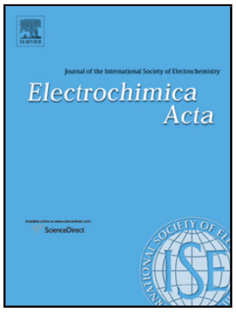

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Phosphate-mediated electrochemical adsorption of cisplatin on gold electrodes

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Research Highlights The potential-dependent adsorption and deposition of cisplatin on polycrystalline gold electrode is mediated by the adsorption of phosphate anions on gold electrode.

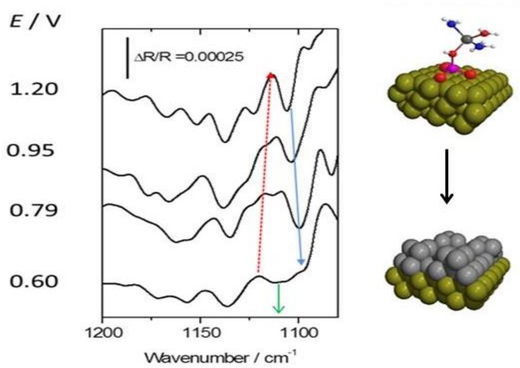
- Quantitative analysis suggests that the stoichiometry of the phosphate species and the cisplatin adsorbed was 1:1.
- Upon reduction of the phosphate-mediated cisplatin adsorption, the platinum deposits are formed by 3D nanoclusters

Abstract

This manuscript reports the potential-dependent adsorption and deposition of cisplatin on polycrystalline gold electrode. It was found that this process is mediated by the adsorption of phosphate anions on the gold electrode and that the maximum coverage of Pt adsorbed is given by the maximum coverage of phosphate adsorbed at a given potential. The interaction of cisplatin with the phosphate groups was confirmed by in situ FTIR spectroscopy under external reflexion configuration. Quantitative analysis suggests that the stoichiometry of the phosphate species and the cisplatin adsorbed was 1:1. Moreover, the relationship between the charge of the Pt deposited and the charge of the electrochemical surface area of the Pt deposited on the gold electrodes indicates that 3D nanoclusters of a few atoms of Pt were formed over the gold electrode upon the electrochemical reduction of the adsorbed cisplatin.

The Pt nanoclusters formed under these conditions were later evaluated for the oxidation of a monolayer of carbon monoxide. The Pt nanoclusters showed a high overpotential for the oxidation of this carbon monoxide monolayer and this high oxidation overpotential was attributed to the absence of adsorption sites for OH species on the Pt clusters: only at potentials where the OH species are adsorbed at the edge between the Pt nanocluster and the gold support, the oxidation of the carbon monoxide on the Pt nanoparticles takes place.

Graphical Abstract



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Keywords: cisplatin; ; ; ; ; ; , gold, adsorption, phosphate, electrocatalysis, size-dependence, carbon monoxide.

1. Introduction

The cost of the Pt catalyst is one of the limitations in the broad commercialization of low temperature fuel cell and water electrolyzers.[1, 2] In the attempt to reduce the cost of the catalyst layer, the scientific community has stablished a race to decrease the loading of platinum through different strategies such as decreasing the particle size, metal alloying or the optimization of the efficiency of the Pt catalyst through metal supported interactions.[3, 4]

Among all the approaches, decreasing the size of the Pt particles has been one of the most exploited since previous works have reported a strong size-dependent electrocatalytic activity of Pt clusters and nanoparticles.[5, 6] To achieve control over the size and particle size distribution of the Pt nanoparticles and supported Pt clusters different physical and chemical approaches have been adopted.[7-10] One of these approaches, the so-called wet impregnation method, includes the spontaneous adsorption of platinum compounds (hexa- and tetra-chloroplatinates) on the support materials with subsequent reduction by chemical or electrochemical means.[11-13]

Significant efforts have been made to understand and control the initial stages of the adsorption of the Pt precursors and the formation of Pt clusters and films on different support materials. Scanning Tunneling Microscopy has revealed that the formation of Pt nanoparticles (3 nm) from haloplatinate complexes is preceded by the formation of long order structures of haloplatinate complexes adlayers on Au(111) prepared by a simple immersion method in $HClO_4$.[14]

In other work, Bakos et al. reported the potential controlled adsorption of hexachloroplatinic acid on gold polycrystalline electrode in sulfuric acid solution. In this work, the authors reported a maximum coverage of 5% platinum on the gold surface independently of the adsorption potential in a region between 0.77 V and 0.95 V RHE. Other works have described the formation of platinum deposits on Au(111) electrodes in sulfuric acid solutions.[15-17] The last works provides full characterization of the structure of the platinum deposits as a function of the deposition time and multiple depositions processes. However the origin and the understanding of the adsorption of the platinum was not discussed. This information is highly relevant since the adequate selection of the electrolyte will contribute in the optimization of the surface coverage of the platinum deposits.

The electrochemical adsorption and reduction of Pt is a complex process and will not only depend on the ligands coordinated to the Pt-centre [18] but also on the affinity of the Pt-centre or the ligands to the surface chemistry of the support where the platinum would be deposited. This manuscript reports for the first time the use of cisplatin ($Pt(NH_3)_2Cl_2$) and phosphate ions to control the coverage of platinum on gold electrodes. We demonstrate that Pt adsorption on gold electrodes can be mediated by the adsorption of phosphate ions on gold and characterise the nature of the phosphate-mediated adsorption of cisplatin on a gold electrode. The potential-dependence of the phosphate-mediated adsorption of the Pt complex allows the control over the surface coverage of platinum atoms over the gold electrode. In addition, upon the reduction of the phosphate-mediated platinum complex, the surface modified electrodes were evaluated towards the electrochemical oxidation of carbon monoxide in acidic media.

2. Experimental

To ensure reproducible and clean conditions of experiments, all the glassware was soaked overnight in acidified solution of potassium permanganate, followed by a rinse with acidified solution of hydrogen peroxide and boiled five times with Milli-Q water (18.2 MΩ cm, 1 ppb total organic carbon).[19] A three compartment electrochemical cell was employed where a high surface area gold flag was used as the counter electrode and Hg/Hg_2SO_4 electrode as the reference electrode. All the results were converted to RHE scale as presented in the manuscript. The cyclic voltammetry measurements were performed on μAutoLab III potentiostat. Prior to experiments, Argon (6N, BOC) was used to deoxygenate electrolytic solutions.

Gold disk electrodes were prepared from high purity (Sigma Aldrich, 99.999%) gold wire. Prior to each experiment, the gold disk electrode was mechanically polished with alumina slurry, rinsed with water, flame-annealed and cooled down under argon atmosphere. The blank voltammetry of the gold electrode was registered prior each experiment to confirm the cleanness of the system (both electrode and electrolyte). The electrolyte and the solutions were prepared from Dulbecco's Phosphate Buffer Saline solution (DPBS, Lonza) or sulfuric acid (Merck Suprapur, 96%).

The adsorption of cisplatin (Biovision, ≥ 98%), on gold surface was completed by immersing the electrode in 2.6 mg L^{-1} solution of cisplatin in DPBS over the period of 60 seconds under potential control. Excess of cisplatin solution, beyond the monolayer, was removed by rinsing with a copious amount of Milli-Q water.

The oxidation of a monolayer of carbon monoxide (BOC, Research grade) was performed as follow. The Pt-modified electrode was immersed in a sulfuric acid solution at 0.1 V vs RHE. Carbon monoxide was bubbled in the electrochemical cell for 1 min. In order to avoid any possible contamination from the formation of metal carbonyls, the carbon monoxide was bubbled through a 1 mol L^{-1} solution of NaOH prior inflowing in the electrochemical cell. The excess of CO was removed by bubbling Ar for 10 mins. The oxidation of the CO monolayer was recorded in a meniscus configuration between 0.1 V and 1.2 V vs RHE at 20 mV s^{-1}.

The peak convolution of the voltammetric profiles were performed using Peakfit v4.12 software, using smoothing, background correction and Lorentzian minimization.

In situ FTIRs experiments were performed with a Bruker Vertex 80V IR spectrophotometer equipped with a MCT detector. A spectroelectrochemical glass cell with a 60° CaF_2 prism was used, designed for the external reflection mode in a thin layer configuration. FTIR spectra were collected with p-polarized light from an average of 200 scans obtained with 4 cm^{-1} resolution at selected potentials, by applying single potential steps from a reference potential (E = 1.25 V vs RHE) in the negative-going direction up to 0.6 V vs RHE. Several sample spectra at different potentials were collected, and the difference with respect to the reference spectrum was evaluated as ΔR/R. In these difference spectra, negative bands (pointing down) correspond to the generation of species at the gold−electrolyte interface and positive bands (pointing up) to the consumption of species.

3. Results and Discussion

3.1 Potential-dependence of the electrochemical adsorption and reduction of cisplatin on gold electrodes in phosphate buffer.

Cisplatin was pre-adsorbed on the gold electrode by immersing a flat gold polycrystalline electrode in a DPBS solution containing 2.6 mg L^{-1} of cisplatin during 1 min at different potentials ranging between 0.65 V and 1.65 V vs RHE. The currents measured during the adsorption process are shown in Figure SI1. Positive currents were recorded during the adsorption of Pt at potentials higher than 1.6 V vs RHE indicating the absence of any adsorption or reduction process (Figure SI2). We attribute the lack of adsorption of cisplatin on the gold surface to the bulk oxidation and formation of gold oxide taking place at these potentials.[20] Large negative currents during the adsorption step at potentials below 0.7 V vs RHE indicated the bulk deposition of platinum. At the adsorption potential of 0.75 V vs RHE, a slightly negative current was recorded suggesting electrodeposition of Pt, however adsorption of cisplatin cannot be discarded. In the potential window between 0.8 V and 1.2 V vs RHE, low values of positive current were observed during the adsorption step. Figure 1A shows the cyclic voltammetry profiles in cisplatin-free DPBS solution of a gold polycrystalline electrode onto which cisplatin had been pre-adsorbed at different potentials.

All the voltammetric profiles present an irreversible reduction signal in the region between 0.6 V and 0.35 V vs RHE. The absence of this reduction peak and the increase of the double layer in a 2nd scan (Figure 1B) confirmed that this reduction peak is associated to the electrochemical reduction of pre-adsorbed cisplatin into metallic Pt according to the reaction:

$$Pt(NH_3)_2Cl_2 + 2e \rightarrow Pt^0 + 2\ NH_3 + 2\ Cl^- \qquad (1)$$

The presence of Pt^0 at the surface was further confirmed by recording the voltammograms in wider potential window (Figure SI3) where two characteristic regions can be observed: the adsorption/desorption of protons and anions in the potential region between 0.05 V and 0.4 V vs RHE, and the oxide formation/reduction region in the potential region between 0.7 V and 1.4 V vs RHE.

Figure 1A also shows that the decrease towards more negative potentials of the pre-adsorption potential of the cisplatin resulted in a shift of the onset potential of the reduction of Pt^{+2} to Pt^0 toward more positive potentials. In addition, the charge associated to the reduction process followed the same trend which confirmed an increase of the cisplatin pre-adsorbed as the adsorption potential decreases. The shift on the onset of the reduction potential and the increase of the total charge matched with the appearance of new features on the voltammetric profiles.

The voltammetric profiles of the reduction of cisplatin on the gold electrode in DPBS contain contributions for the nucleation and growth mechanism of the platinum deposits on the gold electrode. Since different adsorption sites on the surface have characteristic nucleation and growth signals, it should be possible to deconvolute the voltammetric profile to obtain information about the reduction of cisplatin on different sites present on the surface.[21, 22] Understanding each of these peaks might reveal the nature of the reduction process and therefore furthers studies on single crystal electrodes with different orientations and step-densities will be performed in the future.

The reduction feature appearing between 0.6 V and 0.35 V vs RHE revealed an overlapping of 3 separate peaks (Figure 2A-D). The charge associate to each of these peaks and the total charge of the reduction process is presented as a function of the adsorption potential on Figure 3A. When the adsorption potential was as positive as 1.4 V vs RHE, a double peak centred at 0.42/0.5 V vs RHE was observed. At less positive adsorption potentials - 1.25 V, 1.06 V and 0.85 V vs RHE- a new reduction peak appeared at 0.55 V vs RHE, and the charge obtained from the three convoluted peaks increased when the adsorption potential became less positive (Figure 3A). Since the overpotential for the nucleation and growth of Pt particles is dependent on the concentration, changes in the surface concentration of pre-adsorbed cisplatin should result in a shift in the reduction potential of the platinum.[23]

In order to determine the structure of the Pt deposited on the gold electrode as a function of the adsorption potential, the charge associated to the proton adsorption/desorption from Figure SI3 was represented as a function of the number of atoms of Pt deposited on the gold electrode (Figure 3B), which was calculated from the total charge of the reduction process (Figure 3A). A linear relationship between reduction charge and the number of platinum atoms adsorbed (slope $6x10^{-14}$ μC atoms^{-1} Pt) was observed when the adsorption was done between 0.8 V and 1.2 V vs RHE. The deviation of the linear relationship when the adsorption potential was 0.75 V vs RHE is due to the mixed mechanism observed at this potential (adsorption+ bulk deposition). A similar observation has been reported by Bakos et al. for the adsorption of Pt in acidic media.[24] Given that the surface atom density of a Pt(111) is $1.50 \cdot 10^{15}$ atoms cm^{-2} , the hydrogen adsorption on the platinum deposited on the gold electrodes gives a charge density of 90 μC cm^{-2} which is significantly lower than the theoretical value of 240 μC cm^{-2} for a $1e^{-}/1H^{+}$ reaction over a Pt(111) structure.[25] The presence of 2D platinum deposits would result in a charge density closer to the theoretical value of 240 μC cm^{-2}. Given that we are using polycrystalline electrodes, we would expect the value of charge to be smaller and approximately 210 μC cm^{-2}. Thus, we can conclude from here that the reduction of the pre-adsorbed platinum in a potential window between 0.85 V and 1.45 V vs RHE resulted in the formation of 3D nanoclusters over the gold electrode. This result is highly relevant since the final structure of the adsorbed Pt will have an impact on the catalytic activity of the deposited platinum.

Interestingly, the potential window where the adsorption of cisplatin was taking place (0.65 V - 1.4 V vs RHE) coincided with the potential limits of the adsorption/desorption of phosphates on gold electrode.[26] It has been reported that the adsorption of phosphate species appears at approx. 0.65 V vs RHE. At potentials higher than 1.2 V vs RHE, the adsorbed phosphate is displaced by the adsorption of OH that results in a decrease in surface coverage by phosphate. At potentials higher than 1.5 V vs RHE the formation of AuO_x [26] blocks the adsorption of phosphates and therefore the adsorption of cisplatin.

Given the similarities between the reported potential window for the adsorption of phosphates on gold surfaces[26] and the potential window we identified for the adsorption of Pt in these type of surfaces, we suggest that this potential control adsorption of cisplatin is mediated by phosphate anions that are pre-adsorbed on these gold electrodes (Figure 4). Although the interaction of cisplatin with free-phosphate has not been reported to the date, the interactions between Pt-based anti-tumour agents and phosphate groups of organic molecules is well-known.[27-30] For instance, it has been reported that DNA’s phosphate groups have high affinity to polynuclear Pt complexes acting as ‘Phosphate Clamps’ through hydrogen bonds.[28-30] In addition the interaction of cisplatin has been also reported for zirconium phosphate nanoplatelets and calcium phosphates, that can be used as potential delivery agents of cisplatin.[31, 32]

This observation implied that the coverage of Pt was limited by the coverage of the phosphate anions. It was thus important to identify the relationship between the adsorbed phosphate and the potential. Habib et al. has reported that the maximum coverage (i.e. $\theta = 2 \cdot 10^{-12}$ mol cm^{-2}) of phosphate ions on a polycrystalline gold electrode is obtained at approximately 0.8 V vs RHE.[33] An increase in the electrochemical potential results in lower coverage due to the competitive adsorption of OH species and the formation of the surface oxide, in agreement with previous reports[26] and our observations. We thus compared the number of phosphate molecules adsorbed per surface area on Au polycrystalline surfaces[33] with the number of Pt atoms adsorbed that we calculated as a function of the applied potential during the adsorption process (Table 1 and Appendix to Table 1 in SI). Overall, there was a good correlation between the number of Pt atoms and the number of phosphate anions, suggesting a 1:1 binding ratio between this phosphate anion and the molecule of cisplatin.

* Calculated from the value of charge consumed during electrochemical reduction of pre-adsorbed cisplatin assuming no other reductive processes taking place

** Concentrations of phosphate anions has been estimated from FTIR data and radiotracer data presented in the ref. [33]

3.2 In situ FTIR characterization of the adsorption mechanism of cisplatin

In order to demonstrate the mechanism of this phosphate-mediated adsorption of cisplatin on the gold electrode, in situ FTIR experiments under external reflection configuration were performed. Figure 5 shows a series of potential-depended FTIR spectra obtained with p-polarized light of Au polycrystalline flat electrodes in a DPBS solution. In both cases, the spectra were obtained with a reference potential at 1.25 V vs RHE. The left panel was obtained in absence of cisplatin while the right panels were obtained in presence of 8.67 µmol L^{-1} cisplatin.

The spectrum in figure 5A shows two negative bands at approximately 1105 cm^{-1} and 1118 cm^{-1}. This bands were associated to the combination of the δ(OH)+υ(PO) modes of the HPO_4^- according to Yaguchi et al.[26] The spectra below 1080 cm^{-1} was not accessible due to the strong adsorption of the CaF_2 prism. The band at 1118 cm^{-1} showed a blue shift with a stark tuning slope of 19 cm^{-1} V^{-1} demonstrating that this band corresponds to the adsorbed HPO_4^-. However, the negative band at 1105 cm^{-1} increased in intensity between 1.2 V and 0.95 V vs RHE, and decreased at lower potentials. This behavior was in agreement with similar results presented by Yaguchi et al.[26] The bands between 1130 cm^{-1} and 1200 cm^{-1} were attributed to contributions of the fluctuation of the thin layer. Figure 5B shows the potential depended FTIR spectra of Au polycrystalline flat electrode in a DPBS solution in presence of cisplatin. The reference spectrum was collected in absence of cisplatin at 1.25 V. At 1.2 V vs RHE a negative band was observed at 1102 cm^{-1} associated to the υ(P-O-Pt) which increased in intensity between 1.2 V and 0.79 V vs RHE and showed a red shift with a stark tuning slope of 9 cm^{-1} V^{-1}. A negative band at 1120 cm^{-1} was also observable at 1.2 V vs RHE and disappeared at lower potentials. This band can be associated to the disappearance of the combination of the δ(OH)+υ(PO) modes of the HPO_4^- due to the strong interaction of the Pt with the OH group in phosphate. A new negative band was observed at 0.6 V vs RHE which can be attributed to the adsorption of phosphate on the Pt deposited on the gold electrode. Overall, we believe these results are consistent with the phosphate mediated adsorption of platinum proposed on Figure 4B.

3.3. Electrochemical oxidation of carbon monoxide on ultrasmall loadings of Pt nanoparticles on gold electrodes.

In order to evaluate the catalytic activity of the platinum nanoparticles deposited on the gold electrodes, the electrochemical oxidation in acidic media of a monolayer of carbon monoxide was evaluated. The oxidation of a monolayer of carbon monoxide was chosen as a probe of the catalytic activity of the Pt deposit because of the lack of adsorption of CO on gold electrodes in acidic pH.[34, 35] Figure 6 shows voltammetric profiles of the oxidation of a monolayer of carbon monoxide in acidic media on two platinum modified electrodes obtained using the adsorption-reduction of cisplatin. Figure 6 also includes the voltammetric profiles of the oxidation of a monolayer of carbon monoxide on gold electrode modified with cisplatin deposited at 0.65 V, where reduction of Pt should be observed. As can be seen, the oxidation of carbon monoxide on the electrode prepared by deposition of Pt at 0.65 V vs RHE showed two oxidation peaks at 0.8 V and 1.0 V vs RHE. While the appearance of a peak at 0.8 V vs

RHE is in agreement with the oxidation of carbon monoxide on supported platinum nanoparticles[36], the appearance of a second peak at significantly higher overpotentials suggested that the oxidation of carbon monoxide was taking place in two different reactions sites. Interestingly, when the electrode was modified by the phosphate-mediated adsorption and deposition of cisplatin, only this second peak at 1.01V vs RHE was observed.

For over more than 2 decades, understanding the mechanism of CO oxidation on Pt substrates has been subject of intensive discussions and several pathways have been proposed.[37-43] Important considerations, such as adsorption energies, have to be taken into account when comparing results on Pt single-crystal electrodes or with supported nanoparticles.[10, 36, 44] The electrochemical oxidation of CO results from a reaction between neighboring CO_{ads} and the OH generated by the activation of water following a Langmuir–Hinshelwood mechanism (L-H), as proposed by Gilman (Equation 2).[45]

$$\text{Pt-CO}_{ads} + \text{Pt-OH}_{ads} \rightarrow CO_2 + H^+ + e^- + 2\text{Pt}^* \qquad (2)$$

In our system, the low coverage and the restricted mobility of CO in small Pt-islands significantly limits the likelihood of finding adsorbed $^-$OH on nearby sites.[46] Interestingly, the blank voltammograms on Figure 6A and 6B did not show any contributions associated to the oxidation of the Pt catalyst. However, it is important to notice that the onset of the CO oxidation in Figure 6A and 6B coincided with the potential (> 0.95 V vs RHE) where the desorption of sulfates anions and the adsorption of OH species on the gold electrodes at the pH investigated has been reported.[47-49] Therefore, we propose here that the Pt nanoclusters obtained by the phosphate-mediated adsorption of cisplatin on gold are not active towards the CO oxidation on their own. The CO oxidation only takes place at overpotentials where OH replaces the adsorbed phosphate on the gold surface. We propose that on such small Pt nanoclusters, the reaction take place at the edges of the Pt particles following the overall reaction mechanism (Equation 3):

$$\text{Pt-CO}_{ads} + \text{Au-OH}_{ads} \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^- + \text{Pt}^* + \text{Au}^* \qquad (3)$$

4. Conclusions

The phosphate-mediated adsorption of cisplatin on gold electrodes has been investigated. This process is potential dependent and takes place in a potential region between 0.75 V vs RHE and 1.5 V vs RHE. At lower potentials than 0.75 V vs RHE the bulk deposition of Pt takes place and at higher potentials the phosphate replacement by the gold oxide blocks the adsorption of platinum. The maximum coverage of cisplatin is reached at ≈ 0.8 V vs RHE which coincides with the maximum coverage of phosphate.

We propose an adsorption model where each cisplatin is bound to one adsorbed phosphate molecules. In situ FTIR experiments confirmed this interaction of the platinum with the P-O group in the potential range where the adsorption takes place.

Upon electrochemical reduction of the phosphate mediated cisplatin, platinum 3D nanoclusters islands where obtained on the surface of the gold electrodess. The platinum nanoclusters showed high overpotentials for the CO oxidation. The large overpotential was attributed to the low availability of free Pt-sites for the adsorption -OH species. We believe that the oxidation of the CO at high potentials >1.0 V vs RHE is triggered by the displacement of phosphate by OH on gold electrodes.

This manuscript represents the first report of the anion-mediated adsorption/deposition of Pt on an electrified surface. Our findings may open the door for the use of electrochemistry to prepare well-defined monolayer and submonolayers of metals using potential dependence adsorption of anions or other relevant ligands.[50] The ability to control the deposition of metal (sub)monolayers has important implications in the development of core-shell nanostructures for Fuel Cells applications and environmental remediation.[51-54] In future studies, the relationship between the crystal structure of the electrodes, the structure of the anion adlayer and the coverage and structure of the resulting Pt deposit will be studied.[55, 56].

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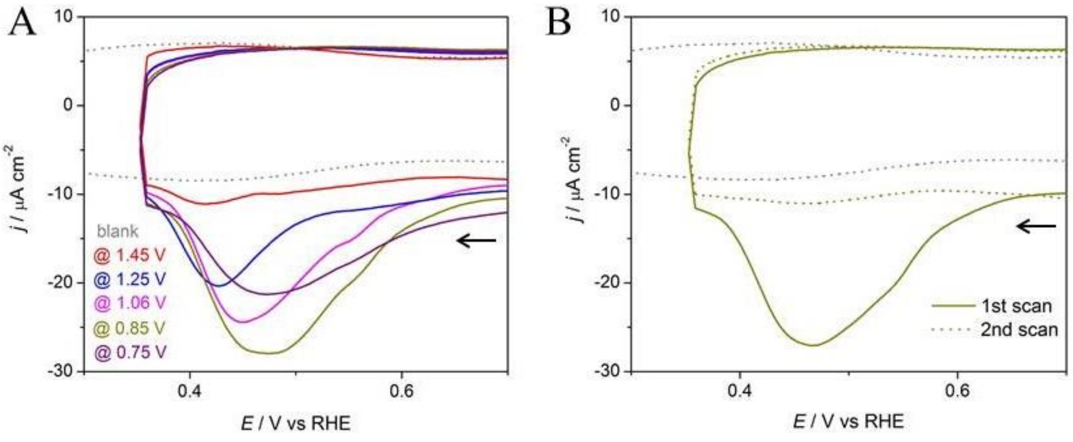

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Figure 1: (A) Voltammetric profiles in a cisplatin free phosphate buffer solution of surface-modified Au(poly) electrode. Surface modified electrodes were obtained by

immersing the electrode in 2.6 mg L^{-1} solution of cisplatin solution during 1 min at different potentials as indicated in the figure. The scan direction is indicated by the arrow in the figure. (B) Consecutive scans of a cisplatin-modified Au(poly) electrode at (@) 0.85 V vs RHE recorded in a cisplatin free phosphate buffer solution Scan rate υ = 50 mV s^{-1}.

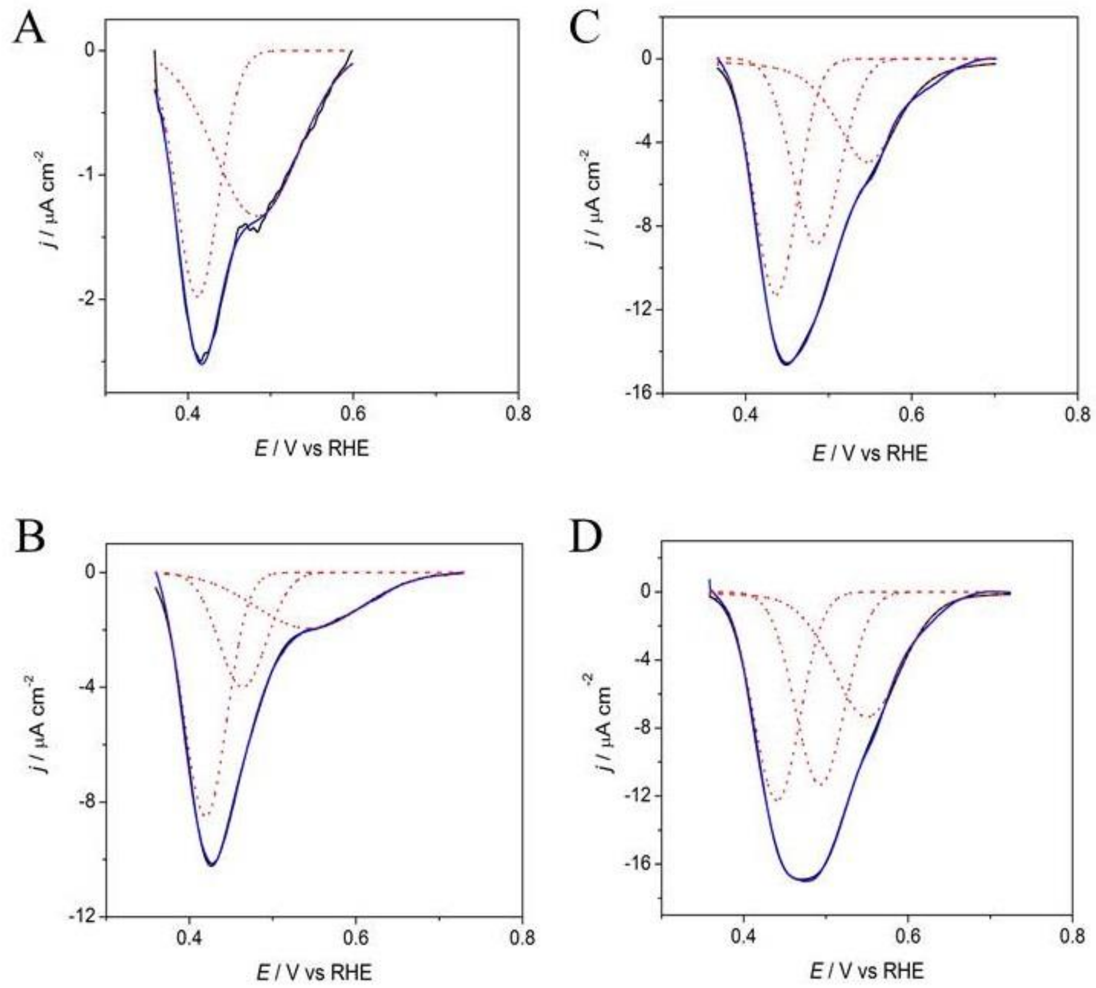

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Figure 2: Voltammetric profiles taken from figure 1A (solid black line), deconvoluted peaks (dashed red lines) and fitting of the convoluted peaks (solid blue lines) after

preadsorption at (A) 1.45 V (B) 1.25 V (C) 1.06 V vs RHE (D) 0.85 V vs RHE. Peaks were smoothed, background-corrected and deconvoluted using PeakFit v4.12 software. [1]

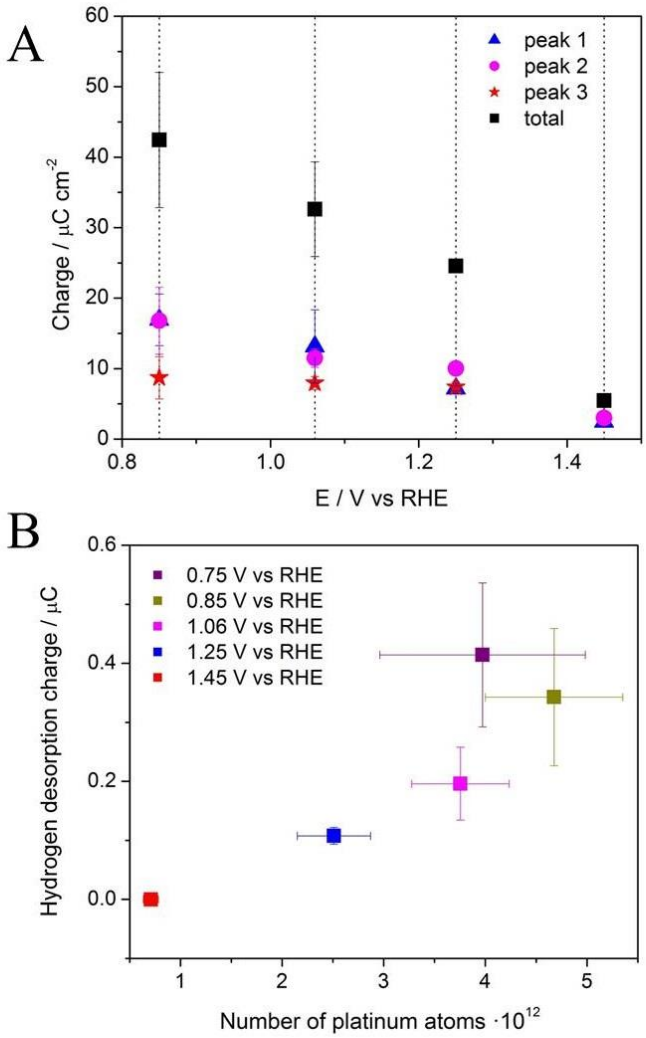

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Figure 3: (A) Integrated charge from the deconvoluted peaks shown in Figure 2 as a function of the adsorption potentials (B) Integrated charge of the hydrogen adsorption/desorption region from Figure SI3A as a function of the number of atoms of

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[1] The shape of the reduction peak is surface structure dependent (Figure S4). This changes are associated to the different arrangements of the phopshate adsorbed over the surface and the precense of low coordinated atoms over the surface.

platinum adsorbed at each adsorption potential calculated from the total charge on Figure 3A.

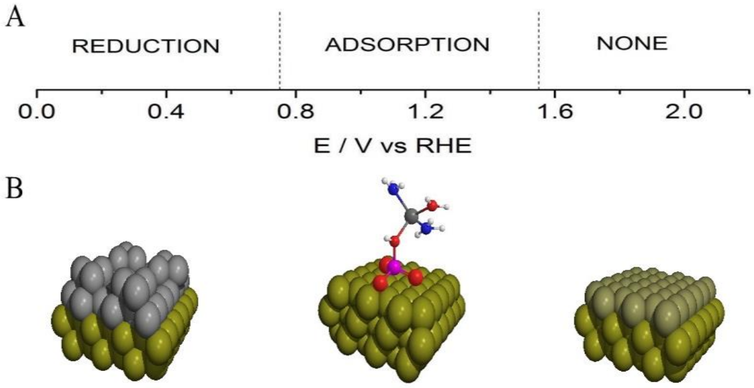

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Figure 4: (A) Scheme of the potential-dependence for the phosphate-mediated adsorption of cisplatin on Au polycrystalline electrode. (B) Hard-sphere model corresponding to the phenomena observed at the range of potentials. Yellow spheres stand for gold, grey spheres stand for platinum, pale yellow spheres stand for gold oxide layer.

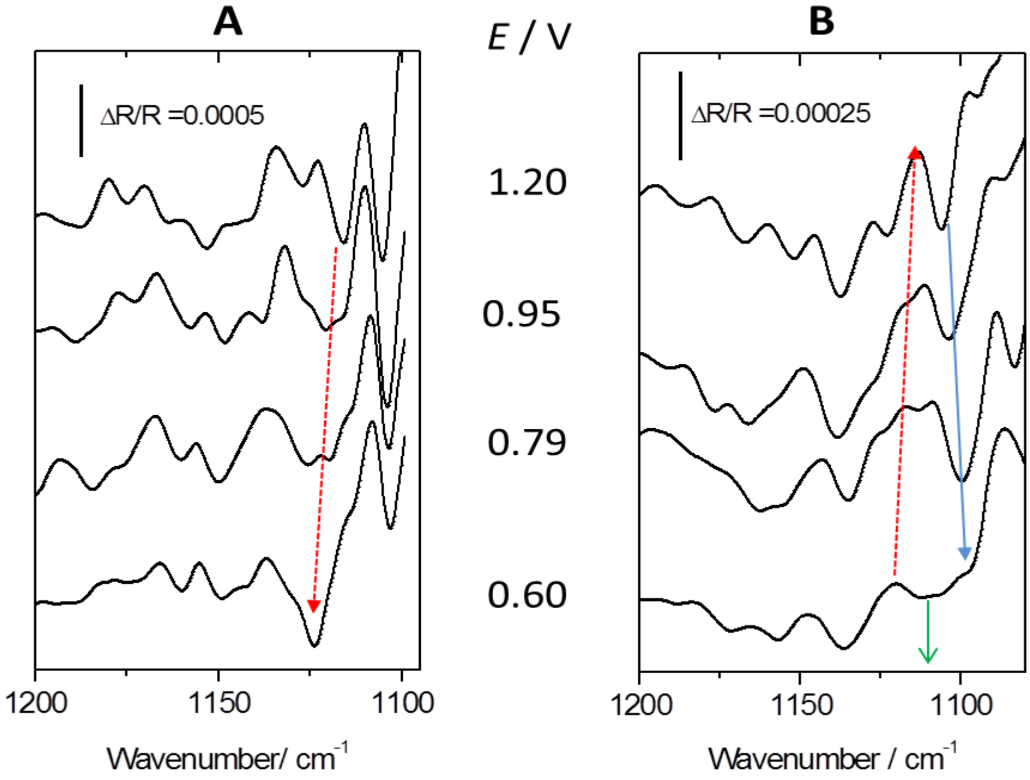

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Figure 5: Potential difference FTIR spectra of Au flat polycrystalline electrode in PBS solution in (A) absence and (B) presence of cisplatin. Both spectra were acquire in absence of cisplatin and are referred to the reference spectrum acquired at E_{ref} = 1.25 V vs RHE prior to the potential step-down to 0.6 V vs RHE.

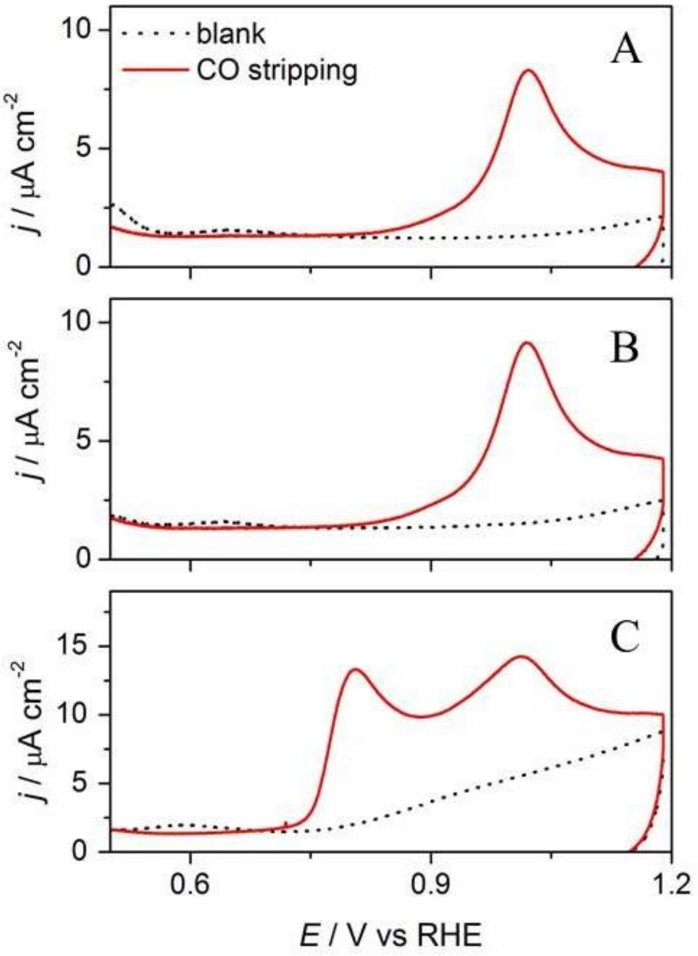

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Figure 5: Voltammetric profiles in 0.5 M H_2SO_4 for the oxidation of a CO monolayer on the Pt-modified gold electrodes prepared at (A) 1.06 V vs RHE, (B) 0.75 V vs RHE, (C) 0.65 V vs RHE; scan rate: 0.02 V s^{-1}.

Table 1. Values of surface concentrations of cisplatin and phosphate anions at different potentials on Au polycrystalline electrode.

	Number of molecules on the surface / $\cdot 10^{-10}$ mol cm^{-2}		
Adsorption potential vs RHE	0.85 V	1.06 V	1.25 V
Cisplatin*	**2.2 ± 0.3**	**1.8 ± 0.2**	**1.1 ± 0.2**
Phosphate anions**	**2.0**	**1.5**	**0.7**