

ARTICLES

Near-Field and Far-Field Scattering by Bimetallic Nanoshell Systems

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We have studied theoretically the far- and near-field scattering response of bimetallic Ag/Au core-shell and alloy nanoparticles. Particular emphasis is put on the near-field study, which is known to play a fundamental role in surface enhanced spectroscopies. The comparison between the scattering spectra of core-shell and alloy particles shows that for particles with a Au/Ag volume ratio greater than 2, the structural difference does not imply any significant difference in the optical response. For such particles, while the retardation effects are not negligible, the scattering at the interface between the two metals in the core-shell case does not seem to modify the scattering behavior. The scattering at the interface is conversely not negligible for particles with a lower Au/Ag ratio, where the particle inner structure seems to be important.

I. Introduction

In the recent past, the study of the optical properties of nanoparticles has received growing attention because of the number of possible applications arising from the peculiarities of nanosized objects. Among these peculiarities, caused by the interaction with electromagnetic fields, one of the most interesting is the scattering response, which can give rise to enormous enhancement of the field amplitude on the surface of the particles (near-field) with respect to the incident field.^{1–3} This property has been exploited to develop spectroscopic techniques, such as surface-enhanced Raman spectroscopy (SERS),⁴ single molecule detection,⁵ and scanning near-field optical microscopy (SNOM).⁶

Out of the many types of existing nanoparticles, the core-shell ones (whose structure can be efficiently controlled by synthetic route⁷ and characterized with noticeable precision⁸) are considered particularly attractive for surface applications. Two main classes of core-shell nanoparticles are typically studied. The first one involves a dielectric core surrounded by a metal shell, and such systems are usually referred to as “nanoshells”, while in the second one, the particles consist of a metal core surrounded by a shell of a different metal. The particular interest in both these kinds of particles is related principally to the modification of their spectral properties induced by the intrinsic core-shell structure.⁹ For instance, nanoshells display a large spectral modification of the surface plasmon resonance wavelength as a function of the surrounding medium, so that, in suitable conditions, by exploiting such a resonance shift they can be used as nanosensors for biological applications.¹⁰

Probably the most important feature of interest in core-shell nanoparticles is the possibility to tune their response properties

by changing one (or more) of the several parameters involved, as for instance the core-shell radius ratio and total radius of the particle. The classical Mie scattering theory predicts, and several experimental data confirm it, that by varying the shell thickness ratio with respect to the overall size, the plasmon resonance of the particle can be shifted at a required wavelength in the range from mid-IR to UV. In bimetallic nanoparticles, in addition, the spectral properties can be tuned by acting on the chemical composition of the particle because of the interplay of the different dielectric behavior of the two metals. This tuning possibility is decisive for many applications (resonant photo-oxidation inhibitors,¹¹ environmental and chemical,¹² or Raman¹³ sensing to mention only a few examples).

As observed, many applications of core-shell nanoparticles are based on their near-field scattering properties. The response of a molecule physisorbed on a surface, or of a group of nanoparticles closely packed together, is clearly dependent on the fields generated at the surface.¹⁴ These can differ noticeably from those characterizing the far-field scattering, apart from the intensity, in the areas of plasmon resonance and line shape.¹⁵ Such differences are expected to be particularly important in core-shell particles, where the presence of additional (core-shell) interactions, usually near the particle-host medium interface, can give rise to further near-to-surface effects through scattering at the interface between the two metals. The study of far-field scattering then cannot be transferred unambiguously into the near-field context, and a comparison between far and near field is needed when dealing with problems involving scattering from a nanoparticle surface. In spite of this, while several works have been focused on the investigation of absorption and far-field scattering response,^{16–18} the study of near-field scattering in bimetallic particles has received little, if any, attention in the past, and experiments on core-shell particles have rather been addressed particularly to the study of surface plasmon broadening.¹⁹ To the best of our knowledge,

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constructive theoretical comparisons of the near- and far-field scattering response in core-shell nanoparticles is essentially lacking up to now.

In this work, we put forward a systematic study through comparisons between far-field and near-field scattering responses evaluated for a single core-shell bimetallic (Ag-Au) nanoparticle of fixed core radius and variable shell thickness. To assess the scattering importance at the metal-metal interface, the same calculations performed for each core-shell particle have been repeated for the corresponding Ag-Au alloy particle of the same composition. Section II is devoted to a concise presentation of the theoretical model employed, while results and conclusions are to be found in sections III and IV, respectively.

II. Theory

All the scattering spectra discussed in this paper have been calculated in the framework of the classical theory developed by Kerker,²⁰ which takes into account retardation effects. These effects, which depend on the size of the particle, as clearly explained in the fundamental book of Kreibig and Vollmer,²¹ are accompanied by spectral band broadening due to electromagnetic retardation, without involving scattering at the metal interface in core-shell particles. A similar mechanism due to pure retardation effects in the electromagnetic response is expected in the case of spherical nanoparticles with identical size, disregarding their internal structure (core-shell or alloyed homogeneous composition), provided their size is large enough. The internal structure of a core-shell particle is taken into account through the correct boundary conditions on the electromagnetic (em) fields which have to be imposed separately on both core-shell interface and external surface.²² Special plasmon modes excited in the core and in the shell as well then become coupled strongly via their interfaces, resulting in complex spectra.

Following Messenger,² the far-field scattering cross section Q_{ff} is a measure of the capability of a sphere to redirect the incident em wave over all solid angles; the near-field scattering cross section Q_{nf} can analogously be thought as the representation of the capability of the sphere to convert power from the incident field near the surface of the sphere. Thus, Q_{ff} is the ratio between scattered and incident power for a given geometric cross-section, and Q_{nf} can be used to calculate the intensity of the electric field near the particle. According to Quinten,¹ for a single spherical particle, Q_{ff} and Q_{nf} can be expressed in the forms

$$Q_{\text{ff}} = \frac{2}{(kR)^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2) \quad (1)$$

$$Q_{\text{nf}}(r) = 2 \frac{r^2}{R^2} \sum_{n=1}^{\infty} \{ |a_n|^2 [(n+1)|h_{n-1}^{(1)}(kr)|^2 + n|h_{n+1}^{(1)}(kr)|^2] + (2n+1)|b_n|^2 |h_n^{(1)}(kr)|^2 \} \quad (2)$$

where R is the particle radius, $k = (2\pi n_0(\lambda))/\lambda$ the wavenumber outside the particle, λ is the incident-field wavelength, and n_0 is the refractive index of the host matrix. The term $h_{n-1}^{(1)}$ denotes a spherical Hankel function of the first kind of order n , and a_n and b_n are the well-known scattering coefficients of the sphere, whose expressions, dependent on the internal structure of the spherical scatterer, are parametrical functions of the dielectric functions describing the particle.²²

The dielectric functions of the nanostructures considered in this paper are calculated according to a semiempirical oversimplified model, widely utilized,^{23,24} based on the Drude theory²¹ and experimental data.¹⁸ For the case of a core-shell particle, core and shell dielectric functions can be defined as follows:

$$\begin{aligned} \epsilon_{\text{core}}(\omega, R) &= \epsilon_{\text{exp}}(\omega) - \epsilon_{\text{bulk}}^{\text{Drude}}(\omega) + \epsilon_{\text{core}}^{\text{Drude}}(\omega, R) = \\ &\epsilon_{\text{exp}}(\omega) + \frac{\omega_p^2}{\omega^2 + i\omega\Gamma_{\infty}} - \frac{\omega_p^2}{\omega^2 + i\omega(\Gamma_{\infty} + \Gamma_{\text{core}})} \\ \epsilon_{\text{shell}}(\omega, R) &= \epsilon_{\text{exp}}(\omega) - \epsilon_{\text{bulk}}^{\text{Drude}}(\omega) + \epsilon_{\text{shell}}^{\text{Drude}}(\omega, R) = \\ &\epsilon_{\text{exp}}(\omega) + \frac{\omega_p^2}{\omega^2 + i\omega\Gamma_{\infty}} - \frac{\omega_p^2}{\omega^2 + i\omega(\Gamma_{\infty} + \Gamma_{\text{shell}})} \end{aligned}$$

where $\epsilon_{\text{exp}}(\omega)$ is the experimental dielectric function value of the pure bulk material,²⁵ ω_p is the plasma frequency (which has been calculated as $\omega_p^2 = \rho e^2 / \epsilon_0 M$, with ρ being the electronic density and e and M being the electronic charge and mass, respectively, and results in $1.372 \times 10^{16} \text{ s}^{-1}$ for Au and $1.365 \times 10^{16} \text{ s}^{-1}$ for Ag), and $\Gamma_{\infty} = v_F / l_{\infty}$, the bulk collision frequency, with v_F being the Fermi velocity and l_{∞} being the mean free path of the conduction electrons in the metal bulk. Γ_{core} and Γ_{shell} are the surface-induced contributions to the damping, given by $\Gamma_{\text{core}} = A_{\text{core}} v_F / l_{\text{core}}$ and $\Gamma_{\text{shell}} = A_{\text{shell}} v_F / l_{\text{shell}}$, with l_{core} (l_{shell}) being characteristic dimension dependent on the geometry and A_{core} (A_{shell}) being a proper parameter describing the loss of coherence by scattering events. All the necessary physical parameters (electronic density, Fermi velocity, and mean free path) have been obtained by the basic text of Ashcroft and Mermin.²⁶ While plenty of works provide an estimate of A_{core} , a reasonable estimate of A_{shell} is not straightforward to infer. In this work, the values used are $A_{\text{core}} = 1$ and $A_{\text{shell}} = 0.5$,¹⁰ while the values of l_{core} and l_{shell} are, as usual, set equal to the radius of the core R_{core} and of the whole particle R_{tot} .

An alloy particle is modeled by us as a sphere of homogeneous material with physical properties obtained by averaging those of Au and Ag.²⁷ Once the total radius and ratio $R_{\text{core}}/R_{\text{tot}}$ are fixed, the relative quantity of gold and silver are the same in a core-shell and an alloy particle with the same radius. For each core-shell particle of given chemical composition considered, an analogous alloy structure has been studied with the same Au/Ag volume ratio. Thus, the dielectric function of the model alloy particles is obtained by averaging over the volume the experimental dielectric functions of the pure components and by calculating the free electron Drude contributions for both bulk and nanostructure and employing the value averaged on the volumes for ω_p , v_F , and l_{∞} . The surface-induced contribution to the damping was obtained according to

$$\Gamma_{\text{alloy}} = A_{\text{alloy}} \bar{v}_F / R_{\text{tot}}$$

with

$$\Gamma_{\text{alloy}} = 1 \quad \text{and} \quad \bar{v}_F = \frac{V_{\text{core}} v_F^{\text{Ag}} + V_{\text{shell}} v_F^{\text{Au}}}{V_{\text{core}} + V_{\text{shell}}}$$

III. Results

Our study collects the results relative to seven different particle sizes, ranging in radius from 22 to 50 nm (precisely 22, 23, 25, 28, 30, 40, 50 nm). The different sampling adopted for particle dimensions smaller or bigger than 30 nm is related

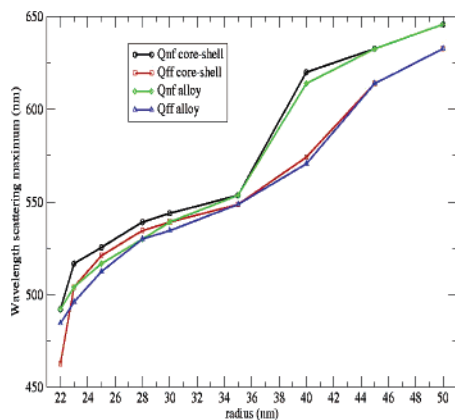


Figure 1. Maximum scattering wavelength (nm) at near and far field versus radius (nm) for core-shell or alloy particles.

to the fact that for particles having a radius between 20 and 30 nm, the plasmon resonance appears in a region between 400 and 550 nm, where the dielectric functions of both silver and gold exhibit a strong dependence on the wavelength. In the same dimension range, moreover, the dielectric function is strongly dependent on the particle dimensions and varies appreciably for small changes of the radius. For these reasons, a dense sampling size in this region is necessary. The studied core-shell particles are composed of a silver spherical core of radius 20 nm, coated by a gold shell of variable thickness. The alloy particles consist of a homogeneous material of permittivity obtained by averaging the dielectric functions of the constituent metals, as explained in section II. This actually means that when the sizes are augmented, in the core-shell structure only the shell radius changes, and for both particle models the ratio between the Au amount and the Ag amount grows as the particle size increases.

We begin our discussion analyzing the plasmon resonance of a single core-shell or alloy particle. In recent papers, experimental data¹⁸ and theoretical analysis¹⁹ have confirmed that the plasmon resonance wavelength shifts to lower energies as the shell thickness grows, while the maximum intensity does not change monotonically. This behavior can be explained by taking into account relative size and geometrical dependence of the imaginary part of the dielectric function of gold and silver in the spectral region considered.¹⁹ The same qualitative behavior is reproducible through the model proposed in section II, as shown in Figure 1, where the calculated near-field and far-field scattering maximum wavelength for a single core-shell or alloy nanoparticle is plotted as a function of the particle size. The isovolumetric particles have the same composition, without consideration with respect to the internal construction.

The trend (maximum position vs radius) appears to be almost unaffected by the internal structure of the particle in both the far and near field. Such a trend is nevertheless different if the far-field and near-field scattering are compared; particularly at a radius larger than 30 nm the behavior of the two curves get clearly separated. This behavior reflects the natural difference in spectral properties at far and near field; we here note that this departure becomes more appreciable as the gold volume fraction in the particle overcomes the silver one.

To go more deeply into this analysis, it is convenient to make a direct comparison between the two different (alloy and core-shell) far-field and near-field scattering spectra size by size, as in Figure 2. As a first comment, we can observe that the agreement between single spectra is not worse in the near-field case than in the far-field one. In both situations, the agreement

is decidedly bad at small dimensions and gets better as the particle size increases or, in other words, as the ratio between the Au amount and the Ag amount increases. The inspection of the left side of Figure 2 suggests that, at far field, while for the alloy particle (red line) the maximum position is in rather good agreement with the one displayed, as already stressed, by the corresponding core-shell (black line), the overlap of the scattering spectra is relatively poor at smaller dimensions and gets better as the particle grows. This is evidence that the band shape is appreciably affected by the internal structure of the particle. In particular, the internal structure of the particle is expected to change the bandwidth as a consequence of the occurrence of scattering at the interface between the two metals, an effect that seems to be not negligible as the thickness of the shell layer is less than 10 nm. We remark, however, that a detailed study of this effect has not been performed, because the utilization of a single Lorentzian function to fit some of the scattering curves obtained proved to be insufficient to obtain a reliable fit. It must be emphasized that the deviations clearly identifiable in some plots from a single Lorentzian function do not seem to be ascribable to multipolar contribution effects to the observed scattering; the repetition of calculations, not reported here, retaining explicitly only the dipolar term, gave essentially the same results. Anyway, the number of multipolar contributions included in the present calculations is fixed according to the recipe in the book by Bohren and Huffman,²² and, being a linear function of particle radius and wavelength, it ranges between 4 (for a particle with radius 22 nm) and 9 (for a radius equal to 50 nm).

To evaluate the role and utility of core-shell and alloy particles in surface enhanced spectroscopy, a more significant property than the far-field scattering cross section is the same response at near field. In the right side of Figure 2, we report the near-field scattering spectra calculated for both core-shell (black line) and alloy particles (red line). As expected,¹ the near-field scattering intensity is much higher (about 2 orders of magnitude) than in the far-field case, a general occurrence observed with nanosized metallic spheres. From the inspection of the last three insets of Figure 2, relative to the scattering spectra of particles with radius equal to or larger than 30 nm, we can obtain confirmation about the agreement between the behavior of alloy and core-shell particles as the radius is increased. It is clearly seen that the difference of response associated with the two structures fades out as the particle size increases. The most interesting feature is to be found in the very different trend displayed by far- or near-field cross sections: while the far-field situation is characterized by cross sections growing linearly with the rise of the radius, at near field, the scattering intensity appears almost constant for different sizes of scatterers.

As already stressed, in the present case, a variation in the particle size implies a variation of composition of the particle. The dielectric function thus changes for two different reasons: in the core shell case, the shell thickness changes (and the same occurs to the Au dielectric function); in alloy particles, the dielectric function changes because radius and composition (ratio between Au/Ag) are varied. Beyond a certain dimension limit, nevertheless, the dielectric function of the Au shell has a weak dependence on the thickness, and the dielectric function of the alloy becomes comparable with that of a particle made of pure Au in the region of plasmon resonance. Thus, beyond this dimension limit, the scattering varies only by virtue of dimension changes, as there is no longer a variation of the dielectric function. We could say that, beyond a certain dimension, a

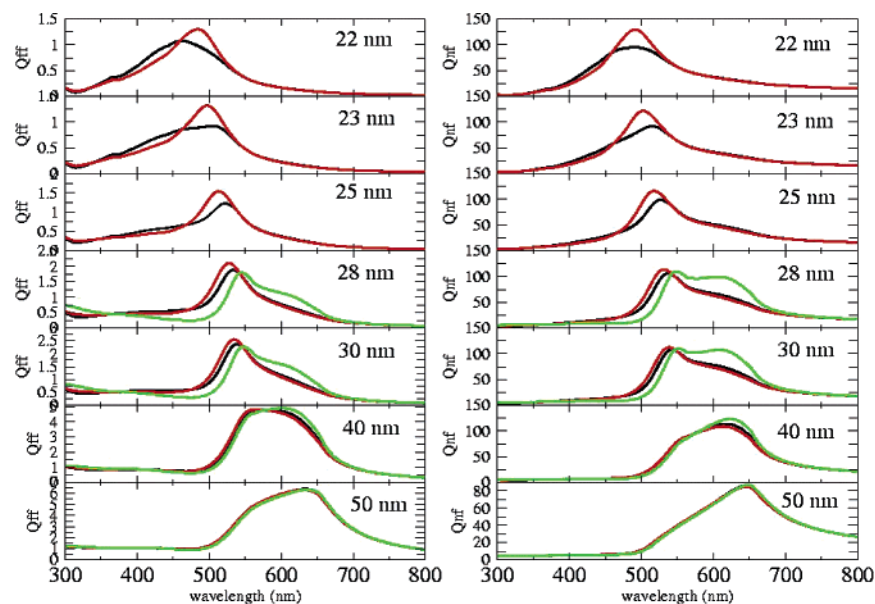


Figure 2. Comparison between scattering spectra of core-shell $\text{Ag}_{\text{core}}/\text{Au}_{\text{shell}}$ (black line) alloy Ag/Au (red line) and Au pure particles (green line) with the same volume and composition put in evidence in each inset, for different radii of 22, 23, 25, 28, 30, 40, and 50 nm. The left side refers to far-field scattering spectra, the right side to the near-field situation.

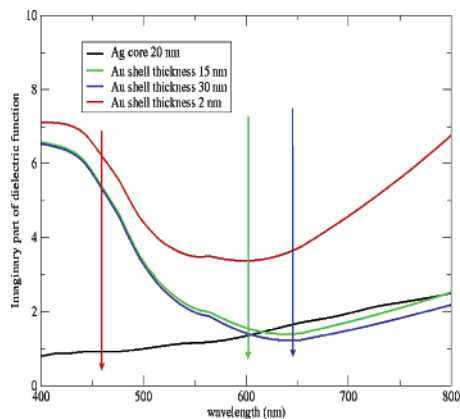


Figure 3. Imaginary part of the dielectric function behavior: the Ag spherical core with $R_{\text{core}} = 20$ nm (black line); Au symmetrical shell, thickness $R_{\text{shell}} = 2$ nm (red line); Au symmetrical shell, thickness $R_{\text{shell}} = 15$ nm (green line); Au symmetrical shell, thickness $R_{\text{shell}} = 30$ nm (blue line). Arrows of corresponding color indicate the near-field scattering maximum wavelength for each shell thickness.

quasi-pure gold metal condition is reached. It is possible to appreciate quantitatively this observation by comparing the green line, which represents the scattering spectra (respectively near and far field) of pure gold particle, with the black line (core-shell) and red line (alloy). It is also straightforward to note that the scattering spectra of the three cases get superimposable when the radius is greater than 30 nm. This means also that the scattering contribution by the Ag core in the core-shell structure is insignificant, and almost all scattering is due to the external gold shell.

The decreasing importance of scattering at the interface between the two metals as the particle size increases can be rationalized by comparing the imaginary part of the dielectric function for the two metals involved in the core-shell particle. These are reported in Figure 3, together with the indication of the related maximum absorption wavelength, for a few situations (particle radius equal to 22, 35, and 50 nm). While the maximum scattering wavelength for a particle with a shell thickness of 2 nm falls in a region where the imaginary parts $\epsilon_2(R, \lambda)$ of the Ag core and the Au shell are very different, because of the role

of interband transitions in Au, the position of maximum scattering for particles with a shell thicker than 15 nm lies in a spectral region where the imaginary parts of the two dielectric functions are quite close. A noticeable effect of the scattering at the interface should then be expected for the first situation but not for particles with a shell thickness equal to 15 nm or larger.

IV. Conclusion

The optical scattering spectra at near and far field for single isolated pure Au or bimetallic Ag/Au particles, with different radii, have been calculated according to a classical treatment. We have taken into account only two possible cases: (i) spherical particles consisting of a Ag core and a Au shell and (ii) homogeneous alloy particles. The results show that, starting with a Ag core with constant radius $R_{\text{core}} = 20$ nm, beyond a definite Au/Ag volume ratio there is small difference between the response observed by core-shell and the response observed by homogeneous alloy particles of identical chemical composition. This indicates that scattering at the interface between the two metals does not significantly affect the plasmon resonance for this system. On the other side, for thin shells (less than 10–15 nm) there is a noticeable difference between the em scattering of the two structures in both far field and near field, and we can reasonably speculate that such a difference is related to the importance of scattering at the metal-metal interface. This effect is expected to be important if, in the spectral region of maximum scattering, the two metals are characterized by imaginary dielectric function values sufficiently far from each other.

The near-field scattering cross sections for particles of radius larger than 30 nm exhibit a red shift of their maximum as the radius increases, but the intensity of these maxima do not grow monotonically.

The qualitative and quantitative behavior observed for far-field and near-field response is appreciably different for all the dimensions considered. Nevertheless, it is interesting to note that the presence of a not negligible contribution from internal surface scattering influences to a similar extent both far- and near-field scattering spectra.

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