How an oxide shell affects the ultraviolet plasmonic behavior of Ga, Mg, and Al nanostructures

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Abstract: The ultraviolet (UV) range presents new challenges for plasmonics, with interesting applications ranging from engineering to biology. In previous research, gallium, aluminum, and magnesium were found to be very promising UV plasmonic metals. However, a native oxide shell surrounds nanostructures of these metals that affects their plasmonic response. Here, through a nanoparticle-oxide core-shell model, we present a detailed electromagnetic analysis of how oxidation alters the UV-plasmonic response of spherical or hemisphere-on-substrate nanostructures made of those metals by analyzing the spectral evolution of two parameters: the absorption efficiency (far-field analysis) and the enhancement of the local intensity averaged over the nanoparticle surface (near-field analysis).

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1. Introduction

The plasmonic response of metallic nanoparticles (NPs) to external electromagnetic fields makes them attractive for a wide range of applications: real-time sensors, surface enhancement spectroscopy techniques, light energy guiding, nanosensing, and electromagnetic cloaking, among others [1]. Applications of plasmonics in biology have produced important advances in the detection and sensing of agents at very low concentrations [2]. Most biological molecules have absorption bands in the UV, so an examination of metal nanostructures with UV plasmon resonances would be desirable, especially for cases in which either fluorescent labeling is not feasible [3] or photobleaching is a problem. Furthermore, growing requirements to detect,
recognize, and/or destroy biological toxins, and the need for improved biological imaging at the nanometer scale, have increased the interest in UV plasmonics over the last few years [4–6]. In previous studies, the plasmonic performance of various metals in the UV has been analyzed. Among them, aluminum (Al) [3, 6–10], gallium (Ga) [7, 10–13], magnesium (Mg) [7, 14], and rhodium (Rh) [15–17] were identified as particularly promising candidates for UV plasmonics, with properties approaching those of silver (Ag) and gold (Au) widely used for plasmonic applications in the VIS-NIR [10,18]. However, the efficiencies of these metals depend sensitively on the surrounding dielectric environment, and all of them, except Au and Rh, form native oxides that wrap the NP with a shell, whose thickness depends on both the metal and the environmental exposure conditions (temperature and pressure). Consequently, it is essential to understand the effect of oxidation on their UV plasmonic response [7, 9, 19]. Also, very recently it was shown that, since oxidation is a means to grow a dielectric shell, its control may be used to tune the plasmonic resonance of NPs [14].

Here we report a detailed numerical investigation into how the thickness of a surface oxide shell affects the UV plasmonic performance of nanostructures made of Ga, Al, and Mg by using the discrete dipole approximation (DDA) method [20] and finite element method (FEM) simulations. We specifically consider isolated spherical and hemispherical-on-substrate particles to mimic typical experimental conditions used in applications like colloidal chemistry or surface enhanced spectroscopy using nanostructures in solution or on substrates, respectively. This investigation considers and compares the plasmonic absorption efficiency and the near-field distribution for each material and geometry, and its dependence with a growing oxide shell thickness.

2. System geometry and methods
Two basic core-shell geometries have been considered: an isolated spherical NP of radius R ("spherical" case), and second, a hemispherical NP with the same radius located on a dielectric sapphire substrate with n = 1.78 ("hemispherical" case). In this way, with the former we mimic experimental conditions for colloidal chemistry and with the latter, the typical experimental conditions for metallic nanostructures on substrates made of either Ga or Mg [11–14]. Although the typical Al NP geometry is usually not hemispherical, we use this geometry to facilitate comparison. Furthermore, Al NPs are often deposited on a dielectric substrate with a large contact surface area [8, 21]. In the present analysis the total NP size will be fixed at R = 40 nm, but the metal oxide shell thickness will vary from 0 nm (bare metal NP) to 20 nm, so the metallic core radius will range from R_{core} = 20 to 40 nm (pure metallic NP) (Fig. 1). Al and Ga have very large enthalpies of oxide formation [22], and the oxide formed is quite dense, preventing oxide diffusion and slowing dramatically the oxidation process after only a few monolayers (Ga) or nanometers (Al). On the contrary, Mg has a moderate enthalpy of oxide formation [22], and the native oxide MgO forms aggressively upon exposure to air, leading to a complete and rapid destruction of the plasmonic response [23] unless this process is performed under controlled conditions [14]. In all these cases, oxide layers of a few nanometers are formed. Taking into account the influence of the ambient conditions on the oxidation processes, it is interesting to analyze the whole thickness range since control of it would allow the UV plasmon resonance to be tuned, as we will see later on.

The system is excited by a monochromatic, linearly polarized plane wave, with normal incidence for the particle-substrate configuration as shown in Fig. 1(b).

The spectral dependence of two parameters has been studied: the absorption efficiency Q_{abs} and the enhancement of the local intensity averaged over the NP surface ⟨|E|^2⟩. Obviously both magnitudes depend on λ, this dependence being the key of our plasmonic study. For particles much smaller than the wavelength, Q_{abs} can be associated with the far-field extinction efficiency and it is defined as the ratio between the particle absorption cross-section (difference
Fig. 1. The two analyzed scattering geometries: a) Isolated spherical geometry, b) Hemi-
spherical geometry on a dielectric substrate. ($R = 40$ nm, $R_{\text{core}}$ will range from 20 nm to
40 nm).

between extinction and scattering cross-sections) and its geometrical cross-section. $\langle |E|^2 \rangle$ gives
an estimate of the local field enhancement or, more precisely, the local enhancement of the local
energy density, close to the particle surface in the near-field regime, whose spectral distribution
is generally red-shifted with respect to $Q_{\text{abs}}$ due to the dominant evanescent character of the
near electromagnetic field [24, 25]. $\langle |E|^2 \rangle$ is useful for predicting the plasmonic performance in
surface-enhanced applications such as Raman (SERS) or fluorescence (SEF) spectroscopy [26],
while $Q_{\text{abs}}$ helps to describe the ellipsometric response of surfaces with metallic nanostructures,
especially that related to the imaginary part of the measured pseudodielectric function [12].

The Discrete Dipole Approximation (DDA) and Finite Element Methods (FEM) like COMSOL
Multiphysics v.5.2 have been employed for the numerical analysis of the $Q_{\text{abs}}$ and $\langle |E|^2 \rangle$. The
DDA method, also known as coupled dipole method [20], is based on a direct-space dipole
discretization scheme to calculate light scattering and absorption by irregular particles and
inhomogeneous structures. In our case, both the NP and the substrate were discretized with a
large number of cells. This number was optimized for each calculation in order to guarantee
convergence in a reasonable time without loss of accuracy (typically $\sim 150,000$). Although for the
isolated core-shell spherical NPs there is an analytical expression that describes the absorption
efficiency [27], it has been also calculated with DDA and checked with the exact solution in
order to be consistent with the hemispherical-on-substrate case [27]. Although $Q_{\text{abs}}$ has a simple
expression for the small particle limit coming only from the dipolar contribution [27], this
approximation is not longer valid for the $R = 40$ nm particles analyzed in this study. The local
electric field distribution and the corresponding $\langle |E|^2 \rangle$ in both core and shell surfaces have been
calculated employing finite-element simulations.

The dielectric constants of Al, Mg, Al$_2$O$_3$, MgO, and Ga$_2$O$_3$ have been taken from di-
ferent sources in the literature [28, 29], but the values for Ga were obtained in situ by spectroscopic
ellipsometry [7] and confirmed by those reported in the literature [30]. Figure 2 plots the real and
imaginary parts of the dielectric function $\epsilon = \epsilon_r + i\epsilon_i$ for the three metals and their corresponding
oxides. Note the similar optical behavior shown by oxides of Mg and Al, while Ga$_2$O$_3$ shows
a clear absorption in the UV region below 300 nm. The optical behavior of the three oxides is
found to be roughly equivalent ($Re(\epsilon) \approx 3 - 4$ with low absorption) above 400 nm.

A dimensionless parameter to quantify the near field enhancement has been recently proposed
by Lalisse et al. [31]. The so called Faraday number ($Fa$) takes the following values for the
analyzed metals at their resonant wavelengths: $Fa^{\text{Mg}} = 6542$, $Fa^{\text{Al}} = 1404$ and $Fa^{\text{Ga}} = 53$.
Whereas $\langle |E|^2 \rangle$ gives an estimate of the local field enhancement averaged over the particles
surface, $Fa$ is a local enhancement indicator at the point where the maximum electric field is
produced. A large value of $Fa$ indicates a higher ability to enhance the optical near field, and it
3. Results and discussion

3.1. Comparative study in the far-field: influence of NP shapes

Ellipsometry has been used to measured the pseudo-dielectric function of particle-on-substrate nanostructures in order to determine their plasmonic response [12, 13]. The measured imaginary part of this pseudo-dielectric function correlates directly with the absorption efficiency that is easier and more accurate to determine numerically. In Fig. 3, the absorption efficiency $Q_{\text{abs}}$ for the two geometries is plotted as a function of the wavelength $\lambda$ and the core radius $R_{\text{core}}$ for NPs with an overall radius $R = 40$ nm. For an isolated spherical nanoparticle made of either magnesium or aluminum (first three plots in Figs. 3(a) and 3(b)), the location of the main resonance is only slightly sensitive to shell thickness and follows a similar tendency as their oxide shell thickens. Specifically, their absorption dipolar resonances increase and narrow as their shells become thicker. For Ga, $Q_{\text{abs}}$ also narrows with increasing oxide thickness, but its strength first increases to a maximum value near $R_{\text{core}} = 30$ nm before decreasing with increasingly thicker oxide shells, a behavior influenced by a given value of the shell thickness, this being related to the higher absorption of its oxide at shorter wavelengths (see Fig. 2). Note that the frequency shift caused by NP oxidation depends on two factors that produce opposite behaviors with increasing oxide thickness: a blue-shift due to a reduction of the core size, and a red-shift due to an increase of the effective refractive index surrounding the core. As the oxide shell increases, the blue-shift compensates and slightly dominates the red-shift for Al, while the red-shift dominates the blue-shift for Mg and Ga. These balanced behaviors are more clearly evidenced in Fig. 3(b).

In Fig. 3(a) some quadrupolar behavior can be observed. For $\lambda > 200$ nm this is clearly visible in form of narrow peaks for Mg between 200 and 300 nm. For Al and Ga, this resonance shifts to the blue, and the quadrupolar response lies out of the analyzed range.

For hemispherical nanoparticles located on a sapphire substrate (bottom row of Figs. 3(a)
For hemispherical nanoparticles located on a sapphire substrate, that can be considered experimentally relevant in surface enhancement techniques (bottom row of Figs. 3a and 3b) [11, 13, 14], the plasmonic performance is substantially modified by the geometry and the substrate. In general, interactions with the dielectric substrate tend to red shift the dipolar resonance with respect to the isolated sphere of the same radius [11]. For aluminum and magnesium the absorption is stronger for the hemispherical case than for the spherical case, probably due to the volume reduction of the metallic core. As a consequence of this, the plasmonic absorption reaches a maximum for these Al and Mg hemispherical nanoparticles for certain values of the core radius.

Fig. 3. (a) Absorption efficiency, $Q_{abs}$, of a core-shell spherical nanoparticle and a hemispherical nanoparticle, for Mg/MgO (first column), Al/Al$_2$O$_3$ (second column) and Ga/Ga$_2$O$_3$ (third column). The particle overall radius is $R = 40$ nm while the core radius varies from $R_{core} = 20$ to 40 nm. (b) 2D color map of the normalized absorption efficiency as a function of the wavelength and the core radius $R_{core}$ for Mg/MgO (first column), Al/Al$_2$O$_3$ (second column) and Ga/Ga$_2$O$_3$ (third column) spherical and hemispherical on substrate NPs.
and 3(b)) [11, 13, 14], the plasmonic performance is substantially modified by the geometry and the substrate. In general, interactions with the dielectric substrate tend to red-shift the dipolar resonance with respect to the isolated sphere of the same radius [11]. For aluminum and magnesium the absorption is stronger for the hemispherical case than for the spherical case, due to the volume reduction of the metallic core. As a consequence of this, the plasmonic absorption reaches a maximum for these Al and Mg hemispherical nanoparticles for certain values of the core radius within the studied interval, in contrast with the isolated spherical nanoparticles for which the absorption increases as the core shrinks. Conversely, the absorption for Ga hemispheres decreases with decreasing core radius but reaches a maximum value for an intermediate spherical core radius. In general, if top and bottom plots of Fig. 3(b) are compared, we can conclude that the overall effect of going from the sphere case to the hemisphere one is a shift of the peak absorption to larger core radius and to longer wavelengths. However, the hemispherical-on-substrate geometry is less sensitive to the value of $R_{\text{core}}$. Note that the substrate and the oxide shell have a similar refractive index, so the effective refractive index surrounding the metallic core is larger for the hemispherical nanoparticles than for the isolated spherical nanoparticle with the same oxide thickness. Consequently, the associated blue-shift produced by the oxidation is less for the hemisphere than for the isolated sphere. Finally, it is worth mentioning that the hemisphere geometry presents weaker quadrupolar resonances.

By considering the dielectric constants of each studied metal and their corresponding oxides (Fig. 2), it would be expected that Mg would have the lowest values of $Q_{abs}$ since it has the smallest values of the imaginary part of the dielectric function, but Al $Q_{abs}$ peaks are lower. This apparently contradictory behavior may be understood by recognizing that it is the area under the $Q_{abs}$ curve, not the peak, that is related to the power absorbed by the particle. The Al absorption peak is weaker but wider than that of Mg, so it is not clear which one absorbs more. Furthermore, the real part of the dielectric function has also an effect on the absorption efficiency. In the region of interest (200-300 nm), Al acts as a better conductor than Mg since the real part of its dielectric constant is more negative and is thus better able to limit field penetration.

### 3.2. Near-field enhancement

The analysis of the near field enhancements is of great interest for Raman (SERS) or fluorescence (SEF) spectroscopy techniques where surface field and its interaction with adsorbed analytes play a crucial role. The local electric field distribution has been calculated and analyzed by FEM method, for the two geometries and for different values of the core size and oxide shell thickness. For brevity, and as a representative example of the general behaviour, in Fig. 4 the local electric field distribution is only plotted for a core-shell (metal-metal oxide) spherical (top row) and hemispherical-on-substrate (bottom row) with $R_{\text{core}} = 30$ nm and a oxide shell of 10 nm. The illuminating beam is a monochromatic linearly polarized plane wave whose propagation ($\vec{k}$) and polarization directions ($\vec{E}$) are indicated in the inset. The illuminating wavelength corresponds to the electric dipolar resonance in the $Q_{abs}$ spectrum. The main conclusion is that hot-spots corresponding to a surface electric field enhancement are observed on both the core and the shell, especially for the spherical case. These enhancements correspond to charge concentrations induced by the polarization of the incident field and are manifested by non-propagating evanescent waves. For thick oxide shells, these evanescent waves remain attached to the metallic core and dissipate within the oxide shell. However, for thin oxide shells, part of this evanescent field reaches beyond the surface of the particle, creating external hot-spots with evident practical interest. For the hemisphere geometry, these hot-spots are located mainly where the metallic core touches the substrate, i.e. where the metallic core has sharp edges. Because they are not accessible from outside, they are of little practical interest.

In order to quantify how these enhancements are distributed between core and shell surfaces, the ratio between the average of $|\vec{E}|^2$ on the core and shell surfaces is represented in Fig. 5.
Fig. 4. Local electric field distribution for an isolated core-shell spherical and hemispherical nanoparticle for each metal, with $R = 40$ nm, $R_{\text{core}} = 30$ nm, and a 10 nm thick oxide shell. The illuminating wavelength in each case corresponds to the one that makes $Q_{\text{abs}}$ maximum.

Fig. 5. Evolution of $\langle |\mathbf{E}_{\text{core}}|^2 \rangle / \langle |\mathbf{E}_{\text{shell}}|^2 \rangle$ for each metal as a function of the metallic core size for a spherical and hemispherical nanoparticle of radius 40 nm at the wavelength at which $\langle |\mathbf{E}_{\text{shell}}|^2 \rangle$ takes its maximum in the electric dipolar resonance.
These are plotted as a function of the core size for the two geometrical configurations at the wavelength at which $|\langle \vec{E}_{shell} \rangle^2 |$ takes it maximum value in the electric dipolar resonance. For both cases, it can be observed that for a small metal core with thick oxide shells, $|\langle \vec{E} \rangle^2 |$ is much higher at the core than in the shell, with $|\langle \vec{E}_{core} \rangle^2 |/|\langle \vec{E}_{shell} \rangle^2 |$ larger than 1. As the oxide shell thins, the value of this ratio generally decreases until the shell enhancement becomes larger than the core enhancement, and the hot-spots are clearly located on the shell surface $|\langle \vec{E}_{core} \rangle^2 |/|\langle \vec{E}_{shell} \rangle^2 |$ smaller than 1. This happens for the spherical geometry for all the three materials analyzed. For the hemispherical geometry, we get similar results, except that this ratio is considerably larger because of the high field enhancements where the metallic core meets the substrate.

Ratios $|\langle \vec{E}_{core} \rangle^2 |/|\langle \vec{E}_{shell} \rangle^2 |$ smaller than 1 can be interpreted by considering boundary conditions for the normal component of the displacement vector $\vec{D} = e \vec{E}$. At hot-spot positions, the near field is mostly composed of evanescent waves, and its electric field direction is predominantly radial, normal to the spherical surface. In this situation, the component of the displacement vector $\vec{D}$ normal to the surface separation between the oxide shell and vacuum is conserved. Because the shell electric permittivity is larger than that of the surrounding vacuum, the electric field inside the shell is smaller than outside of it.

For hemispherical nanoparticles, the electromagnetic field tends to be confined at the edges of the hemisphere (lightning rod effect [32]). Due to this confinement, thinner shells are required to achieve $|\langle \vec{E}_{core} \rangle^2 |/|\langle \vec{E}_{shell} \rangle^2 |$ less than 1; indeed, for Mg this ratio is always larger than 1. As can be seen in Fig. 4, the maximum value $|\vec{E}|^2$ is much larger for all three metals because of this confinement. By contrast, in the isolated spherical geometry the electromagnetic energy is spread in larger regions instead of being bound around the edges.

For practical purposes it is interesting to be in the $|\langle \vec{E}_{core} \rangle^2 |/|\langle \vec{E}_{shell} \rangle^2 | < 1$ region, where the

for the Mg hemisphere this condition can not be fulfilled indicates that this type of structure cannot be used for surface enhanced applications.

Concerning the analyzed materials, magnesium presents the highest values of these electric field enhancements because Mg and MgO are the least lossy materials. On the contrary, gallium and its oxide shell present the poorest plasmonic performance. It is interesting to point out that the core size for the condition $|\langle \vec{E}_{core} \rangle^2 |/|\langle \vec{E}_{shell} \rangle^2 | = 1$ increases as the Faraday number $F_{\text{fa}}$ of the metal becomes larger, but the enhancement depends more sensitively on core radius. Figure 5 indicates that for a given geometry, the sensitivity of $|\langle \vec{E}_{core} \rangle^2 |/|\langle \vec{E}_{shell} \rangle^2 |$ to increasing $R_{\text{core}}$ is larger for the Mg and Al than for Ga.

3.3. Influence of the oxidation on plasmonic performance

Figure 6 plots the evolution of the peak value and wavelength of the dipolar resonance for both $Q_{\text{abs}}$ and $|\langle \vec{E} \rangle^2 |$ in terms of the core radius for both geometries of Ga, Mg, and Al. The way the peak value of $|\langle \vec{E} \rangle^2 |$ evolves with increasing oxide-shell thickness is similar for the three studied metals. Whereas for the spherical particle (red squares-solid line) its value reaches a maximum for the intermediate values of the analyzed shell thicknesses, in the case of the hemispherical nanoparticle (blue squares-solid line), the value of $|\langle \vec{E} \rangle^2 |$ decreases monotonically as the shell becomes thicker. Both behaviors are influenced by two factors: the way the oscillating charges in the metallic core are increasingly separated from the surface where the near field is calculated [33], and the fact that the evanescent field is increasingly confined inside the thicker oxide layers [34]. Since the intensity is calculated as an average of the electric field on the particle surface, its value depends sensitively on the oxide layer thickness.

Regarding the peak location, the hemisphere peaks are red-shifted from the spherical peaks, as expected [11], following the same behavior for both geometries but differing from metal to metal. For Mg and Ga, the resonance peak red-shifts from the bare metal value as the shell thickens,
ultimately approaching a constant value. Although, the Al peak red-shifts with initial oxidation, it then blue-shifts with increasing oxide thickness, eventually to wavelengths shorter than its unoxidized wavelength. These idiosyncratic behaviors derive from the respective dielectric functions of the growing native oxide shell (red-shift) and shrinking metal core (blue-shift) [7,11], an effect foreshadowed in an early investigation of Al NPs [21] and consistent with more recent studies [9, 14].

The characteristic spectral red-shift of the near field $\langle |E|^2 \rangle$ (circles-dashed line) from the far field [24, 25], $Q_{abs}$ (squares-solid line) is clearly observed for all geometries. The magnitude of this shift depends on the value of the imaginary part of the dielectric function [25]. When the imaginary part of the dielectric function is low, as for Mg, the red-shift is smaller, but when its imaginary part is higher, as for Ga, the red-shift is larger. The quantification of this shift allows an optimization of the near fields based on their far-field counterparts, which are, in general, easier to measure.

From an experimental point of view, Al and Mg show an interesting plasmonic behavior in the UV [7], and both are quite stable metals in absence of humidity [14] and at moderate temperatures [35]. They suffer a similar tarnishing process that protects the underlying material from further oxidation [36]. Unfortunately, nanostructures of these metals are quite susceptible to oxidation during or after fabrication, and further investigations are needed to understand and control nanoscale oxide formation [9, 14]. For example, if ambient temperature increases over 400°C, Al can oxidize almost completely due to the high mobility of oxygen [35]. In this way, the heating action produced by a powerful light source interacting with the strong plasmonic absorption of Al NPs could produce a deleterious effect by inducing additional oxidation. Consequently, both humidity and Joule heating can produce efficiency losses in both metals and blue-shifts of the resonances in Al after several uses. Although gallium shows the weakest resonance and strongest oxide sensitivity, it is of interest because its oxide is thin and stable, its resonances in the UV [11, 12] are broad, and its low melting point makes it suitable for eutectic alloys that may improve its plasmonic performance [37].
4. Conclusions

In summary, we have studied the effect of NP oxidation on the UV plasmonic performance of three promising metals: gallium, magnesium, and aluminum [7, 8, 11, 13]. The growth of an oxide shell on a hemispherical NP surface made of Ga, Mg, or Al produces a decrease in the near field amplitude of $\langle |E|^2 \rangle$ for all cases. However, for the spherical nanoparticles, the value of $\langle |E|^2 \rangle$ increases for intermediate values of the analyzed shell thicknesses. The values of $Q_{abs}$ in hemispherical NPs actually increases for the three metals under study for some intermediate value of the oxide thicknesses. For Al and Mg spherical NPs, $Q_{abs}$ increases as the size of the core decreases. On the contrary, for Ga spherical nanoparticles, the $Q_{abs}$ maximum is found for a 10 nm thick oxide shell. The resonance could be red- or blue-shifted depending on the material and the thickness of the shell. Furthermore, the systematic, monotonic reduction of the field intensity on the particle surface may be used as an estimate of the oxide thickness. These results indicate how UV plasmonic resonances of Ga, Mg, and Al may be optimized for SERS-like applications, allowing control of the near field peak intensity and its spectral location.

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