

Effect of surface structure of Au(1 0 0) electrode on phase transitions within adsorbed adlayer of coumarin in halide electrolytes in the presence of tetrabutylammonium cations



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ABSTRACT

Effect of surface structure of Au(1 0 0) electrode on the phase transitions within adsorbed adlayer of coumarin (CUM) in halide electrolytes in the presence of tetrabutylammonium cations (TBAC) was studied by means of cyclic voltammetry and differential capacity measurements. At the nearly unreconstructed surface of Au(1 0 0) electrode in chloride and bromide solutions, TBAC induced this transition, while at the reconstructed surface these cations caused a shift of it to more negative potentials. In KI as the supporting electrolyte, such phase transition was not detected at the reconstructed surface, but it was induced at the unreconstructed one. Additionally, new phase transitions in CUM adlayer have been found at the unreconstructed surface in bromide electrolyte, which are, however, completely inhibited by TBAC.

1. Introduction

Many electrochemical studies have proved that some organic substances, in addition to mere adsorption, showed phase transitions within the adlayer at different electrodes. The phase transitions in organic adlayers on gold surface have been mainly investigated on Au(1 0 0) and Au(1 1 1) electrodes [1–7]. Among a few organic compounds which undergo phase transition at these electrodes there is CUM, a valuable leveling agent used in electroplating. For the first time it has been found that, for the highest possible CUM concentration of about 0.01 M, sharp current spikes occur in the cyclic voltammogram (CV) of a reconstructed Au(1 0 0)-(hex) electrode in perchlorate, sulfate, chloride and bromide electrolytes [7]. Later on the appearance of these spikes has been proposed to be related to a structural transition (disorder–order) within the CUM adlayer at the reconstructed Au(1 1 1)-(√3 × 22) and Au(1 0 0)-(hex) electrodes [1], respectively. The naming of the reconstructed surfaces has originated from low energy electron diffraction terminology [8].

Apart from factors such as the nature and surface structure of the metal, temperature, concentration, pH, also the type of cation of the electrolyte seems to have impact on the phase transitions. It has been reported [9] that condensation of 6-methyluracil at an Hg electrode is possible only in the presence of Na⁺ cations, which appears to be the only example known of such a specific effect of inorganic cation. Recently, we have observed [10] that in sulfate electrolyte at Au(1 1 1)

electrode organic cations, i.e. TBAC, shift the phase transition in the CUM adlayer to much more negative potentials. Incidentally, these cations play an increasing role in electrochemistry. Namely, as follows from the papers published during last year, TBAC were able to influence the rate of polyoxometalates electron transfer during reductive reactions at Pt electrode [11], “invert” the so-called diode effect (from cationic one to anionic) during the ion transport at a titanate nanosheet deposit [12] and initiate the layered-to-spinel phase transition in Li-rich layered cathode in lithium batteries [13]. The finding presented in a third of the above mentioned papers [13] together with ours in [10] encouraged us to enlarge the knowledge on the ability of TBAC to induce the phase transition in an electrochemical system.

In order to choose the appropriate system for investigation we analyzed numerous earlier reports on the electrochemical interfacial behaviour of TBAC [see e.g. ref. 14 and refs. therein] and our results presented in [15,16]. As these studies revealed, TBAC show the structure-sensitive adsorption [15] and affect the other phase transitions e.g. the lifting of the reconstruction and phase transitions within the adsorbed adlayers of halide anions at Au(1 0 0) electrode [16]. In view of this, it seemed interesting to investigate the impact of the structure of the electrode surface on the ability of TBAC to induce a phase transition within the CUM adlayer. As a consequence, in the present communication we have decided to investigate the phase transition under consideration at Au(1 0 0) electrode in the halide electrolytes containing TBAC.

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The detailed motivation for the choice of such a system was twofold. Firstly, the use of Au(1 0 0) electrode provides a unique means of probing the structural effect, i.e. enables us to investigate the influence of TBAC on phase transitions within the adsorbed adlayer of CUM on surfaces of quite different structures. Namely, it has been shown [8] that the flame-annealed Au(1 0 0) surface is reconstructed showing large domains of the (hex) structure in which the atoms have a hexagonal arrangement. This reconstruction is lifted at positive potentials due to the adsorption of anions or organic molecules yielding the unreconstructed (1 × 1) surface with the square lattice arrangement of atoms and hence ~25% smaller packing density than the (hex) one. Besides, the reconstructed (hex) structure of the surface can be obtained not only by flame annealing but also by applying negative potential. This latter transformation of the surface is called potential-induced reconstruction and is much slower than with Au(1 1 1) electrode [8]. The potential induced reconstruction of Au(1 0 0) is so slow that on the negative going CV scan the electrode surface remains nearly unreconstructed. At our experimental conditions ca. 87% of the surface remains unreconstructed (*vide infra*). By the way, from STM pictures (see e.g. in [8]) the large difference between the structure of both surfaces can be easily estimated.

Secondly, the selection of halide electrolytes, in this work, brings a possibility for checking how the halide sensitive interfacial behaviour of TBAC at Au(1 0 0) [16] influenced the phase transition under investigation. Finally, this choice unexpectedly supplied new information on the ability of CUM to undergo the new phase transitions on the unreconstructed surface in TBAC free bromide solution.

Therefore, the main objective of this work is to demonstrate the influence of the surface structure of Au(1 0 0) electrode on phase transitions within the adlayer of CUM in the halide electrolytes containing TBAC. Additionally, new phase transitions within the adlayer of CUM in bromide solution are described.

2. Experimental

The working electrode was an Au(1 0 0) single crystal disc, 4 mm in diameter and 4 mm thick, and oriented to $< 1^\circ$ (MaTecK, Jülich). Before each experiment, the electrode was prepared according to the well-known procedure for preparation of well-ordered gold surfaces [17]. 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. The counter electrode was an Au sheet. The reference electrode was a saturated calomel electrode (SCE) and throughout this work all potentials are reported versus SCE. The voltammetric and capacity measurements were performed using an AUTOLAB system (Eco Chemie). All the voltammograms were obtained at a scan rate of 50 mV s^{-1} . In capacity measurements the potential was stepped in 10 mV divisions with ac voltage of 6 mV amplitude and a frequency of 19 Hz.

The supporting electrolyte solutions were $5 \cdot 10^{-2} \text{ M KCl}$, $5 \cdot 10^{-2} \text{ M KBr}$ and $5 \cdot 10^{-2} \text{ M KI}$ prepared from 99.99% salts from Sigma-Aldrich. Tetrabutylammonium perchlorate (TBAP) purisss (from Fluka) and coumarin (from Aldrich) were used without further purification. All solutions were prepared from Milli-Q water.

All solutions were deaerated by nitrogen before each experiment and a constant flow was maintained over the solution at all times. All experiments were carried out at room temperature $20 \pm 1^\circ \text{C}$.

3. Results and discussion

In Fig. 1 two CVs for the thermally reconstructed Au(1 0 0)-(hex) in $5 \cdot 10^{-2} \text{ M KCl} + 9 \cdot 10^{-3} \text{ M CUM}$ (solid line) and after addition of $5 \cdot 10^{-4} \text{ M TBAP}$ (dotted line) are compared. As can be seen from this figure the former CV agrees with that already presented in [7] indicating that the presence of CUM in chloride solution gives a sharp

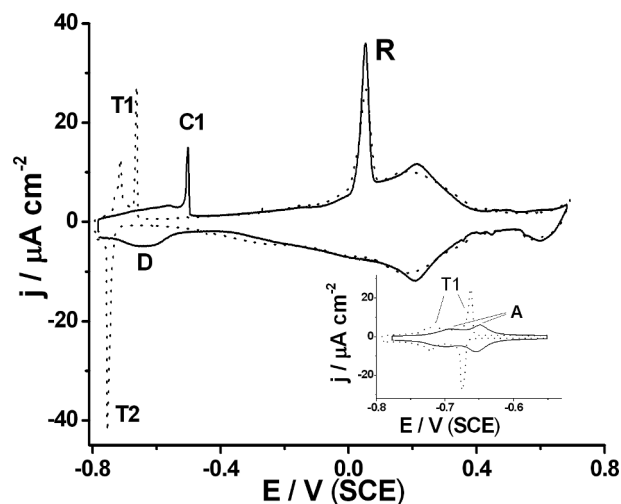


Fig. 1. CVs for thermally reconstructed Au(1 0 0)-(hex) in $5 \cdot 10^{-2} \text{ M KCl} + 9 \cdot 10^{-3} \text{ M CUM}$ (solid line) and after addition of $5 \cdot 10^{-4} \text{ M TBAP}$ (dotted line). Inset: CVs for thermally reconstructed Au(1 0 0)-(hex) surface in $5 \cdot 10^{-2} \text{ M KCl} + 5 \cdot 10^{-4} \text{ M TBAP}$ (solid line) and after addition of $9 \cdot 10^{-3} \text{ M CUM}$ (dotted line) when the anodic limit of the first scan does not exceed the potential of the lifting of the reconstruction.

current spike C1 around -0.502 V on the positive going scan. This spike is believed to be caused by a phase transition within the CUM adlayer.

The addition of TBAP produces a split and acute current spike T1 at much more negative potentials around -0.690 V . The integration of these voltammetric features C1 and T1 leads to almost the same charge of ca. $9.8 \mu\text{C cm}^{-2}$, which confirms that we deal with the same phase transition.

Further inspection of Fig. 1 reveals a large, high and irreversible peak R at ca. 0.060 V , related to the lifting of the reconstruction. In the following figures the peaks assigned to this process are labeled as R.

Besides, as can be seen from Fig. 1, during the negative going scan, which shows the current response on the unreconstructed surface, a very sharp spike T2 is seen, which is not the case for the TBAC-free solution for which a small and broad hump D assigned to the desorption of CUM is observed. The above presented voltammetric results indicate that TBAC only shifts the potential of the phase transition within the adsorbed layer of CUM on the reconstructed surface and induces it on the unreconstructed one. This latter surface, as mentioned in the Introduction, is not in fact fully unreconstructed because of the slow potential-induced reconstruction at Au(1 0 0) [8]. In the following, from the ratio of the areas under the peaks due to the lifting of potential-induced reconstruction and the thermally-induced one, it was calculated that a very significant part (ca. 87%) of the surface is still unreconstructed at the spike T2 potential.

Additionally, the postulated above effect of surface structure on the phase transition under investigation is depicted also in the dissimilarity in the shape of peaks T1 and T2.

Finally, in order to illustrate the impact of TBAC on the phase transition under consideration the inset in Fig. 1 compares two CVs obtained in a solution free of CUM, i.e. $5 \cdot 10^{-2} \text{ M KCl} + 5 \cdot 10^{-4} \text{ M TBAP}$ (solid line) and after its addition (dotted line). A small difference in potentials of peak A related to adsorption of TBAC and spike T1, as well as the similarity in their shape, indicate that the substitution of K^+ cations by TBAC can affect this phase transition. It should be noted that no reconstruction lifting occurs in the potential window used in experiments shown in the inset.

The substitution of Cl^- anions by stronger adsorbing Br^- produces changes in the CV for a solution containing CUM, not reported earlier. Therefore, in advance, it seems worthwhile to describe these changes

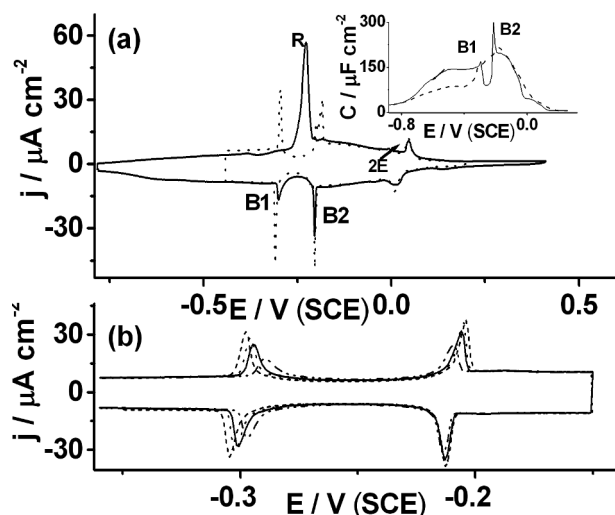


Fig. 2. (a) CVs for thermally reconstructed Au(1 0 0)-(hex) surface (solid line) and unreconstructed Au(1 0 0)-(1 × 1) one (dotted line) in $5 \cdot 10^{-2}$ M KBr + $4.5 \cdot 10^{-3}$ M CUM. Inset: double layer capacitance - potential curves for thermally reconstructed surface (dotted line) and unreconstructed one (solid line) of Au(1 0 0) electrode in the same solution. (b) CVs for the unreconstructed Au(1 0 0)-(1 × 1) surface in $5 \cdot 10^{-2}$ M KBr + $4.5 \cdot 10^{-3}$ M CUM after waiting at 0.250 V for a different lengths of time: 8 s (dot dash dot), 20 s (solid), 35 s (dot) and 75 s (dash).

which are demonstrated in Fig. 2(a) showing the CV for a thermally-reconstructed Au(1 0 0)-(hex) electrode in $5 \cdot 10^{-2}$ M KBr + $4.5 \cdot 10^{-3}$ M CUM (solid line). Namely, as can be seen due to low CUM concentration spike related to the phase transition under consideration (C1) cannot be found and only the reconstruction peak R and spike 2E (related to the transition within the adsorbed anions) are slightly shifted to higher potentials than in the bromide solution (see Fig. 2 in [16]). However, quite unexpectedly, on the negative going scan, two distinct current spikes B1 and B2 appeared. It is noteworthy that spikes B1 and B2 were absent in the solutions of a smaller CUM concentration, e.g. 10^{-3} M, as well as in the chloride solution (*vide supra*). This interfacial behaviour of CUM molecules is also clearly illustrated in the inset of Fig. 2(a) by the capacity of the electrical double layer (C) - potential curves obtained in the same system for the positive (dotted line) and for the negative going scan (solid line), respectively. As shown in the inset, the main difference between both capacity curves is the presence of two very sharp peaks B1 and B2 separated by a minimum on the latter curve. Moreover, as follows from Fig. 2(a), such spikes can be observed also in CV on the positive going scan (dotted line) at almost the same potentials on condition that the scan has been reversed at about -0.450 V, i.e. where the surface is in the (1 × 1) form. These voltammetric and capacity features can point to phase transitions within CUM adlayers only on the Au(1 0 0)-(1 × 1) surface, thus indicating the role of surface structure of the electrode on this process. As follows from literature [18], such phase transitions within organic layers are possible on Au(1 0 0)-(1 × 1), provided that the gold islands due to lifting of the reconstruction have been removed by the so-called electrochemical annealing. We can deal with such a case because the electrode was polarized to rather positive potentials (0.470 V) at which bromide-enhanced mobility of the gold surface atoms could cause the formation of partly island-free Au(1 0 0)-(1 × 1) surface. In order to confirm the origin of these phase transitions the influence of duration of electrochemical annealing on the size and potentials of spikes was investigated in the following experiment: after flame annealing and cooling of the electrode, it was immersed at -0.650 V into the solution in which the reconstruction was preserved. Then the reconstruction was lifted by jumping the electrode potential to 0.250 V and stopped there for different times (from 8 to 75 s). The resulting CVs shown in Fig. 2(b)

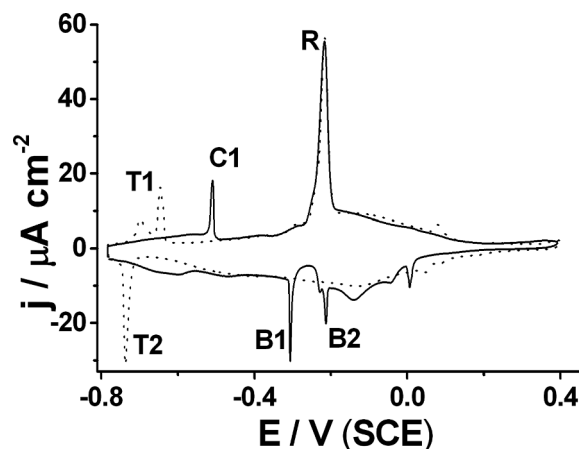


Fig. 3. CVs for thermally reconstructed Au(1 0 0)-(hex) in $5 \cdot 10^{-2}$ M KBr + $9 \cdot 10^{-3}$ M CUM (solid line) and after addition of $5 \cdot 10^{-4}$ M TBAP (dotted line).

reveal that the longer the waiting times at 0.250 V, the greater are both the height and the distance between the spikes thus indicating the decrease of the number of the small gold islands.

The finding and verification of new phase transitions within the adlayer of CUM opens the possibility to investigate the influence of TBAC on such processes not only at the reconstructed surface of Au (1 0 0) electrode but also at the unreconstructed one. The obtained results are displayed in Fig. 3 in which two CVs for a thermally-reconstructed Au(1 0 0)-(hex) electrode in $5 \cdot 10^{-2}$ M KBr + $9 \cdot 10^{-3}$ M CUM (solid line) and after addition of $5 \cdot 10^{-4}$ M TBAP (dotted line) are compared. As follows from this figure, the addition of TBAP causes the replacement of the current spike C1 at ca. -0.505 V, related to the phase transitions within adsorbed adlayer of CUM, by a split and high current spike T1 at more negative potentials and the occurrence of spike T2 during the positive and negative going scans, respectively. It means that the presence of TBAC in bromide solution containing CUM shifts the phase transition under consideration to more negative potentials at Au(1 0 0)-(hex) surface and initiates it at the nearly unreconstructed one. Finally, in the presence of TBAC, the pair of spikes B1 and B2 disappears, which means the inhibition of these phase transitions at Au (1 0 0)-(1 × 1).

Quite a different situation takes place, however, when the supporting electrolyte contains iodides as anions. The first difference can be already observed after the addition of CUM molecules to the supporting electrolyte. This is illustrated in Fig. 4(a) which displays two CVs recorded for the thermally-reconstructed Au(1 0 0)-(hex) electrode in $5 \cdot 10^{-2}$ M KI (dotted line) and after addition of $9 \cdot 10^{-3}$ M CUM (solid line), respectively. As follows from this figure, on the CV recorded at the reconstructed surface in the solution with CUM, there is no current spike, such as observed for Cl^- (Fig. 1) and Br^- (Fig. 3) at ca. -0.500 V, which could be assigned to the phase transition within CUM layer [7]. It means that the adsorbability of I^- anions, which is much stronger than that of smaller halides, inhibits this process. Instead, quite a large and round current peak A is seen at a more negative potential, which precedes the reconstruction peak R. The second difference is the more negative potential (by ca. 19 mV) of this peak than that of the reconstruction one obtained in the supporting electrolyte, i.e. 0.05 M KI. This indicates that the adsorption of CUM molecules in iodide electrolyte, in contrast to chloride or bromide [7], lifts the reconstruction. The comparison of CVs in the more anodic region of polarization reveals also that the pair of spikes (E2) related to the transitions within the adsorbed anions in iodine electrolyte alone [16,19], disappears after the addition of CUM.

On the other hand, examination of the negative going scan on the CV recorded for the unreconstructed surface reveals the counterpart of

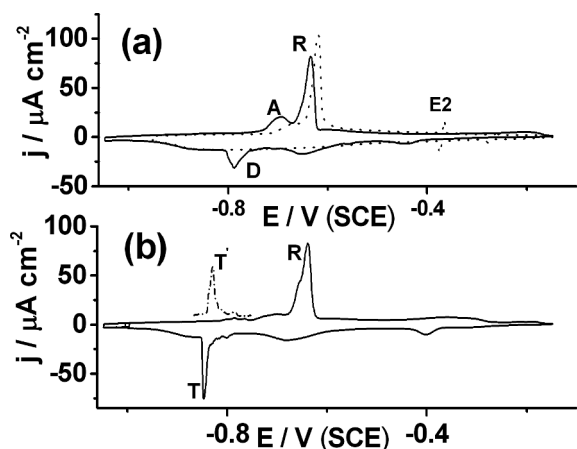


Fig. 4. (a) CVs for thermally reconstructed Au(1 0 0)-(hex) in $5 \cdot 10^{-2}$ M KI (dotted line) and after addition of $9 \cdot 10^{-3}$ M CUM (solid line). (b) CV for thermally reconstructed Au(1 0 0)-(hex) in $5 \cdot 10^{-2}$ M KI + $9 \cdot 10^{-3}$ M CUM + $5 \cdot 10^{-4}$ M TBAP (solid line) and CV for Au(1 0 0)-(1 × 1) surface in the same solution (dash dot line) obtained when the scan had been reversed before the (hex) form was restored.

peak A, i.e. D at ca.

−0.785 V. Such rather broad peaks (A and D) would normally not be considered as indications of a 2D phase transition, and it seems reasonable to attribute them rather to an ads./des. process than to the phase transition of CUM at both surfaces.

Next, as can be seen from CV (solid line) in Fig. 4(b), after the addition of TBAC, both peaks A and D disappear and on negative going scan a high and sharp spike T appears which can be related to a phase transition. This may indicate that at the unreconstructed surface, because of the presence of TBAC, the pure adsorption process is transformed into the phase transition within the adsorbed adlayer of CUM. Fig. 4(b) also presents the part of CV recorded when the scan has been reversed at a potential at which the surface is completely in the (1 × 1) form (dotted-dashed line). This part of CV depicts almost identical needle-like anodic spike T'. It means that in iodide solution TBAC are able to induce such a phase transition at the unreconstructed surface. The occurrence of a phase transition at the unreconstructed surface is due to a quite large adsorption of TBAC at this surface in contrast to the reconstructed one on which such adsorption is inhibited [16].

What can be the rationalization of the surface sensitive nature of the phase transitions within the adsorbed adlayer of CUM in halide electrolytes containing TBAC? This action of TBAC may be understood by assuming that the adsorption of CUM molecules is modified by these cations. In other words, in contrast to smaller potassium cations, TBAC coadsorb with CUM molecules and penetrate among them, which alters the order of molecular packing, e.g. from disordered to ordered one, due to the appearance of short-range forces between TBAC charges and quite a large (4.5 D [20]) dipole moment of CUM molecules. Moreover, as a consequence of surface sensitive adsorption of TBAC [15], the packing of CUM molecules also becomes surface structure dependent, and as a result not only the potential of phase transition is shifted for the reconstructed surface but also its initiation takes place at the nearly unreconstructed surface.

4. Conclusions

The most important outcome of this paper is to show, for the first time, that organic cations have a distinct impact on a phase transition within the adsorbed adlayer, depending significantly on the surface structure of the electrode. The above reported macroscopic

electrochemical observations have demonstrated that, at nearly unreconstructed surface of Au(1 0 0) electrode, TBAC are able to induce a phase transition within the adsorbed adlayer of CUM in chloride, bromide and iodide solutions. In contrast, at the reconstructed surface of Au(1 0 0) electrode the presence of TBAC in chloride and bromide solutions causes only a shift of this process to more negative potentials, while in iodide solution, because of the inhibition of TBAC adsorption, such a phase transition has not been detected.

Additionally, in a bromide solution new phase transitions within the adsorbed adlayer of CUM have been found at Au(1 0 0)-(1 × 1), thus indicating also their surface sensitive nature. These phase transitions are, however, completely inhibited by TBAC.

CRediT authorship contribution statement

W. Gałęczowski: Writing - review & editing. P. Skořuda: Conceptualization, Methodology, Investigation, Resources, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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