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The Effect of Propanal on the Stability Range of the Reconstructed Au(100) Surface in Different Electrolyte

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Voltammetric measurements have been employed to assess the effect of propanal on the stability range of the reconstructed Au(100) surface in different electrolytes. The results show that, depending on the type of anions, propanal reduces or increases or does not change the stability range of the reconstructed surface. The influence of the propanal electrooxidation on this stabilization is considered.

Key words: single-crystal Au(100) electrode, surface reconstruction, electrooxidation, propanal

Surface reconstruction of Au(100) electrode in aqueous solutions is a well-known phenomenon, which has been studied by various techniques [1]. It has been demonstrated that a flame-annealing Au(100) surface is reconstructed (the thermally-induced reconstruction), showing the hexagonal close packed form, hex-form, which contains about 24% more surface atoms than the unreconstructed square lattice, (1×1)-form. The Au(100)-(hex) surface can be obtained also electrochemically [2] at negative potentials (the potential-induced reconstruction).

The reconstruction is lifted, due to adsorption of anions [3] and organic molecules [4], and the structural transition (hex)→(1×1) takes place at the so-called transition potential (E_T) yielding the unreconstructed surface. The influence of organic molecules on the stability of the (hex)-structure has been investigated. For several organic molecules, *e.g.* pyrazine, thiourea [4], the stability range of the hex-structure is reduced. On the other hand, it has been found for coumarine [5] and recently for γ-butyrolactone and cyclohexanone [6] that this stability range is increased, *i.e.* these molecules shift the transition potential to more positive values. The impact of all the above mentioned organic compounds on the stability range of the hex-structure is independent of the applied supporting electrolytes. In the following it is demonstrated that propanal (PAL) acts quite differently. Namely, depending on the type of anions, present in the solution, the addition of PAL shifts the potential E_T either to more negative or to more positive values. Besides, for one system considered no such shift is observed. Additionally, in our systems the lifting of the reconstruction occurs at potentials, at which the oxidation of PAL takes place. This creates a possibility to determine to what extent the latter process influences the lifting of the reconstruction.

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EXPERIMENTAL

The working electrode was an Au(100) single crystal rod, cut and polished at LEI-CNRS (Meudon, France). The geometric area of this electrode was 7.3 mm^2. Before each experiment the electrode was prepared according to the well-known procedure for preparation of well ordered gold surfaces [7]. Namely, the crystal was annealed for 3 min in a Bunsen burner flame, then cooled down to room temperature in a stream of nitrogen. Contact with the electrolyte was achieved by the hanging-meniscus method [8]. In all cases, the counter electrode was a Pt wire and the reference electrode was a saturated calomel electrode (SCE). All potentials are reported versus SCE. The voltammetric measurements were performed using a traditional electrochemical equipment.

All solutions were prepared from Milli-Q water. The supporting electrolyte was 0.05 M KNO_3, 0.05 M Na_2SO_4 or 0.05 M Na_2CO_3 (all Merck Suprapure) with various additions (from 0.001 M to 0.04 M) of distilled propanal (Sigma).

Measurements were carried out by adding the organic compound into the supporting electrolyte solution previously deaerated (for 50 min) by nitrogen. Nitrogen was allowed to flow over the solution during the experiments, carried out at room temperature (24±1°C).

RESULTS AND DISCUSSION

The lifting of the (hex)-reconstruction is particularly clearly seen in the cyclic voltammograms, in which the (hex)→(1×1) transition shows up in a pronounced current peak, due to changes in the potential of zero charge and the amount of adsorbed anions or organics between the reconstructed and unreconstructed surfaces. The reconstruction origin of this peak (which has no cathodic counterpart) can be confirmed additionally by a simple electrochemical test (applied throughout in the present paper), based on recording peaks associated with the lifting of thermally- and potential-induced reconstructions. The latter peak occurs at a potential *ca.* 35 mV less positive than the former one and is usually smaller. The peak potential is a convenient indicator of the stability of the (hex)-structure, whose existence corresponds to its negative side.

In order to investigate the effect of PAL on the potential of the Au(100)[(hex) →(1×1)] structural transition, the current-potential curves were recorded in three different supporting electrolytes of 0.05 M concentration, *i.e.* KNO_3, Na_2SO_4 and Na_2CO_3 with various bulk concentration of PAL. In the following, a scan rate of 50 mV/s has been chosen for the sake of comparison with the results obtained previously [5,6].

Figure 1 depicts three cyclic voltammograms for the thermally-prepared Au(100)-(hex) electrode with the (hex)→(1×1) transition in 0.05 M KNO_3 (supporting electrolyte) and in solutions containing 0.001 M and 0.005 M PAL. The most striking feature in the former voltammogram is the presence of a well developed peak at 0.469 V. This peak in pure electrolyte is interpreted as due to the lifting of the reconstruction. A positive value of E_T confirms [9] a weak adsorption of NO_3^- anions on gold. The addition of PAL modifies the cyclic voltammograms by increasing the current at potentials more positive than 0.250 V at first, owing to PAL oxidation at the

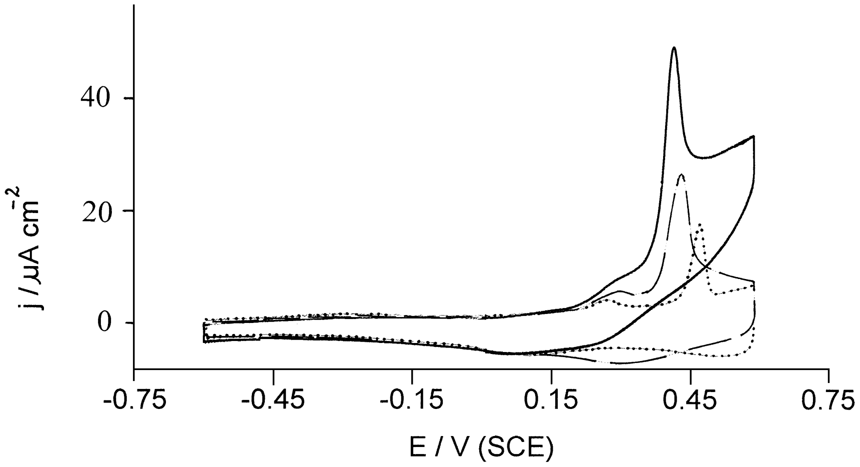

Figure 1. Cyclic current-potential curves for thermally-prepared Au(100) in 0.05 M KNO_3 (· · · ·) and with various additions of propanal 0.001 M (– – – –) and 0.005 M (————). Scan rate 50 mV/ s.

reconstructed surface, and then due to the lifting of the reconstruction. Moreover, the presence of PAL in the electrolyte shifts the peaks towards less positive potentials and simultaneously increases the charge under the peaks. Analysis of the concentration dependence shows that an increase in the PAL concentration (from 0.001 to 0.04 M) shifts the reconstruction peak towards less positive potentials (from 0.431 V to 0.403 V). A similar concentration dependence of E_T is typical of few organic molecules such as pyrazine or thiourea, which lift the reconstruction upon adsorption [4]. This means that in the presence of weakly adsorbed NO_3^- anions the lifting of the reconstruction may be caused by adsorption of PAL or both PAL + intermediate species, as in this potential range the stability of the hex-structure overlaps with that of PAL oxidation. In other words, the considerably positive values of E_T for weakly adsorbed NO_3^- anions of the supporting electrolyte enable the other species, present in the solution, *e.g.* PAL to lift the reconstruction at less positive potentials and as a consequence reduce the stability range of the Au(100)-(hex) surface. However, we are aware that it is difficult to relate these peaks to only a single process, *i.e.* lifting of the reconstruction as one would expect a significantly smaller charge under this peak (in KNO_3 alone such charge is about 2–3 times smaller). It seems, therefore, that an additional process, *i.e.* charge-transfer process, due to the electrooxidation of PAL, contributes to the charge associated with peaks under consideration. In this respect, Roelfs *et al.* [10] have also proposed, that both the charge transfer from the adsorbed thymine molecules to the surface and the lifting of the reconstruction are responsible for the charge under the peak in the voltammogram of the Au(100) electrode.

The situation is different, when the supporting electrolyte KNO_3 was replaced by Na_2SO_4, whose anions show stronger specific adsorbability. This is demonstrated in Fig. 2 where the current-potential curves for a thermally-prepared Au(100)-(hex) surface in 0.05 M Na_2SO_4 with various additions of PAL (0.02 M and 0.04 M) and, for comparison in supporting electrolyte alone, are given. As can be seen, on the anodic wave, due to oxidation of PAL, one can easily notice the current peak whose potential is practically equal to that in the supporting electrolyte. This indicates that the adsorption and electrooxidation of PAL have no impact on the potential, at which the reconstruction is lifted. Moreover, the analysis of the concentration dependence shows that for the PAL concentration varied from 0.001 to 0.04 M, the shift of the potential for the (hex)→(1×1) transition is almost zero. This result suggests that for the system under consideration, the lifting of the reconstruction cannot be caused by PAL or PAL + intermediates adsorption, as is in the above case. On the other hand, the fact that the peak potential, irrespective of PAL concentration, is the same as that in the supporting electrolyte, indicates that the adsorption of SO_4^{2-} anions is responsible for the lifting of the reconstruction. It is worth mentioning that such a change of species, whose adsorption is responsible for the lifting of the reconstruction after the application of different supporting electrolyte, contrasts with the behaviour of the hitherto investigated organic molecules. For example piridine lifts the reconstruction irrespective of the electrolyte anion (see *e.g.* [4] and [11]).

We have examined above the impact of PAL on the lifting of reconstruction in the systems, in which PAL was added to neutral solutions. As a result, the reconstruction was lifted at the potentials, at which the rate of PAL oxidation was rather low. Further insight into the impact of electroxidation on the lifting of the reconstruction can be

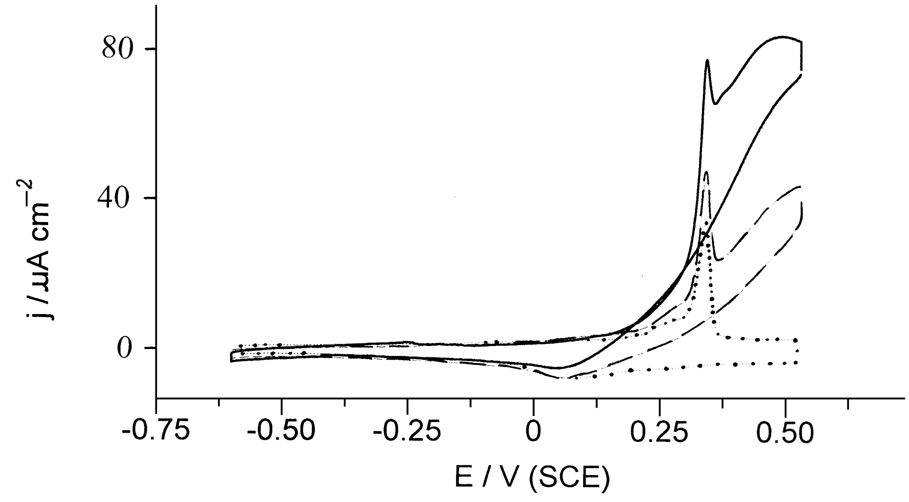

Figure 2. Cyclic current-potential curves for thermally-prepared Au(100) in 0.05 M Na_2SO_4 (· · · ·) and with various additions of propanal 0.02 M (– – – –) and 0.04 M (———). Scan rate 50 mV/ s.

gained from the experiment carried out in alkaline solution, as it is well known that gold is a very active electrocatalyst for electrooxidation of organic compounds [12] in such solutions. However, the application of a strongly alkaline solution, *e.g.* 0.05 M NaOH causes such a high increase in the PAL oxidation current, that it is impossible to determine E_T to a high accuracy. Therefore, we have performed our investigation in a slightly alkaline solution, *i.e.* 0.05 M Na_2CO_3 .

Figure 3 displays the voltammetric curves for the oxidation of PAL on the thermally- prepared Au(100) in 0.05 M Na_2CO_3. The curve obtained in the absence of PAL, which is included, shows the current peak, associated with the lifting of the reconstruction caused by adsorption of anions at 0.131 V. As follows from Fig. 3, in 0.05 M Na_2CO_3 the electrooxidation of PAL not only begins at much more negative potentials, but is also accompanied by a much higher current density than that in the above-mentioned two electrolytes. Moreover, as can be seen, in the positive range of potentials the reconstruction peak occurs on each oxidation wave. Almost the same charge, under each of these peaks as that of the peak associated with the lifting of the reconstruction in the supporting electrolyte, suggests that the anions lifts the reconstruction. However, as follows from Figure 3, addition of PAL shifts the peak potential quite unexpectedly towards more positive values. The concentration dependence analysis shows that an increase in PAL concentration (from 0.001 to 0.02 M) shifts the transition potential towards more positive values (from 0.134 to 0.273 V). Let us add, for the sake of comparison, that a similar extension (*ca.* 130 mV) of the stability range was observed in sulfate electrolyte for twice lower concentration (0.01 M) of coumarin [5] or for nine times greater concentration of cyclohexanone [6]. Addition of these compounds extends the stability range of the hex-structure,

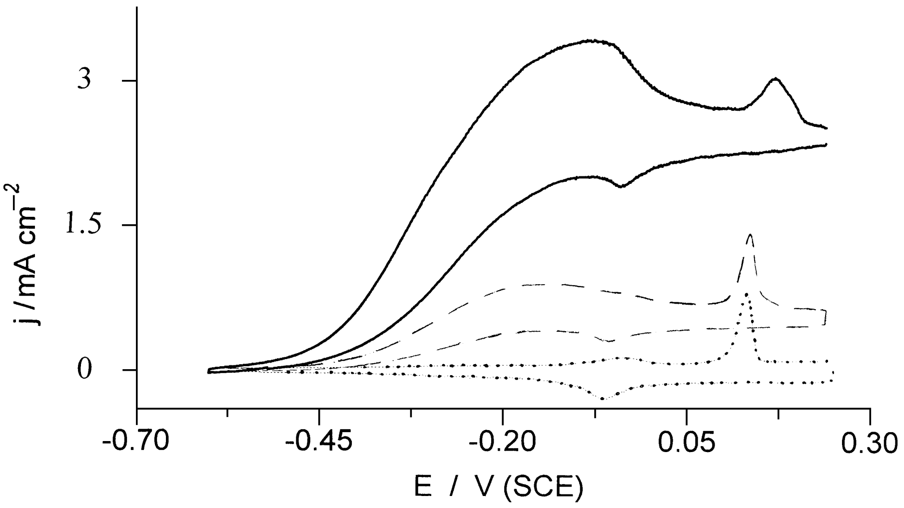

Figure 3. Cyclic current-potential curves for thermally-prepared Au(100) in 0.05 M Na_2CO_3 (· · · ·) and with various additions of propanal 0.001 M (– – – –) and 0.003 M (————). Scan rate 50 mV/ s.

because the adsorption of anions, responsible for lifting of the reconstruction, is retarded by the adsorbed organic molecules. The action of these molecules was explained by strong and structure insensitive adsorption, due to their large size [5] and/or the presence of carbonyl group [6]. However, in the present case we deal with the small molecules of aldehyde and, therefore, it seems that only owing to the presence of the carbonyl group, PAL interacts rather strongly with gold (regardless of the substrate structure) and as a consequence of competitive adsorption can retard the structure sensitive adsorption of anions.

Thus, according to this interpretation, a shift of E_T to more positive potentials could also be expected in sulfate solution after the addition of PAL, which was not the case. For both electrolytes Na_2SO_4 and Na_2CO_3 the lifting of the reconstruction occurs at the potentials at which the oxidation of PAL takes place, however, in the latter one at a greater rate. Therefore, it seems that the rate of the PAL electrooxidation may influence the extension of the stability range of the Au(100)-(hex) surface. Namely, due to electron transfer during the process of electrooxidation of organic molecules the surface electrode charge is changed. At the metal-electrolyte interface charging and adsorption are strongly interrelated, however, very often the amount of adsorbed anions changes in a quasi-linear fashion with the charge on the metal, *e.g.* [9]. For this reason the transfer of electrons appearing in the process of electrooxidation influences the surface charge and, thus, might shift E_T to more positive value, at which the minimum amount of anions necessary to remove the reconstruction is adsorbed. This shift is expected to be the greater, the larger the number of electrons transferred, *i.e.* the greater is the rate of electrooxidation. We probably deal with such a situation, when PAL is oxidised in 0.05 M Na_2CO_3 as the supporting electrolyte. For this system, the potential of the reconstruction peak is more positive than for 0.05 M Na_2CO_3 alone, due to a large number of electrons released in the electrooxidation of PAL molecules. Moreover, an increase in the rate of oxidation by increasing concentration of PAL in the solution is responsible for a further shift of E_T towards more positive values. This allows us to speculate, that the electrooxidation of PAL on the reconstructed Au(100) surface may, at least partly, extend the stability range of the reconstructed surface to more positive potential values. However, we are aware that more studies of this type might help to further elucidate this problem.

CONCLUSIONS

Our findings indicate, that the addition of PAL can, depending on the supporting electrolyte, extend, reduce or do not change at all the stability range of Au(100)-(hex) structure. This contrasts with the behaviour of all hitherto applied organic compounds, which, regardless of the electrolyte, only reduce or only extend this stability range. Our observations point on a different role played by PAL molecules in the lifting of the reconstruction which, to a large extent, depends on both the adsorbability of the oxyanions and pH of the solution.

The addition of PAL to Na_2SO_4 electrolyte does not change the stability range of Au(100)-(hex) surface. The dominant role is played by sulfate anions, whose adsorption is responsible for the lifting of the reconstruction, whereas the adsorption and oxidation of PAL have no impact on this process. By contrast, the importance of PAL addition considerably increases in KNO_3 electrolyte, whose anions show weak adsorbability. Namely, for this system the reconstruction is lifted by adsorption of PAL or PAL + intermediates. As a result of such a change of species, whose adsorption is responsible for the lifting of the reconstruction, the stability range of the reconstructed surface is reduced (as is the case for example for thiourea [4]). In 0.05 M Na_2CO_3, *i.e.* in a slightly alkaline solution, PAL again does not have a tendency to lift the reconstruction but suprisingly extends the stability range of Au(100)-(hex) surface towards positive values of the potential. This action of PAL may indicate, that either PAL hinders anions adsorption similarly as *e.g.* cyclohexanone [6] and/or owing to the high rate of PAL oxidation electrons transfer *via* the surface charge and the surface coverage shifts E_T to more positive values. However, we are aware that this latter explanation calls for more experimental studies.

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