoparticle changes, the resonance frequency of the particle changes. SPR wavelength also changes. The above descriptions eventually imply that there may be a quite sound correlation among the SPR wavelength, size, shape and density which can turn out to be standard equation [5-8].

Standardization of the equation can help the researchers to predict the size, shape and density of the sample without going into further investigations. So, this study is mainly aimed to find

out a standard relation between the SPR wavelength and the physical aspects of nanoparticles. Due to dearth of abundant data, present study concentrates only to size and concentration of the nanoparticles.

Data Sets and Methodology

For formulating an empirical equation, data have been used which is listed in the Table 1 and customized code has been used

in the MATLAB platform. In order to validate the equation, another data set as listed in the Table 2 has been used and standard deviations have been computed and plotted to see the accuracy of the formulated equation.

Calculations for gold nanoparticles

For the calculation of equation relating the concentration, size and wavelength, we had used the data already provided in literature listed in Table 1.

Table 1: Concentration, size and SPR peak wavelength of gold nanoparticle.

Conc. (ppb)(cx109)	Size(nm)	Peak Wavelength (SPR)
5470	5	517
598	10	519
164	15	520
65.4	20	524
17.9	30	526
7.15	40	530
3.51	50	535
1.96	60	540
0.782	80	553
0.384	100	572

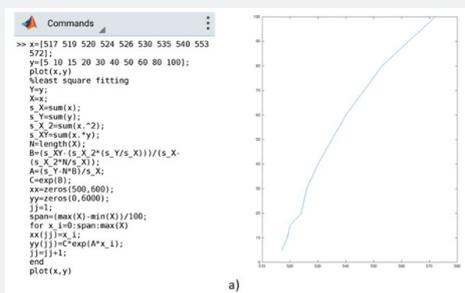


Figure 1A: MATLAB code for plotting size vs SPR wavelength graph and the plotted graph.

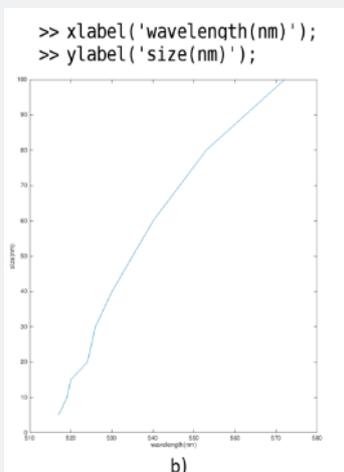


Figure 2: Code for labeling of the axes.

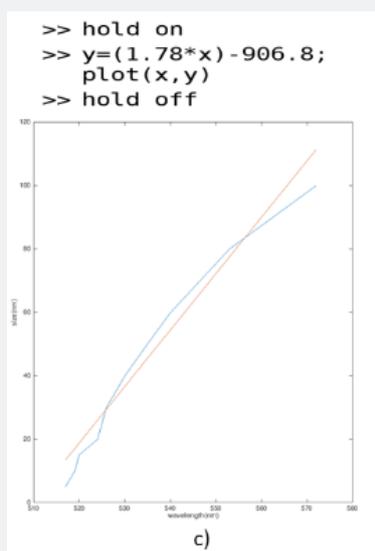


Figure 3: Code and plotting of least square fitting curve for gold metal nanoparticles.

Relation between size and spr wavelength of the nanoparticles

The customized code and respective plots that are used for formulating a relation between the size and peak wavelength of SPR of gold nanoparticles are shown in Figure 1-3.

Accordingly, relation between size and wavelength is linear, which can be defined by equation

$$s_g = (1.8x - 907) \text{ (approx.)}$$

where, s_g is the size of gold nanoparticle and x_g is the SPR wavelength of gold nanoparticles (Figure 4).

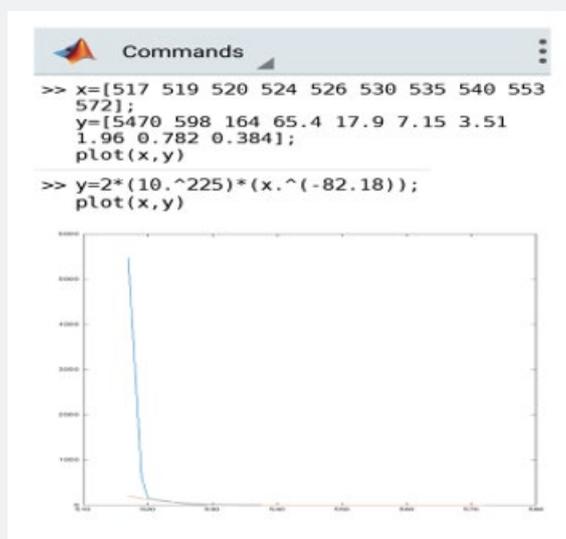


Figure 4: Code for plotting concentration vs wavelength graph and the equation of the curve for gold nanoparticles.

Relation between concentration and wavelength

Here, the equation provides relation between concentration and wavelength that is

$$c_g = 2 \times 10^{225} \times x_g^{-82.18} \quad (2)$$

In equation (2), c_g refers to the concentration of the nanoparticles and x_g is the SPR wavelength. Combining equations (1) and

(2), we derive the relation between SPR wavelength and size and concentration of the nanoparticles simultaneously, viz

$$x_g = 0.36 \times s_g + 196 \times 10^{-0.012 \log c_g} + 324 \quad (3)$$

where x_g is the SPR wavelength, s_g is the size and c_g is the concentration of the nanoparticles. Here c_g is in ppb ($\times 10^{19}$) and s_g is in nm. The deviation of the calculated values from the experimental values of SPR is provided in Table 2 below.

Table 2: Deviation of calculated from experimental values.

SPR Wavelength (experimental)	SPR Wavelength (calculated)	Deviation
517	503	14
519	509	10
520	514	6
524	518	6
526	524	2
530	530	0
535	535	0
540	540	0
553	545	8
572	554	18

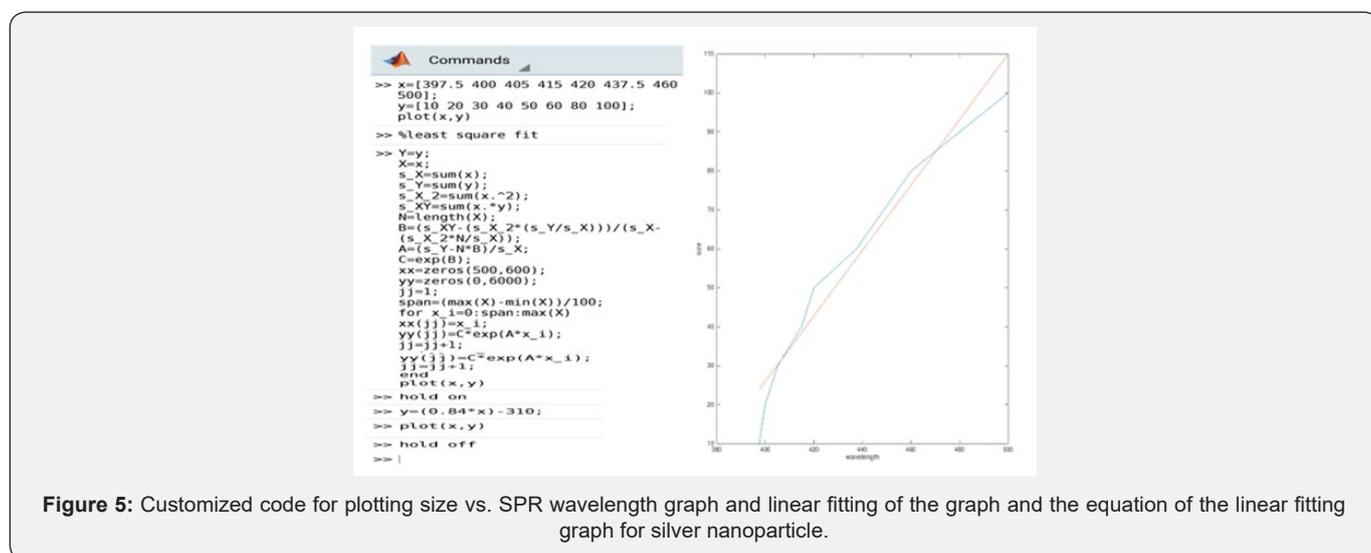


Figure 5: Customized code for plotting size vs. SPR wavelength graph and linear fitting of the graph and the equation of the linear fitting graph for silver nanoparticle.

Table 3: Deviation of calculated from experimental values.

Conc.(ppb) (cx109)	Size(nm)	Peak Wavelength (SPR)
3600	10	397.5
460	20	400
140	30	405
57	40	415
29	50	420
17	60	437.5
7.1	80	460
3.6	100	500

Calculations for Silver Nanoparticles

In similitude to AuNPs, we have performed for silver nanoparticles to establish correlation corresponding to data as listed in Table 3 (Figure 5).

Relation Between Size and Wavelength

Accordingly, we develop the relation between size and wavelength is

$$s_s = (0.84x_s - 310) \text{ (approx) (4)}$$

Where, s_s is the size of silver nanoparticle and x_s is the SPR wavelength (Figure 6)

Relation between concentration and wavelength

Likewise, the relation between concentration and wavelength is given by

$$c_s = 2.64 \times 10^{66} \times x_s^{-24.65} \quad (5)$$

Combining both equations and, we get

$$x_s = 0.54 \times s_s + 266 \times 10^{-0.04 \log c_s} - 168.5 \quad (6)$$

where c_s is in $ppb(\times 10^{18})$ and s_s is in nm.

Deviation of the theoretical data from experimental data

Deviation between theoretical and calculated values is listed in Table 4.

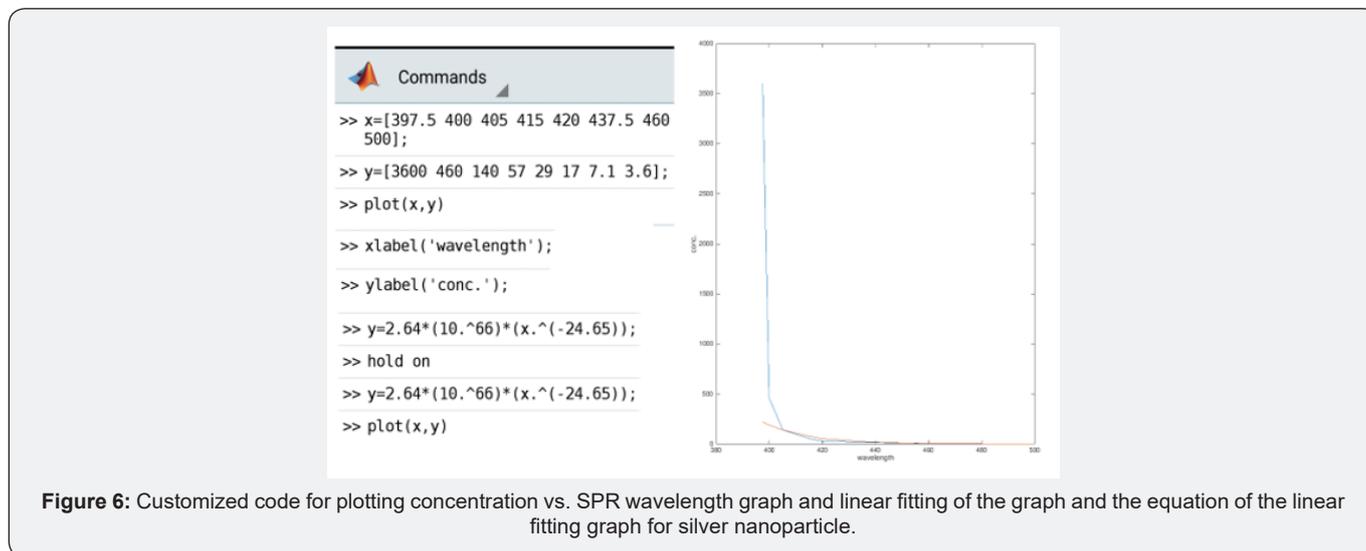


Figure 6: Customized code for plotting concentration vs. SPR wavelength graph and linear fitting of the graph and the equation of the linear fitting graph for silver nanoparticle.

Table 4: Comparison of experimental and computed values..

Peak Wavelength (SPR)	Wavelength (calculated)	Deviation
397.5	366	31.5
400	387	13
405	403	2
415	416	-1
420	428	-8
437.5	438	-0.5
460	458	2
500	475	25

Results and Discussions

In summary, we have tried to formulate correlation between parameters of nanoparticles affecting surface Plasmon resonance wavelength of gold and silver nanoparticles. The available data lead us to two different equations, one for silver and one for gold nanoparticles which correlate their size, concentration and wavelength. For gold nanoparticles, the equation came out to be

$$x_g = 0.36 \times s_g + 196 \times 10^{-0.012 \log c_g} + 324$$

Where conc. is in $ppb(\times 10^{18})$ and size is in nm. For silver nanoparticles, the equation came out to be

$$x_s = 0.54 \times s_s + 266 \times 10^{-0.04 \log c_s} - 168.5$$

Where conc. is in $ppb(\times 10^{18})$ and size is in nm. These equations are then verified with respect to experimental dataset. Our observations reveal that there is matching of the values to a con-

siderable extent. There is lot of scope for development of this work. This work will give us a priori about which concentration of the given solution of nanoparticle of known size will give wavelength (SPR) in required range. The empirical formulations will provide a quicker way to characterize the Au and AgNPs through the allied parameters..

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