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Investigation on gold corrosion by in situ quartz crystal microbalance and atomic force microscopy in self-assembled processes of alkanethiol monolayers

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Abstract

The corrosion behaviour on gold surface in air-exposed solution induced by alkanethiol molecules such as *n*-dodecanethiol in self-assembled process has been for the first time investigated in detail by in situ quartz crystal microbalance (QCM). The gold lost from the in situ QCM has been well explained by the observation of atomic force microscopy (AFM), which shows the evident image of corrosive defects or holes produced on the corresponding surface of gold grains. Both alkanethiol assembled monolayer and existing oxygen would be decisive factors for the gold corrosive dissolution on the substrate. The kinetic equation on the corrosion rate of gold dissolved in the air-exposed alkanethiol solution has been obtained. The initial corrosion rate on gold can be estimated to be 5.8×10^{10} Au atoms cm^{-2} s^{-1}.

Keywords: Gold corrosion; Corrosion rate; Alkanethiol assembly; In situ quartz crystal microbalance; Atomic force microscopy

1. Introduction

Self-assembled monolayers (SAMs) of linear alkanethiols ($CH_3-(CH_2)_{n-1}-SH$) adsorbed onto Au substrates like single crystalline Au(111) or Au(111)/mica surfaces have been widely investigated due to their easy preparation, believable density, long term stability and high structural quality [1–7]. Many interesting applications of SAMs in chemical sensing, biosensing, biomimetics, biocompatibility, and lithography have seen their large amount of growth on their great potential [8–16]. In particular, there were increased reports on the nature of holes or pits in self-assembled thiol monolayers which have been found frequently in scanning–tunneling microscopy (STM) studies [17–22], that may be attributed to thiol-induced dissolution of gold during the adsorption process of organothiol molecules. By atomic absorption spectroscopy of polycrystalline gold substrate, Edinger et al. have presented quantitative data for gold solubility in thiol solution in the presence of oxygen [20]. In addition, the corrosive oxidation of thiols on Au surfaces in air has also been demonstrated by using laser desorption mass spectrometry [23,24].

However, relatively few have monitored the gold corrosion accompanied in alkanethiol assembled processes on line. In the present paper, the corrosion phenomena occurred on the gold substrates have been, for the first time, observed by in situ microbalance method for adsorption of alkanethiol monolayers in air-exposed and oxygen-saturated tetrahydrofuran (THF) solution, combining with atomic force microscopy (AFM) observations at the same time. Because of the complexity of SAM structure, it is still necessary to know the nature of the gold surface during the alkanethiol self-assembled process,

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that will guide people for further surface modification of bio-chips, chemical and bio-sensors, etc.

2. Experimental

2.1. Materials

Alkanethiols ($C_nH_{2n+1}SH$ for $n=3-10$, 11, 12, 16, and 18) were obtained from three sources (Sigma-Aldrich of USA, $n=3$, 5, 7, 9, 11, 18; Eastman Kodak of USA, $n=4$, 10, 12, 16; Wako of Japan, $n=6$, 8). The tetrahydrofuran (THF) solvent was freshly distilled prior to use. All other chemicals used through out the experiments were of reagent grade or better if not stated elsewhere.

2.2. Quartz crystal microbalance

A quartz crystal microbalance (QCM) measurement system used was commercially purchased from USI Corporation, Japan, which consisted of quartz crystal oscillating circuit, temperature controller, and a universal counter (Model 53131A, Hewlett Packard Co., Japan). An AT-cut QCM with a fundamental resonance frequency of 9 MHz (USI Co., Japan) was connected to the circuit and the counter. The QCM substrate was prepared by vacuum thermal evaporation (less than 5×10^{-5} Torr) of high-purity gold (2000~3000 Å) onto the surface of quartz crystal that had been pre-coated with chromium (100 Å) to improve adhesion. The gold substrate of QCM was polycrystalline by thus preparation. All QCM measurements were conducted at controlled temperature of 25 ± 0.1 °C.

2.3. Monolayer preparation

For comparison, alkanethiolate monolayers were deposited by their spontaneous adsorption from air-exposed, nitrogen and oxygen-saturated THF solutions ($4\sim400\times10^{-6}$ M) on gold substrates of QCMs, respectively. The formation of n-alkanethiol monolayers were monitored by in situ QCM device with the immersion time. Upon removal from solution, the thiol-modified QCMs were thoroughly rinsed with pure THF, dried in a steam of pure N_2, and immediately imaged by a scanning probe of AFM.

2.4. Atomic force microscopy

All images were recorded in the contact mode by using a scanning probe microscopy (Nanoscope IIIa, Digital Instruments, Inc., Santa Barbara, CA). The cantilevers used were the silicon nitride probes with the pyramidal tips and the spring constant of 0.06 and 0.12 N/m. The piezo scanners in the AFM had a scan range of 14.1 × 14.1 × 2 μm and 1.2 × 1.2 × 0.7 μm, respectively.

3. Results and discussion

3.1. Alkanethiol-induced corrosive dissolution on gold

In different operation conditions, like in air-exposed, nitrogen and oxygen-saturated solutions, the kinetic adsorption behaviours of self-assembled monolayers of alkanethiols ($C_nH_{2n+1}SH$ for $n=3-10$, 11, 12, 16, and 18) on gold have been examined in detail. As a representative thiol molecule, the n-dodecanethiol with neither short nor long chain was usually subject to in situ QCM measurements and then AFM observations for comparison.

Fig. 1 shows a typical kinetic response curve of n-dodecanethiol self-assembled on the gold surface of QCM with the THF solution exposing to air. Usually, the fundamental frequency of oscillating QCM crystal was stable at AB stage (called as F_0) firstly, whose standard deviation was ±0.34 Hz ($n=350$). After an appropriate amount of n-dodecanethiol solution (40 mM) were injected into the solvent, the output frequency of the crystal decreased rapidly at BC stage and then reached a relatively stable value at CD stage in the bottom (called as F_1), which is called as frequency-decreased (FD) process. It means that there are a plenty of n-dodecanethiol molecules adhered onto the gold substrate of QCM by Au–S bonding interaction in a very short time. However, with the time, the frequency turned to increase at DE stage and then gradually reached a relative equilibrium value at EF stage (called as F_2), which is called as frequency-increased (FI) process. It seems that something gradually left out of the gold surface and dissolved into the solution after exposing the solution to air with the time. One possibility was caused by the n-dodecanethiol monolayer desorption, another was induced by the assembled n-dodecanethiol monolayer and dissolved oxygen from air, that is to say, the organothiols desorption would bring their bonding gold atoms out of the surface into thiol solution while interacting with oxygen. Thereafter, the corrosive oxidation reaction would be occurred on the gold surface between the thiol-bonding gold atoms and the dissolved oxygen from the air into the solution.

From the surface observation with microscopy, the corresponding AFM image on the gold substrate of the QCM in air-exposed

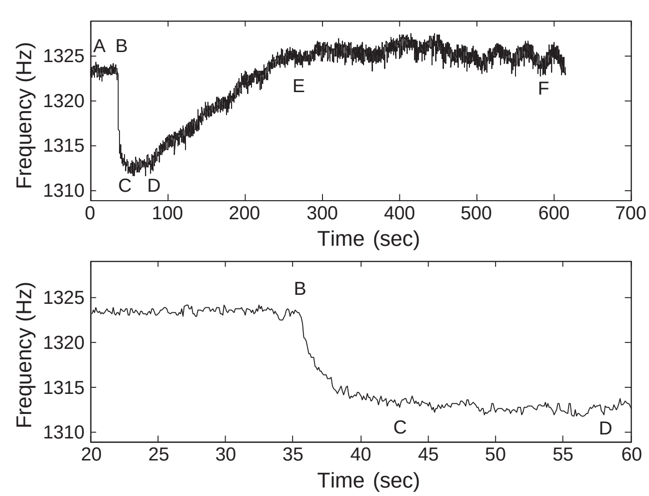

Fig. 1. Typical kinetic response curve of n-dodecanethiol self-assembled on the gold surface of QCM in the air-exposed THF solution with the time (top) and the corresponding magnified part (bottom).