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Authors: O.A. Oviedo, M.M. Mariscal, E.P.M. Leiva

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Theoretical Studies of Preparation of Core-Shell Nanoparticles by Electrochemical Metal Deposition

O. A. Oviedo, M. M. Mariscal* and E. P. M. Leiva^{*,1}

INFIQC, Departamento de Matemática y Física, Facultad de Ciencias Químicas,
Universidad Nacional de Córdoba. Córdoba, Argentina.

Abstract

In the present work we discuss the statistical mechanical framework for predicting the decoration of metallic nanoparticles using electrochemical methods, in thermodynamic equilibrium. It is found that depending on the interactions between the two metals, controlled decoration may be achieved for core-shell nanoparticles in undersaturation and oversaturation conditions. The concept of underpotential deposition is discussed for the case of nanoparticles, with the finding that this phenomenon may be size dependent.

Keywords: nanoparticle, underpotential deposition, core-shell, size effect, nanotechnology.

1. Introduction

Nanoparticles (NP) are conglomerates of hundreds or thousands of atoms that are characterized by a high surface to volume ratio. A consequence of this feature is the

* Tel/Fax: +54 (0351)4344972. Email: eleiva@fcq.unc.edu.ar

¹ ISE members.

generation of an energy excess with respect to the bulk material that make them thermodynamically unstable with respect to the latter [1,2]. The unique nanoscale features of these small particles affect their reactivity, physical and chemical properties [3]. For example, although gold is known to be inert at the macroscopic scale, when the size of Au NP is reduced to a few nanometers, they become extremely effective as catalysts for oxidation and reduction reactions [4-6]. The size dependence of the optical and electronic properties of NP provides another clear example of nano-effect. In this respect, it has been found that the energy band gap increases as the diameter decreases below 6–8 nm [7-9]. These properties are attributed to the confinement of electrons and the existence of discrete electronic states that are absent for larger particles [10]. Another example of the singular behaviour of NP is the size dependence of their thermal properties [11]. Electric and magnetic properties are also known to be related to their size and crystallinity [12,13].

Many size effects could be partially predicted from macroscopic thermodynamics, as a direct consequence of the Laplace-Young equation, but they are strongly pronounced as the size is significantly below 100 nm [14]. For example, Plieth treated the shift of the reversible redox potential of a small particle with its size [15]. A distinctive feature of very small NP (below to 30 nm) is that the surface tension depends on the size and that the derivative of the surface tension must be taken into account in thermodynamic models [16,17]. This size dependence of the surface tension is of great importance in the physicochemical processes of dissolution and phase transformation.

A great number of techniques, including chemical, electrical, and physical processes, have been employed for the preparation of NP [18-28]. Syntheses through simple wet-chemical methods [29] are particularly favored for the cost-effective and large-scale production of such nanostructures. In particular most of the wet-chemical

methods consist of the reduction of a metal salt precursor solution in the presence of a stabilizing reagent. The main advantage of electrochemical methods is that they allow precise adjustment of the supersaturation conditions at the interface, via control of the deposition potential [30,31,32]. Potential adjustment can be achieved by means of straightforward potentiostatic control of an electrode or alternatively by the proper choice of a redox couple. In aqueous media, detergents such as hexadecyltrimethylammonium bromide (CTAB) may be used for the successful syntheses of Au and Ag NPs [33-36]. Nikoobakht and El-Sayed used surfactant-stabilized Au seeds and different amounts of silver nitrate to prepare very high yields of Au NPs having various aspect ratios [24]. Various factors influence the process of NP formation; some examples may be surfactants having chains of different lengths, additives, other metallic ions, etc. [24,37]. It has been suggested that the properties of the surfactants, organic solvents, relative amounts of the reducing agents, and concentration of the seeds are all important parameters for controlling the aspect ratios of NPs when using the seed-mediated growth method.

Another electrochemical method developed to achieve the synthesis of core-shell NPs is the so-called “galvanic displacement method”. This has been originally applied to flat surfaces and then successfully extended to NPs. It allows to control the amount of metal deposited at the monolayer level and has been applied to bimetallic and trimetallic systems [38].

The preparation of bimetallic NP is also of interest to both basic and applied science because they exhibit characteristic electronic, optical, and catalytic properties that differ from those of their individual constituent metallic [3]. Regular rod-shaped Au–Ag core–shell nanostructures have been obtained using NH_2OH to reduce Ag onto the surface of the Au NP [39]. Au–Ag core–shell NP that have different shell

thicknesses can be synthesized by electrochemically depositing Ag onto the surface of Au NP using poly(vinylpyrrolidone) (PVP) as stabilized, and ascorbic acid as a reducing agent under alkaline conditions [40]. Recently Huang *et al.* [41] reported a simple procedure for the synthesis of Au–Ag NP under alkaline conditions (pH 8.0–10.0) from silver and ascorbate ions using Au NP as seeds. The Ag ions that are reduced by the ascorbate ions deposit onto the surfaces of the Au NP to form dumbbell-shaped Au–Ag NP whose morphologies differ depending on the pH and the concentration of Ag ions. These authors suggested that the [111]-facet of the NPs is more accessible to Ag atoms than the [110] facet. By controlling pH, high-quality Au–Ag NP were prepared. On the other hand, Fonticelli *et al.* [42] have proposed an electrochemical method for the generation of bimetallic Au–Ag core-shell NP in solution. In this method, the deposition potential is controlled by means of a redox couple (p-benzoquinone+p-hydroquinone) and pH. The method is based on two well-known electrochemical phenomena: underpotential deposition and the ability of redox couples to control the potential at a given metallic interface. At the initial stage, Au NPs are capped by alkanethiols in order to prevent coalescence, and then the NPs are brought in contact with a solution containing Ag ions. At this stage, Ag ions are able to discharge below the alkanethiol layer, through an electron transfer reaction involving the redox couple. Due to this reaction, a layer of Ag develops on the surface of Au NPs. At the end of the procedure, Au–Ag bimetallic NPs with core-shell structures stabilized by the alkanethiol molecules are observed.

In a previous work [43], we proposed a nanothermodynamic modeling for the electrochemical generation of metallic and bimetallic NPs. We suggested that the spontaneous formation of core-shell NPs depends on several factors, i.e. size and shape of the core, chemical composition of the system, and under/oversaturation conditions.

The behavior of those systems where the binding energy of the adsorbate to the substrate is more positive than that of the bulk adsorbate showed close similarities to that of the classical behavior expected of the growth of pure metal clusters [20,44]. However, when the adsorbate-substrate interaction is stronger than the bulk adsorbate interaction, a manifold of behavior arise depending on cluster size and shape. Recently, we extended this model to consider metastable states [45].

In the present work, we summarize the statistical mechanic features of the new model with special emphasis on their electrochemical relevance and perform an analysis of electrochemical metal deposition on a NP used as a seed. We also report atomistic computer simulations for paradigmatic systems illustrating the relevant points of the present model.

2. Theory

2.1. Statistical mechanical approach

To begin our discussion, we consider an electrolytic solution at temperature T , containing an incompressible metallic nanoparticle (NP) of type S and metallic ions of type Me providing an environment with constant chemical potential μ_{Me} . This configuration of the system aims to describe bimetallic growth on NP used as seeds. As we see below, the growth of a core-shell structure can be considered as a special case, but the basic formulation could be also applied to the formation of nanoalloys and three-shell onion like structures. The grand canonical partition function of this system can be written as [45,46]:

$$\Upsilon(\mu_{Me}, N_S, T) = \sum_{N_{Me}=1}^{\infty} Q(N_{Me}, N_S, T) \exp[\beta N_{Me} \mu_{Me}] \quad (1)$$

where N_{Me} is the number of Me atoms in the nanoparticle, N_S is the number of atoms constituting the metallic core, $\beta = 1/kT$ where k is Boltzmann's constant and $Q(N_{Me}, N_S, T)$ is the canonical partition function of a nanoparticle made of N_{Me} and N_S atoms. Equation (1) can be rewritten in term of excess quantities [45]:

$$\Upsilon(\mu_{Me}, N_S, T) = A \sum_{N_{Me}=1}^{\infty} \exp[-\beta \Delta F(N_{Me}, N_S, T)] \exp[\beta N_{Me} \Delta \mu_{Me}] \quad (2)$$

where $A = \exp(-\beta F_S)$, F_S being the Helmholtz free energy of the naked core and $\Delta \mu_{Me} = \mu_{Me} - \mu_{Me}^0$ is an excess of chemical potential referred to the bulk metal Me . ΔF in equation (2) is an excess of Helmholtz free energy calculated according to $\Delta F = F_{N_{Me}/S} - F_S - N_{Me} \mu_{Me}^0$, where $F_{N_{Me}/S}$ is the free energy of the core-shell nanoparticle. Thus, ΔF is an excess of binding free energy of the Me atoms in the bimetallic nanoparticle with respect to bulk Me . In the case of electrochemistry, the quantity $\Delta \mu_{Me}$ indicating oversaturation (if positive) or undersaturation (if negative) corresponds to an overpotential η measured with respect to a reference electrode made of the same metal Me in the same solution [31]. Thus, for electrochemical applications we can replace $\Delta \mu_{Me}$ by $-zF\eta$, where z is the valence and F is the Faraday constant. In

the electrochemical jargon, $\eta > 0$ correspond to underpotential deposition (UPD) conditions, while $\eta < 0$ correspond to overpotential deposition (OPD) conditions. At first sight it may seem surprising that the quantity $\Delta\mu_{Me}$ may be straightforwardly replaced by the overpotential. In fact, $\Delta\mu_{Me}$ contains the chemical potential of the adatoms in the nanoparticles, thus involving many effects like the size-dependent binding energy of the adatom to the nanoparticle, solvent effects, ion effects, etc. However, it was shown in reference [31] that $\Delta\mu_{Me}$ is equal to the difference of the chemical potentials of the electrons in the working and reference electrodes (equation (5) therein). Thus, if the latter is made of the metal Me and is immersed in the same ionic solution, $\Delta\mu_{Me}$ is the excess of chemical potential of the deposit with respect to bulk Me and η is the corresponding overpotential. Then, within the electrochemical context, we obtain:

$$\Upsilon(\eta, N_S, T) = A \sum_{N_{Me}=1}^{\infty} \exp[-\beta\Delta F(N_{Me}, N_S, T)] \exp[-\beta z F N_{Me} \eta] \quad (3)$$

According to statistical mechanics, this equation contains all we need to calculate thermodynamics properties of the present system, since from it all equilibrium properties may be calculated. However, there are at least two handicaps for such a calculation. One is the calculation of the free energy change $\Delta F(N_{Me}, N_S, T)$, which in turn implies knowledge of the canonical partition function $Q(N_{Me}, N_S, T)$. This calculation involves the sum over all energy states $E_i(N_{Me}, N_S, T)$ compatible with N_{Me} and N_S :

$$Q(N_{Me}, N_S, T) = \sum_i \exp(-\beta E_i(N_{Me}, N_S, T)) \quad (4)$$

Even assuming a lattice model, and thus restricting the positions of the Me and S atoms to a finite number of point in the configurational space, such a calculation appears as computationally demanding due to the number of possible permutations. The other additional problem is the existence of infinite terms in the sum (3). In the underpotential region ($\eta > 0$), there is some hope of convergence for this sum, since for $N_{Me} \rightarrow \infty$ the term $\Delta F(N_{Me}, N_S, T)$ will be approximately constant and the sum of exponentials will converge. However, in the overpotential region the sum (3) will diverge, and some physical considerations must be made to get physical insight into the present problem in spite of this divergence. Both hindrances will be circumvented in the following section. However, an important number of conclusions can be drawn without explicit calculation of the partition function. To show this, let us consider the probability to have N_{Me} metallic atoms deposited on a cluster made of N_S atoms of S -type at the potential η and temperature T :

$$p_{N_{Me}}(\eta, N_S, T) = \frac{\exp[-\beta \Delta F(N_{Me}, N_S, T) - \beta z F N_{Me} \eta]}{\Upsilon(\eta, N_S, T)} \quad (5)$$

Since for given η , N_s and T the partition function is a constant, we have that the product $p_{N_{Me}}(\eta, N_s, T)Y(\eta, N_s, T)$ is monotonic with $p_{N_{Me}}(\eta, N_s, T)$ and also its kT th power:

$$f(N_{Me}) = \left(p_{N_{Me}}(\eta, N_s, T)Y(\eta, N_s, T) \right)^{kT} \quad (6)$$

Thus, representation of this function, that can be calculated from $\exp[-\Delta F(N_{Me}, N_s, T) - zFN_{Me}\eta]$ according to equation (5), yields a straightforward visualization of minima and maxima in $p_{N_{Me}}(\eta, N_s, T)$ without knowledge of $Y(\eta, N_s, T)$. A detailed analysis of local and global minima using $f(N_{Me})$ will be performed in Section 3.

2.2. Computational approach

As stated in the previous section, the present modeling could be applied to any type of bimetallic nanometric systems. With computational purposes, we will restrict our analysis to the family of nanostructures that are addressed with the denomination of core-shells. This is a type of systems where, as described in the introduction, extensive experimental work has been developed.

Instead of calculating $Q(N_{Me}, N_s, T)$, we consider the approximate calculation of $\Delta F(N_{Me}, N_s, T)$ taking into account different contributions to it: translational,

rotational, vibrational, and static [45]. A detailed analysis that we describe somewhere else [45] shows that only the energetic terms are relevant at room temperature in the case of metallic systems like the present ones, where the interaction between particles is strong [43,45,47]. Thus, equation (3) can be roughly approximated by:

$$\Upsilon(\eta, N_s, T) \approx A \sum_{N_{Me}=1}^{\infty} \exp[-\beta \Delta U(N_{Me}, N_s, T)] \exp[-\beta z F N_{Me} \eta] \quad (7)$$

where $\Delta U(N_{Me}, N_s, T)$ corresponds to the excess of internal energy of metal *Me* on the NP with respect to bulk *Me* phase and can be written:

$$\Delta U(N_{Me}, N_s, T) = \Delta U_{tr} + \Delta U_{rot} + \Delta U_{vib} + \Delta U_{stat} \quad (8)$$

Let us analyze each of these contributions. In the case of a bimetallic nanoparticle, the translational energy is given by motion of its center of mass and is of the order of $\frac{3}{2}kT$. However, this is compensated exactly by the translational energy of the naked core yielding $\Delta U_{tr} = 0$. Similarly, the excess of rotational energy can be set $\Delta U_{rot} = 0$. Concerning ΔU_{vib} , previous work where comparison between static and quasi harmonic lattice calculations was made [47] showed that this contribution is of the order of kT per atom at room temperature. Again, the excess should be a small percentage of this quantity. To give a figure, we have calculated by means of molecular dynamic simulations this excess for one, two and three overlayers of Ag on Au(TO_1289) at 300 K. The results are shown in Table 1, where it is found that the vibrational energy excess

per atom amounts at the most a fraction of a meV, so that we will also neglect this contribution. The contribution ΔU_{stat} that involves the binding energy of the system components was approximated using embedded atom potentials [48], which gives a reasonable description of metallic binding. The calculation was made as follows: for a given number of deposited shell atoms (N_{Me}) on the core cluster (N_S) serving as a substrate, the minimum energy configuration was determined by a low temperature simulated annealing. The simulated annealing procedure was started at 300 K and finished close to 0 K. It is quite possible that this procedure will not lead to the global energy minimum of the system, but to a local one. However, the same can be stated for the experiments. Further discussion on these points can be found in references [2,3,45].

	Ag(636)/ Au(TO_1289)	Ag(2735)/ Au(TO_1289)	Ag(2951)/ Au(TO_1289)
ΔU_{vib}	-0.439	1.169	1.275
ΔU_{stat}	12.461	133.943	160.966
$\Delta U_{vib} \cdot x100 / \Delta U_{elec}$	3.5%	0.9%	0.8%

Table 1: Excess of vibrational and static internal energy for deposits made of different number of type *Me* atoms on Au-NP(TO_1289) with respect to the bulk *Me* phase. The temperature was 300 K. All values are given in eV.

3. Results and discussion

In the present section, we analyze within the present approach two different systems where distinct behavior is expected, depending on the relative surface energies of the metals involved. In fact, underpotential deposition is expected on planar surfaces when the surface energy of the adsorbate metal is lower than that of the substrate, while overpotential deposition is expected in the opposite case [49,50].

The first case analyzed corresponds to the adsorption of Ag atoms on Au NP of different sizes. In this case the surface energy σ of the components satisfies the relationship $\sigma_{Me} < \sigma_S$. The second case is the deposition of Pd on Au NP, where the relationship $\sigma_{Me} > \sigma_S$ is satisfied. Special emphasis is made on the truncated octahedral structure (TO_1289).

Figure 1 shows the behavior of $\Delta U(N_{Me}, N_S, T)$ as a function of the number of metal atoms constituting the shell for the two cases analyzed.

At first sight, it appears that in the case of the deposition of Ag on the Au NP the energy of the system shows first a slight decrease ($\partial \Delta U / \partial N_{Me} < 0$), then goes through a shallow minimum and finally increases. This is the expectation for a system where adatoms interact stronger with the substrate than with themselves. However, a magnification of Figure 1a (see inset) shows a more complex saw tooth behavior, with 14 maxima, grouped in two families (6+8). These maxima correspond to a 2-D nucleation and growth phenomenon located on each of the facets of the truncated octahedron. The first six maxima correspond to 2-D nucleation and growth on the [100] facets, the other to a similar process on the [111] facets. The coverage of the 6 [100] and the 8 [111] facets ends up at $N_{Me}=480$, amounting 75% of a complete monolayer on the TO_1289 NP. At this point the system reaches a global energy minimum (see the inset on Figure 1a). In the range $480 < N_{Me} \leq 636$ coalescence of all facets occur,

characterized by $\partial\Delta U / \partial N_{Me} > 0$. A close inspection of the Figure 1a in this region indicates that the derivative $\partial\Delta U / \partial N_{Me}$ is approximately constant, suggesting that this type of process is always not spontaneous at zero overpotential, corresponding to 1D growth at the cluster edges. At $N_{Me} > 636$, the growth of the second and third shell occurs. This process is also characterized by $\partial\Delta U / \partial N_{Me} > 0$, but this value is no longer a constant. At this point, it is important to take into account that fluctuations of thermodynamic quantities for small systems are more obvious than that for macro systems, so that it is pertinent to consider if the energy differences observed in the inset of Figure 1.a are meaningful for experiments undertaken at room temperature. We can get an estimation of the energy fluctuations σ_U from $\sigma_U = (kT^2 N_T C_V)^{1/2}$, where C_V is the specific heat per atom and N_T is the total number of particles in the system. Taking values of C_V between $2 \cdot 10^{-5} \text{ eV}/(\text{atom K})^{-1}$ and $2 \cdot 10^{-4} \text{ eV}/(\text{atom K})^{-1}$, which corresponds to the specific heat of a Au-NP of 55 atoms and the bulk state, respectively, we get fluctuations between 0.5 eV and 1.8 eV, which show that the small features of the inset of Figure 1a will be wiped out by thermal effects. However, this is not the case for the larger changes observed at larger number of atoms. On the other hand, the smaller features could be observed at lower temperatures of with larger clusters.

The second case analyzed corresponds to Pd decoration of Au-NP(TO_1289). At difference with the first case, in Figure 1b it is always found that $\partial\Delta U / \partial N_{Me} > 0$, even in the monolayer region. However, we see a change of the slope $\partial\Delta U / \partial N_{Me}$ at $N_{Me}=636$. This is due to the formation of the second Pd layer on the Au NP.

The effect of the deposition potential on $f(N_{Me})$ for Ag and Pd deposition on NP Au(TO_1289) is shown in Figure 2.

For the following discussion and to connect the present features with those of Figure 1 it is important to make a couple of statements on the nature of the function $f(N_{Me})$. First, we must keep in mind that for $\eta = 0$ a minimum in $\Delta U(N_{Me}, N_S, T)$ corresponds to a maximum in the function $f(N_{Me})$ defined in equation (6). Second, for $N_{Me} = 0$ (naked core), we obtain $f(N_{Me}) = 1$, so that a glance at Figure 2 will tell us, just looking if $f(N_{Me})$ is larger or smaller than one, if some coverage by Me adatoms will be more stable than the naked core structure at the overpotential considered.

Inspection of Figure 2 indicates that the existence or not of decoration in the nanoparticle is strongly dependent on the interaction of the Me atoms with S . While decoration of the nanoparticle is expected at different overpotentials for the system Ag/Au(TO_1289), no decoration is predicted for the system Pd/Au(TO_1289) in a wide potential range. We can correlate these observations with the strength of the interaction of Me atoms with S on perfect planes, infinite surfaces. The latter has been considered by us [47] within the EAM in previous work with the results summarized in Table 2. There, we present the excess of binding energy for Me adsorption on different S single crystal surfaces. From this table we see that the present choice of system represent two clearcut cases of adsorbate-substrate interaction. In the first, Ag/Au, the interaction of Me atoms with S atoms in flat surfaces is stronger than the interaction between Me atoms in the bulk state. This is an UPD system and the consequence of this is the formation of a monolayer of Me on S at underpotentials. In the other system, the interactions of Me with S is smaller than the bulk Me cohesive energy and overpotential deposition is expected. Thus, in a first approach we could conclude that decoration of a core may be predicted on the previous knowledge of the similar process for the planar surfaces. However, nanoparticles have an additional feature, its size, and this will be analyzed in Section 3.3.

Me-S / Face	(111)	(100)	(110)
Ag(<i>Me</i>)/Au(<i>S</i>)	-105	-143	-192
Pd(<i>Me</i>) /Au(<i>S</i>)	165	142	135

Table 2: Excess of binding energy per atom for a monolayer of metal *Me* adsorbed on a single crystal surface of a substrate *S*. The excess of binding energy was defined as the binding energy of the adsorbate on the substrate with respect to the bulk cohesive energy of *Me*. Values are given in meV and were taken from reference [47].

Going back to the effect of the application of an overpotential η to the system, equation (5) shows that it adds a linear contribution to the free energy term, which has increasing weight for large N_{Me} . The effect of this overpotential becomes stronger for large N_{Me} values because the contribution is proportional to number of *Me* atoms. Figure 2 shows the effect of η for the two systems analyzed here. Depending on its sign, η has different consequences that will be analyzed in the following sections.

3.1. Underpotential Deposition region ($\eta > 0$)

To analyze the thermodynamic stability of structures obtained at different coverage degrees in the UPD range, $\eta > 0$, we denote the value of $f(N_{Me})$ at $N_{Me}=98$ by a_i and the corresponding value at $N_{Me}=480$ by b_i , where i ($i = 2, 4$, and 6) denote different η conditions, as marked in the Figure 3. For η relatively close to the bulk

deposition potential of Me, $0 < \eta < 4$ mV, the system presents the highest probability at $N_{Me}=480$ (note $a_2 < b_2$ in the Figure 3). In this region an ensemble of systems should be mainly composed of core-shell NP with a coverage close to 75%. At $\eta \approx 4$ mV the system has $a_2 \approx b_2$ and therefore we could observe the coexistence of particles with two different coverages. At larger η , in the range of $4 \text{ mV} < \eta < 13 \text{ mV}$, the highest probability density is for a coverage close to 15%, where $N_{Me}=98$. This value corresponds to the decoration of all [100] facets. At $\eta \approx 13$ mV a new coexistence is found, corresponding to $N_{Me}=98$ and $N_{Me}=0$. If we further increase η , setting $\eta > 13$ mV, no N_{Me} values other than zero satisfy the relationship $f(N_{Me}) \geq 1$. In this η range, an ensemble of particles should be composed of Au-NP(TO_1289) cores without Ag decoration. Table 3 synthesizes the previous analysis.

UPD region	N_{Me}	%
$0 < \eta < 4$ mV	480	75
$\eta \approx 4$ mV	480-98	75-15
$4 \text{ mV} < \eta < 13$ mV	98	15
$\eta \approx 13$ mV	98-0	15-0
$\eta > 13$ mV	0	0

Table 3: Different overpotential regions corresponding to Ag UPD on a Au(TO_1289) nanoparticle and number of adsorbed *Me* atoms which have the largest probability of occurrence under these conditions. The coverage of the pseudomorphic monolayer is reported as a percentage.

3.2. Overpotential Deposition region ($\eta < 0$)

In the OPD region, $\eta < 0$, equations (5-6) predict an increase of the function $f(N_{Me})$ that becomes more pronounced for higher N_{Me} values. For growing N_{Me} , the term $zFN_{Me}\eta$ in the exponential of (5) becomes increasingly important and finally the function $f(N_{Me})$ diverges in the limit $N_{Me} \rightarrow \infty$. However, at small negative η , the region where $f(N_{Me})$ starts its steep exponential increase is well separated from that corresponding to the decoration of the nanoparticle in the submonolayer region.

It is interesting that also in the OPD region the two present prototypical system show interesting differences in their behavior.

Let us analyze first the case of Pd deposition on Au(TO_1289), a typical system where $\sigma_{Me} > \sigma_S$. Figure 2b shows that even under the application of an important negative overpotential, ($\eta = -450$ mV), all states between $N_{Me}=1$ and the beginning of the exponential increase in $f(N_{Me})$ are less probable than the existence of the empty Au core. Then, it appears that for the present system, it is not possible to control thermodynamically the Pd coverage with the application of overpotential. It must be emphasized that the present model considers only core-shells structures and do not consider stabilizers.

Let us analyze the other case, Ag deposition on Au(TO_1289), a system where $\sigma_{Me} < \sigma_S$. We have seen above in Figure 2a that when $\eta = 0$, the present system presents a stable state at $N_{Me}=480$. When the system is subjected to the condition $\eta < 0$, this state turns to be metastable, that is, it corresponds to a maximum in the probability density but it is less stable than the bulk *Me* material. More properly speaking, when

$\eta < 0$ there are infinite many states which become more stable than the state with $N_{Me}=480$. If η is small, these states are separated from the metastable state by a region where $f(N_{Me})$ is negligible. Thus, we have the possibility of confining the system in this state, as long as the region separating this metastable state from steep exponential growth in $f(N_{Me})$ is relatively wide. This region acts as a bottleneck, separating the core-shell from the bulky region by a kinetic hindrance.

To analyze comparatively the stability of the core-shell NP in the OPD region at different η , it is useful to define a normalized probability density, $g(N_{Me})$, according to:

$$g(N_{Me}) = \frac{f(N_{Me})}{f(N_{\max})} \quad (9)$$

where $f(N_{\max})$ is the probability density at the $N_{\max}$ state, which corresponds to the metastable state with the highest probability of occurrence for a given η . Figure 4 shows $g(N_{Me})$ as a function of the number of Ag atoms that conforms the shell on Au(TO_1289) for different η . At η relatively close to the bulk deposition of Ag ($-35 \text{ mV} < \eta < 0$), the system has a metastable state with the highest probability density at $N_{Me}=480$ (black curve in Figure 4). This state corresponds to the same configuration as that found in UPD conditions ($\eta > 0$). In the range of $-37 \text{ mV} < \eta < -35 \text{ mV}$ we observe a shift of the most probable metastable state from $N_{Me}=480$ to $N_{Me}=576$. The corresponding structures are shown in the Figure 4. At more negative η , in the range $-210 \text{ mV} < \eta < -37 \text{ mV}$, the most probable metastable state corresponds to a coverage of 90% of the pseudomorphic Ag monolayer (see red curve in Figure 4). Under these

conditions, the Ag atoms have covered all the [100] and all the [111] facets plus all the edges between [111] and [100] facets. The edges between neighboring [111] facets remain unfilled. At even more negative overpotentials ($\eta < -210$ mV), the most probable metastable state corresponds to the complete monolayer $N_{Me} = 636$ (see blue curve in Figure 4). Table 4 synthesizes the previous analysis.

OPD region	N_{Me}	Coverage in %
$0 > \eta > -35$ mV	480	75
-35 mV $> \eta > -37$ mV	480-576	75-90
-37 mV $> \eta > -210$ mV	576	90
-210 mV $\approx \eta$	576-636	90-100
-210 mV $> \eta$	636	100

Table 4: Different regions of overpotential deposition studied for the system Ag Au(TO_1289) and the number of Me shell atoms N_{Me} which present the highest probability of occurrence. The coverage by Me atoms is given in percent units.

3.3. Size-dependent UPD-OPD transition

In this section we consider the formation of core-shell structures depending on particle (nanometric) size. The stability analysis was performed at zero overpotential with different sizes of the NP cores, for the Ag-Au(TO) system, where $\sigma_{Me} < \sigma_S$. We expect a similar qualitative behavior for systems satisfying the previous condition.

Figure 5 shows the behavior of $g(N_{Me})$ as a function of the number of Ag atoms deposited on Au NP of different sizes used as growth seeds. In first place, it must be noted that for small NP the highest normalized probability density is found at $N_{Me}=0$. This indicates the non occurrence of UPD. Something very different is found for large NP, where two important phenomena are observed comparing the results for TO_1289 and TO_2406. First, $g(N_{Me})$ becomes relatively more important with respect to the other local minima in $g(N_{Me})$ as N_s increases. Second, the coverage of the NP increases with increasing N_s . In fact, at $\eta=0$ the most probable coverage for Ag on Au-NP(TO_1289) is 75% while for Au-NP(TO_2406) it is 80%. It is interesting to remark at this point how new properties at the nano scale have been emerged naturally from the present statistical mechanics model.

To understand this effect, we must analyze the fraction of different types of surface atoms, which depend on the nanoparticle size for a given geometry of the core. To make a quantitative statement, let us consider the different members of the TO family, identified by the integer N . The following relation allows determining the number of atoms building the TO as a function of N [2]:

$$N_s = 16N^3 + 15N^2 + 6N + 1 \quad (10)$$

From this equation, we find that for the members $N = 1, 2, 3, 4, 5 \dots$, the number of constituent atoms is 38, 201, 586, 1289, 2406... . A more detailed study of the geometry allows the prediction of the number of surface atom of different types, and thus different

adsorption sites on the NP. Table 5 gives the equations that predict the number adsorption sites on the surface of a TO NP, where Me atoms may adsorb.

Symbol	Site type	Number of adsorption sites
$N_{S(100)}^{2D}$	[100] facet	$6N^2$
$N_{S(111)}^{2D}$	[111] facet	$24N^2$
$N_{S(100)}^{1D}$	[111]-[100] border	$24N$
$N_{S(111)}^{1D}$	[111]-[111] border	$12N + 12$

Table 5: Different site types and number of adsorption sites for different members of the truncated octahedron (TO) family. The first column gives the symbol used to denote the number of sites given by the third column.

With the information of Table 5 at hand, let us consider now the results presented in Figure 5 for $\eta = 0$ and $N_S = 1289$. In this case, we found that the most probable structure corresponded to a coverage of 75% of a full monolayer, that is, $N_{Me} = 480$. This corresponds exactly to the prediction that we can make from the equations in Table 5 for $N = 4$, that is, $N_{S(100)}^{2D} + N_{S(111)}^{2D} = 480$ atoms. More generally, we can define a percent coverage corresponding to the decoration of all the 2D-faces for the different members of the TO family, $X_{faces}^{\%}(N)$, according to the relationship:

$$X_{faces}^{\%}(N) = \frac{N_{S(100)}^{2D} + N_{S(111)}^{2D}}{N_{S(100)}^{2D} + N_{S(111)}^{2D} + N_{S(100)}^{1D} + N_{S(111)}^{1D}} \times 100\% = \frac{30N^2}{30N^2 + 36N + 12} \times 100\% \quad (11)$$

$X_{faces}^{\%}$ gives the value corresponding to the complete coverage of the faces as a function on the NP size. Since according to the present calculations this occurs at $\eta = 0$ from $N=4$ on, this equation should be useful to predict this coverage for larger members of the TO family. Equations (8) and (9), can be used to get the coverage of the faces as a function of the number of constituent atoms of the core, $X_{faces}^{\%}(N_s)$. This quantity is presented in Figure 6 as a function of the number of core atoms and radius of core. We see from the picture that $X_{faces}^{\%}(N_s)$ converges slowly to the macroscopic limit of 100 %.

4. Conclusions

In the present work we have discussed the possibility of controlling the decoration of metal nanoparticles by electrochemical methods. This was made in terms of a statistical mechanical model that assumes the control of the chemical potential of the species being deposited via an applied overpotential. As paradigmatic cases, we have analyzed here two systems where, depending on the adsorbate-substrate interaction, decoration at zero overpotential on planar surfaces is expected or not. The former case corresponds to the phenomenon of underpotential deposition (UPD), while

the second involves deposition under application of an overpotential (OPD). The present formalism, valid for an analysis under equilibrium conditions, shows that in UPD systems, controlled deposition on different facets of nanoparticles may be achieved in the undersaturation region (positive overpotentials). For this type of systems, core-shell nanoparticles may be also metastable in the oversaturation region, withstanding overpotentials of a couple of hundreds of millivolts before evolving towards a bulky deposit. Calculations with core nanoparticles having different number of atoms also show that the decoration of nanoparticles in the undersaturation region is very sensitive to nanoparticle size. In this respect, a transition from underpotential to overpotential deposition is expected for decreasing nanoparticle size.

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Figures and Captions

Figure 1: Excess of internal energy as a function of the number of shell atoms for the pseudomorphic growth of a) Ag and b) Pd on Au(TO_1289) at zero deposition overpotential. The vertical broken lines show the point at which the deposition of one and two layers is completed. The inset in (a) shows the detailed energy profile for the decoration of the first shell, in which the decoration of six (100) and the eight (111) facets can be clearly observed.

Figure 2: Probability density of having N_{Me} atoms deposited on Au(TO_1289) as a function of the number of atoms in the shell N_{Me} at different overpotentials η . a) $Me=Ag$ and b) $Me=Pd$. The upper curve (red) shows the deposition at $\eta < 0$, the center (black) at $\eta = 0.0$ mV, and the lower (blue) at $\eta = 2.0$ mV.

curve (black) deposition at $\eta = 0$ and the lower curve (blue) deposition at $\eta > 0$ (UPD).

The inset in b) shows a zoom at low N_{Me} . (See colors in the electronic version)

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Figure 3: Probability density of observing N_{Me} Ag atoms deposited on a Au(TO₁₂₈₉) core as a function of the number of atoms that conform the shell at different positive overpotentials (η). The upper curve (black) corresponds to $\eta = 2$ mV, the central one (red) to $\eta = 4$ mV and the lowest (blue) to $\eta = 6$ mV. The inset shows a schematic view of the configurations for $N_{Me} = 98$ and $N_{Me} = 480$. (See colors in the electronic version)

Figure 4: Normalized probability density of having N_{Me} Ag atoms deposited on Au(TO_1289) as a function of the number of shell atoms at different negative overpotentials. The black curve corresponds to $\eta = -5$ mV, the red one to $\eta = -100$ mV and the blue one to $\eta = -220$ mV. The inset shows a zoom of the transition region. The atomic configurations shown involve $N_{Ag} = 480$, $N_{Ag} = 576$ and $N_{Ag} = 636$, which correspond to 75%, 90% and 100% respectively of a perfect monolayer.

Figure 5: Normalized probability density of having N_{Me} Ag atoms deposited on different Au(TO) cores as a function of the number of atoms conforming the shell at zero overpotential. The core sizes are $N_S=38, 201, 586, 1289$, and 2406 .

Figure 6: Percentage of adsorption sites on the faces of a NP as a function of the number of atoms N_S conforming the core (a) and as a function of nanoparticle radius r (b).