

## A Clay Self-Assembled on a Gold Surface

Yuji Hotta, Keiichi Inukai,<sup>†</sup> Masahiro Taniguchi, and Akihiko Yamagishi\*

*Devision of Biological Science, Graduate School of Science, Hokkaido University, Sapporo 060*

<sup>†</sup>*National Industrial Research of Nagoya, Nagoya 462*

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A smectite-type clay having alkanethiol groups on a basal plane has been synthesized. The clay has been revealed to be self-assembled on a gold surface by applying the quartz crystal microbalance (QCM) and the atomic force microscopy (AFM) methods.

A molecular self-assembly provides a useful synthetic route to the constructions of supramolecular devices including second harmonic generation,<sup>1</sup> photoinduced electron transfer<sup>2</sup> and biosensing applications.<sup>3</sup> Among a number of self-assembling techniques, the use of an alkanethiol is most prevalent in preparing the self-assembled monolayers of organic compounds on a gold surface. As far as we know, however, only a few attempts have been reported to apply the method to inorganic layered compounds.<sup>4</sup>

Recently the syntheses and structures of the inorganic/organic hybrid layered materials have been reported by Tani et al.<sup>5</sup> According to the method, silyl reagents were reacted with magnesium chloride in an aqueous alkaline suspension at room temperature to produce smectite-type clay materials. In the present communication, a clay containing thiol groups was prepared on the basis of the above method and was revealed to be self-assembled on a gold surface. In comparison to the reported multilayer formations of inorganic compounds,<sup>6,7</sup> the present system is characterized by the following aspects: (I) the coverage of a self-assembled monolayer is controlled by changing reaction time; (II) the thiol groups on the external surface of a monolayer can be used for further functionalization; (III) it is possible to prepare a new functional film of various natures (e.g. redox, luminescence and magnetizm) by choosing metal ions in the inorganic part of the inorganic/layer hybrid.

Magnesium chloride (1.0 g,  $4.9 \times 10^{-3}$  mol) was dissolved in

methanol (50ml). 3-Mercaptopropyltrimethoxysilane (3.1 g,  $1.6 \times 10^{-2}$  mol) was added to the above solution under stirring. 200 ml of deionized water and 10 ml of 1 N NaOH was added and stirred for 72 h at room temperature. After being centrifuged, the precipitate was washed with water and freeze-dried. The material was denoted as an HS-Mg layer. From the elemental analyses, the chemical formula of an HS-Mg layer was given by  $[(C_{36}H_{24}O_{12}Si_{12}S_{12})Mg_2(OH)_3] \cdot 21H_2O$ ; obs. H (4.9%), C (23.4%) and S (20.9%); calc. H (3.7 %), C (23.4%) and S (20.8%). The FT-IR spectrum of the material showed the absorption at  $2553\text{ cm}^{-1}$ , confirming the presence of thiol groups. The X-ray diffraction pattern of the powder sample showed the (001) and (020) peaks at 14.7 and 4.2 Å, respectively.

The quartz crystal microbalance (QCM) was applied to follow the adsorption of an HS-Mg layer on gold. An AT-cut quartz crystal with a gold-coated area of  $1.4\text{ cm}^2$  (Maxtex, Inc.) was

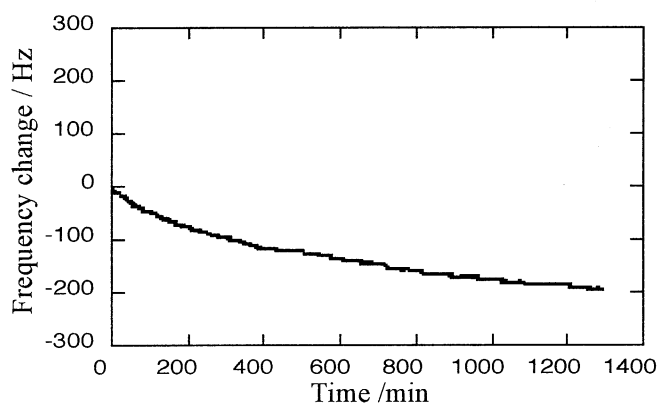


Figure1. The relation with frequency change (Hz) and time (min).

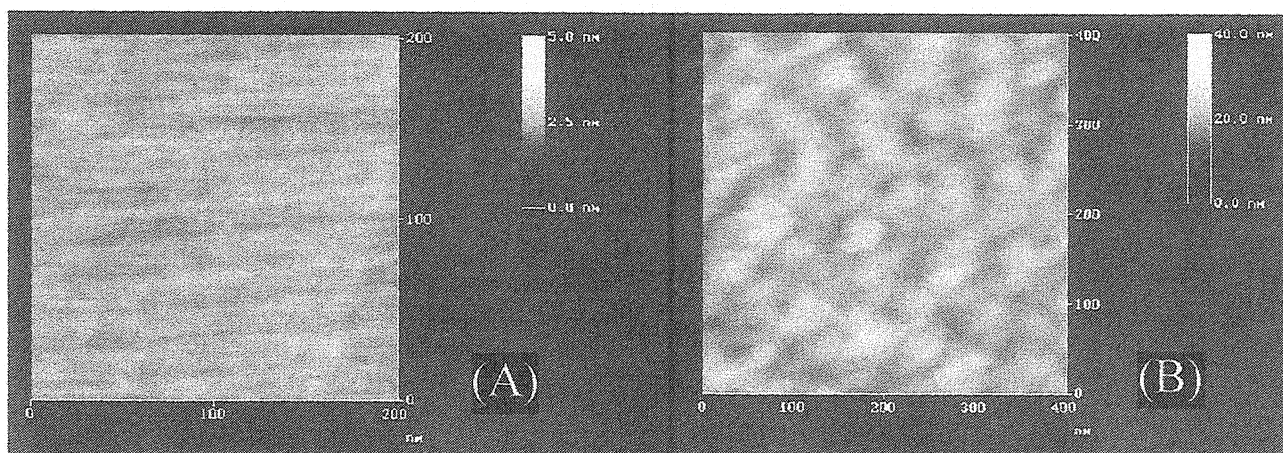


Figure 2. AFM images; (A) a bare gold surface and (B) a gold surface treated with an HS-Mg layer for 48 h.

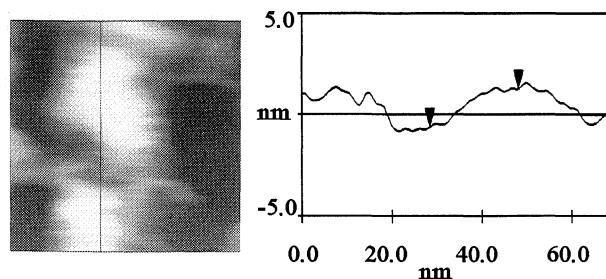
used and its oscillation frequency was 5 MHz. The crystal was soaked in a chloroform suspension of an HS-Mg layer ( $3.33 \times 10^{-3}$  g/l). As shown in Figure 1, the resonance frequency of the electrode decreased with time until it was levelled-off at -190 Hz after about 21 h. According to the following relation<sup>8</sup>

$$\Delta m (\text{ng}) = \Delta f (\text{Hz}) S$$

$$\text{with } S = -17.7 \text{ ng / Hz cm}^2,$$

the total mass change was obtained to be  $3.3 \times 10^3$  ng/cm<sup>2</sup>. The value was compared with the theoretical calculation of  $1.0 \times 10^3$  ng/cm<sup>2</sup> when the single layers of an HS-Mg layer covered a gold surface completely. In the calculation, the unit cell of an HS-Mg layer was assumed to be  $5.0 \times 8.4 \text{ \AA}^2$  on the basis of the X-ray diffraction data. Since the experimental value was 3 times larger than the theoretical one, it was concluded that an HS-Mg layer was deposited to be overlapped at least partially.

We used an atomic force microscope (AFM) to observe the surface structures when an HS-Mg layer was self-assembled on a gold surface. A gold crystal was prepared by annealing a gold wire and soaked in the chloroform suspension of an HS-Mg layer (0.0025 g/25 ml). After 48 h, the gold was washed with chloroform. The AFM measurement was carried out at room temperature in air with a Nanoscope III scanning probe microscope (DI Instruments, USA). Nanoprobe cantilevers [ $\text{Si}_3\text{N}_4$ ] integral tips with spring constant of  $0.06 \text{ nm}^{-1}$  (Park Scientific) were used. The AFM images were obtained in the contact mode with filters off. Figures 2 (A) and (B) compare the AFM images of a bare gold surface and a gold surface treated with an HS-Mg layer, respectively. The surface of a bare gold was rather flat with the variation of ca. 0.3 nm, while the surface of the latter sample was covered with the particles of ca. 30 nm in diameter. Figure 3 shows the section analysis of the AFM image when a gold was treated with an HS-Mg layer for one hour. Although the particles existed on a surface, they did not cover the surface completely. The maximum height of the particle from the bottom of the gold surface was measured to be 1.9 nm. By subtracting the height variation of a bare gold surface from this value, the height of the particle was estimated to be 1.6 nm. This value well coincided with the interlayer distance of the



**Figure 3.** The section analysis of the AFM image when a gold was treated with an HS-Mg layer for 1 h.

material as determined by the X-ray diffraction measurements. Thus these AFM images really manifested the self-assembling of an HS-Mg layer particle on a gold surface.

The present work may open a way to develop an insulator film or a monolayer modifying an electrode on a molecular scale.

## References

- 1 D. Li, M. A. Ratner, T. J. Marks, C. H. Yang, and G. K. Wong, *J. Am. Chem. Soc.*, **112**, 7389 (1990).
- 2 S. W. Keller, S. A. Johnson, E. H. Yonemoto, E. S. Brigham, and T. E. Mallouk, *J. Am. Chem. Soc.*, **117**, 12879 (1995).
- 3 P. A. DiMilla, J. P. Folkers, H. A. Biebuyck, R. Harter, G. P. Lopez, and G. M. Whitesides, *J. Am. Chem. Soc.*, **116**, 2225 (1994).
- 4 H. C. Yang, K. Aoki, H.-G. Hong, D. D. Sackett, M. F. Arendt, S.-L. Yau, C. M. Bell, and T. E. Mallouk, *J. Am. Chem. Soc.*, **115**, 11855 (1988).
- 5 Y. Fukushima and M. Tani, *J. Chem. Soc., Chem. Commun.*, **1995**, 241.
- 6 E. R. Kleinfeld and G. S. Ferguson, *Science*, **256**, 370 (1994).
- 7 G. Cao, H.-G. Hong, and T. E. Mallouk, *Acc. Chem. Res.*, **25**, 420 (1992).
- 8 D. A. Buttry, "Electrochemical Interfaces; Modern Techniques for In-situ Interface Characterization," ed by H. D. Abruna, VCH Publishers, New York (1991), p. 531.