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# Electrochemical STM study of the Adsorption of Adenine on Au(111) Electrodes

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## Abstract

An Electrochemical Scanning Tunneling Microscopy (EC-STM) study of the adsorption of adenine on Au(111) electrodes was undertaken in the pH range between 1 and 7, aiming at achieving a deeper knowledge on the structure and organization of adenine chemisorbed on gold, and at confirming previous conclusions obtained from combined electrochemical and in-situ IR spectroscopy measurements. This study confirms that chemisorption of adenine induces the lifting of the Au(111) surface reconstruction. Furthermore, the 4% excess gold atoms of the reconstructed surface which are expelled during lifting of the reconstruction do not diffuse away from the reconstruction rows. We observe, in contrast, the formation of nanometric islands arranged forming chains along the directions previously followed by the reconstruction solitons. Chemisorbed adenine adlayers consist of short chains of adenine molecules roughly aligned along the three main crystallographic directions of the substrate and stabilized by  $\pi$  stacking. These chains tend to align parallel to each other, forming very small domains and yielding an adlayer with a very short-range order. The same adlayer structure is observed at all the studied pH values. The STM results also confirm that, in very acidic media, and at low potentials, adenine adsorbs very weakly on the reconstructed Au(111) surface.

## Keywords

Adenine adsorption, Au(111) electrodes, electrochemical scanning tunneling microscopy, surface reconstruction,  $\pi$ -stacking.

## 1. Introduction

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The study of the adsorption of DNA bases on well defined electrode surfaces bears interest due to their biological relevance and to the technical importance of the preparation of biocompatible materials and biosensors. In this context, we have recently focused our studies on the adsorption of adenine on gold single-crystal and thin-film electrodes [1-4].

Initially, we characterised the adsorption of adenine on low-index gold single-crystal electrodes by cyclic voltammetry and impedance measurements [1]. Adenine adsorption showed a significant sensitivity to the reconstructed or unreconstructed state of the electrode surface. Chemisorption of adenine was found to lift the reconstruction on all three low-index surfaces, and the thermodynamic study of the adsorption/desorption of adenine on Au (111) surfaces by means of chronocoulometry established that the chemisorption is weak, and that adenine behaves as an electron donor [1]. The thermodynamic analysis also provided a projected area of the adsorbed molecule of  $44 \text{ \AA}^2$ , this being compatible with a tilted orientation of the molecular plane relative to the electrode surface. A study of the kinetics of the adsorption process using electrochemical impedance spectroscopy [2] revealed a mixed control of the adsorption rate by both mass transport and activation steps.

In order to obtain information about the microscopic aspects of the adsorption process, in-situ IR spectroscopy was applied [3], both in the external reflection-absorption (IRRAS) configuration with Au (111) electrodes, and in the attenuated total reflection-surface-enhanced infrared absorption (ATR-SEIRAS) configuration with nanostructured gold thin-film electrodes. The assignments of the surface-active IR signals, and the analysis of their potential dependence, confirmed a tilted orientation of the adsorbed adenine molecular plane relative to the electrode surface, and that the molecular orientation does not change with the electrode potential, respectively.

The influence of the pH on the IR spectra of adsorbed adenine [4] allowed us to conclude that adenine adsorbs in its neutral (unprotonated) form even at pHs below its  $pK_1$  (4.2). On the other hand, in very acidic media and at low adenine concentrations, ATR-SEIRAS revealed the existence, at potentials below the onset of the chemisorption of adenine, of a second form of adsorbed adenine, which was identified as physisorbed protonated adenine. IR spectra also suggested the co-adsorption of water in acidic media.

The structure of adenine adlayers on solid substrates strongly depends on the chemical nature of the substrate [5-9]. A combined STM and electron energy loss spectroscopy (EELS) study in ultrahigh vacuum (UHV) revealed that adenine adsorbs on Cu(110) with the molecular plane parallel to the substrate with a tilted C-NH<sub>2</sub> bond, forming chains that order themselves into chiral domains linked by H-bonding interactions [5]. On graphite electrodes [6-8], adsorbed adenine forms incommensurate condensed layers with a structure strongly dependent on the applied potential. The STM images obtained for the adsorption of adenine on Au(111) electrodes at potentials around the open circuit potential [9] suggest a different organisation, with adenine molecules aligned along the main crystallographic directions, and with intermolecular distances clearly shorter than those corresponding to hydrogen bonding interactions.

The above-mentioned recent information about adenine adsorption on Au(111) electrodes provided by combining electrochemical methods with in-situ IR spectroscopy has induced us to

revisit the problem using STM, which can help to clarify the role played by the pH, the potential, the reconstructed or unreconstructed state of the surface, and the nature of the adenine-adenine interactions. We report here an electrochemical STM study of the adsorption of adenine on Au(111) electrodes as a function of the electrode potential in the pH range between 1 and 7. Structural information about the arrangement of adenine molecules within the adlayer, and about the nature of the corresponding intermolecular interactions is provided. The adlayer structure is found to be potential-independent within the chemisorption region. Moreover the role of adsorbed adenine in the surface reconstruction phenomenon is clarified.

## 2. Materials and methods

A Pico LE and a Pico Plus Molecular Imaging microscopes with PicoScan 2100 and 2500 controllers, respectively, were employed. Tungsten tips were electrochemically etched in 2 M NaOH from a wire 0.25 mm in diameter, and were then covered either with an electrophoretic lack or with polyethylene based thermal glue (ethyl-vinyl-acetate) from a polyethylene glue gun. All the images were obtained in the constant-current mode with currents lower than 2 nA, because, at higher tunnelling currents, we often observed that the structure of the adenine adlayer was destroyed by the STM tip during scanning.

The electrochemical STM cell was fabricated in PCTFE (Kel-F), with a capacity of ca. 100 $\mu$ L. It was left overnight in "piranha" solution, and thoroughly rinsed with ultrapure boiling water before each measurement. The working electrode was a Au(111) disk 12 mm in diameter and 2 mm thick from MaTeck (Jülich, Germany), which was flame annealed before each experiment. A platinum wire was used as pseudo-reference electrode, but all the potentials in the text are referred to the saturated calomel electrode (SCE). A gold wire was used as the auxiliary electrode.

Working solutions with pH between 1 and 7 (0.1 M in HClO<sub>4</sub>, 0.1 M H<sub>2</sub>SO<sub>4</sub>, 0.1 M KClO<sub>4</sub>, and (0.1 - x) M HClO<sub>4</sub> + x M KClO<sub>4</sub>) containing 1 mM adenine were prepared with ultrapure Milli-Q water (18 M $\Omega$  cm, < 3 ppb TOC), 70-72% HClO<sub>4</sub> (Merck, p.a.), 96% H<sub>2</sub>SO<sub>4</sub> (Merck Suprapur), 99% KClO<sub>4</sub> (Merck, p.a.) and 99% adenine (Fluka, p.a.). The working electrode was put in contact with the adenine-containing solution under potential control, negative of the onset of the lifting of the reconstruction, in order to avoid the lifting of the thermally-induced reconstruction formed during flame annealing [10].

## 3. Results and discussion

Figure 1 shows the cyclic voltammogram of Au(111) in 0.1 M H<sub>2</sub>SO<sub>4</sub> + 1 mM adenine, and a sequence of STM images obtained in the same solution at different electrode potentials in a separate experiment. Similar results were obtained in all the solutions used. The STM experiment was started with a freshly flame annealed electrode at the negative potential limit, and the potential was then stepped to successively higher values. At potentials lower than the onset of chemisorption of adenine, only the herringbone structure characteristic of the thermally-induced reconstruction can be observed (Figure 1a and 1b). At these conditions,

physisorbed protonated adenine has been detected on the Au(111) surface by ATR-SEIRAS [4]. The persistence of the reconstructed surface confirms that the interaction of protonated adenine with the electrode surface at these potentials is very weak. The failure to image physisorbed adenine with the STM might be due to adenine molecules being swept away from the electrode surface by the tip during scanning or, alternatively, to a high mobility of the adenine molecules in the physisorbed adlayer.

As the potential increases, the reconstruction rows first become sharper and finally disappear, as can be observed in Figures 1b and 1c. These changes have been recently shown to be characteristic of the transition from the reconstructed to the unreconstructed surface in a detailed study in several supporting electrolytes of the initial stages of the lifting of the surface reconstruction on Au(111) electrodes [11], that was shown to occur always through the same sequence of dislocation networks. It was also shown there that, independently of the nature and concentration of the supporting electrolyte, the lifting of the reconstruction process starts always at a surface charge density of  $-5 \mu\text{C cm}^{-2}$  and concludes at a surface charge density of  $28 \mu\text{C cm}^{-2}$ , when the dislocations disappear and the surface reaches its unreconstructed state. Similar morphologies, but in the reverse process, have been recently observed by He and Borguet [12]. It must be noted, however, that Wu et al. [14] have demonstrated that, at similar charge densities, the adsorption of some organic molecules on the unreconstructed surface is thermodynamically more favourable and, therefore, has a significant contribution to the driving force of the lifting of the reconstruction.

Concomitantly with the lifting of the reconstruction, gold islands with a diameter between 2 and 10 nm and of monatomic height appear on the surface in order to accommodate the 4% excess atoms of the reconstruction (Figures 1d-1f). Contrary to the behaviour in adenine-free sulphuric acid or perchloric acid/perchlorate solutions, in which islands grow by Ostwald ripening and/or diffuse to the edge of neighbouring terraces, in the presence of adenine they remain frozen at the positions where the atoms were ejected, and decorate the surface by aligning themselves along the directions previously occupied by the reconstruction lines (Figure 2a). These results are similar to those reported by Dretschkow et al. [13] in a study of the adsorption of uracil on Au(111) electrodes. These authors found that, by applying a sufficiently negative potential for at least 60 min, the electrochemically-induced reconstruction forms, but the resulting morphology has a shorter-range order than the thermally-induced reconstruction formed during flame annealing, [13]. The observed freezing of the gold islands at the locations where they are initially formed and the slow formation of the electrochemically-induced surface reconstruction, are both a consequence of the adsorbate-induced low mobility of gold surface atoms, in agreement with the conclusions reached by Wu et al. concerning the adsorption of other organic molecules, [14].

On the unreconstructed Au(111) surface adenine chemisorbs forming short chains that tend to align parallel to each other, and that roughly follow the main crystallographic directions of the substrate (Figure 2b). Some of the adenine rows are perfectly straight, while some others run in zig-zag. The adenine rows decorate the whole surface of the one-atom high islands formed during the lifting of the reconstruction, whose dimensions seem to be related to the number of adsorbed adenine rows that can be accommodated on top of the islands.

Higher resolution images reveal that every single adenine strand is composed of brighter spots with a periodicity of approximately 3-3.5 Å (Figure 2c), in good agreement with the results obtained without potential control by Tao et al. [9]. Assuming that each spot corresponds to an adenine moiety, this excludes hydrogen bonding as the responsible for chain formation, because any of the possible hydrogen bonds would involve distances between molecules between 5.8 and 7.8 Å [9]. We suggest, hence, that the chains of adenine molecules are stabilized by  $\pi$ -stacking interactions, a suggestion which is also compatible with the presence of both straight and zig-zag adenine chains.  $\pi$ -stacking electronic interactions have been described for purine basis in solution [15]. The distance between chains is of ca.  $9 \pm 2$  Å, which is too long for hydrogen bonding. We suggest, therefore, that the arrangement of adenine chains parallel to each other is governed by van der Waals interactions.

#### 4. Conclusions

Chemisorption of adenine on Au(111) electrodes provokes the lifting of the reconstruction. The one-atom high gold islands formed by the 4% excess atoms ejected during the lifting of the reconstruction do not suffer Ostwald ripening nor coalesce with neighboring terrace steps, due to the very low rate of atomic diffusion induced by the presence of chemisorbed adenine.

On the unreconstructed Au(111) surface, adenine molecules form chains that tend to follow the three main crystallographic directions of the substrate, although with frequent direction changes that impede the formation of long chains. The chains align parallel to each other forming very small domains, resulting in an adlayer with a very short-range order. The intermolecular distances within chains, and the interchain distances, suggest that chain formation is driven by  $\pi$ -stacking interactions, while parallel alignment of the chains is governed by van der Waals interactions.

This structure was observed in the whole pH range investigated (between 1 and 7), thus confirming that chemisorbed adenine is deprotonated even at pHs lower than the  $pK_1$  of adenine. STM observation of physisorbed protonated adenine, as recently detected by IR spectroscopy at low pHs and at potentials negative of the lifting of the reconstruction, was not possible, either because the physisorbed molecules are too mobile to be imaged by STM, or because, due to their very weak interaction with the surface, they are swept away by the STM tip during imaging.

#### 5. Acknowledgements.

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## Figure legends.

Figure 1.- 50 x 50 nm<sup>2</sup> EC-STM images of a Au(111) electrode in 0.1 M H<sub>2</sub>SO<sub>4</sub> + 1mM adenine.  $I_t = 1$  nA;  $U_t =$  ranging from 0.15 V (tip positive) to -0.35 V (tip negative), obtained sequentially at a) -0.2 V vs SCE, b) -0.09 V vs SCE, c) -0.04 V vs SCE, d) -0.01 V vs SCE, e) 0.03 V vs SCE, f) 0.06 V vs SCE and g) 0.2 V vs SCE. h) Cyclic voltammogram at 20 mV s<sup>-1</sup> in the same solution obtained in a separate electrochemical experiment.

Figure 2.- EC-STM images of a Au(111) electrode at 0.200 V vs SCE in 0.1 M KClO<sub>4</sub> + 1 mM adenine.  $I_t = 1$  nA;  $U_t = 0.35$  V (tip negative). a) 400 x 400 nm<sup>2</sup> area showing the one-atom high islands formed upon lifting of the reconstruction aligned along the directions originally followed by the reconstruction solitons; b) 50 x 50 nm<sup>2</sup> area showing the adenine chains on the unreconstructed Au(111) electrode; c) High resolution (11 x 11 nm<sup>2</sup>) EC-STM image of the adenine adlayer,  $I_t = 0.6$  nA .

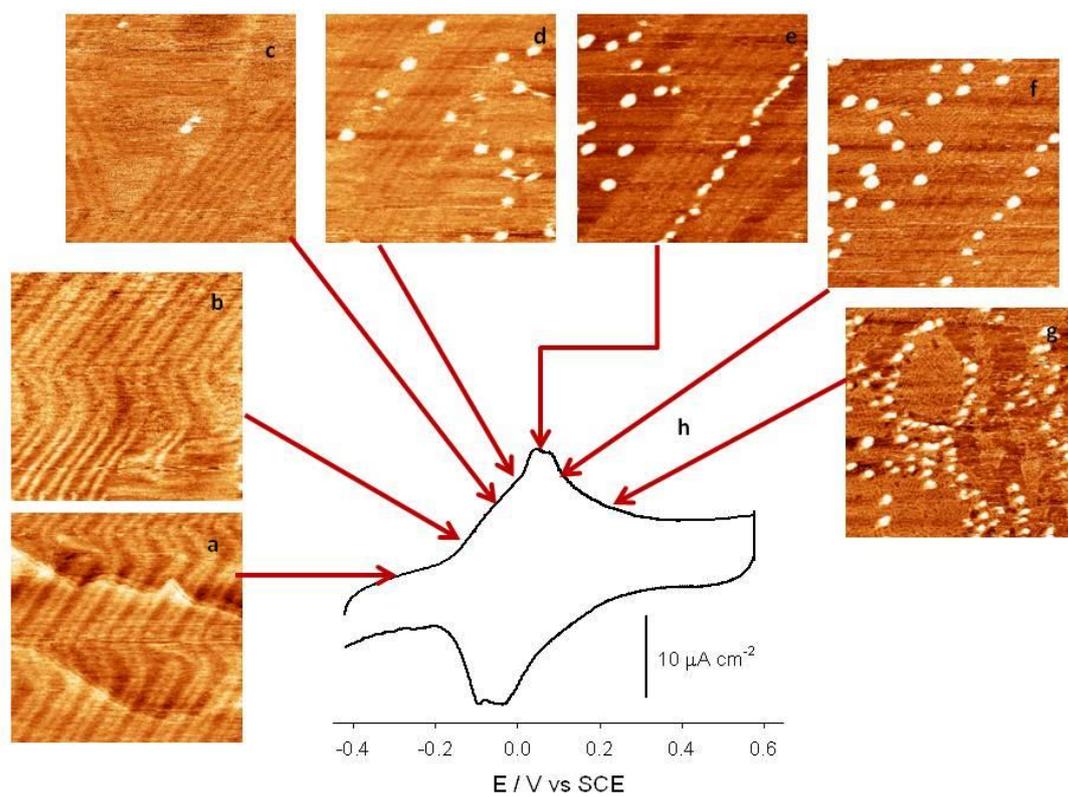


Figure 1

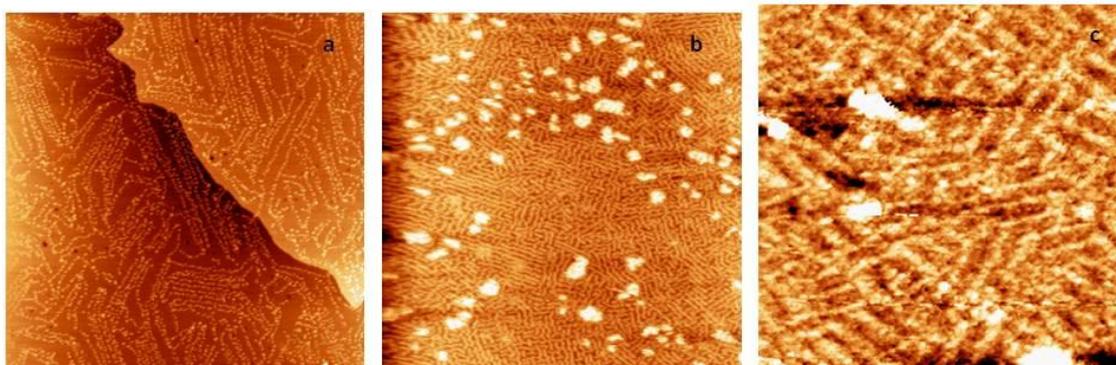


Figure 2

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**Highlights**

Chemisorbed adenine reduces the mobility of gold adatoms.

The adlayer of chemisorbed adenine adopts the same structure in the pH range 1 to 7.

The structure consists of short chains along the main crystallographic directions.

Intermolecular distances suggest  $\pi$ -stacking interactions within the chains.

Interchain distances suggest van der Waals interactions between chains.

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