



Underpotential deposition: From planar surfaces to nanoparticles



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ABSTRACT

An overview is given of selected theoretical, experimental and computer simulation research on thermodynamic modeling applied to the metal underpotential deposition. Focus is made mainly on the last 20 years. The *upd*-theory on planar surfaces is revisited and the thermodynamic framework is extended to consider underpotential deposition on nanoparticles and to include anion coadsorption, solvation and double layer charging. Results from molecular dynamics and Monte Carlo simulations are shown for systems of experimental interest. At the end some perspectives for further advanced modeling of the present problem are given.

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1. Introduction

1.1. 20 years of progress in underpotential deposition. General aspects

The last two decades have witnessed major advances in the characterization and development of a new generation of nano- and molecular devices. Nanoscience and nanotechnology have been the branches of science dealing with these systems. The main purpose of nanotechnology is the manufacture, manipulation and integration of nanoscale devices in order to obtain products with novel physicochemical properties, and nanoscience is providing the basic support for these achievements. Manufacture of items in this scale can be accomplished via two strategies: a (so as to say) conventional manufacturing, starting from large objects going down to progressively smaller ones (also called top-down) and a molecular manufacturing (also called bottom-up). The first is the strategy that has characterized the innovations of the last century, while the second is expected to predominate in the present century [1]. Today we are facing a transitional stage between these two strategies.

In the bottom-up strategy, tiny individual parts are linked together to form larger components with a higher hierarchy, which in turn are linked with each other to form a larger system, and so on. This mechanism has been inspired by nature as it happens, for example, with the assembly of a protein. The central idea in this strategy is to manipulate the reaction conditions and interaction forces to obtain controlled growth of the desired structure at will, so that the building blocks self-assemble and the desired product is obtained. Addressing the growth mechanism of such structures is not an easy task and this constitutes a source for new challenges and paradigms. A wide variety of building blocks exists, such as fullerenes, nanotubes, DNA, quantum dots,

dendrimers, copolymers, and nanoparticles. Currently, joint efforts between different branches of science are undertaken in order to find better synthetic strategies and to improve the kinetic and thermodynamic stability of the resulting structures or devices. Thanks to these efforts, our understanding of the processes involved in the formation of nanostructures at the atomistic level has increased considerably in the last 20 years. This has been possible in part through the development and improvement of experimental techniques such as scanning tunneling microscopy, electron microscopy and those derived from synchrotron light. Nowadays, it is possible to monitor the behavior of a small set of atoms or even a single molecule directly and in real time. On the other hand, our knowledge in the area has improved thanks to the development of theoretical models and computational techniques. The development of information technology has generated more computing power, which has increased concomitantly with the size of the hardware. It is possible today to compare experimental measurements with an atomistic view generated from a molecular simulation. This synergy allows the validation (and/or refinement) of models and can even contribute to the development of new synthetic strategies in a more accurate, efficient and faster way than in the previous decades.

Getting into the electrochemical field, it comes out that various strategies, originally used for the modification of flat surfaces, are nowadays successfully applied to design and modify nano-sized structures. Among these, the modification of a metal surface by underpotential deposition (*upd*) is of great interest, which consists in metal deposition on a foreign substrate at potentials positive with respect to the Nernst thermodynamic prediction. Although it sounds awkward, the term *upd* was developed to mark the contrast with the current metal deposition, which always involves an overpotential deposition (*opd*) due to kinetic hindrances. The potential utility of *upd* is due to the relatively rapid, simple and precise modification of the reaction conditions, which allow controlling the degree of coverage of the adsorbate metal on the substrate surface. The

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main obstacle to the implementation of *upd* for a large number of systems is the fact that this phenomenon is limited in many cases to the deposition of a less noble metal on a more noble one. In the case of electrocatalytic applications, this situation is right the opposite of the desired one. One way to circumvent this problem is to use a technique that denominated galvanic replacement (*gr*). In this method, the substitution of a sacrificial *upd* sub/monolayer by the desired noble metal atop in circuit allows obtaining the desired catalyst. Applied together, *upd* and *gr* allow reducing the quantity of noble metal used to a minimum amount, thus reducing the economic costs of the final product. This is a key objective for potential industrial applications. Thus, both *upd* and *gr* appear as attractive bottom-up methods, with great prospects for the development of novel nanomaterials. The contribution of the present work is directed to discuss research on some basic aspects of *upd* that have brought new insight into this phenomenon in the last two decades.

1.2. Overview on recent experimental and theoretical progress

Although there is not currently a book exclusively devoted to the discussion of *upd* phenomena, there are various review articles [2,3,62] and book chapters on it [4–12]. The present article is not intended to summarize all the work in the field, but rather to focus the discussion on some recent advances on this phenomenon, especially concentrating on the theoretical point of view in the last two decades.

The formation of core@shell structures may be considered as the nano-counterpart of heterogeneous metal growth on planar foreign substrates. While in the latter case the occurrence of overpotential and underpotential deposition phenomena is well known and there are whole books devoted to their analysis [4], the possibility of occurrence of *upd* and *opd* on nanoparticles has been rather seldom mentioned in the literature and its theoretical analysis dates back to 2008. Concerning experiments, Selvakannan et al. [13] showed in 2004 that tyrosine molecules used as surface stabilizers of Au NPs may also reduce Ag ions present in the electrolyte solution to yield core@shell NPs of the type Au@Ag. The protonation of the phenolic group of tyrosine, which is responsible for its reductive ability, was found to be controlled via the pH of the solution, thus allowed tuning the reductive power of this molecule. Fonticelli et al. showed in 2007 [14] that p-benzoquinone (a molecule with similar characteristics to those of tyrosine) can be used to reduce Ag ions on the surface of a Au-NP coated with thiol molecules. The main difference between the experiments of Selvakannan et al. and those of Fonticelli et al. is that in the first case the reducing molecules were on the surface of the NP, while in the second they were free in solution. This is a slight but significant difference, since the reducing molecules on the surface of the NP may be influenced by the presence of a second material, thereby affecting the deposition process. The final results of the synthesis of Fonticelli et al. were Au@Ag thiol stabilized NPs. This work also showed that the electric potential for metal deposition on a NP freely suspended in solution can be tuned using molecules with acid–base activity, in very much the same way that a potentiostat is used to control the surface potential of an electrode. Thus, in this picture, the NP resembles a nanoelectrode that can be wired to a desired potential via a redox system. However, here the question arises concerning the similarities and the differences between an infinitely large electrode and a NP used as electrode. Wood and Plieth [15–17] tackled this problem already in the '80s. Wood noted that the work function, that is, the work to extract an electron right outside the surface a NP of radius r is given by:

$$\phi^{NP} = \phi^{bulk} + \frac{3}{8} \left(\frac{e_0^2}{r} \right) \quad (1)$$

where ϕ^{bulk} is the work function of the bulk material ($\phi^{bulk} > 0$) and e_0 corresponds to the elementary charge. The second term on the *rhs* of Eq. (1) is always positive, indicating that $\phi^{NP} > \phi^{bulk}$ for a finite r . In this way, extracting an electron from a NP always involves a larger work

than taking it out from the corresponding bulk material and this work will become larger the smaller the NP. Thus, this early work showed that curvature effects may become important in electrochemical processes where the work function is known to play a relevant role, like for example determining the potential of zero charge of the electrode. However, the relevance of NP size for *upd* had to wait much longer to be considered.

In 2008 Leiva and coworkers [18,19] modified the existing *upd* thermodynamic framework to consider the process of electrochemical deposition in systems with curvatures at the nanometric level. This development, based on nanothermodynamic concepts developed by Hill [20] allowed the study of new scenarios for *upd* at the nanoscale. The new modeling anticipated novel behaviors for nanosystems: in those with negative curvatures, such as nanocavities, *upd* should be favored, while in those with positive curvatures such as NPs, the opposite should occur. Following these ideas, Oviedo et al. [19,63–65] used computer simulations to study the process of Ag *upd* on Au-NPs and found that this phenomenon could reach a limit for small NPs. Something similar should happen for Pd deposition on Au-NPs [21]. Then, Compton and coworkers [22–24] showed experimental evidence indicating that the *upd* phenomenon could disappear in the case of deposition of Pb and Cd on Ag-NPs of relatively small size. The occurrence of a *upd*–*opd* transition is of great relevance, since this would set a limit to bottom-up layer-by-layer techniques [25,12].

One of the behaviors observed at the nanoscale that has no counterpart on single crystal flat surfaces is the selective decoration of the facets of a NP. It is known that on flat surfaces *upd* is more prone to occur on open surfaces. Thus, a proper choice of the deposition potential enables deposition at the more open facets of a NP. This effect has been used to block (or promote) growth on these facets and thereby control crystal growth. This strategy has been employed in the Ag/Au system [26,27] to get a variety of NP shapes.

Upd may be strongly modified by anion coadsorption [66]. Electronic structure calculations indicate that the coadsorption of sulfate plays a key role in making possible *upd* Cu on Au(111) [28] and something similar happens with Cu deposition of Pt-NPs [29]. Langille et al. [30] have analyzed in detail the effect of including other anions like chloride, bromide and iodide in NP growth under *upd* control. On the other hand, Tran and Lu [31] have analyzed the effect of the presence of Pd and Ag ions on Au NP growth. Overall, this strategy allows obtaining NPs with high index facets, as well as NPs with concave facets that are very important for technological applications in electrocatalysis.

As mentioned above, one of the main handicaps of *upd* is the need to deposit a less noble metal on another more noble one. One way to circumvent this problem is to produce a galvanic replacement, where the *upd* sub/monolayer is used as a sacrificial deposit [32–34]. Thus, the successive use of *upd* and *gr* allows synthesizing nanomaterials with a minimal use of precursors, lowering the end cost of the product [35]. Inclusion of a third metal and/or performing several *upd*–*gr* cycles allows the construction of complex sandwich structures, which exhibit properties different from those of the separated materials [36].

Recent progress has also been made in determining the various thermodynamic contributions to the *upd* process. Some studies based on the lattice gas have analyzed the configurational entropic contributions in comparison with the energetic ones [3]. These studies have demonstrated that the formation of the bond between the adsorbate and the substrate, that is, the potential energy of the metal interactions, delivers the main contribution to *upd*. The latter has been confirmed for pseudomorphic systems, where atomistic computer simulations have shown that the contribution of vibrational entropy to *upd* does not exceed 5% [37]. Conway and Chacha [38] have studied experimentally the entropic contributions to Pb-*upd* on polycrystalline Au, on the basis of the analysis of the change of the *upd* shift [44–46] with temperature. From their measurements, they estimated entropic contributions to *upd* shift ranging between 185 and 307 mV. Taking into account that the *upd* shift estimated in Ref [39] for Pb deposition on Au(111) is 215 mV, the values of

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