In situ STM study of self-assembled mercaptopropionic acid monolayers for electrochemical detection of dopamine

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Abstract

An Au(111) electrode coated with a self-assembled monolayer of 3-mercaptopropionic acid (MPA) has been investigated by square-wave voltammetry for electrochemical detection of dopamine in the presence of ascorbic acid and characterized by in situ STM. The electrode is found to shift selectively the unwanted oxidation of ascorbic acid to higher potentials while leaving the oxidation of dopamine unchanged. The selectivity is lost below ~ −0.5 V (Ag | AgCl | 3 M KCl) due to a reductive desorption of MPA, and also above ~ 1.2 V where the Au electrode begins to oxidize. STM shows that even a brief oxidation results in large change in the molecular packing structure of the MPA monolayer. Before the oxidation, the MPA molecules in the monolayer pack into several phases. The most dominant phase is an incommensurate \( \frac{p}{p10} \) structure, while commensurate phases, \( \frac{5}{p10} \), \( \frac{6}{p10} \), \( \frac{8}{p10} \), and \( \frac{10}{p10} \) have also been observed frequently. In some areas, the molecules pack into a superlattice \( \frac{3}{p10} \) that can be attributed to a periodic mixing of two discrete conformations of MPA. After cycling the potential to the oxidation potentials, the ordered structures transform into a less compact disordered structure. The exposed bare Au electrode in the disordered structure is believed to be responsible for the loss of the electrode selectivity. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Ordered organic monolayers self-assembled on electrode surfaces are of great interest for both fundamental and practical reasons [1]. One of the best known systems is that of organosulfur compounds on gold electrodes [2–5]. The sulfur end of the molecules is linked to gold via the strong S–Au bond, while a functional group attached to the other end controls the surface properties of the electrodes that can be engineered for various applications [6–10]. Understanding how individual molecules are arranged on the electrode surfaces is, perhaps, the most fundamental task in any attempts for a microscopic understanding of the functional of the surfaces. To date, a variety of spectroscopies [11], diffraction [12–14], and microscopy (i.e. STM [15–20] and AFM [21,22]) have been used to determine the molecular packing structure of the self-assembled monolayers (SAMs). However, the most studied and understood SAM is that of CH₃-terminated alkanethi-olates (CH₃(CH₂)ₙS⁻) on Au(111) surfaces. For \( n \geq 9 \), the SAM is commensurate with the underlying Au(111) and forms a simple \( \sqrt{3} \times \sqrt{3} \) R30° lattice. A \( c(4 \times 2) \) superlattice of \( \sqrt{3} \times \sqrt{3} \) R30° has also been observed and attributed to two discrete thiol conformations [14,18]. For shorter chains, the molecular packing appears to be less well ordered because the lateral van der Waals forces between the tails is not sufficiently strong to align the tails in parallel. For example, for butanethiolate \((n = 3)\) and hexanethiolate \((n = 5)\), a two-dimensional liquid phase and ordered domains with a unit
and NH$_2$, are more important than CH$_3$. For example, many applications, terminal groups, such as COOH prove the selectivity of the electrodes for detection of dopamine.

2. Experimental

Dopamine (DA) and L- (+) ascorbic acid (AA) were obtained from Sigma. Solutions of DA and AA were prepared in 25 mM phosphate buffer (pH 7) using water from a bioresearch-grade Nanopure system (Barnstead) fed with campus distilled water. All buffer materials were reagent grade and used without further purification. Self-assembled monolayers of MPA (purchased from Fluka) on Au electrodes were obtained by soaking the electrodes in an aqueous 1 mM MPA solution. The soaking time was varied from 30 min to 3 days. For the STM experiments, Au (111) films grown epitaxially on mica under ultrahigh vacuum conditions were used as substrates. Each substrate was briefly flame-annealed in a H$_2$ flame before experiment. For the electrochemical measurements, Au balls formed by melting gold wires (1 mm dia.) in a H$_2$ flame were used as electrodes. The surface of the electrodes are well-known to have many (111) facets [34,35]. We have also used Au(111) films for the measurements and found no obvious difference in the dopamine and ascorbic acid oxidation peaks in the voltammograms. The electrochemical measurements were carried out on a Model CS-1090 potentiostat (Cypress) using Pt wires and Ag | AgCl | 3 M KCl as counter and reference electrodes, respectively. The STM experiments were performed in a Pico-STM system (Molecular Imaging) using a typical bias voltage between −0.05 and 0.1 V and a tunneling current of 120 pA. The STM tips were etched electrochemically from 0.25 mm diameter Pt$_{0.8}$Ir$_{0.2}$ wires, which were then coated with Apiezon wax. A Pt wire was used as a counter electrode, and an Ag wire was used as a quasi-reference electrode, which was calibrated against the Ag | AgCl electrode.

3. Results and discussion

3.1. MPA-coated electrode for electrochemical detection of dopamine

On a bare Au(111) electrode, ascorbic acid oxidizes at a peak potential that is about 0.15 V less positive than the oxidation potential of dopamine (Fig. 1). This is similar to the electrochemical oxidation of the molecules on bare carbon fiber, glassy carbon and graphite electrodes [24–26,33]. However, it does not agree with a previous cyclic voltammetry study of mixed dopamine and ascorbic acid on a bare Au wire microelectrode which found that ascorbic acid oxidizes.
at a more positive potential than dopamine [23]. The discrepancy may be attributed to the difference between the well-defined Au(111) electrode used in this study and the polycrystalline Au microelectrode.

After coating the Au(111) electrode with a MPA monolayer, we have measured square wave voltammetry in 5 mM ascorbic acid and in 1 mM dopamine, respectively, in 25 mM phosphate buffer. We found that the oxidation peak of ascorbic acid is broadened and shifted towards a more positive potential by \(0.45\) V, compared to the peak on the bare Au(111) electrode (shown as inset of Fig. 2). These findings agree qualitatively with the previous study [23]. The positive potential shift for ascorbic acid may be attributed to a repulsive interaction between the negatively charged ascorbic acid and the negatively charged COO\(^-\) group of the MPA monolayer and an increased distance between the molecules and the electrode due to the MPA layer. Around pH 7, the amine group of dopamine is expected to be charged positively, and the electrostatic attraction between dopamine and the MPA layer would also affect the dopamine oxidation. However, we found that the MPA layer has no significant effect on the oxidation of dopamine — both the peak position and width are similar to those obtained with the bare electrode (Fig. 3). One possible explanation is that the effect of the electrostatic attraction may be cancelled out by the increase in the electron transfer distance between dopamine and the electrode because of the presence of the MPA layer which slows down the electrochemical oxidation. We have also measured the voltammogram of the dopamine and ascorbic acid mixture and found no synergetic effect.

We have studied the stability of the MPA-coated electrode upon repeated cycling of the electrode potential. We found that the electrode is quite stable in terms of keeping the oxidation of ascorbic acid at more positive potentials than those of dopamine as long as the electrode potential stays within a window between \(-0.5\) and \(0.8\) V. At very negative potentials, MPA is known to be reduced and desorbs from the electrode surface which has been studied thoroughly [22,36,37]. Increasing the potential beyond \(0.8\) V, we found that the shifted oxidation peak at \(0.5\) V decreases while the peak observed on the bare Au electrode increases (Fig. 4). As we will return to this in the next section, this degradation in the electrode performance is related to the oxidation of the Au(111).

In order to prepare a compact alkanethiol monolayer from an ethanolic solution, the Au electrode is typically left in the solution for more than 12 h. We have examined the effect of the time that the Au(111) electrode is exposed to the MPA solution by varying the time from 30 min to 3 days and found that the exposure time has little effect on the electrochemical response of the electrode (Figs. 2 and 3). This means that the formation of a compact monolayer for MPA on
Fig. 4. Square wave voltammograms of the MPA-coated Au electrode in 25 mM phosphate buffer solution containing 5 mM ascorbic acid as the upper limit of the electrode is raised gradually to 1.2 V. Solid line: first sweep to 0.7 V; Dotted line: second sweep to 1.2 V; Dashed line: third sweep to 0.7 V. Square wave frequency; 10 Hz, peak-to-peak pulse amplitude, 25 mV; potential step increment, 4 mV (pulse)^-1.

Au(111) is rather fast, a fact that has also been confirmed by our STM studies.

3.2. Molecular ordering of the MPA monolayer

Fig. 5 shows two typical STM images of the MPA monolayer in 25 mM phosphate buffer. The image shows that the SAM consists of pits of about 2.5 Å deep corresponding to a single gold atomic layer. Higher resolution images reveal that the pits are also covered by the MPA. Similar pits have been observed in the SAMs of more well studied CH₃-terminated alkanethiolates although the cause of the pits is still a subject of debate [5,17,38]. Zooming in onto the SAM, several different molecular packing structures have been identified which are discussed as follows.

3.2.1. 3 × 4/3 superlattice

In some areas, domains of a rectangular superperiodic structure with lattice constants of \( a = 8.7 \pm 0.2 \) Å, \( b = 20.0 \pm 0.4 \) Å and \( \gamma = 92 \pm 2^\circ \) were observed (Fig. 6A). Within each unit cell, blob-like features with two different apparent heights are clearly visible. A superlattice of \((\sqrt{3} \times 3) R30^\circ\) structure has been observed previously in CH₃-terminated alkanethiolates with much longer chains, and has been attributed to two discrete azimuth angles of the S–C bond of the molecules [14,18]. Assuming the interpretation holds also for the MPA monolayer, all the features observed in the image can be explained by the model shown in Fig. 6B. In the model, the MPA molecules occupy the hollow sites of the Au(111) lattice, but the periodic blending of the MPA molecules with two azimuth angles gives rise to the superperiodic rectangular lattice. The superperiodic lattice can be described as \(3 \times 4\sqrt{3}\) whose lattice constants are \(a = 8.64\) Å, \(b = 19.95\) Å and \( \gamma = 90^\circ\), which are in excellent agreement with the measured values. We note that the distance between two nearest molecules varies between 4.32 Å (1.5 \(a_{\text{Au}}\)) and 5.76 Å (2 \(a_{\text{Au}}\)) rather than a uniform 5.0 Å (\(\sqrt{3} a_{\text{Au}}\)) as observed in the superlattice of CH₃-terminated SAMs. However, the average area per molecule is 21.6 Å² which is the same as that of CH₃-terminated SAMs.

3.2.2. Disordered structure

Between domains of ordered structures, small areas of disordered structure are often observed (Fig. 7). Similar to the superperiodic structure, the individual molecules are revealed as ‘blobs’ with different apparent heights. The distance between two nearest molecules is between 4.5 and 5.5 Å. The disordered structure is not entirely due to a random mixing of the molecules with different conformations; the individual MPA molecules also occupy different lattice sites of Au(111). The average area per molecule is 24 ± 1 Å², which is about 10% greater than that in the superlattice.

Fig. 5. STM image of a MPA monolayer on Au(111) in 25 mM phosphate buffer at rest potential. Image sizes are 50 × 50 nm² for (A) and 20 × 20 nm² for (B).
3.2.3. $p \times \sqrt{3}$ structure

The most dominant structure, however, is a stripe-like structure as shown in Fig. 8A. The parallel stripes can rotate by 120°, corresponding to the symmetry of the Au(111) lattice. The separation between two adjacent parallel stripes varies between $\sim 14$ and $\sim 35$ Å. Higher resolution images reveal that the stripes are due to a variation in the apparent height of the molecules. Along the stripes, the molecules align periodically with a repeat of $5.1 \pm 0.2$ Å. At first glance, the stripes in the perpendicular direction appear also periodic, but after a careful examination of the images one can see that the molecules usually do not repeat the same pattern exactly (Fig. 8B, C). So in the perpendicular direction, the MPA lattice is not commensurate with the underlying Au(111). Because the incommensurate structure arises from the competition between the adsorbate–substrate and adsorbate–adsorbate interactions, the incommensurate structure in the MPA monolayer indicates the importance of the intermolecular interactions in the molecular packing structure. The structure may be denoted as $p \times \sqrt{3}$, where $p$ is an irrational number for a truly incommensurate phase or a very large integer for a higher order commensurate phase. The apparent heights of the molecules in the perpendicular direction of the stripes do not oscillate between two discrete values, instead, they can vary smoothly between a maximum and a minimum. This observation means that the blending of the molecules with two different conformations alone is not adequate to explain the variations in the apparent heights of the molecules. We believe that a variation in the adsorption sites of the molecules is responsible for the gradual height variations observed in the STM images. The average area each MPA molecule occupies determined from STM images is $20.2 \pm 0.5$ Å$^2$, which is about 5% smaller than that in the commensurate superlattice and in the $(\sqrt{3} \times \sqrt{3})$ R30° structure of CH$_3$-terminated alkanethiolate monolayers. The more compact molecular packing in the incommensurate phase indicates an attractive force between the adsorbed MPA molecules. This seems in contradiction with the expected repulsive force between charged COO$^-$ groups of the MPA molecules. One possible explanation is that the electrostatic repulsion is screened by positive counter ions present in the solution.

Although the incommensurate packing is the most dominant structure, several commensurate structures have been observed frequently (Fig. 9). One of them has lattice constants, $a = 5.1 \pm 0.2$ Å, $b = 14.5 \pm 0.4$ Å and $\gamma = 91 \pm 2^\circ$ (Fig. 9A). Interpreting each blob-like feature in the image as a MPA molecule, this structure...
In order to understand why the MPA-coated electrode loses its selectivity after cycling the potential to \( \sim 1.2 \text{ V} \), we have studied the stability of the MPA monolayer as a function of potential in 5 mM ascorbic acid. As the potential approaches the 1.2 V, the image becomes streaky and the surface becomes rough. In the absence of MPA coating, the electrode is known to oxidize at \( \sim 1.1 \text{ V} \). So we believe that the change in the surface at \( \sim 1.2 \text{ V} \) is due to the oxidation of the Au(111) surface. If the potential is lowered to a smaller value, the surface is still covered with a layer of MPA but the molecular packing of MPA appears to be much

is modeled as a \( 5 \times \sqrt{3} \) structure (Fig. 9B). One unexpected observation is that the smallest distance between two nearest neighbors appears to be only about 3 Å, which is too small unless chemical bonds are formed between the two nearest molecules. Another possibility is that not all the blob-like features can be interpreted as individual molecules since STM probes the local electronic density of states of the adsorbate + substrate system whose maxima do not always coincide with the geometrical centers of the molecules. The average area per molecule is 24.0 Å\(^2\). The number is greater than that in the superlattice because of the missing row in the structure (pointed by an arrow in the image). A second commensurate structure has lattice constants, \( a = 5.0 \pm 0.2 \text{ Å} \), \( b = 19.5 \pm 0.5 \text{ Å} \) and \( \gamma = 89 \pm 2^\circ \) (Fig. 9C), which can be modeled as \( 7 \times \sqrt{3} \) (Fig. 9D). Similar to that in the \( 5 \times \sqrt{3} \) structure, the smallest distance between two nearest neighbors is only about 3 Å. The average area per molecule is 21.6 Å\(^2\), the same as that found in the superlattice structure. Two other commensurate phases found are \( 8 \times \sqrt{3} \) (Fig. 9E and F) and \( 10 \times \sqrt{3} \) (Fig. 9G and H), and the corresponding average areas per molecule are 19.2 Å\(^2\) and 20.6 Å\(^2\), respectively.
Fig. 10. After raising the potential to 1.2 V in 25 mM phosphate buffer containing 5 mM ascorbic acid, the MPA monolayer becomes disordered due to the oxidation of the Au(111). Image sizes are 25 x 25 nm² (A) and 4.8 x 4.8 nm² (B).

less ordered and contains more defects (Fig. 10). Based on the STM images, the two oxidation peaks (Fig. 4) for ascorbic acid after cycling the potential to ~1.2 V can be understood in terms of the oxidation at defect sites and on the residual MPA layer. At the defects, the oxidation of ascorbic acid takes place at the potential of a bare Au electrode, while the oxidation on the residual MPA is at higher potentials. For application in the electrochemical detection neurotransmitters, it is, therefore, important to keep the potential below the oxidation potential of the Au electrode.

4. Conclusions

We have studied the performance of the Au(111) electrode coated with a self-assembled monolayer of 3-mercaptopropionic acid for electrochemical detection of dopamine. The electrode does not change the rapid oxidation of dopamine while the unwanted oxidation of ascorbic acid shifts towards more positive potentials by ~0.45 V. In comparison to many other methods used to modify electrodes for electrochemical detection of neurotransmitters, the self-assembled MPA monolayer provides a well defined coating of the electrode without sacrificing the rapid response of the electrode. The MPA-coated electrode is stable as long as the electrode is kept within a window between −0.5 and +1.1 V. Below −0.5 V, MPA becomes reduced and consequently desorbs from the electrode. Above 1.1 V, the oxidation of the Au electrode destroys the compact and ordered molecular packing in the MPA monolayer. We have investigated the molecular packing structure of the MPA monolayer as a function of the electrode potential with STM and identified several different phases. The most dominant phase is an incommensurate \( p \times \sqrt{3} \) structure, while commensurate phases with, \( 5 \times \sqrt{3}, 6 \times \sqrt{3}, 8 \times \sqrt{3} \) and \( 10 \times \sqrt{3} \) have also been observed. In some areas, the molecules pack into a superlattice with lattice constants, \( a = 8.7 \pm 0.2 \) Å, \( b = 20.0 \pm 0.4 \) Å and \( \gamma = 92 \pm 2^\circ \), which can be modeled as \( 3 \times 4/\sqrt{3} \), due to a periodic mixing of two discrete conformations of MPA. At the boundaries of the ordered phases, a disordered phase in which the MPA molecules do not occupy the Au lattice in a periodic manner has been observed. Increasing the potential to the oxidation potential of Au(111), the molecular packing of MPA changes irreversibly to a disordered structure which is responsible for the loss of selectivity of the electrode.

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