Formation Kinetics and Structure of 3-Octylthiophene Self-Assembled Monolayers on Gold Surfaces

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The self-assembly process and the structure of a monolayer of 3-octhylthiophene (OTP) on gold surfaces were monitored and characterized by *in situ* surface plasmon resonance spectroscopy (SPS) and scanning tunneling microscopy (STM). The formation of well-ordered OTP self-assembled monolayers was confirmed for the first time.

Well-ordered and close-packed self-assembled monolayers (SAMs) prepared by alkanethiols and dialkyl disulfides on metal surfaces have been extensively studied because of the fundamental interest in surface science as well as the possibility of a variety of technical applications.[1-3] Other sulfur-containing molecules have been used for the preparation of SAMs on metal surfaces.[4-6] Interestingly, the fabrication of SAMs by π-conjugated polymers like polythiophene on gold surfaces has been attempted to develop novel organic electronic devices.[7] Theoretical studies have suggested, however, that thiophene would not interact with gold.[8] In contrast, recent STM observations show that thiophene molecules do adsorb on the Au(111) surface.[9] To our knowledge, however, there are no further detailed studies reported in the literature on thiophene SAMs. As a matter of fact, understanding the details of monolayer formation by thiophene is required for any technical application with SAM systems utilizing the thiophene moiety. In this study, we have observed for the first time SAM formation by OTP using *in situ* SPS, which is one of the most sensitive techniques to measure thickness and formation kinetics of SAMs on metal surfaces. Furthermore, we have investigated the surface structure of the SAMs by STM. It is well known that van der Waals interactions as well as molecule-substrate interactions play a major role in SAM formation.[10,11] Therefore, we used OTPs with relatively longer alkyl chains to examine both adsorption of the sulfur atom in a thiophene group on a gold surface and the effect of alkyl chain length in the ordering process. In addition, we compared the OTP SAM with one prepared with octanethiol (OT) having the same alkyl chain length.

The OTP was obtained from Tokyo Chemical Industry Co. Ltd. and used without further purification. The gold substrates for SPS[12] and STM[13] measurements were prepared by thermal deposition under conditions of high vacuum. The SPS measurement was carried out using a laboratory-built experimental setup.[14] The optical density was transformed to the thickness of the adsorbed monolayer using the same procedure reported previously.[12] SAMs were prepared by exposing the gold substrates in a freshly prepared 1 mM ethanol solution of OTP and OT for 1 day. After the substrates were removed from the solutions, the SAM samples were thoroughly rinsed with pure ethanol to remove physisorbed molecules from the surface. STM imaging was carried out in air at room temperature, and STM images were acquired in the constant current mode using a Pt/Ir tip.

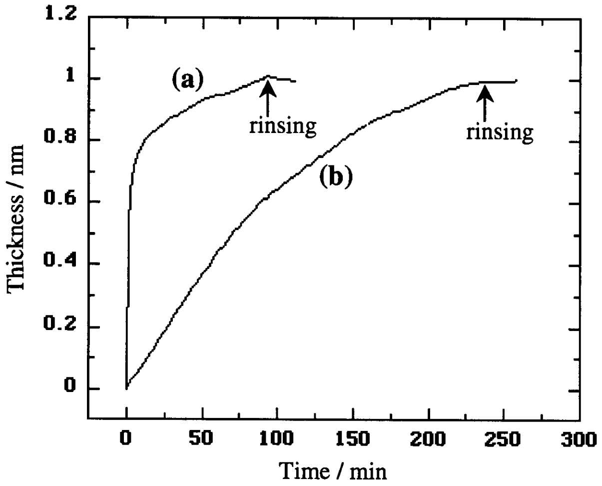

Figure 1. Comparison of formation kinetics for (a) octanethiol and (b) 3-octylthiophene SAMs on a gold surface. The corresponding 1 mM ethanol solutions were introduced into a flow cell for *in situ* surface plasmon resonance spectroscopy at 23 °C.

Figure 1 displays formation kinetics for OT and OTP SAMs on a gold surface observed by *in situ* SPS. Adsorption kinetics of OT on a gold surface obeys Langmuir isotherm. The kinetic curve for OT changed quickly with steep slope at the beginning of the adsorption process showing the high affinity of these molecules for the gold surface. A slower rearrangement process to optimize lateral interactions between the adsorbed molecules on the gold surface followed, and then the kinetic curve reached a plateau, implying the formation of relatively stable monolayers. However, adsorption kinetics of OTP shows deviation from Langmuir isotherm. The kinetic curve of OTP shows a gradual slope, and it takes a longer time to reach final stage compared to OT molecules. This deviation may be due to a lower affinity of thiophene molecules for the gold surface. In addition, this can also be attributed to the fact that the two-dimensional ordering process due to van der Waals interactions between alkyl chains would require to overcome the relatively strong interaction between the π-conjugated system of the thiophene ring and the gold surface in a striped phase where the molecular axes are oriented parallel to the gold surface.[15] Therefore this SAM growth stage may need a longer time to reach a plateau. In addition, to confirm the existence of the physisorbed multilayers, *in situ* rinsing experiments were performed. The arrows in Figure 1 are the starting points for rinsing with ethanol. However, neither kinetic curve showed any clear change in thickness reflecting the formation of the chemisorbed monolayers.

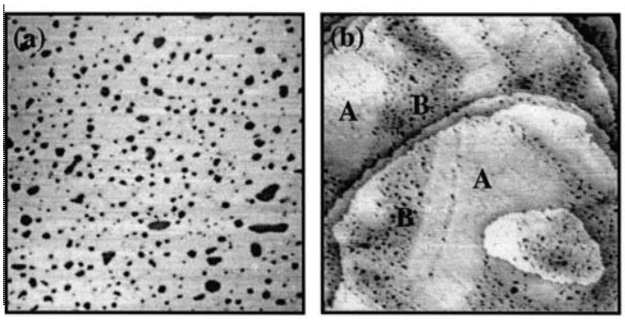

Figure 2. STM images of (a) octanethiol and (b) 3-octylthiophene SAMs on Au(111) obtained after 1 day deposition. (a) Imaging conditions: 250 × 250 nm^2, $I_t = 0.14$ nA, and $V_b = 0.50$ V (sample positive). (b) Imaging conditions: 250 × 250 nm^2, $I_t = 0.19$ nA, and $V_b = 0.50$ V (sample positive).

Figures 2(a) and 2(b) represent surface morphologies showing the formation and distribution of etch pits observed from SAMs prepared using OT and OTP in large scan areas, respectively. These pits are usually observed in the course of the formation of chemisorbed monolayers, such as alkanethiol and dialkyl disulfide SAMs.[10,13,16] In the case of these SAMs, the depth of the pits is 0.24 nm, which is identical to the monoatomic step on the Au(111) surface, and these pits are somehow uniformly distributed over the monolayer as shown in Figure 2(a).

On the other hand, etch pits were also observed on the SAMs formed by OTP. This result strongly implies that OTP SAMs form through a chemical reaction between the sulfur atom in thiophene and the gold surface. Interestingly, however, the surface morphology of the monolayer is considerably different from the usual SAM systems. Close-packed domains (region A) and etch pit domains (region B) were clearly phase-separated from each other. Such a structure for SAMs has not been reported elsewhere to date. In a previous report, thiophene SAMs showed uniformly formed etch pits, not localized ones.[9] Hence we consider that such a SAM structure might originate from a two-dimensional ordering process to maximize lateral interactions between alkyl chains through diffusion of adsorbed molecules on the surface. In this stage, etch pits can be expelled from close-packed domains.

The STM image in Figure 3 exhibits the well-ordered and close-packed monolayer structure observed in region A of Figure 2(b). Although this image did not show individual molecules, molecular rows with an inter-row distance of about 0.59 nm were clearly observed. This value corresponds to nearly half of the 1.2 nm revealed in thiophene SAMs,[9] which means an increase in surface molecular density. This result strongly suggests the importance of van der Waals interactions between alkyl chains in self-assembly ordering process by OTP as well.

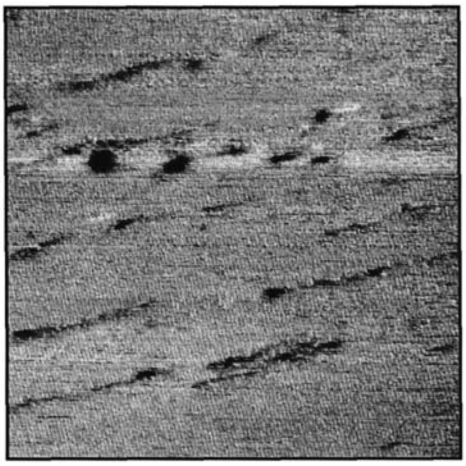

Figure 3. Well-ordered and close-packed structure of 3-octylthiophene SAMs on Au(111): 53 × 53 nm^2, $I_t = 0.15$ nA, and $V_b = 0.41$ V (sample positive).

In conclusion, SPS and STM results clearly show SAM formation on the gold surfaces by 3-octylthiophene. In addition, it was revealed that an alkyl group attached at the 3-position of thiophene plays an important role in the self-assembly process.

References and Notes

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