

# Tuning and Exploitation of the Surface Plasmon Resonance on Gold/Cadmium Sulfide Nanoshell for Performance Enhancement in Photocatalytic

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**Abstract** Core-shell nanoparticles based on Au or Ag nanoshell core and cadmium sulfide semiconductor shell with different sizes have been simulated using Mie and Drude approach. The results show that gold nanosphere coated by cadmium sulphide results has a maximum wavelength at 530 nm. This plasmon peak corresponds to a ratio equal to 1.66. The optimized nanoshell allows light absorption in the visible region before cadmium sulfide coating. Thus, these materials Au/CdS especially are good candidates for the design of functional nanocomposites used for photocatalytic application due mainly to its good light transparency.

**Keywords:** core-shell, gold, silver, cadmium sulfide, mie theory, nanoparticles

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## 1. Introduction

Solar energy is free and almost unlimited, thus its exploitation obviously raises great hopes. The exploitation of solar energy, free and almost unlimited, obviously raises great hopes. The photovoltaic cell a priori is one of the privileged means to directly convert the solar rays into electricity. Among the materials used for this conversion is cadmium sulfide (CdS), which has been in great demand due to its good physicochemical properties. Indeed, the CdS has made it possible to achieve relatively high photovoltaic conversion efficiencies using easily implemented techniques such as the chemical bath deposition (CBD) technique [1] or by evaporating chemically synthesized [2].

CdS is a II-VI compound, n type semiconductor with energy gap of 2.45 eV. It is used in photovoltaic, photonic and optoelectronics. In detail, cadmium sulfide thin film have received considerable attention due to their applications in the fabrication of photoconductors [3], space charge limited diodes [4], photovoltaic devices [5,6] and transistors [7].

Metal-semiconductor hybrid nanoparticles are promising candidates for applications in solar energy conversion [8], photocatalysis [9,10] and electronic devices [11]. The nanoscopic dimensions of their components, result in size and shape-dependent electronic and optical properties. These mainly result from quantum confinement in the

semiconducting part ("exciton") and the dielectric confinement ("surface plasmon") in the metal part, leading to a very high polarizability at the plasmon frequency. Surface plasmons are collective excitations of the electrons at the interface between a conductor and an insulator and are described by evanescent electromagnetic waves that are not necessarily located at the interface. Surface plasmon appear in a number of different phenomena, including the optical response of materials at different scales, to Casimir and van der Waals forces between macroscopic bodies [12]. Plasmonic nanoparticles are appreciable for scientific research because of their interesting applications in the field of photonics, electronics, optical sensing, imaging [13,14,15]. Surface plasmon resonance is a function of size, shape, inter-particle distance, surface coverage and surrounding medium [12,16].

Plasmonic nanoparticles compensate high losses in solar cells, occurring due to partial absorption of the solar spectrum and thermalization losses of photons. These losses are the primary challenge that has generally been addressed to overcome the limitations of photovoltaic efficiency. The incorporation of these nanoparticles enhances the light scattering in the photoactive absorb layer, which improves the overall performance of solar cells.

In this article, we use gold and silver nanoparticles for solar cell applications because their localized surface plasmon resonance have been performed and are localized in the visible range. For gold nanoparticles resonance plasmon is at 515nm [17,18] and at 400 nm for silver nanoparticles [19,20].

We compare theoretical calculations results based on extinction measurements of hybrid Au/CdS and Ag/CdS nanoparticles. Thus, the optical properties of CdS-Au and CdS-Ag hybrid particles arise from a complex interplay of the components. The rapid electron transfer from the semiconductor to the metal leads to quenching of the fluorescence from the semiconductor part [21,22]. The optical properties of these nanostructures, for example, often exhibit interesting deviations from either their individual components or from a physical mixtures of the two components. These optical effects include a shift in the plasmon resonance of noble metal nanocrystals when combined or coated with other materials or changes in the photoluminescence intensity of semiconductor nanocrystals which can be attributed to the overlap for the electronic structures of the different components [23].

In this article, we simulated the optical properties of Au/CdS and Ag/CdS core-shell nanospheres using the solution of Maxwell's equations for spherical particles using Mie-Gans theory combined with Drude model. We calculate the optical cross section area, properties such as the extinction, absorption and scattering cross sectional area for gold/cadmium sulphide (Au/CdS) and silver/cadmium sulphide (Ag/CdS) using Matlab software.

## 2. Method and Material

At this point, it is usual to define absorption and scattering cross-sections of the sphere core/shell by dividing  $\sigma_{abs}$  and  $\sigma_{sca}$ . A definition of cross-sections as characteristic quantities only for the scattering particle is a serious unsolved problem. Nevertheless, we define cross-sections  $\sigma_{abs}$  and  $\sigma_{sca}$  as [24].

$$\sigma_{abs} = \frac{2\pi}{\lambda\epsilon_0} \text{Im}(\alpha) \quad (1)$$

$$\sigma_{sca} = \frac{k^4 |\alpha|^2}{6\pi\epsilon_0^2} \quad (2)$$

So the absorption and scattering cross-sections are both functions of  $\omega$  and  $\lambda$ . And the total extinction cross-section  $\sigma_{ext}$  as

$$\sigma_{ext} = \sigma_{abs} + \sigma_{sca} \quad (3)$$

Where,  $k$  and  $\alpha$  are defined as:

$$k = \frac{2\pi\sqrt{\epsilon_3}}{\lambda} \quad (4)$$

$$\alpha = 4\pi R_2^3 \epsilon_0 \left\{ 1 - \frac{3 \left[ \begin{array}{l} (\epsilon_2 - \epsilon_1) R_1^3 \\ + (2\epsilon_2 + \epsilon_1) R_2^3 \end{array} \right] \epsilon_3}{\left[ \begin{array}{l} 2(\epsilon_2 - \epsilon_1)(\epsilon_3 - \epsilon_2) R_1^3 \\ + (2\epsilon_2 + \epsilon_1)(2\epsilon_3 + \epsilon_2) R_2^3 \end{array} \right]} \right\} \quad (5)$$

The optical constants such as real part  $\epsilon_r$  and imaginary part  $\epsilon_i$  of the complex dielectric function, the refractive index  $n$  and extinction coefficient  $k$  are the determining parameters for electronic polarizability of the nanoparticles. Thus, there are two sets of quantities that are often used to

describe optical properties: the real and imaginary parts of the complex refractive index  $\tilde{n} = n + ik$  and the real and imaginary parts of the complex dielectric function (or relative permittivity)  $\epsilon = \epsilon_r + i\epsilon_i$ . These two sets of quantities are not independent. Either may be thought of as describing the intrinsic optical properties of matter. The relations between the two are [25]

$$\epsilon = \epsilon_r + i\epsilon_i = \tilde{n}^2 = (n + ik)^2 \quad (6)$$

The drude model dielectric function is

$$\epsilon = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (7)$$

Where  $\omega$  is the angle frequency of incident light,  $\gamma$  is the damping constant which is related to electron scattering processes,  $\omega_p$  is the plasma frequency.

**Table 1. Values of the plasma frequency  $\omega_p$ , the damping constant  $\gamma$  and  $\epsilon_\infty$**

Metal	$\hbar\omega_p$ (eV) [26]	$\hbar\gamma$ (eV) [27]	$\epsilon_\infty$ [28]
Gold [Au]	9.03	0.0708	2.2715
Silver [Ag]	9.01	0.0212	1.7381

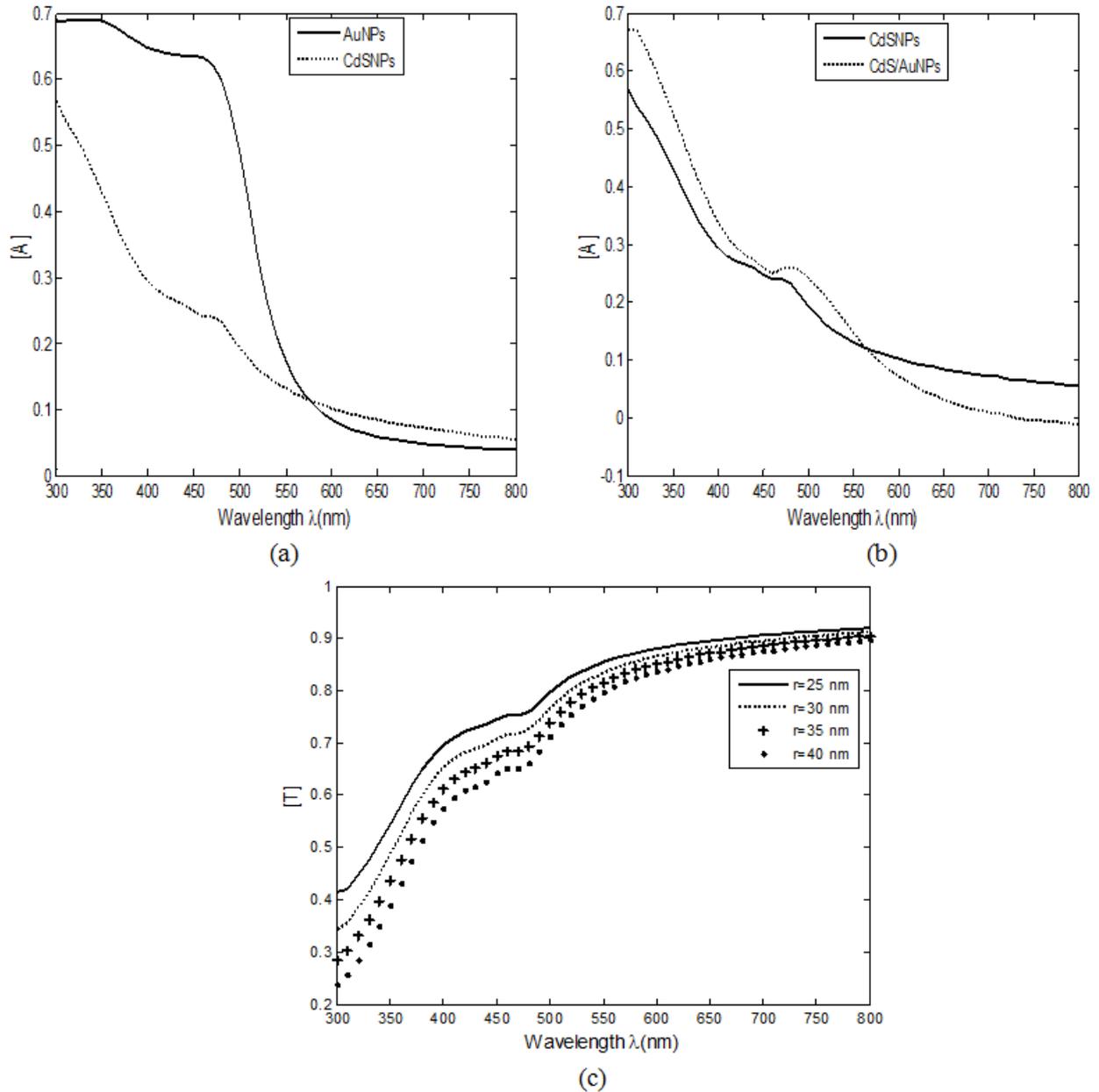
The simulation was done using the optical values ( $n$ ,  $k$ ) suggested by Hossam ElAnzeery and al [29] for CdS.

## 3. Results and Discussion

### 3.1. Absorption and Transmittance of CdS Nanoparticles

For the purposes of illustration we will use the model developed in our previous article [30] to calculate the optical properties of the gold and cadmium sulphide. The particles are considered to be spheres of radius  $r=25$  nm distributed on the surface of the substrate. For the substrate we take the optical values ( $n$ ,  $k$ ) and considered the surrounding medium as air. The calculated absorption (e.g. Figure 1.a, b) and transmittance (e.g. Figure 1.c) of the gold and cadmium sulfide nanoparticles, depending on the wavelength, varies between 300 to 800 nm.

It is known that semiconductor nanoparticles have unique size-dependent chemical and physical properties [31,32]. As shown in these articles, the size of semiconductor particles decreases to the nanoscale, the band gap of the semiconductor increases, causing a blue shift in the UV-Vis absorption spectra. Our study first shows a decreasing evolution of CdS absorption with increasing wavelength. This absorption varies from 74.99% to 8.66% for wavelengths from 300 to 800 nm, respectively. The experimental work of Ramamurthy et al. [33], showed exactly the same evolution of CdS nanoparticles absorption. This allows us to validate our study code. Figure 1.a indicates, CdS materials exhibit an absorption peak of about 482 nm. The spectrum of the gold capped CdS nanoparticles are shown in Figure 1.b. As illustrated in Figure 1.b, the CdS/Au nanoparticles exhibited an absorption peak at 485nm (let an offset of 3 nm).



**Figure 1.** Absorption spectrum of Au, CdS (a), CdS/Au (b) and transmittance spectrum of CdS (c)

In the absorbance spectra of the gold nanoparticles, there were two obvious turning points in the temporal evolution of the absorption spectrum during the simulation of gold nanoparticles. Absorbance properties of metal nanoparticles is dependent on shape and size of metal nanoparticles, which results in a strong absorbance band in the visible region (300 nm-500 nm) more than 60% and after 500 nm, there is a decreasing trend to less than 10% in the range 500 nm to 800 nm. Figure 1.b, shows the obtained results after deposited gold nanoparticle on the CdS. There is a slight increase in the 300-500 nm region and a decrease in the 500-800 nm range. In Figure 1.c, the transmission spectrum of a CdS nanoparticle is presented. Contrary to the absorption phenomenon, an opposite evolution of transmittance is observed for CdS. The transmission in the high-energy region extends up to 300 nm. CdS nanoparticles presented a good optical transmission. According to the Figure 1.c, when the radius CdS increase (25-40 nm), the transmission rate decrease.

### 3.2. Optical Properties: Extinction Cross Section

The optical properties of gold, silver and cadmium sulphide nanospheres are highly dependent on the nanospheres radius. The extinction cross section area diagrams of Au, Ag and CdS nanospheres with radius of 15 nm and immersed in a medium with a refractive index of 1.333 (water).

All spectra have a peak resonance at visible spectrum, caused by the oscillations of the nanosphere electrons on the surface. The simulation results are given in Figure 2 in comparison with the experimental result. As the measured spectra are for a dilute solution of nanoparticles dissolved in water with a well defined size and shape, we model the nanoparticles as isolated hybrid particles that are not interacting with each other. For gold, silver and cadmium sulphide we obtained following plasmon resonances. For gold nanoparticles, the plasmon resonance peak is located around 515 nm, and at 410 nm for silver

nanoparticle. For cadmium sulphide, the simulation obtained a small plasmon peak at around 475 nm.

In addition, the surface plasmon resonance peak positions of the simulated spectra show an excellent agreement with

those values corresponding to experimentally measured spectra. These reference works are in [17,18] for gold, [19,20] for silver and [34] for cadmium sulphide nanoparticles.

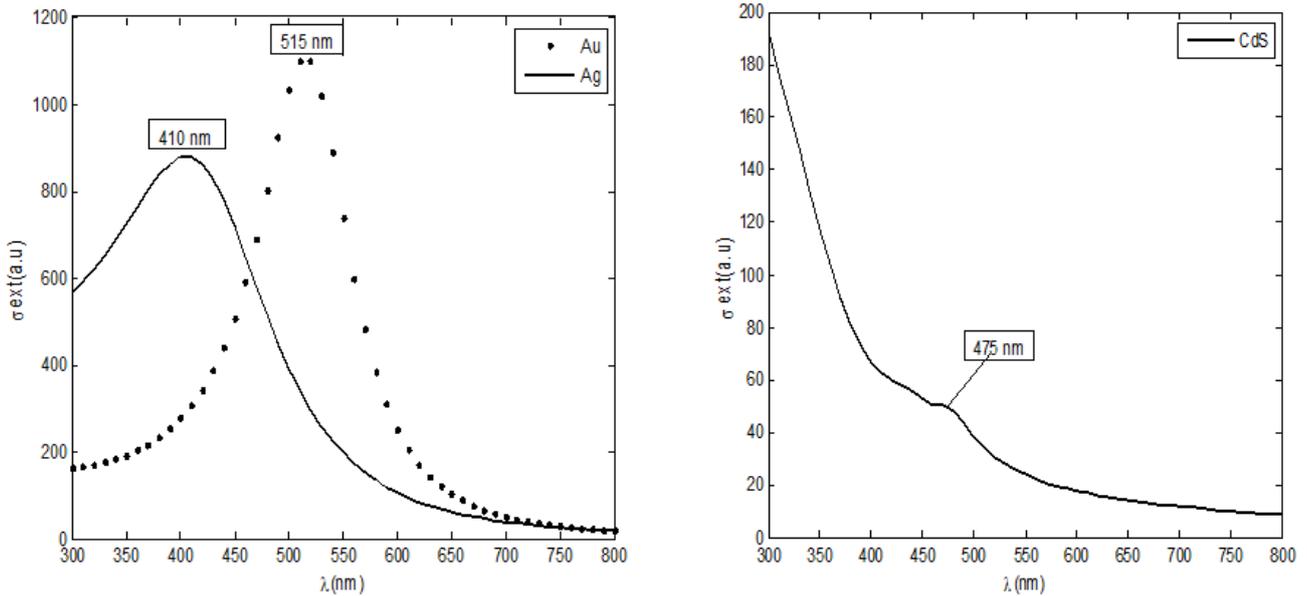


Figure 2. Extinction cross section of gold, silver and cadmium sulphide

### 3.3. Optical Properties of Core/Shell Nanoparticles

Core-shell nanoparticles are a class of nanostructured materials that have recently received increased attention owing to their interesting properties and broad range of applications in catalysis, biology, materials chemistry and sensors.

#### 3.3.1. Effect of the Core Material and Shell Size

In order to examine the influence of CdS shell size on extinction spectrum of composite nanoparticle, R1 core size is fixed to 15 nm. The extinction spectra with different shell sizes are shown in Figure 3 and the results

of the simulations are summarized in Table 2. The spectra of conventional core/shell structure of Au/CdS and Ag/CdS are also presented for comparison. As illustrated in Figure 2, the extinction efficiency of Ag/CdS composite nanoparticle is selectively improved in the visible region as CdS shell size varies. This is attributed to the excitation of localization surface plasmon resonance on silver surface at corresponding wavelength. As shown in the Table 2, there is an evolution of plasmon resonance towards the long wavelength of 410 nm corresponding to silver metal alone at 470 nm after the addition of a CdS layer of size 30 nm. It can clearly be observed in Figure 3 that these spectra follow the same trend with CdS size.

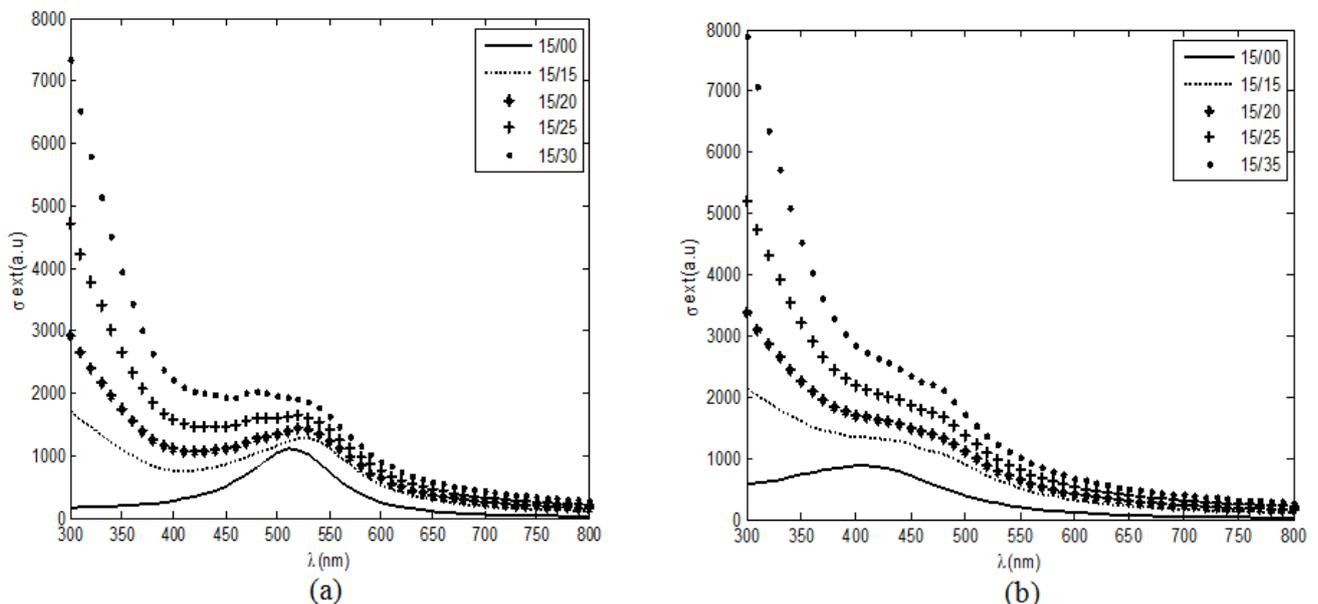


Figure 3. Relationship between extinction properties and shell thickness of metal/CdS: Au/CdS (a) and Ag/CdS (b)

In the case of gold nanoshells, when the core radius is fixed to 15 nm, as shown in Figure 3.a, the extinction spectra of nanoparticles with different CdS layer thicknesses (00, 15, 20, 25, 30, 35 nm) show an evolution quite different from that of nanoshells with silver as core. After a maximum for Ag/CdS (15/15), corresponding to a resonance plasmon of 525 nm, the resonance wavelength is blue shifted from 525 to 475 nm as the shell radius varies from 15 to 35 nm. Of these two materials, simulation results indicate well that the resonance of silver nanoparticle is boosted up as the ratio of intermediate layer thickness to core radius decreases (as shown Figure 3.b). Considering the evolution of the extinction spectra shown in Figure 3, it is possible to propose the following mechanism for the formation and growth of the Au/CdS and Ag/CdS nanoparticles for visible application such as photocatalysis or photovoltaics. This is how, our results reveal that of localized surface plasmon resonance should be excited in wavelength range below 525 nm and 475 nm for Au/CdS and Ag/CdS, respectively. A very important aspect to consider in the reasons of the evolution towards the CdS peak is the value of the dielectric constant of the envelope (i.e.  $\epsilon_{CdS}=7.11$  [35] which is much higher than that of gold (i.e. less than  $\epsilon_{Au} \approx 4$ ) and silver (less than  $\epsilon_{Ag} \approx 0.25$ ) metal [36].

Table 2. Localized surface plasmon resonance

Composite Au@CdS	$\lambda_{max}$ (nm)	Composite Ag@CdS	$\lambda_{max}$ (nm)
15/00	510	15/00	410
15/15	525	15/15	420
15/20	523	15/20	440
15/25	520	15/25	470
15/30	500	15/30	470
15/35	475	15/35	475

### 3.3.2. Core Size Effect on Surface Plasmon Band

The simulation extinction cross section spectra is plotted in Figure 4, for various core thickness ranging from 15 nm to 40 nm. During this exercise, shell thickness is kept constant and equal to 15 nm. These particles are immersed in surrounding medium of refraction index  $n=1.333$ . As shown in Figure 4, spectral location of surface plasmon resonance is gradually red-shifted with respect to corresponding rise in the value of the core size. The simulation characterization of core/shell particles show that with increasing core thickness or otherwise by increasing the ratio of core size to shell size the intensity of the resonance band increases and sifted toward the higher wavelength region

Quantitatively, surface plasmon resonance is localized at 525 nm, 527 nm, 530 nm, 530 nm, 530 nm and 530 nm for core radius equal to 15 nm, 20 nm, 25 nm, 30 nm, 35 nm and 40 nm, respectively. As it is shown in Figure 4 and Table 2, it can be said that the maximum resonance band is reach when the gold thickness is 25 nm and cadmium sulfide thickness is 15 nm or a ratio of 1.66. We note that, after reaching a wavelength of 530 nm, the resonances band are no longer sensitive to the change into the ratio core/shell but the plasmon band increased in intensity.

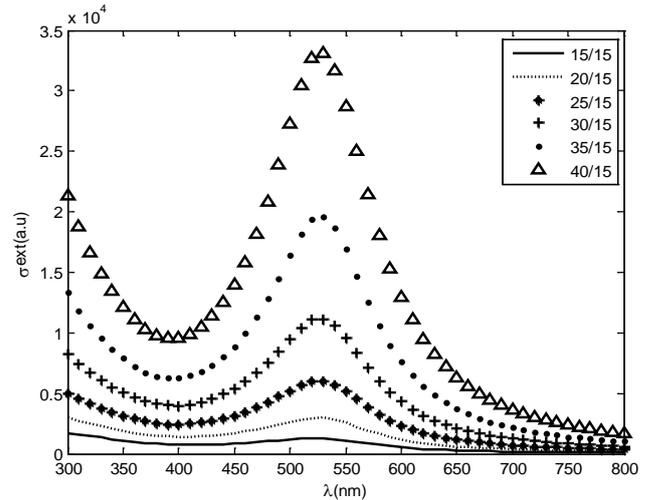


Figure 4. Extinction cross section for Au/CdS nanospheres at varying radius core at shell thickness of 15 nm

## 4. Conclusion

In this paper, we demonstrated the capabilities of the Mie theory and quasi-static approximation to calculate the optical response of the metallic nanoshell. We have implemented a simple method that allows us to optimize A/CdS and Ag/CdS nanoshells. The method presented in this study results in the formation of Au and Ag surrounded by CdS semiconductors with different thicknesses. The results show clearly that wavelength of plasmon resonance of gold and silver / cadmium sulfide nanospheres are highly dependent on the core/shell ratio. Thus, three parameters are fundamental to correctly identify the plasmon resonance band: surrounding medium, shell thickness and core size. The quantitative information deduced from the simulation analysis shows, the maximum peak resonance response of Au/CdS nanoshell is observed in the visible region at 530 nm with a ratio Au/CdS=1.66.

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