

Turnability of the Plasmonic Response of the Gold Nanoparticles in Infrared Region

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Abstract We report on the modulation of the optical properties namely the Surface Plasmon Resonance (SPR) of gold nanoparticles core-shell as function of the surrounding medium (water, ethanol). We have study two different combinations (1) silica thin film coating gold nanospheres and (2) gold thin film coating silica nanoparticles. The optical model used is based on Mie theory by considering spherical gold nanoparticles core-shell and the simulation is done using Matlab program. The results show an important influence of the surrounding medium and the size of the core as well as the shell thickness, on the optical properties with a redshift of the Surface Plasmon Resonance (SPR). By using Mie theory and Drude model for the simulation of the Surface Plasmon Resonance model of spherical nanoparticles showed that for the control of the Surface Plasmon Resonance of the gold thin film coating silica nanoparticles it is important to considered three parameters (i) the size of core (ii) the surrounding medium and (iii) shell thickness, which enable the turning of the SPR through the near infrared; where as gold nanosphere coated by silica results has a maximum wavelength at 530 nm, this Plasmon peak corresponding a R_1/d ratio of 1.6. Thus, this work enabled optimizing core-shell structure with well-controlled sizes for biomedical application.

Keywords: *Nanospheres particles, Nanospheres, shell thickness, Surface Plasmon Resonance*

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1. Introduction

Spite the significant efforts made in medical research for cancer treatments, it remains one of the major causes of death in the world. Various methods of treatment bringing into play a laser, microwaves, radio frequencies...etc, were tested for local heat treatment of cancerous area to destroy it. The cancer cells are naturally more sensitive to the radiation than the normal cells. However, these treatments by microscopic, cause not only the destruction of the tumoral cell but also the destruction of healthy surrounding cells and thus produce many side effects [1].

Nanosciences and Nanotechnologies open new ways towards better, adapted and more targeted treatment. Indeed, du to their sizes effects, nanoparticles can be utilized for the simultaneous removal of cancer. The nanotechnology allows the production of nanoparticles, which is at the origin of Surface Plasmon Resonance [2].

Surface Plasmon Resonance is collective excitations of the electrons at the interface between a conductor and an insulator and it is described by evanescent electromagnetic waves that are not necessarily located at the interface [3,4].

Noble metal nanoparticles are of advantages because they are not degraded under laser irradiation and allow also an important reduction laser power, this is du to their high absorption cross section [5]. Noble metals nanoparticles

present remarkable optical properties, which explain all the interest of their usage. Besides their optical properties, noble metal nanoparticles have found applications in many different fields; we can quote electronics, optics, catalysis and nanomedicine [3,6]. Gold nanoparticles have numerous promising applications in nanomedicine field, they are used to produce thermal tumor ablation and new therapeutic agents.

Most of these applications use the unique optical properties of gold nanoparticles, which is the Surface Plasmon Resonance [4], photoluminescence and Surface Enhanced Raman Scattering (SERS) effect [2]. Gold plasmonic i.e. SPR nanoparticles are widely used in biological applications, such as contrast agents for cancer detection, photothermal therapy [7]. Properties of SPR are used to the diagnostic of cancer, for example gold nanoshells with solid silica cores have great potential for cancer photothermal therapy [8].

With regard to the application of the nanoparticles in biology, gold nanoparticles are the metal nanoparticles most frequently used due of their properties. First of all, gold is not toxic. Like silver and copper, gold presented a strong absorption in visible spectrum, called the Plasmon band. Gold nanoparticles resonance is localized in visible spectrum [9], Christina Graf and co-workers, affirmed-that the Surface Plasmon Resonance (SPR) of gold nanospheres of 5 nm of radius embed in water are localized at 520 nm [10] whereas SPR of silver nanospheres is localized towards 410 nm [11,12]. Broader Nikolai G. khlebtsov

reported gold nanospheres in water having radius in the interval $5 \text{ nm} < R < 20 \text{ nm}$, their Plasmon resonance is observed at 520 nm [13]. The most important feature of the SPR is its position in the spectrum and its band intensity. To enable biomedical applications, the resonance plasmon frequency of the nanoparticles should be however in the near infrared (NIR) region [14]. Principal approach to enable use of nanoparticles for biomedical application is to fabric nanostructures (core/shell). Core/shell nanoparticles are a new type of nanoparticle composed of a dielectric core such as metallic oxide or polymer coated with metallic layer, which is typically gold. P. Mulvaney and al [15] established absorption of a film of nanoparticles core shell Au/SiO₂ at 525 nm . By rationally tuning the cores as well as the shells of such materials, a range of core-shell nanoparticles can be produced with tailorable properties that can play important roles in various applications in medicine for cancer diagnostic and offer sustainable solutions to current diagnostic cancer problems. Indeed, the SPR wavelength depends on the nanoparticles shape (sphere, rods, cubic...), size and local environment [2,4,6].

In this work, we have simulated the absorption cross-section of spherical core/shell nanoparticle using Matlab like simulation program. Nanospherical gold is characterized by appearance of only one Plasmon band [2,16]. Two models were used to explain the physical aspect of Surface Plasmon Resonance: Drude-Maxwell model [2,17] and Mie theory [2,18]. We used the solution of Maxwell's equations for spherical particles using Mie-Drude theory. According to this theory, we can calculate the optical cross section area, using MATLAB 2011 software for different materials such as gold nanospheres and core-shell nanostructures.

2. Material and Methods

According to M. M. Alvarez et al. [19], when the noble metal particles (gold, silver and copper) are subjected to an electric field, the dielectric function decomposed in two terms: an inter-band contribution (IB), corresponding to the response of 5d electron and an intra-band contribution (ID) or contribution of free electrons. These transitions are in the infrared range. According to the generalized Drude theory, the permittivity of the particle can be written as follows:

$$\varepsilon(\lambda) = \varepsilon_r + i\varepsilon_i. \quad (1)$$

And the real (ε_r) and imagery (ε_i) part of the dielectric function are respectively given by equations (2) and (3) [20,21].

$$\varepsilon_r(\omega) = \varepsilon_{rIB}(\omega) + \varepsilon_{rD}(\omega) \quad (2)$$

$$\varepsilon_i(\omega) = \varepsilon_{iIB}(\omega) + \varepsilon_{iD}(\omega). \quad (3)$$

Inter-bands contributions are taken from the literature (see Table 1) and intra-bands values are defined by the equations (4) and (5).

$$\varepsilon_{rD}(\omega) = \varepsilon_\infty - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2} \quad (4)$$

$$\varepsilon_{iD}(\omega) = \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)}. \quad (5)$$

Table 1. Optical parameters of gold

Metal	gold	References
τ (second)	$(9.3 \pm 0.9) * 10^{-15}$	[20]
ε_{rIB}	6.9	[20,25]
ε_{iIB}	2.45	[26]
λ_p (nm)	145	[27]
ε_∞	2.2715	[28]

For metals at near-infrared frequencies, these equations become (6) and (7).

$$\varepsilon_{rD}(\omega) \cong \varepsilon_\infty - \frac{\omega_p^2}{\omega^2} = \varepsilon_\infty - \frac{\lambda^2}{\lambda_p^2} \quad (6)$$

$$\varepsilon_{iD}(\omega) \cong \frac{\omega_p^2}{\omega^3 \tau} = \frac{\lambda^3}{\lambda_p^2} \tau_r \quad (7)$$

Where ε_∞ , the high frequency is limit dielectric constant given in the literature, λ_p is the plasma wavelength given in the literature and τ_r is relaxation time given by equation (8).

$$\tau_r = 2\pi c\tau \quad (8)$$

Where τ is the electron lifetime in seconds and C is the velocity of light ($C = 8 * 10^8 \text{ m/s}$).

For metallic oxide and/or polymer, the optical parameters n and k which respectively designate the refraction index describing the speed of the wave phase and extinction index describing the absorption of the wave during propagation in the material, are respectively expressed by the following relations (9) and (10).

$$\varepsilon_r = n^2 - k^2 \quad (9)$$

$$\varepsilon_i = 2 * n * k. \quad (10)$$

The real and imaginary parts of the complex dielectric function of the particle ε_r and ε_i are related to the dielectric function of core noted ε_a and the dielectric function of shell noted ε_b (see Figure 1) by the relations (11) and (12).

$$\varepsilon_a = \varepsilon_r + i\varepsilon_i \quad (11)$$

$$\varepsilon_b = \varepsilon_r + i\varepsilon_i \quad (12)$$

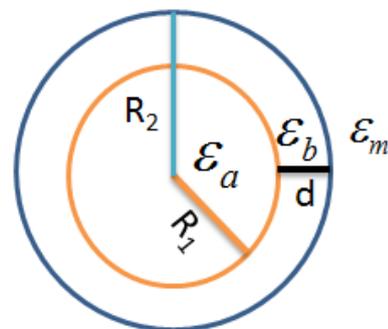


Figure 1. Spherical core/shell nanoparticle

The optical parameter (n, k) of SiO₂ data are obtained from E. Palik [22]. In the case of a sphere multi-layer (by example core-shell system) the expression of the absorption cross section is solved on the basis of the Laplace equations. For more detail see article [23] and

document [24]. It is assumed that the particle diameter is much smaller than the wavelength of the incident field. Then, we can obtain the absorption cross section from the polarizability defined by equation (13).

$$\alpha = 4\pi R_2^3 \varepsilon_0 \left\{ 1 - \frac{3 \left[(\varepsilon_b - \varepsilon_a) R_1^3 + (2\varepsilon_b + \varepsilon_a) R_2^3 \right] \varepsilon_m}{2(\varepsilon_b - \varepsilon_a)(\varepsilon_m - \varepsilon_b) R_1^3 + (2\varepsilon_b + \varepsilon_a)(2\varepsilon_m + \varepsilon_b) R_2^3} \right\}. \quad (13)$$

From Mie scattering theory the absorption cross section is given by equation (14).

$$\sigma_{abs} = \frac{2\pi}{\lambda \varepsilon_0} \text{Im}(\alpha) \quad (14)$$

Where $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of vacuum and ε_m is the dielectric constant of surrounding medium ($\varepsilon_m = n^2$) with n is refractive index. The extinction coefficient of a small particle is determined by its absorption $\sigma_{abs} = \sigma_{ext}$; in the general case we have the following relation between the extinction (σ_{ext}), absorption (σ_{abs}) and scattering (σ_{sca}) cross section $\sigma_{ext} = \sigma_{abs} + \sigma_{sca}$ [13,24].

The constant values taken from the literature and that are necessary for this study, are shown in Table 1 with the corresponding references.

3. Results and Discussion

Nanoparticles can be categorized based on single or multiple materials into simple and core/shell or composite nanoparticles. In general, simple nanoparticles are made from single material whereas core/shell particles are composed of two or more materials. Moreover of gold nanoparticles we have used silica material for the formation of nanoshell particles. According to Maria Vallet Regi and Francisco Balas [29], they report that different silica-based materials can be employed for designing devices for biomedicine either for drug delivery systems or for bioactive materials in prosthetic applications. In this study, the spectra extended into from visible to the near infrared region (200-1200 nm) were measured.

3.1. Optical Properties of Single Metal Nanoparticles

Equation (14) can provide the absorption spectra of a metal nanoparticle as function of the particle radius R and the refractive index of the medium in which it is embedded. In Figure 2, we have plotted the absorption spectrum of a particle with a 20 nm radius, embedded in a medium with a refractive index of 1.333 (water).

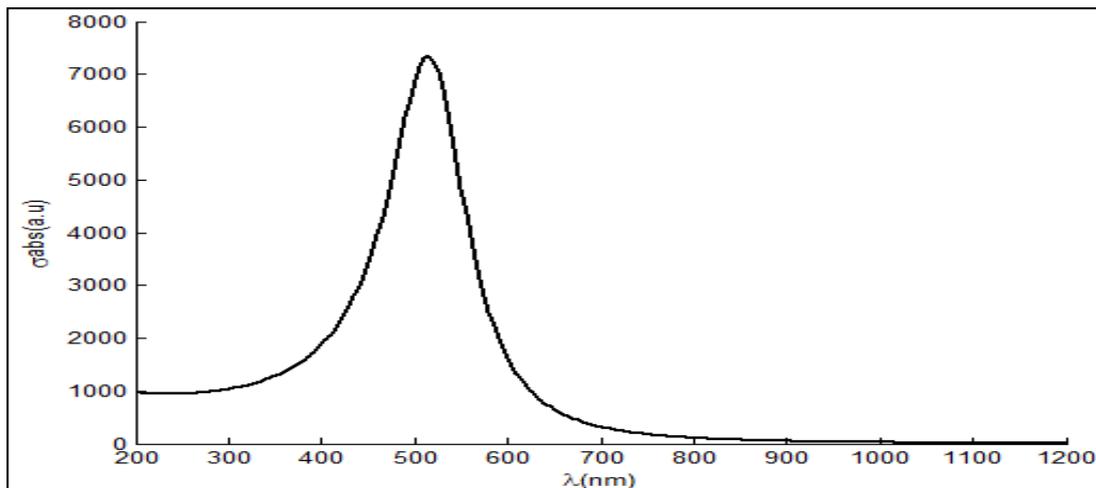


Figure 2. Absorption cross section of gold nanosphere

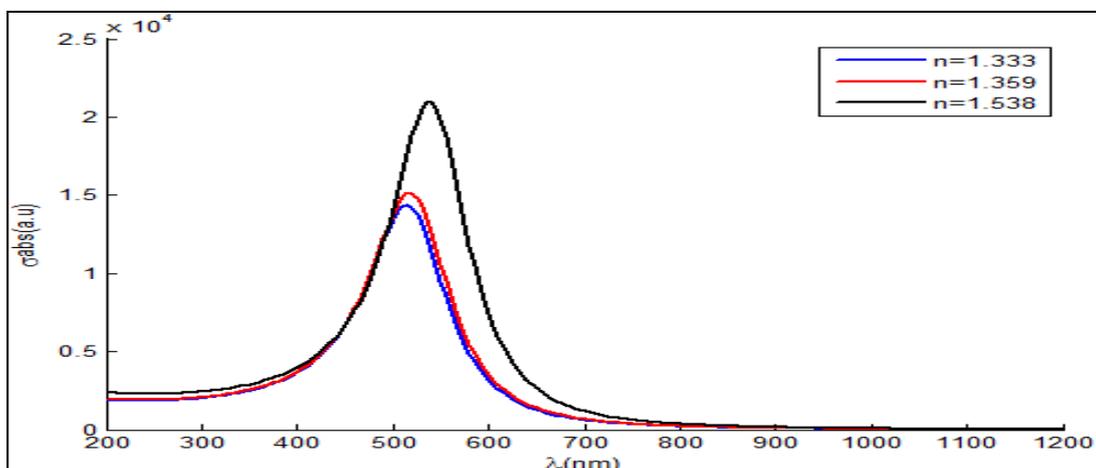


Figure 3. Surrounding medium effect on the optical properties

As expected, the spectrum of gold nanosphere reveals one only resonance located around at 515 nm in water, caused by the collective plasma oscillation of the free electron gas. The maximum absorption was obtained at wavelength 515 nm characteristic the formation of gold nanosphere nanoparticles. This value is in good agreement with experiments measure, which has been confirmed our model of studies of the optical response. The simulation results for gold nanosphere resemble the experimental spectrum. According to [30] Azim Akbarzadeh and co-workers are obtained a maximum absorption at 518 nm. Whereas this band can be influences by surrounding medium as shown in Figure 3.

Figure 3 shows the absorption cross-section spectra of gold nanospheres in different medium: water, ethanol and benzyl acid. The refractive indexes used are fixed values: 1.333 (water), 1.359 (ethanol) and 1.538 (benzyl alcohol). The optical properties of the gold nanosphere particles shows that with increasing refraction index the intensity of the Plasmon band increases and absorption shifts toward the higher wavelength region as shown in Figure 3. But also band becomes wider. These three bands are localized at 515 nm, 520 nm and at 540 nm for 1.333, 1.359 and 1.539 for refraction indexes values respectively. These results, allow considering a significant factor, which is the surrounding medium. These results confirmed according to the equation (14) that the dielectric constant of the surrounding medium plays a predominant role in the position of the Plasmon peak and its intensity.

3.2. Optical Properties of Core/Shell Nanostructure

We have coated the gold nanoparticles with silica to study their optical properties. The advantage of these

nanostructures (core/shell) is the possibility to modify the resonance Plasmon from visible region to near infrared region, and thus the absorption wavelength by changing the core to shell ratio. For $d=0$ nm (i.e. without any shell of SiO_2) the Surface Plasmon Resonance of the gold nanoparticles is localized at 515 nm in water and 520 nm in ethanol (bleu curve in Figure 4). We have study two different combinations (1) silica thin film coating on gold nanospheres and (2) gold thin film coating on silica nanoparticles.

3.2.1. Silica Coating on Gold Nanosphere

Figure 4 shows the evolution of the Plasmon band when silica is used as a shell to coat the gold nanoparticle. In this case we have considered a gold core of 30 nm of radius (R_1) and the SiO_2 shell thickness (d) vary from 0 nm to 50 nm. First, the silica shell is known to diminish the bulk metal conductivity and improves the chemical and physical stability of the core component [31]. Second, silica can be used to block the core surface from making contact with a biological environment and also silica particles produced via the Stöber Method have been shown to be chemically biocompatible [32].

The obtained core/shell nanoparticles are emerged into the two different surrounding mediums (water and ethanol). The non-coated gold nanoparticle ($d=0$ nm), the gold nanoparticles had a characteristic surface plasmon resonance at a wavelength of 515 nm in water and at 520 nm wavelength in ethanol.

Figure 4 shows globally that all the core/shell nanospheres irrespective to the surrounding medium, their SPRs move toward red shifted but remain in visible region. Therefore the increase into the thickness of the shell increases the Surface Plasmon Resonance wavelength, which is gradually red, shifted and its intensity increases as well.

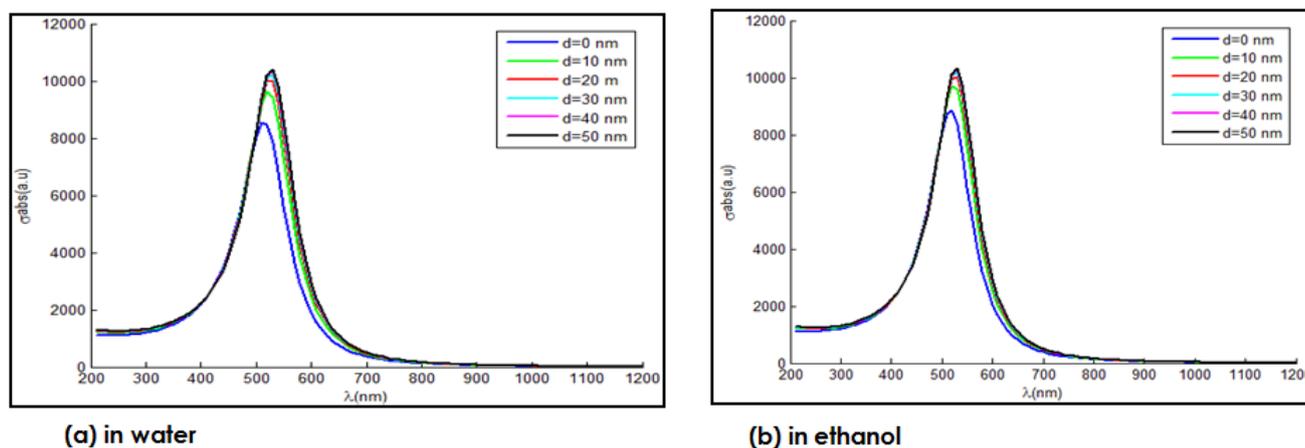


Figure 4. Absorption cross-section for Au/SiO₂ (core/shell) nanospheres at varying thickness shell at core radius of 30 nm

Table 2. Maximum absorption of the Au/SiO₂ (core/shell) nanospheres as function of the core/shell ratio at each surrounding medium (water and ethanol)

Au/SiO ₂ Medium Refraction index n=1.333	SPR _{max} (nm)	Au/SiO ₂ Medium Refraction index n=1.359	SPR _{max} (nm)
5/3	530	5/2.5	530
10/6	530	10/5	530
20/12	530	20/10	530
30/18	530	30/15	530
40/25	530	40/20	530
50/30	530	50/25	530

As it shown in Figure 4, we remark that the maximum absorption is reach when the silica thickness is between 10 and 20 nm in both mediums and the frequency of resonance is positioned at 530 nm wavelength for the two surrounding medium. After reaching a wavelength of 530 nm, the SPRs are no longer sensitive to the change into the shell thickness but the plasmon band increased in intensity. After we have looked at the influence of the ratio between the core size and the shell thickness on the SPR wavelength; Table 2 summaries the ratio between size of core and thickness of shell for to reach the maximum absorption. Thus a maximum wavelength of 530 nm is achieved at an R_1/d ratio of 1.6 (Cf. Table 2) irrespective to the surrounding medium. The experimental results reported by Yusuke MORIGUCHI and co-authors [33] have showed a very weak variation of the SPR when it increases silica thickness coated with gold nanosphere. We can also quote the work on references [31] and [34] in which the authors have carried experimental studies on the optical properties of Au/SiO₂ nanoparticles. According to these three references [31,33,34], experimental and simulated data are in reasonable agreement with respect to the SPR position in the visible spectrum.

In summary, the thickness of the silica shell does not modify significantly the plasmon response. When particle is emerged in water, Au/SiO₂ red shifted about of 25 nm and 10 nm in ethanol (see Figure 3). In addition, increase core size give the same results as increasing of shell thickness. After the first step of silica coating on gold, the results show clearly that Au/SiO₂ structure SPRs slightly. Samantha Soulé and al [6] have obtained a redshift (resonance peak toward 800 nm) into their system, by experimental method with the Ag/Au/SiO₂ structure,

where in their experiment the core was composed of Ag and Au nanoparticle.

3.2.2. Gold Coating on Silica

In this step, gold is considered as the coating thus the shell and silica nanoparticle the core. The simulation absorption cross section spectra are plotted in Figure 5 and Figure 6, for various shell thickness from 3 nm to 20 nm in different dielectric constants of the surrounding medium. In this party, we report the results obtained for gold nanoshells with (silica core radius/gold shell thickness) parameters of (10-50 nm/4-100 nm). These particles are emerged in surrounding medium of refraction index $n=1.333$ and $n=1.359$ which is water and ethanol respectively, all results of simulation are summarized in Table 3.

Figure 5 shows the absorption cross section of SiO₂/Au core/shell nanospheres with six shell thicknesses that are 3 nm, 4 nm, 7 nm, 10 nm, 14 nm and 20 nm. These gold layer are used to coat different size of core, radius of core used in this step are $R_1=50$ nm, $R_1=30$ nm, $R_1=15$ nm and $R_1=10$ nm.

It is important to notice that silica particles do not show any absorption peak from the visible range to the infrared region. It is interesting to notice a relation between the shell thicknesses, the core size and the SPR wavelength. It is well known that, if the thickness of the shell decreases, resonance wavelength red-shifted and band intensity decrease. These results are according to reference [35,36]. But we observe that, on increasing the core size of metallic oxide (i.e. silica), the Surface Plasmon Resonance re-shifted far away and its intensity increases.

For the same shell thickness, core particle with bigger size are highly red-shifted as shown in Figure 6.

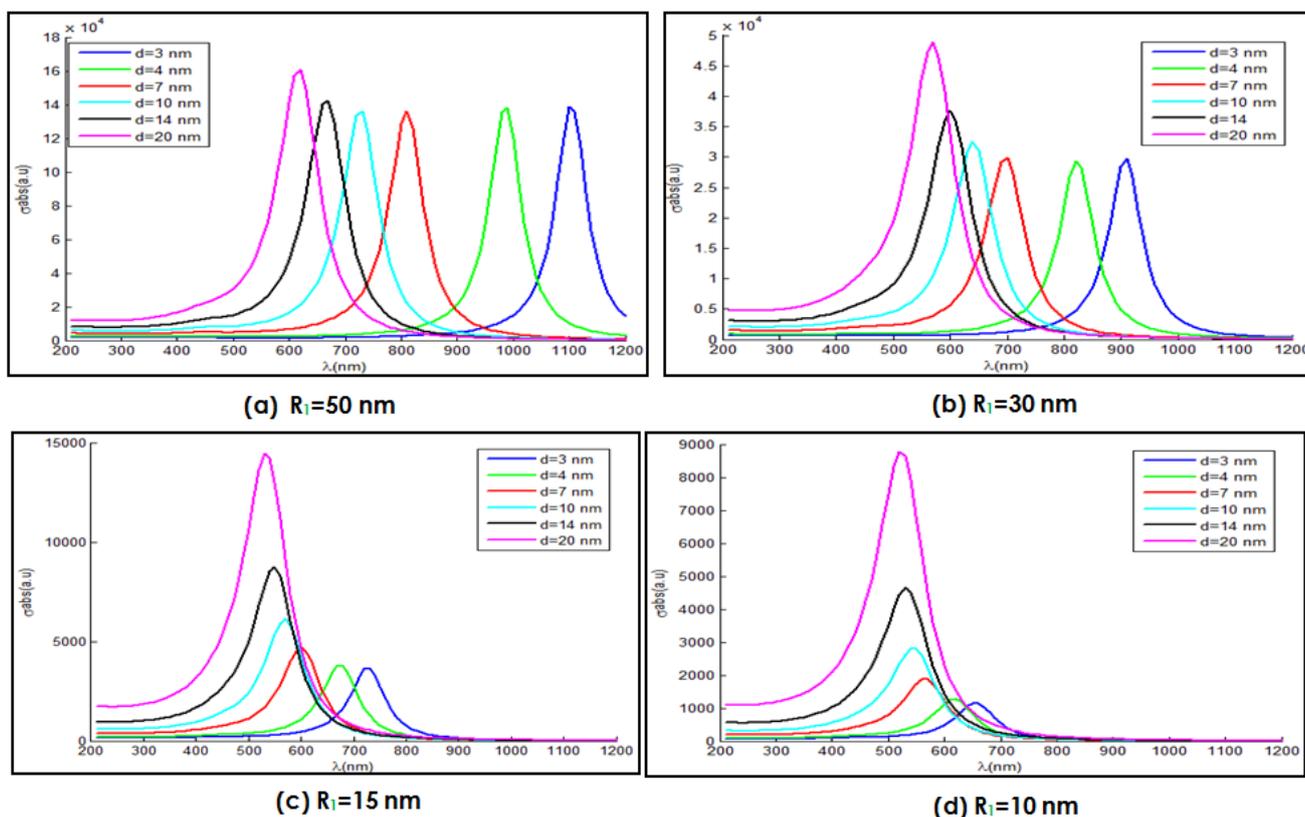


Figure 5. Absorption cross section for SiO₂/Au core/shell nanospheres at varying thickness shell in water for different core radius

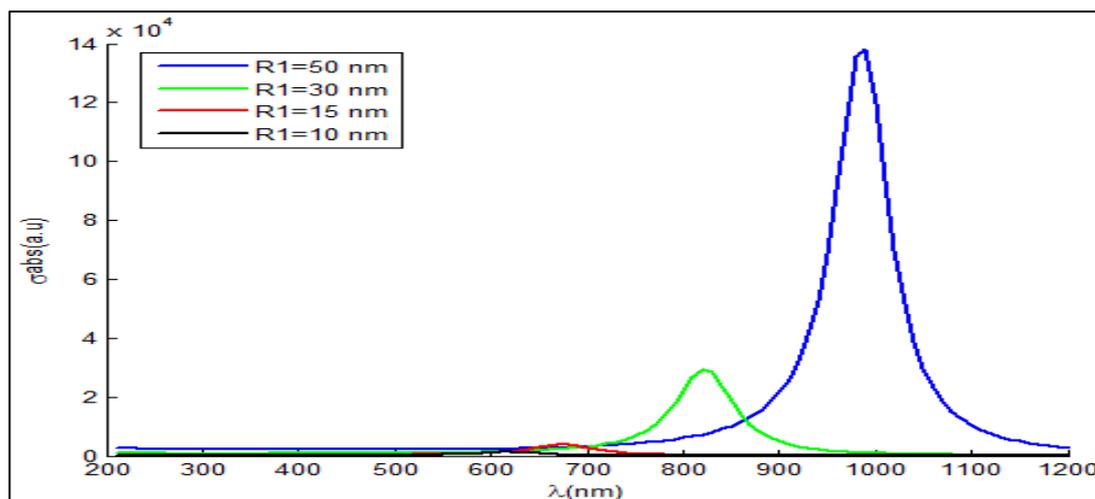


Figure 6. Absorption cross section for SiO₂ core /Au shell a radius core function

Table 3. Wavelength of the resonance band according with the surrounding environment, shell thickness and size core

Gold thickness (nm)	Resonant wavelength (nm)									
	Nanospheres: SiO ₂ /Au									
	R ₁ =10 nm		R ₁ =15 nm		R ₁ =20 nm		R ₁ =30 nm		R ₁ =50 nm	
	n=1.333	n=1.359	n=1.333	n=1.359	n=1.333	n=1.359	n=1.333	n=1.359	n=1.333	n=1.359
4	620	620	670	680	730	730	820	830	990	1000
7	570	570	600	610	630	640	700	700	810	820
10	550	550	570	570	590	600	640	650	730	730
14	530	540	550	550	570	570	600	600	670	670
20	520	530	530	540	550	550	570	570	620	620
30	520	520	520	530	530	530	550	550	580	580
40	520	520	520	520	520	530	530	540	560	560
50	515	520	520	520	520	520	530	530	550	550
60	515	520	520	520	520	520	520	530	540	540
70	515	520	515	520	520	520	520	520	530	540
80	515	520	515	520	520	520	520	520	530	530
90	515	520	515	520	515	520	520	520	530	530
100	515	520	515	520	515	520	520	520	520	530

The thickness of the shell is fixed at 4 nm and the influence of core particle size is study in water. The core size effect reveals a clear high displacement into the infrared as the radius of core increase.

Surface Plasmon Resonance is located at 990 nm, 820 nm, 670 nm and at 620 nm for the core radius equal to 50 nm, 30 nm, 15 nm and 10 nm, respectively. Therefore the surface plasmon band increase in intensity within the increase of the size of the core. Core size is known to be a very important feature that can significantly influence the physical properties of the material. The result indicates that the Plasmon band of SiO₂/Au is more sensitive to the big nanospheres with a big core.

All simulation results are reported in Table 3 in, which we report on the effect of core size on SPR. The thickness of gold layer shown in Table 3 was estimated to be 4, 7, 10, 14, 20, 30, 40, 50, 60, 70, 80, 90 and 100 nm and study is done in to two surrounding medium as reported into Table 3.

From the results obtained, we can say that silica (core)/gold (shell) SPR can be easily shifted in to near infrared region by simple variation of ratio core radius/shell thickness. As shown in Figure 5 and Table 3, for gold coating silica, according to the nature of the

medium and thickness of the gold shell but also size of SiO₂ core material, SiO₂/Au nanosphers absorb light in the near infrared region thus can be use biological applications.

Table 3 shows that more the ratio becomes high, nanospheres particles SPR can be shifted in near infrared region. For example in water, for the ratio SiO₂/Au= 2.5; 3.75; 5; 7.5 and 12.5, these particles have shifted at 620, 670, 730, 820 and at 990 nm, respectively.

In summary, we have studied the general behavior of the Surface Plasmon Resonance on small and large nanoparticles in different surrounding environment. For instance, the location of these resonances of these nanospheres are depending on four parameters which can influences their optical properties (i) the core radius (ii) thickness of shell (iii) surrounding medium (iv) the surface geometry of core-shell configuration.

With the aim to optimize the materials in near infrared region, the results are showed in Table 3. This work shows that the particles with large core give the resonance at longer wavelength more than the small core (Figure 6). When the core size of the particle increases, the Surface Plasmon Resonance becomes red shifted more and more important. Study shows that coating silica as core and

gold as shell can be use to turn the gold nanosphers SPR in the near infrared region.

4. Conclusion

In this work we have study the turn-ability of the gold nanoparticle SPR to two different combinations (1) silica thin film coating on gold nanospheres and (2) gold thin film coating on silica nanoparticles. And the SPR have been probed into two different mediums (water and ethanol).

The results show initially that wavelength of plasmon resonance of a simple Au/SiO₂ nanosphers does not much depending on the surrounding medium whereas for the SiO₂/Au nanosphers three parameters are considered for the control the optical response of the material: surrounding medium, shell thickness and core size.

Note that the results show that SiO₂/Au nanosphers are composed of a dielectric core of silica covered by a thin gold shell their SPR is highly red-shifted and can be ideal candidates for enhancing cancer treatment, cancer detection. Important remark can be pulled in this study, SiO₂/Au nanosphers with large core absorbed more light.

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