

The underpotential deposition that should not be: Cu(1x1) on Au(111)

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Abstract: Underpotential deposition of copper on Au(111) is analyzed in the light of first-principles calculations. The existence of a 1x1 Cu monolayer on Au(111) at underpotentials can be only understood taking into account the free energy excess delivered by the adsorption of sulphate anions. While a naked copper pseudomorphic monolayer results thermodynamically less stable than bulk copper, accounting for the interaction with sulphate ions delivers an underpotential shift which is comparable with the experimental value.

Keywords: underpotential deposition, anion adsorption, monolayer

1.1 Introduction

Underpotential deposition (UPD) is a well-known electrochemical process that may occur during metal adlayer formation onto a metallic substrate. When a metal working electrode is cathodically polarized, ions of a second, less noble metal may be deposited onto the substrate forming a monolayer or submonolayer film at potentials more positive than the Nernst potential of the metal being deposited. UPD has been the subject of extensive experimental research, and in the nineties many theoretical approaches bloomed to tackle this problem [1,2]. A first-step towards the understanding of UPD was taken by Kolb et al. [3], who found that the UPD shift ($\Delta\varphi_{upd}(\theta)$, the difference between the potential of the stripping peak of an adlayer of a metal M adsorbed on a foreign substrate S and the potential of the peak corresponding to the dissolution of pure M) correlated to the difference between the work functions of the substrate and the adsorbate. It was also emphasized that $\Delta\varphi_{upd}(\theta)$ is related to the difference between the chemical potentials of the atoms being deposited, $\mu_{(S)M}$ and those of the bulk material, μ_M :

$$\Delta\varphi_{upd}(\theta) = (1/ze_0)(\mu_M - \mu_{(S)M}) \quad (1)$$

Schmickler[4] devised a thermodynamic cycle putting into evidence the role of the binding energy of the metals involved in the UPD phenomenon, thus providing a straightforward theoretical framework for the calculation of underpotential shifts. Using this approach, Sanchez et al. performed first-principles calculations to assess the role of the binding energy in determining the underpotential shift for a number of systems [5,6,7]. While in general the density functional calculations yielded results in good agreement with the experimental results, the remarkable exception was the UPD of Cu on Au(111) surfaces, for which the binding energy of a Cu(1x1) monolayer was predicted to be smaller, in absolute value, than the bulk binding energy of Cu. The difference of binding energies, 0.5 eV in favour of the bulk material, indicated that the formation of a Cu(1x1) monolayer should take place with an overpotential of ca. 0.25 Volts with respect to the bulk Cu deposition potential. Recent calculations by Greeley [8] also predicted negative shifts for Cu deposition/dissolution on Au(111) in 3, 4 and 6-fold coordination. It appears, thus, as a blatant paradox that the behaviour of the probably most-studied UPD system cannot be explained in terms of thermodynamics and high-quality quantum mechanical calculations, not only quantitatively, but even at the qualitative level.

Cyclic voltammograms of copper UPD on Au(111) in sulphuric acid solutions show two well defined processes, evidenced by two anodic and two cathodic peaks. The most positive of these couples, occurring at $0.21 \pm 0.01V$ [9] vs. a Cu/Cu^{+2} reference electrode in the same solution, has been assigned to a honeycomb superlattice of copper atoms adsorbed on threefold hollow sites, stabilized by sulphate anions that occupy the honeycomb centers [10,11], adopting a $\sqrt{3} \times \sqrt{3} R 30^\circ$ structure. Typically, only the sulphate superlattice can be observed using AFM [12]. Using STM, the sulphate superlattice is observed if the tip is biased negative with respect to the surface [13,14], but the copper honeycomb can be imaged if the tip is biased positive [14]. The nature of this structure is now accepted as well understood, and there have been numerous simulation studies by Blum and Huckaby [15,16] and Wieckowski and coworkers [17,18], all of them based on heuristic interatomic potentials. To the best of our knowledge, only Xu et al. [19] have undertaken first-principles calculations on this system, concluding that without sulphate co-adsorption, the honeycomb structure of Cu adsorption is unstable. No attempt to compare the stability of the sulphate-containing honeycomb structure with that of the Cu(1x1) was made.

The most negative couple of voltammetric peaks occurs at $0.05 \pm 0.03V$ vs. a Cu/Cu^{+2} electrode in the same solution and has been assigned to the formation/oxidation of a (1x1) Cu monolayer on the Au(111) surface [9].

The coadsorption of Cu and sulphate on Au(111) was quantitatively assessed by Shi and Lipkowski [20,21,22], who found that when the complete copper

monolayer is formed, sulphate coverage drops to a limiting value close to that found in the case of the copper free Au(111) surface, suggesting that the sulphate ions are adsorbed on top of the copper atoms, in agreement with EXAFS measurements[23]. Several reviews discuss how this and other anions change UPD of Cu on Au(111)[24,25,26].

The Cu (1x1) structure on Au(111) has been far less investigated than that of the $\sqrt{3} \times \sqrt{3} R 30^\circ$ phase. The transition from the latter to the epitaxial monolayer has been found to occur via a nucleation and growth process which is responsible for a linear decrease in the stress change with coverage in this regime[27]. However, in vacuum the complete Cu monolayer is not pseudomorphic with the bulk terminated gold surface, showing striking differences with respect to the electrochemical environment, and indicating that the nature of the electrolyte plays a very important role[27].

According to the previous picture, the proper way to assess from a theoretical perspective the role of anions in determining the puzzling stability of Cu(1x1) on Au(111) is to include them in first-principles calculations. The main hindrance to do this is the incomplete knowledge of the nature of the structure of the anion to be considered on the top of the Cu(1x1) monolayer. In this regard, two recent experimental contributions come to help. On one side, Vasiljevic et al. [28] found, using STM, an ordered sulphate (2×2) structure on the pseudomorphic Cu(1x1) UPD layer on Au(111) in sulphuric acid solutions. On the contrary, based on X-ray absorption spectroscopy, Lee et al. [14] have proposed the existence of a $\sqrt{3} \times \sqrt{3} R 30^\circ$ sulphate overlayer on the Cu-(1x1) UPD layer on Au(111) in sulphuric acid solutions. In the present contribution, after establishing a suitable thermodynamic framework, we present stability calculations for these structures. We have also considered a $\sqrt{3} \times \sqrt{7}$ structure of adsorbed sulphate on the Cu(1x1) UPD adlayer, because this is the structure formed upon sulphate adsorption on bulk Cu(111) [29].

Both sulphate and bisulphate could come into question as the species coadsorbed with Cu. We have chosen the first alternative based on the experimental and theoretical evidence[29].

1.2 Materials and Methods

First-principles calculations were performed within the framework of DFT with the SIESTA code [30,31]. Valence electrons were described with a set of double-z polarized basis. The number of k -points was chosen to obtain convergence in the system energy better than 0.002 eV / atom, finally resulting in a sample of $5 \times 5 \times 1$ k -points. The separation between the metal slabs in the z direction, made of 2 Cu and 5 Au layers, was of 15 Å. The metal layers were symmetrically arranged and all of them but the central one were relaxed. Exchange and correlation effects were described using the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof functional [32]. The *energy shift* used to confine the electrons in the pseudo-atomic orbitals was 0.005 eV.

1.3 Results and Discussion

1.3.1 Thermodynamic modelling

We consider a working electrode, denoted S , with a Cu-UPD layer in equilibrium with a solution containing Cu^{2+} and SO_4^{2-} (SO_4H^-) ions, as shown in the left of figure 1. In order to assess the stability of the different structures, we define the following free energy function:

$$G_S = G_{Cu(SO_4^{2-})-Au(111)} - N_e^S \bar{\mu}_e^S - N_{Cu^{2+}}^S \bar{\mu}_{Cu^{2+}} - N_{SO_4^{2-}}^S \bar{\mu}_{SO_4^{2-}} \quad (2)$$

Where $G_{Cu(SO_4^{2-})-Au(111)}$ is the free energy of the metal slab covered by N_{Cu}^S copper adatoms and $N_{SO_4^{2-}}^S$ sulphate anions, $\bar{\mu}_{Cu^{2+}}$ is the electrochemical potential of the Cu^{2+} ions in solution, $\bar{\mu}_{SO_4^{2-}}$ is the electrochemical potential of SO_4^{2-} anions in solution and $\bar{\mu}_e^S$ is the electrochemical potential of the electrons in the reservoir to which the S electrode is attached. The last three terms on the right-hand side of this equation corresponds to a Legendre transformation taking into account the equilibria of the left electrode involving:

- Electrons provided by the foreign source at the electrochemical potential $\bar{\mu}_e^S$
- Sulphate ions in solution at the electrochemical potential $\bar{\mu}_{SO_4^{2-}}$, since these may freely cross the metal/solution interface.
- Copper ions in solution at the electrochemical potential $\bar{\mu}_{Cu^{2+}}$

An equation analogous to (2) may be written for the electrode on the right:

$$G_M = G_{Cu} - N_e^M \bar{\mu}_e^M - N_{Cu^{2+}}^M \bar{\mu}_{Cu^{2+}} - N_{SO_4^{2-}}^M \bar{\mu}_{SO_4^{2-}} \quad (3)$$

Where G_{Cu} is the free energy of the bulk Cu electrode and the remaining symbols have an analogous meaning to those in equation(2). The upper index indicates that the quantities correspond to the M electrode.

We consider the transfer of a Cu^{2+} cation from the M to the S electrode, allowing the formation on the S electrode of the following structures: $SO_4^{2-} \sqrt{3} \times \sqrt{3} R30^0$ with $\theta_{Cu} = 0.66$ (honeycomb), $SO_4^{2-} \sqrt{3} \times \sqrt{3} R30^0$ adsorbed on Cu(1x1), $SO_4^{2-} p(2 \times 2)$ adsorbed on Cu(1x1), and $SO_4^{2-} \sqrt{3} \times \sqrt{7}$ on Cu(1x1).

At equilibrium, the total free energy change must be nil:

$$\delta(G_S + G_M) = 0 \quad (4)$$

With the conditions:

$$\delta N_{Cu^{2+}}^S = -\delta N_{Cu^{2+}}^M = 1 \text{ (mass balance for } Cu^{2+} \text{ ions)} \quad (5)$$

$$\delta N_{SO_4^{2-}}^S = \begin{cases} 1/2 \text{ for } SO_4^{2-} \sqrt{3} \times \sqrt{3} R30^0 \text{-Cu honeycomb} \\ 1/3 \text{ for } SO_4^{2-} \sqrt{3} \times \sqrt{3} R30^0 - Cu(1 \times 1) \\ 1/4 \text{ for } SO_4^{2-} p(2 \times 2) - Cu(1 \times 1) \\ 1/5 \text{ for } SO_4^{2-} \sqrt{3} \times \sqrt{7} - Cu(1 \times 1) \end{cases} \quad (6)$$

$$\delta N_e^M = -2 \text{ (chargebalance at M)} \quad (7)$$

$$\delta N_{SO_4^{2-}}^M = 0 \quad (8)$$

$$-\delta N_e^S + 2\delta N_{Cu^{2+}}^S - 2\delta N_{SO_4^{2-}}^S = 0 \text{ (chargebalance at S)} \quad (9)$$

Substitution of (2), (3) and (5) into eqn. (4) yields:

$$\delta G_{Cu(SO_4^{2-})-Au(111)} - \delta N_e^S \bar{\mu}_e^S - \delta N_{SO_4^{2-}}^S \bar{\mu}_{SO_4^{2-}} + \delta G_{Cu} - \delta N_e^M \bar{\mu}_e^M = 0 \quad (10)$$

Replacement of (5), (7) and (9) into (10) and rearrangement leads to

$$\delta G_{Cu(SO_4^{2-})-Au(111)} + \delta G_{Cu} + 2 \left(\delta N_{SO_4^{2-}}^S - 1 \right) \left(\bar{\mu}_e^S - \bar{\mu}_e^M \right) + \delta N_{SO_4^{2-}}^S \left(-\bar{\mu}_{SO_4^{2-}} + 2\bar{\mu}_e^M \right) = 0 \quad (11)$$

To consider quantities that may be calculated we subtract the chemical potential μ_{SO_4} of neutral sulphate species to obtain:

$$\begin{aligned} & \delta G_{Cu(SO_4^{2-})-Au(111)} + \delta G_{Cu} - \delta N_{SO_4^{2-}}^S \mu_{SO_4} - 2e_0 \left(\delta N_{SO_4^{2-}}^S - 1 \right) \left(\Psi_S - \Psi_M \right) \\ & + \delta N_{SO_4^{2-}}^S \left(-\bar{\mu}_{SO_4^{2-}} + \mu_{SO_4} + 2\bar{\mu}_e^M \right) = 0 \end{aligned} \quad (12)$$

Where we have replaced the difference of electrochemical potentials $\left(\bar{\mu}_e^S - \bar{\mu}_e^M \right)$ by the corresponding electric work $-e_0 \left(\Psi_S - \Psi_M \right)$. Rearranging (12) we get:

$$\left(\Psi_S - \Psi_M \right) = - \frac{\left(\delta G_{Cu(SO_4^{2-})-Au(111)} + \delta G_{Cu} - \delta N_{SO_4^{2-}}^S \mu_{SO_4} + \delta N_{SO_4^{2-}}^S K \right)}{2e_0 \left(1 - \delta N_{SO_4^{2-}}^S \right)} \quad (13)$$

Where $K = -\bar{\mu}_{SO_4^{2-}} + \mu_{SO_4} + 2\bar{\mu}_e^M$

Eqn. (13) reduces to equation (1) if $\delta N_{SO_4^{2-}}^S = 0$. In the presence of anions, the first three terms can be obtained from first-principles calculations, while the last

term, containing the parameter K , is more complicated to assess, since it involves important entropic contributions, the solvation free energy of the anions, as well as the electrostatic potential difference across the bulk Cu electrode/solution interface. To circumvent this problem, we estimated first the parameter K performing calculations for the $\sqrt{3} \times \sqrt{3} R30^0$ structure and using for $(\Psi_s - \Psi_M)$ the underpotential shift of this phase (0.21 V). Then, with this K value we calculated, according to equation (13), the underpotential shift for the $Cu(1 \times 1)$ structure, assuming different structures for the sulphate ions on the (1×1) Cu deposit.

Table 1 shows results for the underpotential/overpotential shift as obtained from DFT calculations for the different structures analysed. The left column shows the potential shift for a $Cu(1 \times 1)$ pseudomorphic layer on $Au(111)$. In agreement with previous results [7,8], no UPD is predicted for a pseudomorphic monolayer of copper on $Au(111)$. On the other hand, when the underpotential shift is predicted according to the thermodynamic argument developed above, positive underpotential shifts result for the $SO_4^- - p(2 \times 2) / Cu 1 \times 1$ and $SO_4^- - \sqrt{3} \times \sqrt{3} R30^0 / Cu 1 \times 1$ structures. From these two, the first one appears to be slightly more stable, the predicted UPD shift being slightly more positive. No UPD is predicted for $SO_4^- - \sqrt{3} \times \sqrt{7}, Cu 1 \times 1$.

1.4 Conclusions

It can be asserted that the coadsorption of SO_4^- anions may explain by itself the stability of the $Cu 1 \times 1$ monolayer on $Au(111)$. Furthermore, the most stable structure predicted coincides with that found experimentally using STM, although another structure, also proposed on the basis of X-ray absorption experiments, follows very close in stability. The contribution of another coadsorbed species, like water or hydronium ions, cannot be ruled out, and would require further experimental and theoretical research, but the present results unambiguously show that the coadsorption of anions provides the major energetic contribution to the observed UPD of Cu on $Au(111)$.

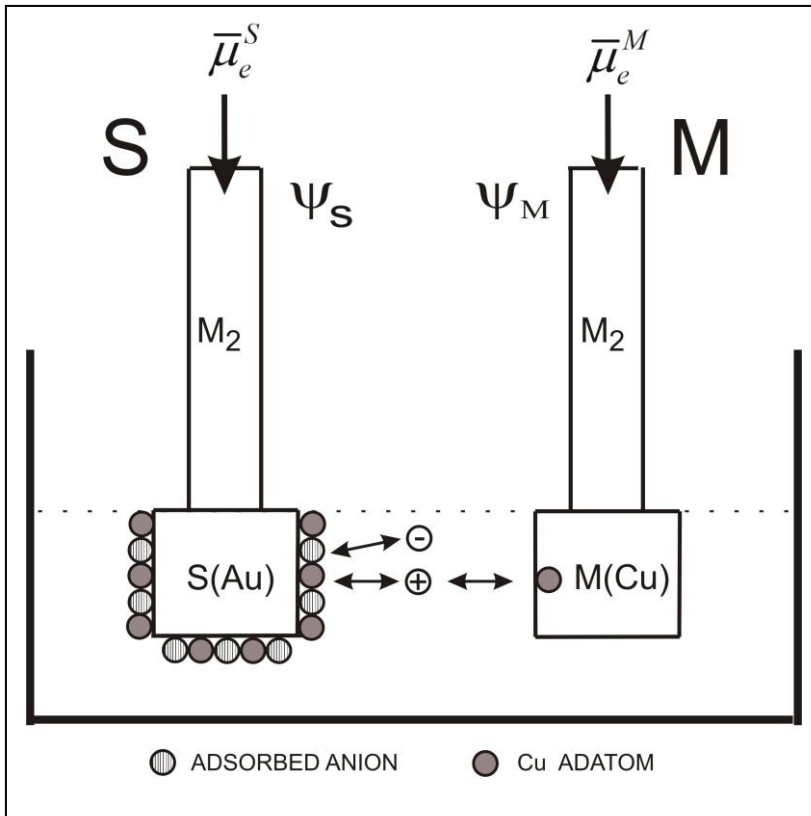
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Table 1: Calculated underpotential/overpotential shifts, $\Psi_S - \Psi_M$, using equation (13) for different systems. All values are given in volts. The experimental values are $\Psi_S - \Psi_M = 0.21 \text{ V} \pm 0.01 \text{ V}$ for the Cu submonolayer (honeycomb structure) and $\Psi_S - \Psi_M = 0.05 \pm 0.03 \text{ V}$ for the Cu monolayer respectively [9].

System	$\text{Cu}(1 \times 1)$ on $\text{Au}(111)$	$\text{SO}_4^- -$ $\sqrt{3} \times \sqrt{3} R30^\circ$ $\theta_{\text{Cu}} = 0.66$	$\text{SO}_4^- -$ $p(2 \times 2)$ on Cu 1×1	$\text{SO}_4^- -$ $\sqrt{3} \times \sqrt{3} R30^\circ$ on Cu 1×1	$\text{SO}_4^- -$ $\sqrt{3} \times \sqrt{7}$ on Cu 1×1
Theory	-0.27	0.21 (fitted)	0.03	0.02	-0.04

Figure 1: Scheme of an electrochemical cell where the potential difference is measured between an electrode made of a substrate S on which a metal M is deposited, and a bulk M electrode. The left electrode is in equilibrium with electrons at the electrochemical potential $\bar{\mu}_e^S$, and the right one with electrons at the electrochemical potential $\bar{\mu}_e^M$. The Cu^{2+} ion cores of both electrodes are in equilibrium via the dissolved Cu^{2+} ions at the electrochemical potential $\bar{\mu}_{Cu^{2+}}$. SO_4^- anions adsorbed on the S electrode are in equilibrium with dissolved SO_4^- at the electrochemical potential $\bar{\mu}_{SO_4^-}$.



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