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Combination of the quartz crystal microbalance and the electrochemical technique for the characterization of self-assembled monolayers of octadecylmercaptan on gold surfaces

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Quartz crystal microbalance (QCM) technique has been applied to the direct mass measurement of a self-assembled monolayer of octadecylmercaptan (OM) on a gold surface deposited onto a quartz-crystal. Repeated rinsing of the modified electrodes with used solvent was conducted to get self-assembled monolayers of OM. From the resonance frequency change, 2.5 nm molecular occupied area of OM on gold was obtained. The advantage of the combination of QCM and electrochemical methods was emphasized for the characterization of self-assembled monolayers.

1. Introduction

Spontaneously organized monolayer assemblies of thiol compounds from solutions on gold surfaces via chemisorption have been attracted from a variety of research fields. These fields include surface chemistry, electrochemistry, corrosion, molecular membrane chemistry, molecular-electronics and analytical chemistry [1]. A variety of the physical methods such as FT–IR spectrometry, ellipsometry, contact angle measurement, electrochemical method (cyclic voltammetry, impedance analysis) and XPS (X-ray photoelectron spectroscopy) have been presented for identifying and characterizing these organic ultra-thin monolayers on Au [1–9]. It is one of the most fundamental requirements to know the packing densities or degree of surface coverages of self-assembled monolayers on electrodes. Quartz crystal microbalance (QCM) is known to provide extraordinary sensitive mass monitoring at nanogram-level based on the change in resonance frequency of the oscillator [10–11]. Recently, Shimazu and co-workers [12] described *in situ* monitoring of the self-assembling and redox processes of a ferrocenylundecane–thiol monolayer by electrochemical quartz crystal microbalance. We describe here the combination of QCM and electrochemical techniques [9] to characterize the self-assembled monolayers of octadecylmercaptan on Au surfaces.

2. Experimental procedure

Gold was vapour-deposited on silver electrodes of piezo-electric crystal (AT cut, 9 MHz, amounts of deposited Au: ca. 0.1 mg 0.60 cm^{-2}), and the piezo-crystal was connected to a fragrance meter (Sogo Pharmaceutical Co. Ltd., SF-101) equipped with a frequency counter and an oscillation circuit. Resonance frequencies were measured under reduced pressure (2 mmHg). Then, piezo-crystal was immersed in a 10 mM *n*-octadecylmercaptan (OM) ethanol solution for 1 min at 25 °C. Following this, it was dipped in pure ethanol for 1 min to remove excess adsorbate and was allowed to air-dry. Then a resonance frequency was measured. The OM modified piezo-crystal was rinsed again in ethanol for 1 min, air-dried and the resonance frequency was measured again. These procedures (rinse, air-drying and resonance frequency measurement) were repeated two more times (four times in total). After this, the modified piezo-crystal was immersed again in OM ethanol solution (1 mM) for given times (total immersion times: 2 min, 5 min, 10 min, 20 min, 30 min, 1 h, 1.5 h, 2 h, 3 h and 6 h) and then the same procedure, ie. recycled rinse, air-drying and resonance frequency measurements were performed. It took about 1 h to get a constant resonance frequency under the reduced pressure.

Cyclic voltammetry (equipment: TOHO Technical Research, Polarization unit PS-06) of the OM monolayer electrodes was conducted in 0.1 M KCl aqueous solution containing 2 mM potassium ferricyanide or methylviologen as electroactive markers. A saturated calomel electrode (SCE) and a platinum electrode were used as the reference and the counter electrode respectively.

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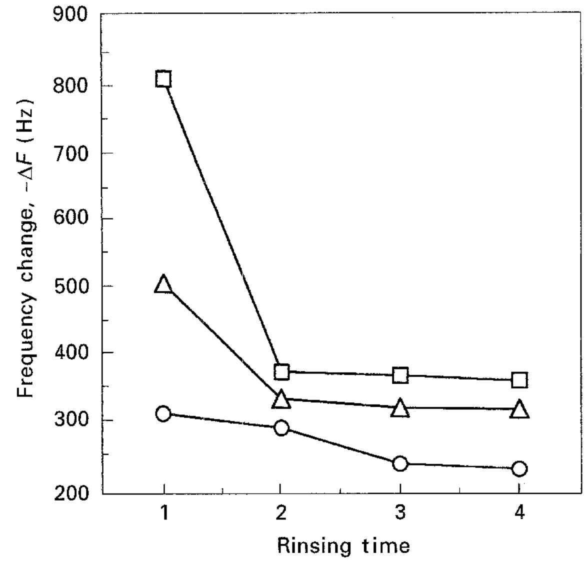

Figure 1 Effect of repeated rinsing in ethanol on the resonance frequency change for the adsorption of octadecylmercaptan (OM) on piezo-crystal gold electrode. Dipping time of the electrode in 10 mM OM in ethanol are 1 min (○), 20 min (△) and 60 min (□). The resonance frequencies were measured under reduced pressure (2 mmHg).

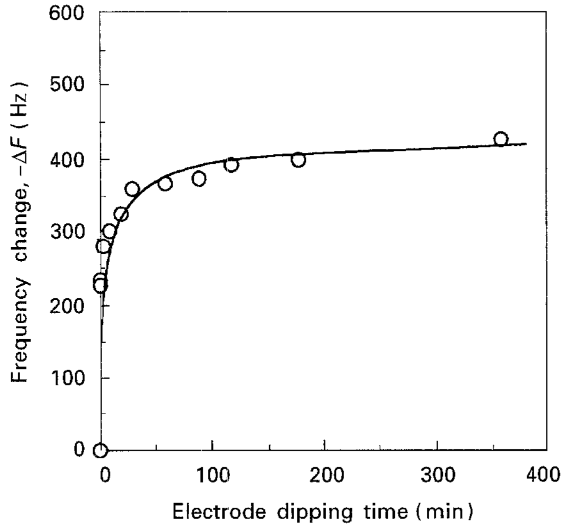

Figure 2 Frequency change as the function of dipping time of a piezo-crystal gold electrode in 10 mM solution of OM in ethanol.

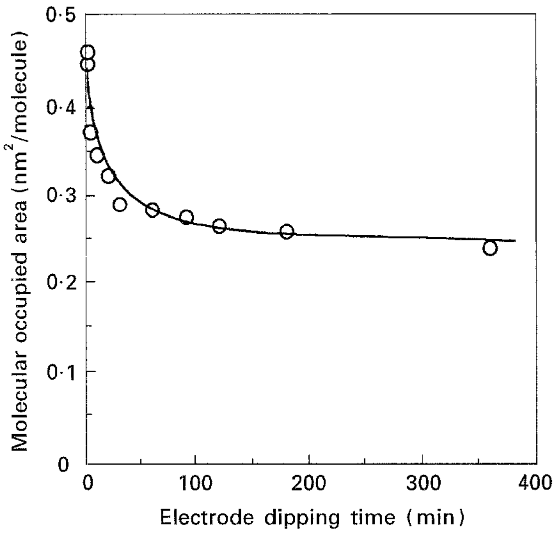

Figure 3 Molecular occupied area of octadecylmercaptan (OM) on gold on piezo-crystal calculated by Equation 1 as the function of total immersion time of the QCM electrodes in 10 mM solution of OM in ethanol.

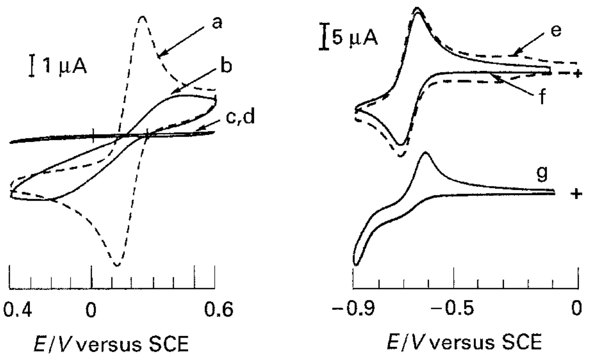

Figure 4 Cyclic voltammograms for a bare (dotted lines) and OM monolayer modified (solid lines) piezo-crystal gold electrodes in the presence of 2 mM $K_3Fe(CN)_6$ (a–d) and 2 mM methylviologen (e–g) in deoxygenated 0.1 M $KClO_4$ aqueous solution. Electrode dipping times in 10 mM OM in ethanol for the preparation of each OM monolayer on piezo-crystal gold electrodes are as follows. (a, e) 0 s; (b) 30 min; (c) 1 h; (d) 2 h; (f) 2 h; (g) 3 days. Scan rate, 0.2 V s^{-1}. 25 °C.

3. Results and discussion

Fig. 1 shows the influence of repeated rinse in ethanol on the shift of frequency resonances (ΔF) of the OM-modified piezo-crystal (results for the piezo-crystal of 1 min, 1 h, 6 h dipping are shown as examples). The results indicate that it is necessary to rinse at least two to three times to remove excessively incorporated OM molecule in the OM monolayer formed by the co-ordination with gold.

Frequency change caused by the adsorption of OM molecules on gold was plotted as a function of immersion time of a bare Au piezo-crystal electrode in a OM ethanol solution (Fig. 2). The frequency change after being rinsed four times was adopted. This result shows that several hours of dipping is found to be required to reach saturated adsorption of OM on the electrode. A frequency change of the shear mode quartz crystal is related to the mass change by the Sauerbrey equation [10]. Molecular occupied area, A (nm²/molecular) can be calculated by the following equation (Equation 1), where a is the gold electrode area (nm²), S is the sensitivity (Hz g^{-1}), M_w is molecular weight and ΔF is the resonance frequency change (Hz)

$$A = \frac{a \times S \times M_w}{\Delta F \times 6.02 \times 10^{23}} \qquad (1)$$

A values determined by this method were plotted as a function of total immersion times of the piezo-crystal in OM ethanolic solution (Fig. 3). Obtained saturated A value is 0.25 nm², which is close to the cross-section area of OM. When *trans*-conformation of all C–C bonds in OM with dense-packing in the monolayer are postulated, 0.25 nm²-molecular occupied area means that the long-axis of OM tilts by 30° from the perpendicular packing. This almost agrees with that reported by Porter and co-authors [13].

Fig. 4 shows cyclic voltammograms for the OM-modified monolayer electrodes prepared in this study in the presence of an electroactive marker. It is evident that an OM modified monolayer electrode, prepared by 30 min dipping, does not block sufficiently the electrochemistry of potassium ferricyanide, while no electrochemistry attributable to ferricyanide was observed at the OM electrodes prepared by 1 h and 2 h dipping. These results should correlate with that of the time dependent adsorption of OM onto Au piezo-crystal. However, when methylviologen was used as an electroactive marker, electrodes prepared by 1–2 h dipping in OM solution in ethanol the decrease in the faradaic current of the voltammograms was 10% at most (Fig. 4). A very long time immersion (3 days) of an electrode in the OM solution was found to give a smaller redox current (Fig. 4, trace g). These results indicate that packing density of OM on piezo-crystal gold electrode still is gradually increasing after several hours dipping of electrodes in the OM solutions, although by the QCM method 2 h dipping seems to be enough to get fully packed OM monolayer on gold.

In conclusion, we demonstrate that QCM is a convenient technique to determine the mass and molecular occupied area of self-assembled thiol monolayers on gold surfaces. This also emphasizes the importance of rinse in ethanol for the preparation of the monolayers. However, the QCM technique was not sensitive to characterize the self-assembled monolayers on gold with very high surface coverages. Electrochemical methods were useful for the characterization of such monolayers.

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