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Computational Study of Nanostructured Materials
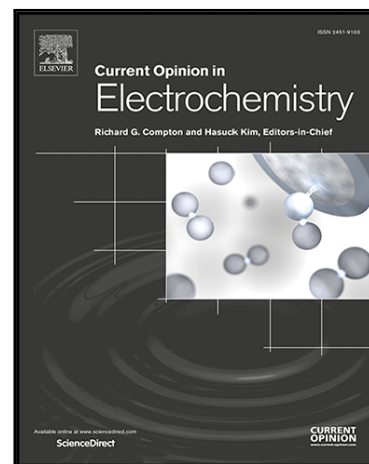
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**Highlights**

- Theoretical achievements to understand systems at the nanoscale are discussed.
- Metal electrodeposition on nanoparticles may yield peculiar metastable states
- Non-noble metals on carbonaceous nanostructures may catalyze hydrogen evolution
- Doped carbon nanostructures may catalyze the oxygen reduction reaction.

# Computational Study of Nanostructured Materials

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Since their early times, by the 50s, computational software and hardware have been growing in importance, to become today one of the key tools for the development and generation of knowledge. Increased computing power has radically transformed the way we make nowadays research. Today, it is possible to perform complex computational experiments with high quality and accuracy for model systems that are similar to those studied experimentally. This starts to be reality both considering sizes and timescales, and in many cases this is strictly true at the nanoscale. The global trend shows a significant increase in the interrelationship between groups of theoretical and experimental research. Addressing the problem from a combined perspective (theory, simulations and experiments) is becoming a rule in high impact publications and although a lot is still to be done, this synergy shows huge advantages. This is so because this new perspective allows greater deepening in the understanding of the basic aspects of the systems at the atomic or molecular level.

A comprehensive review on computer simulations applied to underpotential deposition (UPD) at the nanoscale, of interest for materials scientists, has been presented very recently [1**].

Here, we discuss some challenging theoretical and computational achievements in systems of electrochemical interest at the

nanoscale, providing a close correlation with experiments.

## 1. Challenging Theoretical Models for Nano-electrodeposition

The most important concept to understand the growth of heterogeneous systems is surface free energy, and probably the most widespread model used to compute such properties is the classical nucleation theory (CNT). Nowadays, this concept is applied to the design of shape controlled nanoparticles (NPs) on the basis of kinetic control of the reaction conditions, something that was originally proposed by LaMer in the 50s.
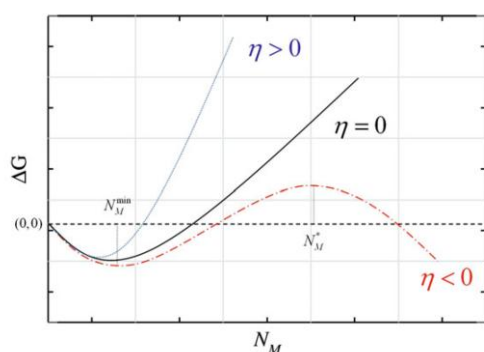


*Figure 1: Scheme of the excess free energy as a function of the number of atoms for heterogeneous electrodeposition in a nanosystem when the interaction substrate/adsorbate is larger than that between depositing atoms. A minimum appears in the free energy landscape. This minimum will subsist at zero or slightly positive overpotentials, defining a global extremum. This minimum could also remain for slightly negative overpotentials, defining a metastable state. Reprinted with permission of Reference [3].*

CNT was not developed for the electrochemical context, thereby effects as the equilibrium with charged species, ligands, solvent, etc. were not included in it [2]. A challenging picture of electrodeposition, based on nanothermodynamics, was presented in References [3**,4]. **Figure 1** shows qualitatively this new approach. The previous picture has allowed to rationalize selective growth of facets [5,6], vanishing of UPD for small NPs [4,7*,8*,9,10*,11], the relevance of anions or ligands for electrodeposition [12,13*,14], and has been used to analyze the first stages of Li adsorption on defective graphene [15].

## 2. Advanced Computer Simulations applied to fundamental electrochemistry

The description of the interactions between particles is the heart of computer simulations. In the present context, the description of charged

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species is very important. This is done through two methods: density functional theory (DFT) calculations or semiempirical potentials based on the theory of bond order.

## 2.1. Density Functional Theory

DFT is one of the most frequently used computational tools in electrochemistry [1,16,17]. DFT energy calculations have typically an uncertainty of 0.3 eV, which is an order of magnitude larger than thermal energy at room temperature. Thereby, a further comparison with experimental data is imperative as discussed by Exner *et al* [18].

A methodic DFT-work analyzing the structure and properties of a complex electrochemical system was performed by Escudero-Escribano *et al* [19*,20]. Non-covalent interactions were found to be responsible for the occurrence of honeycomb structures observed in STM images (see **Figure 2**).
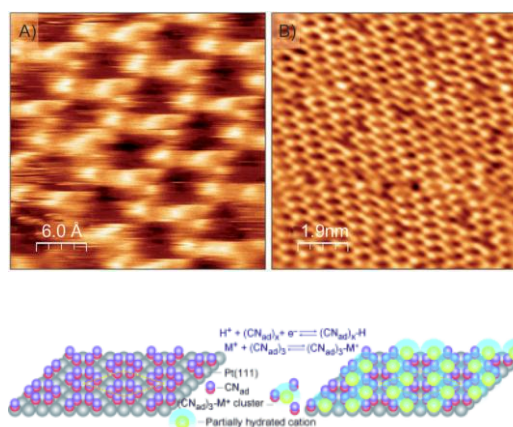


*Figure 2:* STM-image and the DFT-optimized model used to understand the nature of non-covalent interactions leading to honeycomb structures. Modified with permission of Reference [19].

The interaction of ligands and/or solvents molecules with nanostructures is an important topic in electrodeposition. A meaningful contribution on this topic was made by Carino *et al* [21,22*]. The calculated binding energies were found to correspond well with the peaks observed in the CVs of Cu UPD on Pt.

DFT-based Kinetic Monte Carlo (KMC) has gained popularity because adsorption energies and activation barriers are accessible via DFT calculations [16,17, 23 ]. KMC is a stochastic method that directly incorporates reaction mechanisms. It allows to predict experimental quantities such as rates of product

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formation, reaction orders, reaction paths and evolution of the system on the experimental time-scale. It also allows access to observables that are difficult to obtain from experiments, such as the instantaneous surface concentrations of different species. Many of these results have been recently compiled in Reference [1]. New advances have extended this methodology to include atom exchange [24,25] or larger jumps [26]. This innovation has allowed to analyze different categories of deposition systems, such as homoepitaxy, heteroepitaxy, multi-layer, decoration of step edges, and confined regions [1, 25-27].

DFT-based KMC is being used to model current/voltage curves experimentally observed, but special attention must be paid to the selection of the model and a further comparison with experimental data is imperative [28]. Furthermore, different DFT-parameters sets lead to substantial differences either in the overall kinetics or in the surface configuration.

Transport phenomena may also be analyzed using KMC. This was for example made in a recent work by Blanquer *et al* [29]. These authors presented a new application of KMC in three dimensions, in order to explain the increase in capacity observed for lithium oxide batteries. It was found that improvement of the mobility of the species, dilution or increase of $Li^+$ diffusion coefficient should lead to greater and more effective discharge. These predictions were confirmed by experiments.

## 2.2. Semi-empirical Potentials

Advances on empirical potentials are based on the concept of bond order. One of the advantages of their use is the ability to emulate systems of more than $10^6$ atoms on time scales of the order of 40 ns [30]. These heuristic potentials have become a concrete alternative to simulate nano-electrochemical complex environments. They have allowed to simulate relevant characteristics of the electrochemical environment: for example simulations show that in aqueous media, oriented nanocrystals should grow yielding single crystal forms [31]. Recent advances are the inclusion in the growth process of high electric fields [32] and the possibility of simulating complex chemical reactions at high temperatures [33,34,35].

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## 3. Work related to energy generation and storage

### 3.1. First principles modeling of electrocalytic reactions

In recent times, the use of renewable energy resources as well as more efficient energy storage systems have been favorite topics on the agenda of most influential governments and international organizations. A sustainable energy system is urgently required by the modern society due to issues like global warming effects, fluctuating oil price, and contamination produced by fossil fuel combustion. This situation has led, within the area of scientific research, to the quest for improved electrochemical storage systems that can safely store energy from sustainable sources, such as wind and solar power, and also provide the energy needed, for example, for transportation and residential uses. Hydrogen fuel cells are one of the devices foreseen to fit into these needs, and two electrocatalytic reactions are of primarily importance for these devices. One of them is the Hydrogen Evolution Reaction (HER), which, although it is not involved in the fuel cell, it is required to provide its fuel: hydrogen.

The other one is the reaction limiting the performance of hydrogen-air fuel cells: the Oxygen Reduction Reaction (ORR). We revise the newest relevant theoretical results for these two problems in the scope of the present article.

### 3.1.1. Hydrogen Evolution Reaction

The best current catalysts for this reaction are of high-cost due the fact that they are based on Pt. Thus, it is urgent to employ low-cost and earth-abundant materials to replace them and make this technology more economical. Unfortunately, very abundant 3d transition metals (like Fe) are not stable in acidic medium since they dissolve. Recent work has been devoted to develop metallic nanostructures (Fe, Co, FeCo, CoNi alloys) covered by carbonaceous shells doped with nitrogen that protect them from corrosion **[36,37\*\*]**. DFT calculations have been decisive to understand the way in which these catalysts operate. The three elementary steps for the HER are:

$$H^+ + e^- + * \rightarrow H^* \qquad (1)$$

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$$H^+ + e^- + H^* \rightarrow H_2 \qquad (2)$$

$$2H^* \rightarrow H_2 \qquad (3)$$
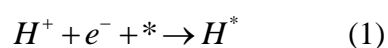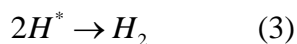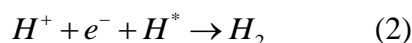
where * denotes an active site on the catalyst.

The Tafel slopes obtained with the previous metal/C nanostructures indicated that the HER for these compounds occurred by the Volmer-Heyrovsky mechanism(1)-(2). The application of DFT calculations to this problem was manifold:

a) Calculation of the adsorption free energy of hydrogen. This is a descriptor of the HER [38]. Either very large or very low values showed to be detrimental.

b) Calculation of free energy along the reaction coordinate. The results also supported the Volmer–Heyrovsky mechanism to be operative here.
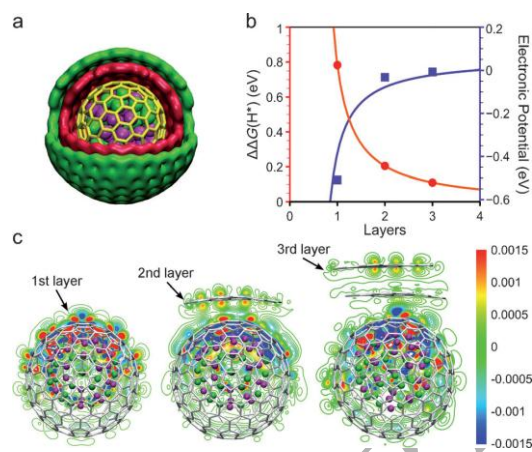
c) Analysis of the electrostatic potential.



***Figure 3****: a) Schematic illustration of a CoNi alloy encapsulated in three-layer graphene. b) Change in the adsorption free energy of hydrogen.* $\Delta\Delta G(H^*)$ *(red line) and electronic potential (blue line) as a function of the number of graphene layers, where* $\Delta\Delta G = \Delta G(\text{without metal}) - \Delta G(\text{with metal})$ *. c) Redistribution of the electron densities after the CoNi clusters have covered by one to three layers of graphene. The red and blue regions are regions of increased and decreased electron density, respectively. Reprinted with permission of Reference [36].*

d) Analysis of differential electronic density plots. These results and the previous ones showed that stabilization of the $H^*$ species should originate from the increase in the electron density on the graphene shells near the metal clusters.

**Figure 3** shows the model of metal core covered by a graphitic layer and results for the free energy of adsorption,

electronic potential and differential electronic density plots for different numbers of graphene layers covering the metal core. DFT calculations have also been applied to understand related systems, like the HER on $MoS_2$ doped with metal atoms [39*], on different nanostructures of $MoS_2$ [40] and on iron-nickel sulfide (INS) [41]. In the latter case, the higher activity of the INS nanosheets with respect to pristine NiS nanosheets in acid solutions was attributed to the lower energy barrier for $H^+$ adsorption and the higher exothermicity for hydrogen formation.

### 3.1.2. Oxygen Reduction Reaction

Similarly to the case of the HER, Pt based catalyst have dominated the scenery of the materials used for the ORR [42]. In acidic solutions, the ORR may proceed over two different processes:

$$O_2 + 4H^+ + 4e^- = 2H_2O \qquad (4)$$

$$O_2 + 2H^+ + 2e^- = H_2O_2 \qquad (5)$$
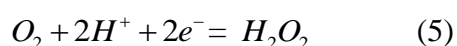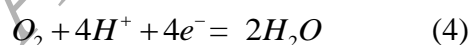
where the second process is unwanted in energy generation processes. In the case of the ORR, the d-band center of the metal and the free binding energy of oxygen are the favorite descriptors used to analyze the activity of catalysts [43]. The potential of this approach in combination with the analysis of experimental data has been shown recently to analyze the ORR and HER on Pt catalysts supported by transition metal carbides [44]. Sabatier principle becomes manifest in so-called typical volcano plots, where some property representing the catalytic activity (*i.e.* Exchange current density) is plotted as a function of the binding energy of a relevant adsorbed species.

A maximum is found at intermediate binding energies for these reactive intermediates, which serves to screen for other good candidates fitting the binding energy under consideration.

As in the case of the HER, recent effort is devoted to develop Pt-free catalyst that make the use of catalysts economically feasible. A breakthrough in this situation aided by the DFT study of the mechanisms of the four-electron pathway on nitrogen doped graphene can be found in the work of Zhang *et al* [45*]. A similar situation was shown by Yang *et al* [46] for boron-doped carbon

nanotubes (NT). In this case, the positively charged boron atom was found to be favorable to capture of the oxygen molecule, which is slightly negatively charged upon approaching the NT. Recent work in the previous direction was undertaken to rationalize the ORR on a series of graphenes doped with nonmetal elements: nitrogen, boron, oxygen, sulfur and phosphorus [ **47 \*\*** ]. DFT calculations were performed to predict exchange currents $j_0^{theory}$ and the adsorption free energies $\Delta G(OOH^*)$ of the intermediate $OOH^*$, which is formed upon $O_2$ adsorption and dissociates subsequently to yield $O^*$ . These two quantities were predicted to follow a volcano-shaped plot (red line in **Figure 4**), which correlated very well with the same representation of the experimental exchange currents $j_0^{exp}$ , blue squares therein. In the same plot a hypothetical system with the maximum catalytic activity is denoted with X-G and marked with a full square. This would correspond to a system with a $\Delta G(OOH^*)$ close to the volcano center, presenting an activity 5 times higher than that of a Pt/C catalyst. The authors proposed that such an X-Graphene should be sought by doping with

multiple elements, introducing structural defects or any possible combination of these effects.
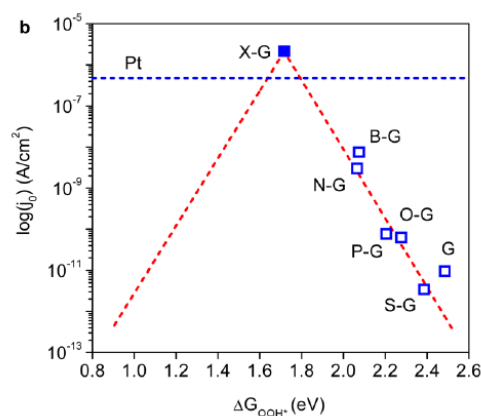


**Figure 4**: *Volcano plots between* $j_0^{theory}$ *and* $\Delta G(OOH^*)$ *as calculated in Reference* **[47]**. *Blue hollow squares are experimental values of* $j_0^{exp}$ *from Tafel plots and DFT derived* $\Delta G(OOH^*)$ *for each doped graphene catalyst. The* $j_0$ *experimental value for Pt is shown by the blue dashed line.*

Very recent work based on multi-scale modeling of the ORR must be highlighted as an appealing new approach to this problem**[48\*]**.

# 4. Acknowledgements

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## 5. References and recommended reading

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* of special interest

** of outstanding interest.

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