

Surface plasmon resonance of capped Au nanoparticles

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In this Rapid Communication we show the relationship between surface plasmon resonance damping and the intensity of surface bonding for capped Au nanoparticles, (NPs). Up to now the influence of capping has been included as a phenomenological modification of the scattering constant. It is indicated here that the effective NP size is the parameter mainly affected by surface bonding. Experimental results in different Au-thiol NPs are shown to be in excellent agreement with the expression we propose for damping. Moreover, according to our model the resonance profile gives a deep insight of the interface bonding strength.

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Surface plasmon resonance (SPR) is the most remarkable optical property of metallic nanoparticles (NPs).^{1,2} Besides the fundamental interest in understanding the physical interactions at the nanoscale, the SPR is in the basis of many technological applications, as they are DNA analysis chips and protein recognition devices.^{3,4} SPR consists on a collective oscillation of the conduction electron inside the NPs. The excess of charge produced at the surface because of electron movement acts as a restoring force, while the electron movement is damped mainly because of the electron interaction with atomic cores and NP surface. The system behaves as a damped oscillator with a resonance frequency that for most of the transition metals lies on the ultraviolet-visible part of the spectrum.^{1,5} Hence the NPs exhibit an absorption band in this region of the spectrum. As the damping constant depends strongly on the particle size,^{1,2,6} so does the shape of the SPR. Within the frame of the Mie theory (that is, assuming well-dispersed spherical NPs), the SPR full width at half maximum (FWHM) is given by:^{1,2}

$$\Gamma = \Gamma_0 + A \frac{v_F}{R}, \quad (1)$$

where A is a constant that includes the details of the scattering processes, v_F is the Fermi velocity for the metal, and R stands for the particle radius. Figure 1 shows the FWHM for Au NPs calculated according to the Mie theory and using a size-dependent dielectric function given in Ref. 2. As can be observed in the inset, the value of Γ follows Eq. (1) up to $R \sim 25$ nm. The exact values of A are slightly different depending on the authors but they are always below 1 and mainly between 0.8 and 0.9 (in units of \hbar).

An intrinsic feature of the NPs is the large fraction of atoms located at the surface that are modified when the particle is capped with different chemical species. Thus the capping agents can alter significantly the whole NP properties. An example of strong interaction between the NPs and the capping agent are the thiol-capped Au NPs. It has been shown that the thiols induce changes in the electronic con-

figuration of the NPs, increasing the hole density at the 5d Au level.⁷⁻¹³ As a consequence of these changes in the electron configuration, the physical properties of the NPs change significantly; the most outstanding one is the ferromagnetic-like behavior of thiol-capped Au NPs despite the diamagnetic character of bulk gold.⁹ Thiol-capped Au NPs also exhibit a wider SPR than bare NPs, which is associated with an extra damping due to the interaction of conduction electrons with the thiols.^{2,14,15} In some cases, thiol capping even yields to the absence of a SPR absorption band in the spectrum.^{8,9} The mechanism responsible for these changes in the optical properties of Au NPs induced by the thiols is not clear. Furthermore, there is a controversy even about the metallic or insulating character of small (below 2 nm size) thiol-capped Au NPs.^{14,15} In the present paper, the effect of the capping molecules in the SPR band of Au NPs is experimentally studied to clarify the influence of the capping agent on the

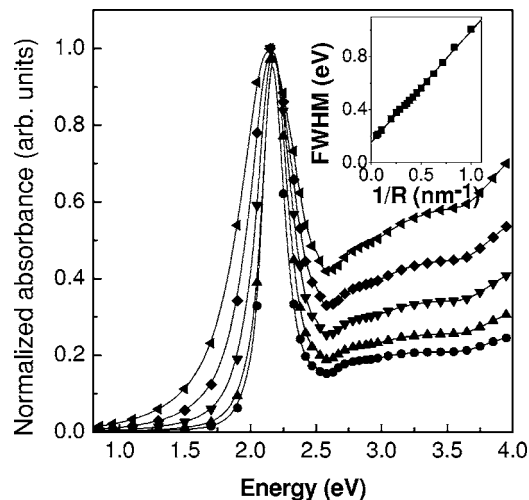


FIG. 1. SPR spectra for Au NPs embedded in a media with $n=1.78$ calculated according to the Mie theory for $R=2$ nm (\blacktriangleleft), 3 nm (\blacklozenge), 5 nm (\blacktriangledown), 10 nm (\blacktriangle), and 20 nm (\bullet). The inset shows the FWHM of the SPR as a function of the inverse of particle radius.

electronic configuration of the NPs, and consequently, on their physical properties.

The sample preparation procedure of dodecanethiol-capped NPs (named hereafter thiol-capped NPs) is based on the route proposed by Brust¹⁶ using a ratio of thiol:gold of 2:1 to decrease the average particle size. Au thiol-capped glyconanoparticles (named hereafter as maltose-capped NP), were prepared by using a maltoneglycoconjugate as a thiol linker species.¹⁷ In this case the metal clusters are at the same time protected and functionalized with the organic molecule. Tetraalkylammonium ($R_4N^+X^-$) protected gold NPs with a weakly interacting dipole capping molecule were also prepared.¹⁸ In this case, the sample was obtained with tetractyl ammonium bromide as the surfactant molecule.

In any analysis of the surface plasmon resonances of Au NPs, the possible effects of aggregation must be kept in mind. TEM analysis of the samples studied here showed that there was no aggregation.⁹ Moreover, it is well known that NP aggregation shifts the position of the resonance toward lower energies (the red and infrared part of the spectrum) while the plasmons analyzed here showed the resonance located at the position that correspond to well-dispersed nanoparticles. We also measured the optical absorption in the red and infrared part of the spectrum but we found no signal in this region, so we can discard aggregation effects in our samples.

As stated above, thiol-capped Au NPs exhibit SPR clearly wider than that corresponding to bare Au NPs.^{2,15} There are two proposed explanations for the changes induced in the SPR of Au NPs by thiol capping: the reduction of electron density in the NPs and the increase of damping due to charge localization at the NP surface.

In a recent work,¹⁵ Lica *et al.* proposed that the changes in the SPR of thiol-capped NPs are due to the decrease in Au 5d electrons because of the charge transfer from Au atoms at the NP surface to S atoms at the end of the thiol chain. Their experimental measurements of SPR could be fitted to those calculated on the basis of a jellium model, assuming that each S-Au bond reduces in one electron the charge of the NPs. However, several extended x-ray absorption fine structure Extended X-ray Fine Absorption Spectroscopy (EXAFS) experiments of thiol-capped Au NPs showed that the charge transfer at the Au-S bond is about 0.04 electron per atom.^{7,9} Although the calculations reproduce the experimental results, the parameters used have no physical meaning and therefore the electron density decrease cannot be invoked as the unique reason for the changes in the SPR.

The other argument proposed to explain the changes induced in the SPR by thiol capping is the charge localization at the Au-S bond. This covalent bond blocks the electrons involved in the bond at the NP surface. The localized charge will have an electrostatic interaction with the NP conduction electrons, inducing an extra damping in the electrons oscillation (called chemical interface damping) and therefore, enhancing the SPR bandwidth.^{2,8,9} Recent theoretical studies showed that the interaction of small Au NPs with capping thiols is quite complicated and not fully understood.^{10,12,13} Therefore, simple phenomenological models are used to study the SPR of thiol capped Au NPs. Within the frame of these models, the FWHM of the SPR is usually given by the expression:^{2,15}

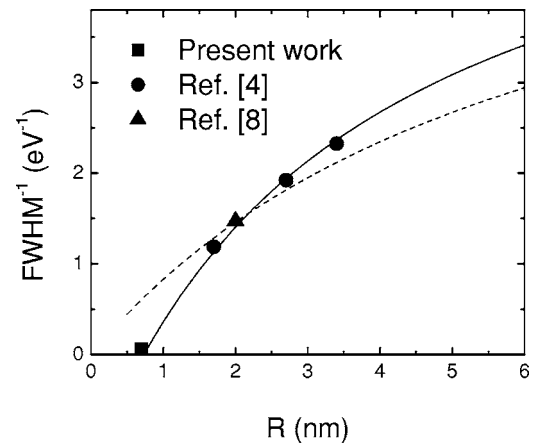


FIG. 2. FWHM for SPR band of thiol-capped Au NPs. Symbols correspond to the experimental values from Refs. 4,8 and from our samples as indicated in the graph. Dashed line corresponds to the best fit using Eq. (2) with $A^*=1.04$ and solid line shows the fit to Eq. (3) with $r=0.7$ nm and $A=0.8$.

$$\Gamma = \Gamma_0 + A^* \frac{v_F}{R}, \quad (2)$$

where A^* is a phenomenological parameter. Although A^* has not a clear physical meaning, large values of A^* are associated with strong chemical interface damping. Thus, for thiol-capped Au NPs, typical values of A^* are between 1 and 1.2.

Following this equation, the region where electrons can oscillate freely is reduced by the chemical interface damping in a factor A/A^* , and it means that this reduction is proportional to the particle size. However, considering that the charge distribution at the interface is determined by the atoms present at this interface and the nature of the bond, this region of localized charge is expected to be independent of the particle radius. It is meaningless to suppose that the region of charge localization at the surface has a thickness, r , which increases linearly with the NP radius. Therefore, we propose that the value for the FWHM of the SPR should be given by an expression as

$$\Gamma = \Gamma_0 + A \frac{v_F}{(R-r)}, \quad (3)$$

where r results independent of the particle size, and A is the same constant than for bare Au NPs. From this latter equation it is expected that the chemical damping becomes more important for small NPs; in particular for those with r close to R , since for these particles the second term in Eq. (3) increases very fast. Actually, this latter equation can explain experimental results of small NPs. It has been found by several authors^{8,9} that 1.5-nm thiol-capped NPs exhibit no SPR, which is understood as an infinite damping. Following Eq. (2) it should yield to an infinite value of A^* , (which is hard to understand), while for larger particles, its value is close to 1. On the contrary, according to Eq. (3), the lack of SPR should correspond to a value of $r=R$. This value of r can also explain the changes in the SPR observed in larger particles. Figure 2 shows the SPR full width at half maximum of thiol-

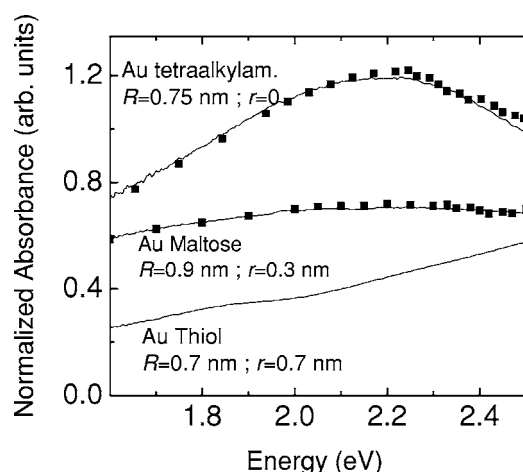


FIG. 3. Optical absorption spectra of Au NPs capped with different species. Solid lines correspond to experimental measurements. The symbols represent the best fit according to Mie theory assuming different values of r as indicated in the figure. A linear background was added to take into account the absorption from the rest of the sample.

capped Au NPs and also results from other authors, as a function of the particle size measured by TEM. The dashed line corresponds to the best fit to Eq. (2) that can explain the results obtained for particles with sizes over 2 nm (with $A^* = 1.04$). However, for smaller particles, the experimental results deviate from the fit and can not explain the absence of SPR for particles smaller than 2 nm. On the contrary, the solid one, showing the fit to the Eq. (3), allows to fit the experimental data from NPs with different sizes with a unique value of $r=0.7$ nm (as it can be expected from a sole bond nature) and $A=0.8$, which is the value given for bare Au NPs.

The parameter r has a clear physical meaning: It is the thickness of the shell where electrons cannot oscillate because of the interaction with capping agents and, therefore, it provides an estimation of the strength of the interaction between these capping molecules and NP atoms. Hence, the SPR can be used as a probe to analyze this interaction. Analyzing the SPR curve in terms of Mie theory we get information about the free electron oscillation volume ($R-r$), whereas TEM measurements will give information about NP size (R). Comparing both values we get the thickness of the blocking shell (r), which, as explained above, is a measurement of the strength of the capping agent–NP interaction. As an example, Fig. 3 shows the SPR of Au NPs capped with different chemical species. For the NPs capped with tetraalkylammonium, which is known to interact very weakly with the NPs, the SPR band can be fitted with the Mie theory using a size $R=0.7$ nm, which corresponds to the same value found by TEM measurements,⁹ confirming that the capping agent merely passivates the NPs and does not modify its electronic structure ($r=0$). For the maltose-capped Au NPs (intermediate interaction strength) with $R=0.9$ nm according to TEM measurements,¹⁹ the SPR band is fitted assuming a particle size of $R=0.6$ nm (that is, $r=0.3$ nm). Finally, for strong interacting thiol-capped Au NPs, the TEM measurements indicated $R=0.7$ and the absence of SPR is understood

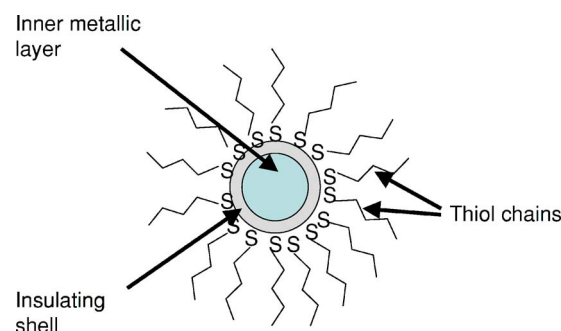


FIG. 4. (Color online) Scheme of a thiol-capped Au NP with an external insulating shell where electron movement is damped by interaction with thiols, and an inner metallic core.

as $R=r$ (and therefore $r=0.7$ nm). Although in both cases, maltose-capped and thiol-capped NPs, the Au atoms at the NP surface are bonded to S atoms, recent calculations indicate that the Au-S interaction at the NP surface depends on the S atom environment,¹³ explaining the different results obtained for both samples. Furthermore, it is worth observing the parallelism in the changes of optical properties, the modification of electronic configuration and magnetic properties of Au NPs as a function of the interaction with capping agents.⁹ EXAFS experiments showed that tetraalkylammonium-capped Au NPs have the same density of $5d$ Au electrons than bulk Au and resulted diamagnetic (as bulk Au). Maltose-capped NPs presented a slightly decreased density of $5d$ electrons with respect to bulk Au, while magnetic measurements indicated weak ferromagnetism.¹⁹ Finally, thiol-capped NPs exhibited an intense decrease of $5d$ electron with respect to bulk Au and presented surprisingly ferromagneticlike behavior up to room temperature.⁹

The proposed model can also explain the controversy about the metallic or insulating character of thiol-capped Au NPs. For NPs below 2 nm in size, several authors observe localized charge behavior^{9,20,21} while recent studies showed the presence of free electrons.^{14,15} According to our model (see Fig. 4), those particles will consist of an outer shell where electrons will be localized and therefore with typical insulating behavior (thickness ~ 0.7 nm), and a inner core of metallic Au. For particles larger than $R=1$ nm metallic character (presence of SPR) is always found, that arises from the inner metallic layer. However, for NPs smaller than $R=0.7$ nm, the size of the insulating shell is about the whole NP size, and therefore, it will show typical insulating behaviour. In the limit between these two regimes, slight changes in the preparation methods (and hence in the thiol-NP interaction) can determine the metallic or insulating character of the NPs. Some recent results showed that thiols can be bond not only to the outer shell of Au atoms but also to some internal ones, increasing in this way the thickness of the blocking shell⁹. This fact should account for the contradictory results obtained by different authors when the NPs are around this size.

In summary, we propose a model to describe the effects of strong interacting capping agents onto the properties of SPR. The capping agents localize charge in a shell close to the

surface with a thickness that depends on the strength of its interaction with NPs, whereas the inner core presents metallic behavior. The model does not use phenomenological parameters but those with physical meaning as the surface thickness of localized charge in which electrons can not os-

cillate freely. The proposed expression also conciliates the apparently contradictory results found by different authors on this kind of materials. This model has been tested with experimental results obtained for Au NPs capped with different agents showing excellent agreement.

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