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# An In Situ Analysis of a Self-Assembly Process of an α-Imidazolyl-ω-Alkanethiol on Gold by a Quartz Crystal Analyzer

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# An In Situ Analysis of a Self-Assembly Process of an α-Imidazolyl-ω-Alkanethiol on Gold by a Quartz Crystal Analyzer

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A self-assembly process of N-[2-(4-imidazolyl)ethyl]11-mercaptoundecan-amide (Im-SH) on gold surface was monitored by in situ measurements of the resonant frequency and the resonant resistance of a quartz crystal analyzer (QCA) together with optical and atomic force microscopy. The Q factor was applied to evaluate the homogeneity of the adsorbed monolayer. A two-step process was involved in the monolayer formation. At the first stage, a fast adsorption to the surface up to 90 % was produced, and then the dot-like Im-SH monolayers became to reorganize and reassemble to form a much larger aggregated monolayer.

*Keywords:* imidazole; monolayer; self-assembly; QCA; AFM

## INTRODUCTION

The self-assembly monolayers best studied so far are those formed by long-chain n-alkanethiols or disulfides[1]. And, most of the examinations of the monolayers on gold have been virtually performed on already formed monolayers prior to examination, and a few effort has been spent on understanding the elementary steps in the formation of the monolayers[2]. Therefore, we have little information on the growth steps of the monolayers

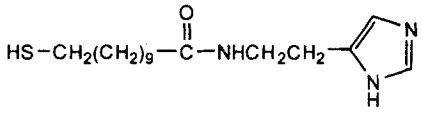
except for the simple alkanethiols[3]. We report herein the synthesis of an imidazole-functionalized alkanethiol and their self-assembly process on gold surface. The self-assembly process was monitored by in situ measurements of the resonant frequency and the resonant resistance of a quartz crystal analyzer together with optical and atomic force microscopies.



## EXPERIMENTALS

### Material

The α-imidazolyl-ω-alkanethiol, N-[2-(4-imidazoly)ethyl]11-mercaptoundecanamide (Im-SH), was synthesized from condensation reaction of 11-bromoundecanoic acid with histamine and following substitution to thiol. The chemical structures were determined from FTIR, $^1$H-NMR, and elemental analysis.




Im-SH

### Measurement

An impedance analyzer (Yokogawa Hewlett-Packard, Model 4192A) was used for monitoring the resonant frequency and the resonant resistance. An incubator (Advantec, Model PE-314) was used for a temperature control. A Pt thin layer sensor and a voltmeter (Advantec, Model TR6840) was used for measuring and storing the temperature of an incubator. A 9-MHz AT-cut quartz crystal, which has a 3 Hz/deg Celsius temperature dependence at room temperature, was used. The quartz crystal was immersed in the DMF solution of Im-SH during the measurement.

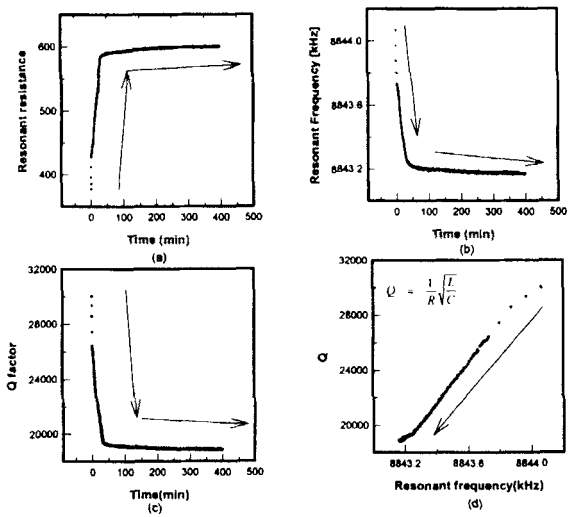



FIGURE 1 Self-assembly process of Im-SH on a quartz crystal. Responses of (a) resonant resistance, (b) resonant frequency, (c) Q factor, and (d) relations between the frequency and Q factor.

## RESULTS AND DISCUSSION

### Analysis of Im-SH Monolayer Formation by QCA

Fig. 1 shows responses of resonant resistance, resonant frequency, Q factor, and relation between the frequency and Q factor. A rapid decrease or increase of resonant frequency or resonant resistance continued during the first 35 min and then the values changed slowly for further 400 min, i.e., fast adsorption of Im-SH to the surface up to 90 % was produced during the first 35 min. As shown in Fig. 1d, most of the Q factor changed linearly along with the resonant frequency except for the nonlinear beginning and the last stage owing to the located adsorption on the QCA, that is, not homogeneously spread all over the surface, or swelling of the adsorbed films[4].

**Morphology of Im-SH Monolayer on Gold Electrode of QCA**

Two types of optical microscope images were found from the gold surface of QCA (not shown here). During the rapid adsorption of Im-SH, small dots spread uniformly all over the gold surface were observed. The small dots have combined together to larger area when observed the gold surface after one week, i.e., the Im-SH monolayer reorganized and reassembled to form a much larger densely aggregated monolayers. The AFM images obtained from the larger area showed more than two kinds of two-dimensional lattices as shown in Fig. 2.

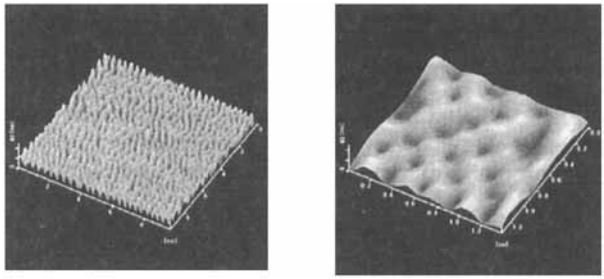


FIGURE 2 AFM images of Im-SH monolayer on gold electrode of QCA. Dimensions are 10x10 $nm^2$ and 1.4x1.4 $nm^2$ (enlarged).

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