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Size dependence of refractive index of gold nanoparticles

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Abstract
The extinction spectra of spherical gold nanoparticles suspended in a homogeneous media were measured and the results were adjusted with Mie's theory together with an appropriate modification of the optical properties of bulk material considering the limitation that introduces the size of nanoparticles on the dielectric function. Usually, the contribution of free electrons to the dielectric function is modified for particle size, while the contribution of bound electrons is assumed to be independent of size. This work discusses the separated contribution of free and bound electrons on the optical properties of particles and their variation with size for gold nanoparticles. The effects of dielectric function and its changes with size on extinction spectra near plasmon resonance are considered. The damping constant for free electrons was changed with size as usual and a scattering constant of $C = 0.8$ was used. For the bound electron contribution, two different models were analysed to fit the extinction spectra: on the one hand, the damping constant for interband transitions and the gap energy were used as fitting parameters and on the other, the electronic density of states in the conduction band was made size-dependent. For the first model, extinction spectra corresponding to particles with radius $R = 0.7$ nm were fitted using two sets of values of the energy gap and damping constant: $E_g = 2.3$ eV and $\gamma_b = 158$ meV/$\hbar$ or $E_g = 2.1$ eV and $\gamma_b = 200$ meV/$\hbar$. For the second model, a simple assumption for the electronic density of states and its contribution to the dielectric function in terms of size allowed to adjust extinction spectra for all samples explored (from 0.3 to 1.6 nm radius). This last model uses only one parameter, a scale factor $R_0 = 0.35$ nm, that controls the contribution of the bound electrons in nanoparticles. Contrast between the maximum and the minimum in the extinction spectra near the resonance at 520 nm or alternatively the broadening of the plasmon band can be used to determine the size of gold nanoparticles with radius smaller than 2 nm.

1. Introduction

Metal nanoparticles show very complex and interesting optical properties known from the beginning of the last century. Recent advances in the production, manipulation and measurements on the nanometre scale have revitalized this field in recent years. Applications of nanoparticles to biological sensors [1] and optoelectronic devices, among others, are now receiving increasing attention. Guiding light in integrated optical systems and interfacing with electronic components remain important challenges for research and development today. Nanostructured metals are believed to

be one of the key components of such future optoelectronic devices [2].

One of the most characteristic features encountered in metal nanoparticles is electromagnetic resonances due to collective oscillations of the conduction electrons named 'plasmons'. Plasmons excited by light lead to strong light scattering and absorption together with an enhancement of the local electromagnetic field. Plasmon modes in metals such as gold and silver fall in the visible spectral region. The spectral characteristics of plasmons have been used frequently to characterize the size of gold nanoparticles in the range 10–100 nm radius [1].

Recently, we have shown a method for sizing gold nanoparticles below 7 nm by fitting extinction spectra with Mie's theory together with a conveniently modified bulk refractive index [3]. The modification follows the idea of Kreibig and von Fragstein [4], who considered that the damping constant in Drude's model is increased due to additional collisions of free electrons with the boundary of the particle. This fact produces a size dependence of the dielectric function and consequently of the refractive index. As usual, the real part of the dielectric function evaluated for the bulk was used without any modification, but the effect of size limitation on the imaginary part of the dielectric function was considered. Recently, Arbouet *et al* [5] made similar assumptions: only free electrons were considered and only the imaginary part of the dielectric function was modified by size.

For noble metals, transitions of bound electrons to conduction levels contribute appreciably to the dielectric function. Recently, Pinchuk *et al* [6] have analysed the influence of interband electronic transitions on the frequency, amplitude and bandwidth of the surface plasmon resonance in small metal clusters in the Rayleigh approximation. Their theoretical results for silver and gold, including the interband transitions in the model, lead to a more reasonable value for the plasmon bandwidth, although the experimental results are still different from calculated values.

The size effect over the dielectric function will be studied further in this work in order to analyse the influence on the extinction spectra of gold nanoparticles. Both free and bound electron contributions will be considered and the values of the different parameters involved in the model will be determined.

2. Experimental section

The gold nanoparticles used in this work were synthesized as 'reverse micelles' in water–hydrocarbon phases and isolated with a stabilizer. Details of the preparation of the particles can be found elsewhere [7]. The particles are capped with the stabilization agent and this fact helps to maintain the gold particles in a dispersion state in organic solvents. For this reason samples were dispersed in heptane for the UV–visible extinction measurements.

Extinction spectra of a suspension of gold nanoparticles in heptane were recorded between 300 and 900 nm using a Beckman Spectrophotometer (Model 600). The optical density for a 1 cm light path was kept below one to avoid multiple scattering effects. The spectrum for a gold sample named ATS-6 is shown in figure 1. The insets show a TEM image (JEOL 1010, at 80 kV) of this sample and the corresponding

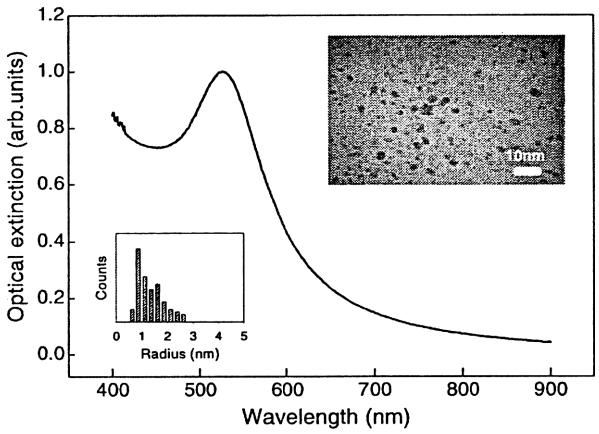

Figure 1. Optical extinction spectra and TEM image of gold ATS-6 sample ($R = 1.3$ nm).

histogram. The nanoparticle shape is nearly spherical. The mean radius was determined from statistical analysis of the histogram of this picture discarding obvious superposition. For this sample, the mean radius was determined as 1.3 nm.

Optical extinction spectra of other samples corresponding to particles prepared with different stabilization agents ATS, *N*-[3-(trimethoxysilyl) propyl] diethylenetriamine (Aldrich Tech.), AES, 3-(2-aminoetilaminopropil) trimethoxisilane) (Aldrich, 97%); and APS, 3-aminopropyltrimethoxysilane (Aldrich, 97%); were measured. Particles prepared with APS and AES are expected to be smaller than samples prepared with ATS, that range between 1.3 and 1.9 nm radius. Spectra of some of them will be shown in section 4, where the main feature is a reduction in the contrast between the maximum at the plasmon band and the minimum near 440 nm in the extinction. Unfortunately, no good microscopic images of all the samples are available, due mainly to coalescence when they were prepared for observation.

3. Theoretical framework

For noble metals, where there is a substantial bound electron component, the dielectric function for the bulk can be decomposed into two terms, a free electron term and an interband, or bound electron, term [8]. Since the dielectric function is additive, it can be written as

$$\varepsilon_{\text{bulk}}(\omega) = \varepsilon_{\text{bound-electrons}}(\omega) + \varepsilon_{\text{free-electrons}}(\omega). \quad (1)$$

For bound electrons, the complex dielectric function can be calculated taking into account the interband transitions from the d-band to the conduction sp-band near the L point in the Brillouin zone of gold [9]. Inouye *et al* [10] have shown a simplified expression of this calculation assuming that the curvature of the d-band can be ignored. The following expression, where a misprint in the original paper is corrected, will be used throughout this work:

$$\varepsilon_{\text{bound-electrons}}(\omega) = Q_{\text{bulk}} \int_{\omega_g}^{\infty} \frac{\sqrt{x-\omega_g}}{x}[1 - F(x,T)] \times \frac{(x^2 - \omega^2 + \gamma_b^2 + \mathrm{i}2\omega\gamma_b)}{(x^2 - \omega^2 + \gamma_b^2)^2 + 4\omega^2\gamma_b^2}\,\mathrm{d}x, \quad (2)$$

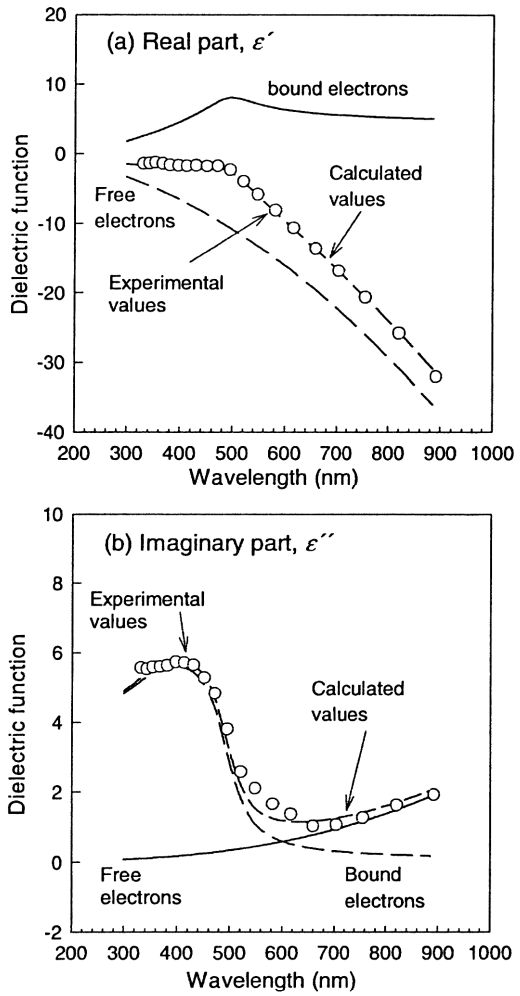

Figure 2. Dielectric function for bulk gold calculated with equations (1), (2) and (3) (lines) and experimental values (hollow circles) from Johnson and Christy [11]. The fitting parameters used are given in table 1.

where $\hbar\omega_g$ is the gap energy (E_g) for gold; $F(x, E_F, T)$ is the Fermi energy distribution function of conduction electron of energy $\hbar x$ at the temperature T with Fermi energy E_F; γ_b represents the damping constant in the band to band transition and Q_{bulk} is a proportionally factor.

The complex dielectric function for the free electrons can be written as usual:

$$\varepsilon_{free-electrons}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma_{free}\omega}, \tag{3}$$

where ω_p is the bulk plasma frequency and γ_{free} is the damping constant (the inverse of the collision time for conduction electrons) in the Drude model.

Figure 2 shows the results of our calculations for the bulk dielectric function using equations (1)–(3). For the free electron contribution, values given by Johnson and Christy [11] and Granqvist *et al* [12] for γ_{free} and ω_p, respectively, were used. For the bound electron contribution, the damping constant γ_b given by Inouye *et al* [10] was used. Other parameters in equation (2), such as Q_{bulk}, E_g and E_F, were adjusted to fit the experimental values for bulk gold. The experimental optical properties for gold were taken from Johnson and Christy [11]. This dielectric function yields n and k values similar to those given by Palik [13]. All the parameters used in this work for bulk gold are summarized in table 1.

For metallic particles, the plasma frequency ω_p can be calculated from

$$\omega_p^2 = \frac{N/V}{m\varepsilon_0}e^2, \tag{4}$$

where N is the amount of free electrons in a volume V, m is the effective mass of an electron (near the free electron mass in the case of gold) and e and ε_0 have the usual meaning. Each atom of gold contributes with one free electron to N and the density N/V remains constant for different sizes. For this reason the plasma frequency ω_p is assumed independent of the size. However, the damping, related to the mean free path for free electrons, is strongly affected by the size. In particles smaller than the mean free path of conduction electrons in the bulk metal, the mean free path is dominated by collisions with the particle boundary [4, 12, 14, 15]. For small particles, the damping constant for the free electron contribution is increased due to additional collisions with the boundary of the particle, and it can be written as

$$\gamma_{free}(R) = \gamma_{bulk} + C\frac{v_F}{R}, \tag{5}$$

where v_F is the electron velocity at the Fermi surface and R is the radius of the particle. A value $v_F = 14.1 \times 10^{14}$ nm s^{-1} was used in the calculations [12]. C is the scattering constant that includes details of the scattering processes. Its actual value is not free from controversy; values from 0.1 to 2 have been theoretically justified [16].

For the contribution of bound electrons, no functional form is known to change the parameters in equation (2) as a function of the size of the particle. However, we can assume that, similarly to the change made in the damping constant for the free electron contribution, the value of γ_b can be made size dependent. Besides that, E_g can change also with size. Alternatively, Logunov *et al* [17] introduced the idea that the electronic density of states is different for nanoparticles of different size. This fact affects equation (2), where part of the integrand is just the density of states in the upper band. Since small particles have larger spacing between electronic states, it is valid to conclude that the density of states will be smaller for very small nanoparticles. We propose to take account of this fact by changing the proportionality factor Q_{bulk} in the contribution of bound electrons from its value accepted for the bulk to $Q_{size} = Q_{bulk}[1-\exp(R/R_0)]$, where R is the radius of the particle and R_0 is the scale factor, that represents the range for which the density of states can be considered to reach the value of the bulk.

To calculate the optical extinction spectra corresponding to the studied small gold nanoparticles we assumed that only the dipole absorption in the Mie calculation contributes to the cross section [8, 18],

$$\sigma(\lambda, \text{size}) \propto \frac{R^3 n_0^3 \varepsilon''_{size}/\lambda}{(\varepsilon'_{size} + 2n_0^2)^2 + (\varepsilon''_{size})^2}, \tag{6}$$

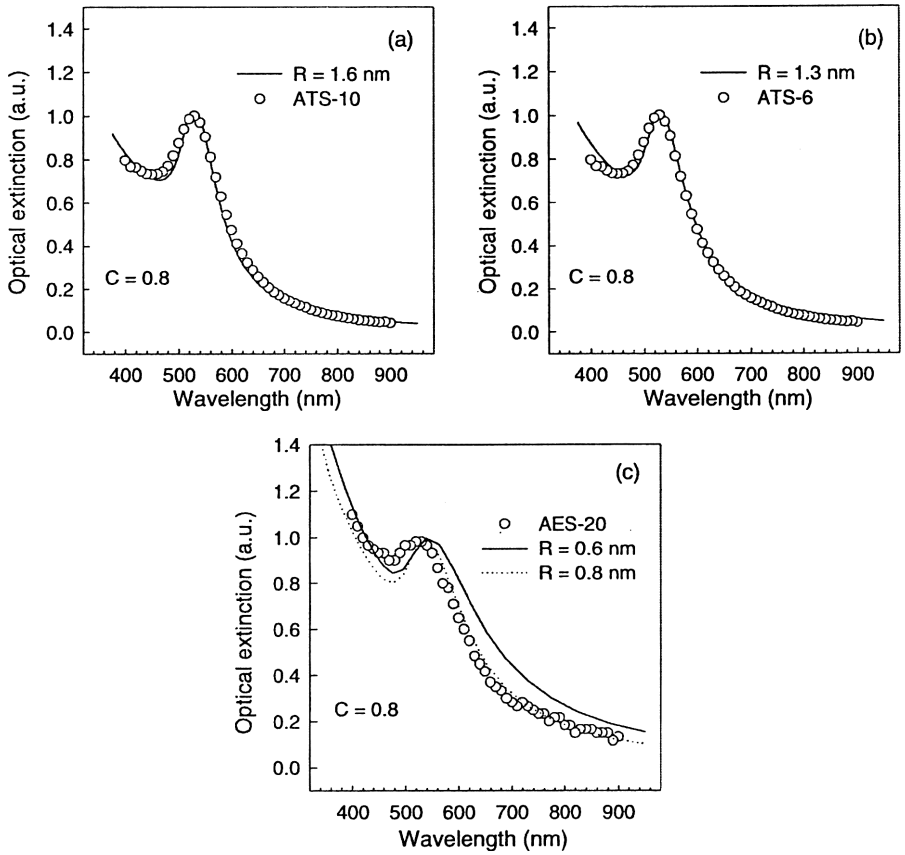

Figure 3. Optical extinction spectra for three samples: (a) ATS-10, (b) ATS-6 and (c) AES-20. Hollow circles correspond to experimental results and lines represent the fits obtained using the parameters for the bulk given in table 1 and $C = 0.8$. Good agreement with experimental spectra can be seen in (a) and (b), for 1.6 and 1.3 nm radii, respectively. However, for smaller radii, (c), no good fit can be obtained for any particle radius using parameters for the bulk.

Table 1. Optical parameters of bulk gold used and determined in this work.

Parameter	Symbol	Value	Reference
Plasma frequency	ω_p	13×10^{15} Hz	Granqvist
Dumping constant for free electrons	γ_{bulk}	1.1×10^{14} Hz	Johnson and Christy
Coefficient for bound electron contribution	Q_{bulk}	2.3×10^{24}	This work
Gap energy	E_g	2.1 eV	This work
Fermi energy	E_F	2.5 eV	This work
Damping constant for bound electrons	γ_b	158 meV/$\hbar$ (2.4×10^{14} Hz)	Inouye

where n_0 is the refractive index of the medium (heptane) and λ is the wavelength for frequency ω. The experimental refractive indices of heptane for 434, 486, 589 and 656 nm were used to calculate values for other wavelengths with Sellmeier's dispersion equation [19].

4. Results

The optical extinction spectra for three samples (ATS-10, ATS-6, and AES-20) are shown in figure 3, together with calculated spectra. For these theoretical fits, we consider that the real (ε') and imaginary (ε'') parts of the dielectric function are composed by addition of the bound electron contribution corresponding to the bulk and the free electron contribution corrected for size through the damping constant.

The fits shown in figure 3 were obtained using the parameters accepted for the bulk given in table 1 and $C = 0.8$. A good agreement with the experimental spectra can be seen in figures 3(a) and (b), where 1.6 and 1.3 nm radius were used respectively. These values were obtained by TEM, as mentioned in a previous work [3]. The optical extinction spectrum depicted in figure 3(c) shows a less pronounced contrast than in the previous ones, indicating that it corresponds to smaller particles. However, it was not possible to find a good fit for any particle radius. For $R = 0.8$ nm, the long wavelength tail is well adjusted but the short wavelength region is not. For $R = 0.6$ nm, the fit is slightly improved in the short wavelength region but it is quite bad in the tail. Unfortunately, a microscope image is not available for this sample but its radius was determined by a fitting procedure in a previous work as 0.7 nm [3].

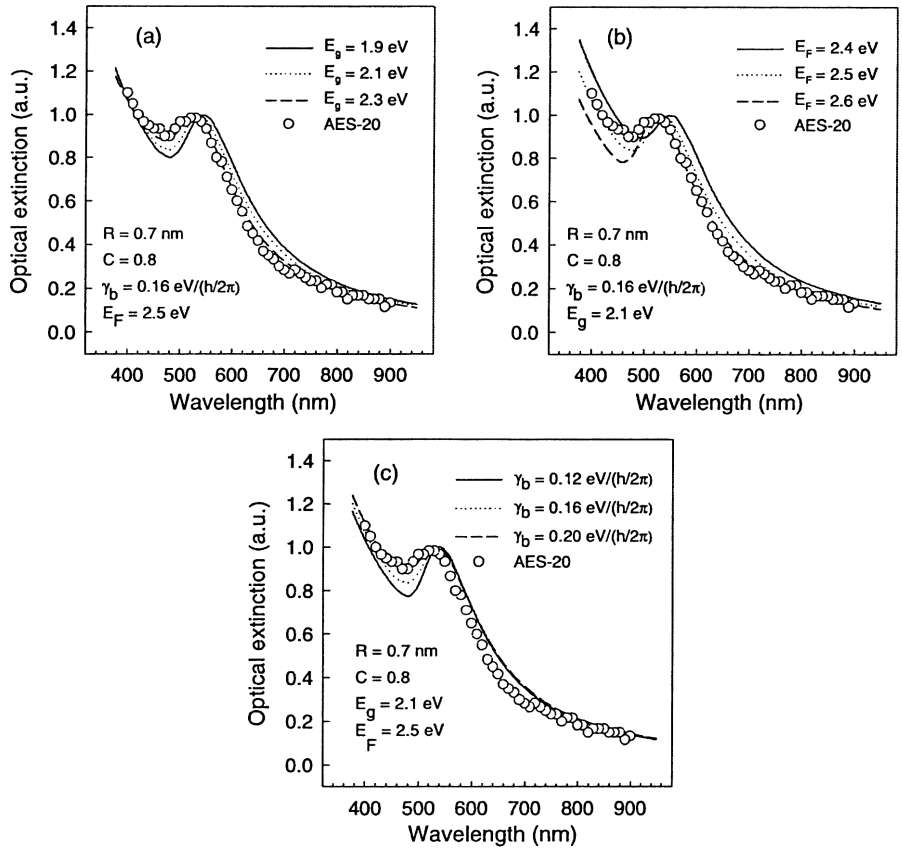

Figure 4. Influence of different parameters for bound electrons on the extinction spectra of small gold nanoparticles: (a) the energy gap (E_g), (b) the Fermi energy (E_F) and (c) the damping (γ_b).

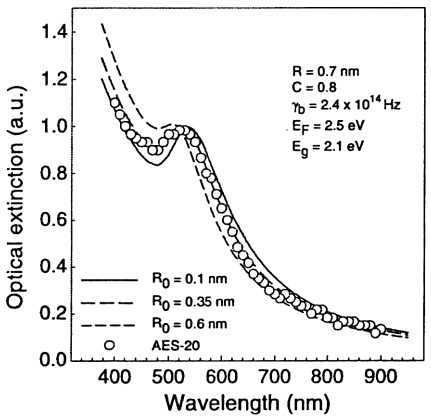

Figure 5. Optical extinction spectra of AES-20 gold nanoparticles. The fitting values correspond to different R_0 values, $C = 0.8$, and other parameters are for bulk gold. The best fit corresponds to $R_0 = 0.35$ nm.

It can be argued that, for the smallest particles, it is necessary to include some size-dependent correction to the contribution of the bound electrons in the dielectric function. In order to study the influence of the different parameters involved in the extinction spectra of gold nanoparticles, we explore the changes introduced by different values of E_g, E_F, and γ_b of equation (2) over the extinction spectra given by equation (5). A radius of 0.7 nm was assumed in this calculation. Experimental results for sample AES-20 are included in figure 4 for reference. Figure 4(a) shows the influence of E_g on both the position of the maximum of the extinction spectra and its contrast. We can observe that the position of the maximum is slightly shifted to lower wavelengths when E_g is increased from its bulk value. Simultaneously, the contrast is reduced. Reasonably good fitting was obtained for $E_g = 2.3$ eV. Figure 4(b) shows the effect of E_F on the positions of the maximum and minimum in the extinction spectra: when E_F increases, both extremes are noticeably shifted to lower wavelengths. No good fit can be obtained by changing only this parameter. Figure 4(c) shows the behaviour of the extinction spectra when γ_b is varied within a certain range. For wavelengths larger than that of the maximum, the spectra are not altered, while for smaller wavelengths different contrast values are observed. By increasing γ_b from its bulk value to 0.20 eV/$\hbar$, the fit is improved in the short wavelength part of the spectra, although the fit for the tail is not good.

The results of figure 4 show that extinction spectra of small gold nanoparticles can be adjusted reasonably well assuming that the Fermi energy is similar to the bulk value but the gap energy or alternatively the damping constant must be increased from its bulk values. For particles with $R = 0.7$ nm, best fits were obtained for two sets of values, $E_g = 2.3$ eV and

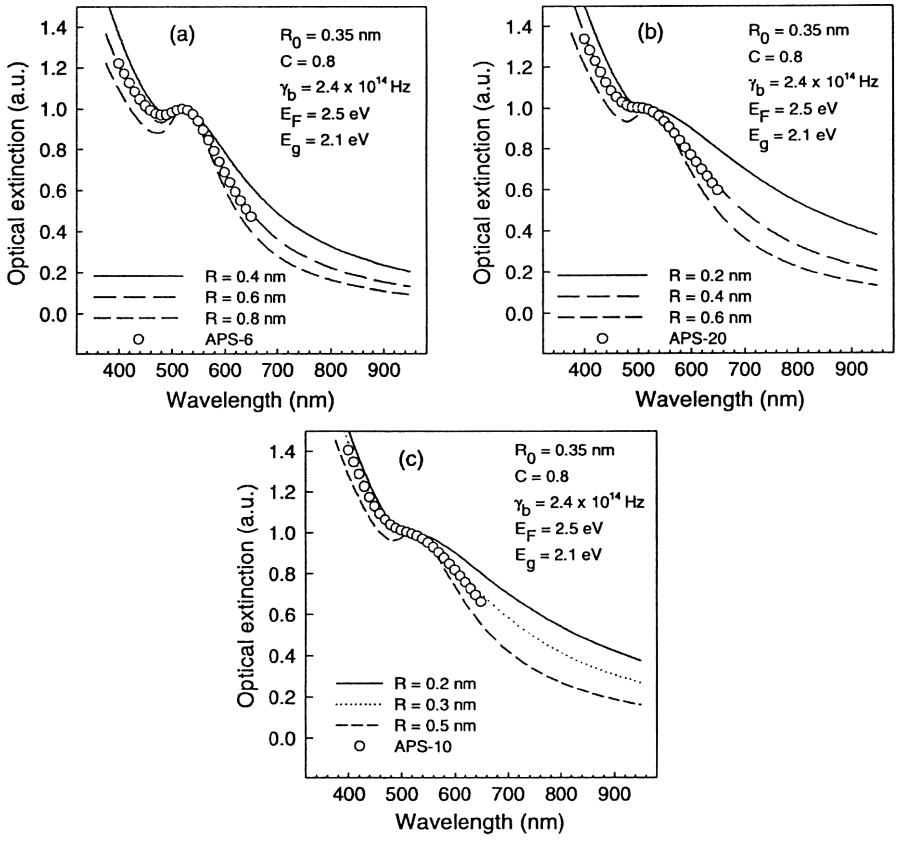

Figure 6. Optical extinction spectra (hollow circles) and fitting results (lines) for APS samples. Best fits correspond to: (a) radius 0.6 nm for APS-6; (b) radius 0.4 nm for APS-20 and (c) radius 0.3 nm for APS-10.

Table 2. Optical parameters of gold nanoparticles used and determined in this work.

Parameter	Symbol	Value
Scattering constant	C	0.8
Gap energy and damping constant for bound electrons (R = 0.7 nm)	E_g, γ_b	E_g = 2.3 eV, γ_b = 158 meV/$\hbar$ E_g = 2.1 eV, γ_b = 200 meV/$\hbar$
Coefficient for bound electrons contribution	Q_{size}	$2.3 \times 10^{24} \times [1 - \exp(R/R_0)]$ R_0 = 0.35 nm

γ_b = 158 meV/$\hbar$ (bulk) or alternatively for E_g = 2.1 eV (bulk) and γ_b = 200 meV/$\hbar$.

As was mentioned in section 3, there is another model used to calculate the influence of the size over the contribution of the bound electrons on the dielectric function. Small particles with larger spacing between electronic states have smaller density of states than larger particles that resemble the bulk material. This fact can be taken into account by making the proportionality factor Q_{size} a function of the size in the form

$$Q_{size} = Q_{bulk}\left[1 - \exp\left(\frac{R}{R_0}\right)\right], \qquad (7)$$

where R is the radius of the particle and R_0 is a scale factor. This expression can be introduced in equation (2) to calculate the contribution of the bound electrons to the dielectric function, and its results are then used in equation (6) to calculate the extinction spectra. Results for sample AES-20 with particles of 0.7 nm radius are shown in figure 5.

Excellent fit was obtained for R_0 = 0.35 nm.

Table 2 summarizes the optical parameters used to adjust the experimental spectra of gold nanoparticles by the two models proposed in this work. The expression given by equation (7) suggests that, for particles with radius bigger than 3 R_0, the correction over Q_{bulk} is negligible. This fact was checked over the bigger nanoparticles (R = 1.6 and 1.3 nm) where the fitting spectra did not show any modification relative to data shown in figure 3. By using this last model, that modifies the density of electronic states in the conduction band according to the size of the nanoparticles, it was possible to fit the extinction spectra of other samples prepared with a different surface modifier, namely APS. The results are shown in figure 6, where it is clearly seen a small contrast in the extinction spectra that predicts the presence of very small

particles. The best fit corresponds to $R = 0.6$ nm (APS-6); $R = 0.4$ nm (APS-20) and $R = 0.3$ (APS-10). TEM results for these samples show strong clustering due to coalescence and are not reliable for the determination of size. Optical extinction spectroscopy is well suited for measurements in solution and allows one to obtain good results for sizing very small nanoparticles.

5. Conclusions

In this work we have shown that the extinction spectra of gold nanoparticles can be fitted using Mie's theory, taking into account the dependence of the optical properties with size. While the change with size of the free electron contribution to the dielectric function has been explored in many works, we show for the first time that the bound electron contribution must be modified as well in order to fit extinction spectra of very small nanoparticles. The contribution of electron transitions from the d-band to the conduction band was modelled using the expression given by Inouye *et al* [10]. First, the different parameters of this expression were obtained by fitting the bulk dielectric function as a sum of free electron and bound electron contributions. After that, two different models were used to include the size dependence on the bound electron contribution: one uses the energy gap and the damping constant as adjustable parameters to fit the experimental extinction spectra, and the other changes the electronic density of states in the conduction band in terms of size. The latter model allows one to fit the spectra of all the samples explored. The dependence of the electronic density of states with size proposed in this work is a good representation of the fact that small particles have larger spacing between electronic states, but the proposed mathematical expression ($\propto 1 - \exp(R/R_0)$) is of course not necessarily unique. This expression suggests that for particles with radius larger than 1 nm, the correction over the bound electron contributions in negligible.

We did not observe a fine structure on the optical extinction spectra for any sample. This feature can be explained due to fact that the samples are not strictly monomodal and present a small dispersion around the mean value. This situation does not represent a restriction when the mean radius is to be determined. Contrast between the maximum and the minimum in the extinction spectra near the resonance at 520 nm or alternatively the broadening of the plasmon band can be used to determine the size of gold nanoparticles, as was suggested previously [3].

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