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# Thermodynamic stability of electrochemically decorated Au–Pd core@shell nanoparticles

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ABSTRACT

The electrochemical decoration of Au and Pd nanoparticles by Pd and Au atoms respectively is discussed in a statistical mechanical framework. It is found that depending on precursor nanoparticle size and shape, controlled decoration may be achieved in undersaturation or oversaturation conditions. Multilayer deposition is also considered, with the finding that this phenomenon is also size dependent.



## 1. Introduction

Nanoparticles (NPs) have shown to present unique optical, electrical and catalytic properties [1,2]. In particular, bimetallic nanoparticles (nanoalloys) constitute a promising type of catalysts, mainly due to the fact that their chemical and physical properties may be tuned by varying the composition and atomic ordering as well as their sizes and shapes [3]. Among nanoalloys, Pd–Au appears as one of the most attractive systems in catalysis. Alloyed and core@shell Au–Pd structures have been used as catalysts in the oxidation reaction of CO at low temperatures [4], acetylene to ethylene conversion [5], oxidation of alcohols to aldehydes and production of vinyl acetate monomers, among others [6–14]. Due to the wide range of applications of Au–Pd catalysts, it is of great interest to study the thermodynamic stability of pure and bimetallic systems.

It has been experimentally found that, depending on the synthesis conditions, nanoalloys of various sizes, composition and structures can be obtained. Several configurations have been reported in different studies, *i.e.* Pd(core)@Au(shell) [15–17,4], Au(core)@Pd(shell) [12,13,18,19], random solid solutions [12,20,21], and three layer "onion-like" structures [22]. Similarly, synthetic control allows the Pd/Au catalytic properties to be tuned. This can be accomplished by controlling the sizes and shapes of core nanoparticles [13], shell thickness [15], and/or by using a different temperature conditions to regulate the extent of surface alloying [14,23]. The previous point is very important for future development of multicomponent nanoparticles to be used in advanced catalytic applications. This wide variety of structures observed makes the study of this system even more attractive from a basic point of view.

The energetics, structures and segregation (chemical ordering) of Pd–Au nanoalloys have been reported, using a genetic algorithm [24,25] for global geometry optimization. In that work, the binding energy and the second difference in energy were used as stability criteria. Using different parameterizations of the Gupta potential the authors found Pd(core)@Au(shell) segregation, and Pd–Au mixing, generally leading to mixed Pd–Au nanoalloys. Very recently, Neyman et al. [26], reported results from density functional theory (DFT) calculations showing that segregation of Au atoms to the NP surface is thermodynamically favorable, where the most stable sites for Au substitution are located at the edges of the Pd-NPs. Moreover, the formation of structures with Au atoms located in the core of the nanoalloys was found to be energetically unfavorable with respect to monometallic Pd and Au NPs of the same shape and size.

In a previous work [27], we have presented a thermodynamic analysis and computer simulations corresponding to the formation of pure and core@shell nanoalloys, in a situation where the chemical potential of a metal compounding the shell is controlled to produce its deposition onto a seed NP. As stability criteria we adopted the Gibbs free energy, since the usual electrochemical conditions (very frequently found in synthesis methods) are

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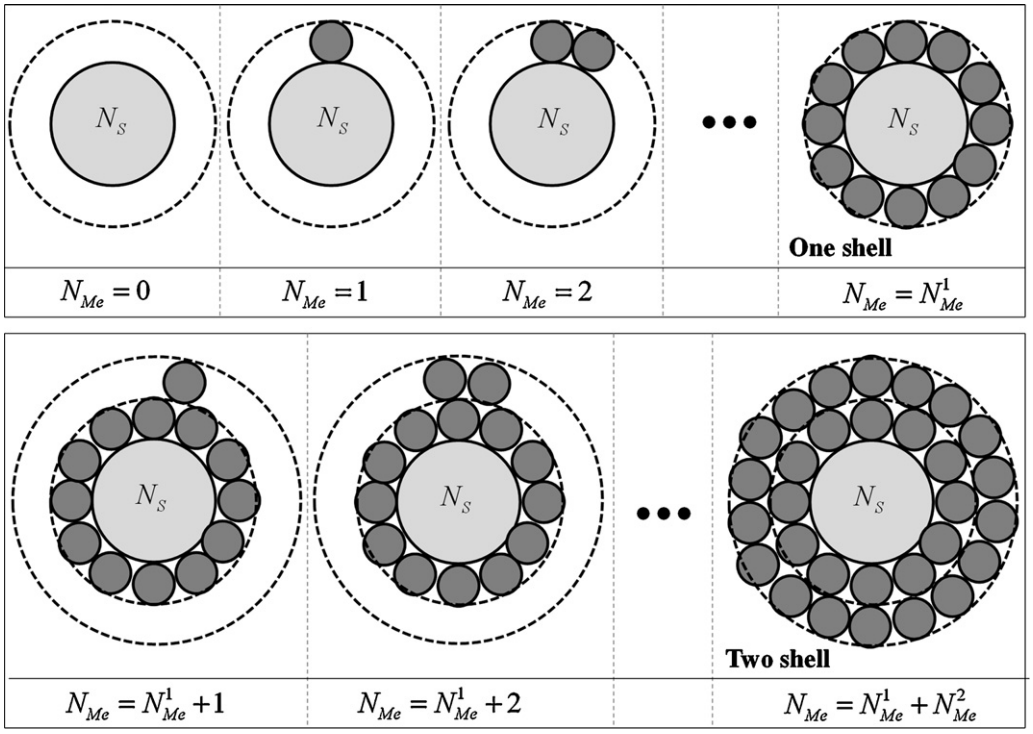


**Fig. 1.** Schematic representation of the ensemble employed to study core@shell NP growth. We have omitted, for simplicity, the electrolytic solution.

constant pressure and temperature. In the electrochemical environment, potential control and the presence of cations in solution corresponding to those of the shell should allow for controlled decoration of the NPs. The potentiality of electrochemical control to set the coverage of NPs has been demonstrated in recent experiments, where it has been found that remarkable size effects occur when NP size is reduced below 50 nm, where the so-called underpotential deposition phenomenon seems to vanish [28–30].

In the present work, we apply our previous thermodynamics analysis to study the stability of Pd–Au core@shell NPs. A brief discussion on the model is made illustrating its application with computer simulations using a parameterization of the embedded atom method (EAM) developed by Foiles et al. [31].

## 2. Theoretical considerations and calculation method

We introduce our theoretical discussion considering an electrolytic solution at temperature $T$, containing $Me^{z+}$ type ions and an incompressible metallic NP ($S$) used as a seed. On this seed, we will allow deposition of metal atoms of type Me providing an environment with constant chemical potential $\mu_{Me}$. As shown in a recent publication [32], this can be achieved using a proper redox couple that fixes the electrochemical potential of the electrons in the free NP. Fig. 1 shows a 2D-scheme of the present model system.

The partition function of the nanoalloys considered as a semi-open system can be written as [33]:

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

where $N_{Me}$ is the number of Me atoms on the seed NP, $N_S$ is the number of atoms constituting the metallic seed, $\beta = 1/kT$ where $k$ is Boltzmann's constant, and $Q$ is the corresponding canonical partition function. Fig. 1 shows a scheme of the most relevant atomic configurations corresponding to some of the first terms of the sum in Eq. (1).

Taking into account the free energy excess with respect to the bulk material, Eq. (1) can be written as [33]:

$$\gamma(\mu_{Me}, N_S, T) = C\sum_{N_{Me}} \exp[-\beta\,\Delta F(N_{Me}, N_S, T)]\exp[-\beta z F N_{Me}\eta] \quad (2)$$

where $C$ is a constant which depends only on the nature of the seed, $\Delta F(N_{Me}, N_S, T)$ defines an excess of binding Helmholtz free energy of the Me atoms in the nanoalloy referred to bulk Me, $z$ is the valence and $F$ is the Faraday constant. The electrochemical stability of the bi-NP is related to the argument of the exponential in Eq. (2):

$$\Delta\tilde{F}(\eta, N_S, T) = \Delta F(N_{Me}, N_S, T) + zFN_{Me}\eta \quad (3)$$

where $\Delta\tilde{F}$ corresponds to the excess of the Helmholtz free energy with respect to the bulk material, now including the electrochemical term $zFN_{Me}\eta$. The present modeling could be applied to any type of bimetallic nanometric systems. However, with computational purposes, we will restrict our analysis to the family of nanostructures that are usually addressed with the denomination of core@shell. This is a type of systems where, as described in the introduction, extensive experimental work has been developed.

In the case of bimetallic systems, where the interaction between particles is strong, only the static energetic term is relevant at room temperature. Thus, we will be roughly approximate $\Delta F(N_{Me}, N_S, T) \approx \Delta U(N_{Me}, N_S, T)$, where $\Delta U$ is an excess of the static internal energy and will be calculated using EAM potentials. Here, we neglect entropic contributions, a more thorough discussion on them can be found in Ref. [33].

For the computational modeling of the system, we use seed structures with different sizes on which different number of atomic layers of the adsorbate are located. We select two different NP shapes. On one hand, the first five members of the truncated octahedral (TO) family, which present fcc structure, on the other hand, the first nine members of the icosahedral (ICO) family (non-fcc structures). A total of 47 systems are analyzed. We will use the notation "$S_m$ (structure)@$Me_{n\text{-layers}}$" to specify the nature of the NP in terms of the number of atoms that make up the seed ($m$) and the number