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Fabrication of Odor Sensor Surface Recognizing Substructure of Odorant

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In biological systems, odor receptors receive odor molecules by recognizing molecular information. Recent studies have shown that the size and electrical dipole of molecules are important for odor reception. We developed an odor code sensor that recognizes essential molecular information for reconstructing the odor code of odor molecules. The substructure of odor molecules is a candidate target property of a developed odor code sensor. The substructures of odorants are received at the sensor surface; therefore, the design of surface functionality is important. In this study, a self-assembled monolayer (SAM) was used to construct a nanospace that fits the substructure of odor molecules. A surface that can recognize substructures was fabricated by the mixed SAM method. A competitive method and a replacement method were examined for SAM surface preparation. The mixed SAMs obtained were analyzed by contact angle measurement, ellipsometry, and an electrochemical method. Finally, the surface was evaluated through odorant responses, and the specificity to odorants was confirmed.

1. Introduction

Odor detection is important in many areas, *e.g.*, quality evaluation of foods, explosive detection, health state, biometric identification, and environmental measurements. In a biological olfaction system, ca. 350 different kinds of odor receptors in humans exist, while far more than 10,000 different odorants exist. An odor molecule interacts with multiple odor receptors; each receptor recognizes not the whole structure of the odor molecule but its substructures. Thus humans can identify odors by the combination of activated receptors.⁽¹⁻³⁾ This combination is essential for odor quality measurement and is called the odor code. The aim of this study is to develop a transducer that can extract essential molecular information of the odor code.

Important molecular properties of odorants are size, shape and electrical polarization inside molecules. Size and shape can be measured using the nanoscale structure of a sensor surface. Self-assembled monolayers (SAMs) are good candidates for the present sensor surface with nanospace.⁽⁴⁾ It was confirmed that an appropriate mixture of SAMs

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with nanospace or roughness fit to the size of target odor molecules has affinity to odor molecules.⁽⁵⁻⁷⁾ Nanotechnology makes it possible to confer affinity to an appropriate surface for various molecules. We have developed an artificial olfactory epithelium integrated into a multichannel electrode for measuring the electrochemical impedance of an electrode surface changed by the adsorption of odorants. Each channel has a certain substructure specific to benzene or alcohol.

The method used for the multichannel sensor entails the competitive adsorption of benzene and alkane thiol. However, it is difficult to construct a precise structure that has an appropriate distribution of complementary electrical charges, which form a hydrogen bond as an intermolecular force with target odor molecules. Furthermore, the previous methods do not enable easy control of objective nanospaces with appropriate sizes and charge distributions. Therefore, a better surface for obtaining information on molecular size and electrical charge distribution is required.

In this study, sensor surfaces with mixed SAMs for detecting essential parts of odor molecules, where a hydrophilic part is buried inside a certain nanoscale hydrophobic space, were fabricated. Their structure could serve as detection sites for essential parts of odor molecules, which are composed of electrical dipoles and small hydrophobic parts.

2. Materials and Methods

2.1 Surface preparation

To form a nanospace on a sensor surface, mixed SAMs were formed on an electrode surface (Fig. 1). Mixed SAMs were monolayers composed of two different thiol compounds. A mixture of two alkane thiols on an electrode having different alkane lengths might form a rough surface. Such a surface can be used as a nanospace for adsorption sites of odor molecules. The difference in alkane chain length would correspond to the nanospace size. In the case of mixed SAMs composed of alkane thiols, a nanospace is hydrophobic. If one of the thiols has a functional group on its terminal, a hydrophobic nanospace might have an electronic dipole inside the space and might work

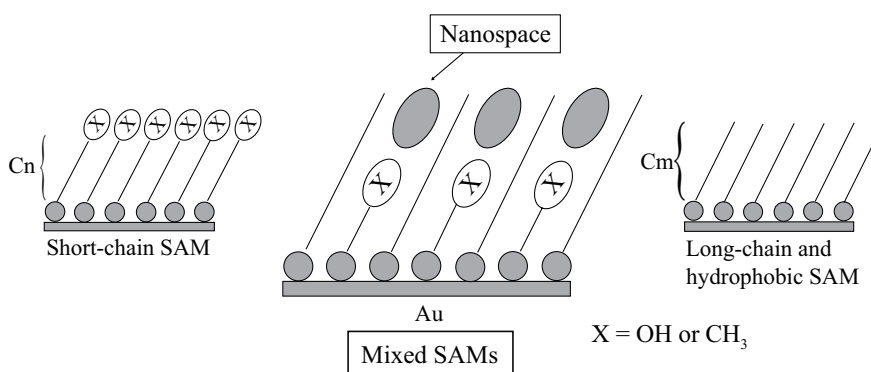


Fig. 1. Alkane thiols, and designed SAM surface.

as an adsorption site for the counterpart of odor molecules.

Mixed SAMs were fabricated on gold substrates. For surface analyses, such as ellipsometry, stripping voltammetry, contact angle measurement and electrochemical impedance spectroscopy (EIS), 200-nm-thick Au substrates electron-beam-evaporated on 20-nm-thick Ti and glass (Corning 1737) layers were used, while mirror-polished quartz crystal microbalance (QCM) electrodes (USI Co.) were used for QCM measurement.

Thiols were adsorbed from ethanol solutions of a certain thiol compound onto gold surfaces. Au surfaces were cleaned beforehand in 90°C aqueous solution of H₂O₂ and ammonium.

In order to fabricate SAMs with a nanospace, two methods, namely, the competitive and replacement methods, were adopted. In the competitive method, SAMs were formed from a mixed ethanol solution of different thiol compounds; two thiol compounds competitively adsorb onto the electrode. In the replacement method, a Au surface was incubated in ethanol solution of certain thiol compounds, then transferred into ethanol solution of another thiol compound; the preceding SAM was partly replaced with thiol compounds and the surface was covered with a mixture of two thiol compounds.

The thiol compounds used were alkane thiols of the formula CH₃(CH₂)_{*n*-1}SH where *n* = 8, 10, 12, 14, 16, 18, and mercaptoalcohol, HO(CH₂)₈SH. In this study, the alkane thiols used and mercaptoalcohol were abbreviated as *Cn* and C8OH, respectively.

2.2 Surface analyses

SAM thickness was measured using an ellipsometer (SpekEI-2000-VIS, Mikropack GmbH). Electrochemical methods were also used to analyze the mixed SAMs using a potentiostat (Autolab PGSTAT12, EcoChemie), which is a frequency response analyzer installed for measuring the impedance of an electrode. The amount of thiols adsorbed could be evaluated by stripping voltammetry, where integrated current, i.e. the total charge of reductive reaction, is denoted as the amount of adsorbing thiols. The types of thiol could be determined by measuring the electrode potential at which reduction current occurs, because thiols with different alkane chains have different adsorption energies and reduction potentials. Electrochemical impedance spectroscopy was also used to investigate the formed surface. The contact angle of the water drop was measured to determine the hydrophobicity and hydrophilicity of the SAM surface. Static contact angle was measured using a digitized instrument (DM-500, Kyowa Interface Science Co.).

2.3 Odor responses

Some odorants were used to confirm the fabricated nanospaces. A quartz crystal microbalance (UQ-200, USI Co.) was used to evaluate the adsorption property of odor gases (Fig. 2). Ethanol and phenethyl alcohol were used as sample gases. These odor molecules have an alcohol hydroxyl group, which is adsorbed by the terminal hydroxyl group of thiol compounds, and have a certain length of hydrophobic alkane chains. All gases were generated using a computer-controlled flow system. In the system, saturated gases were diluted by mixing them with a certain volume of clean air.

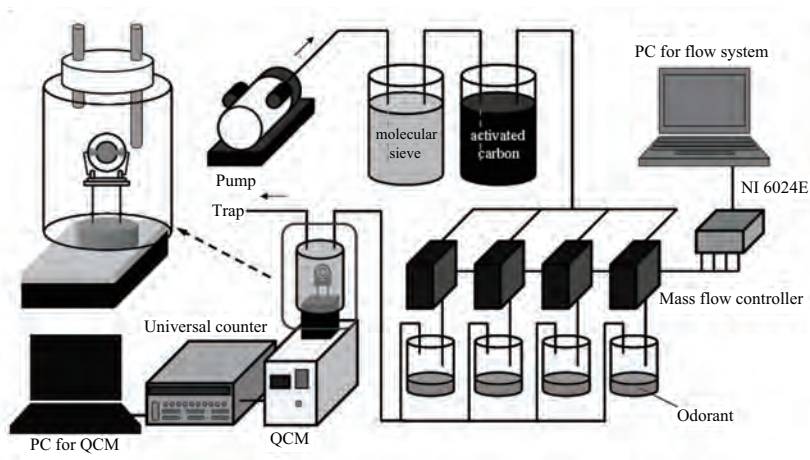


Fig. 2. QCM setup with flow system.

3. Results and Discussion

3.1 SAMs fabricated by competitive method

Mixed SAMs were fabricated by the competitive method and the obtained surfaces were evaluated. Figure 3 shows the amount of thiol molecules on Au surfaces measured by stripping voltammetry, where thiols were competitively adsorbed from a solution of C8 and C18. When the concentration ratio of C8 solution to C18 solution was set from 1:10 to 1:20, mixed SAMs having equal amounts of two thiols were obtained. C18 produces firm SAMs owing to the intermolecular force between its adjacent alkane chains; therefore, a concentration smaller than that of shorter-alkane thiol C8 is required to produce mixed SAMs. Figure 4 shows the thickness of mixed SAMs obtained. The thickness obtained by the ellipsometer denotes the average thickness of an organic thin film. Therefore, the concentration ratio of C18:C8 = 1:20 is favorable from the standpoint of thickness.

3.2 SAMs fabricated by replacement method

Figure 5 shows the thickness of C10- C_n ($n = 12, 14, 16$) mixed SAMs. The surfaces of C10- C_n mixed SAM electrodes were prepared by a C8- C_n replacement method. The C10 thiol SAM formed on the Au surface was replaced with a longer-alkane thiol, C_n . The incubation times for C10 and C_n were both 24 h. All replaced SAMs were thicker than the original C10 film and thinner than the C_n film. Thus, mixed SAMs were obtained by the replacement method. The occurrence of replacing was also confirmed by EIS (data not shown).

We could obtain mixed SAMs and a control mixture ratio of thiol compounds by both competitive and replacement methods; however, the surface properties evaluated by the electrochemical impedance spectroscopy of the mixed SAM surfaces were less

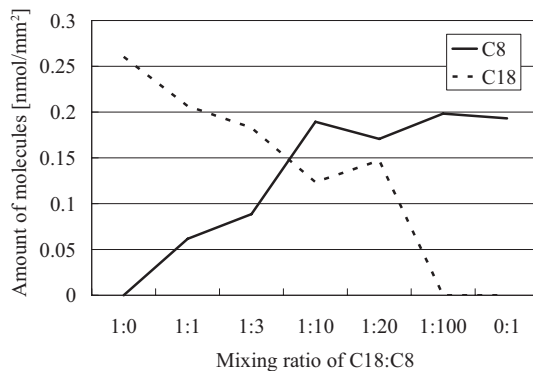


Fig. 3. Amounts of molecules adsorbed onto C8/C18 mixed SAMs measured by stripping voltammetry. Surfaces were prepared by a C8/C18 competitive method.

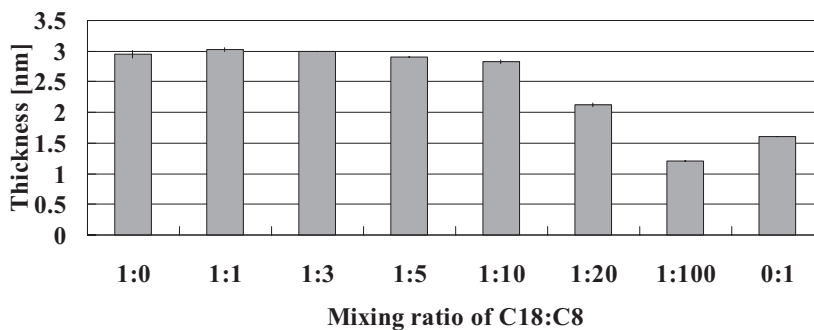


Fig. 4. Thicknesses of C8/C18 mixed SAMs. Surfaces were prepared by a C8/C18 competitive method. Vertical bars denote standard deviations.

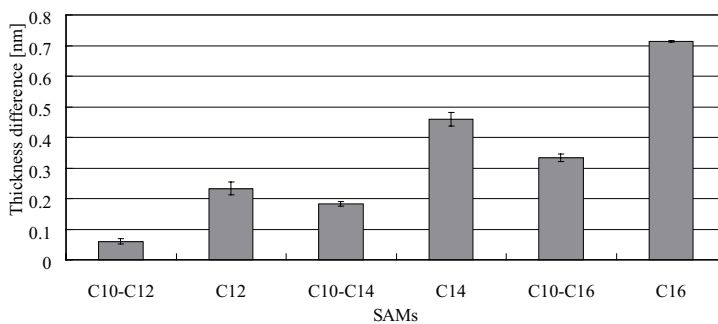


Fig. 5. Thicknesses of C10-C n ($n = 12, 14, 16$) mixed SAMs. Differences from C10 SAM are displayed. Surfaces were prepared by a C10-C n replacement method. Vertical bars denote standard deviations.

reproducible in the case of the competitive method. It was easy to control the mixture ratio by regulating the immersion time in the replacement method. Consequently, we adopted the replacement method for the following mixed SAM fabrication and odor sensor evaluation.

Mixed SAMs having an appropriate hydrophilic surface were prepared by mixing C8OH and C_n . Figure 6 shows the contact angle of C8OH- C_n mixed SAMs. A smaller angle means a more hydrophilic surface. Therefore, the C8OH SAM surface was hydrophilic and the C12 surface was hydrophobic. The intermediate contact angles of C8OH-C12 mixed SAMs suggest that C8OH was replaced with C12 thiol. A short incubation time for C8OH led to a hydrophobic surface, because a small number of hydrophilic C8OH molecules existed on the mixed SAM surface. In the case of C8OH-C16, the same contact angle could be obtained as in the case of C8OH-C12.

Figure 7 shows real and imaginary impedance plots of EIS results measured in 500 mM Na_2SO_4 aqueous solution. The impedance of mixed SAMs had a large real value (Z')

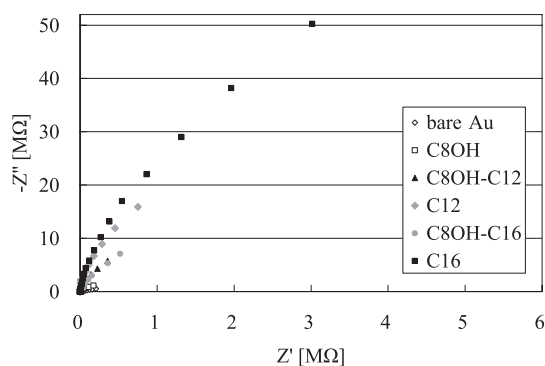


Fig. 6. Electrochemical impedance spectra of C8OH- C_n ($n = 12, 16$) mixed SAMs. The measured frequencies were from 100 mHz to 10 kHz. Surfaces were prepared by a C8OH/ C_n replacement method.

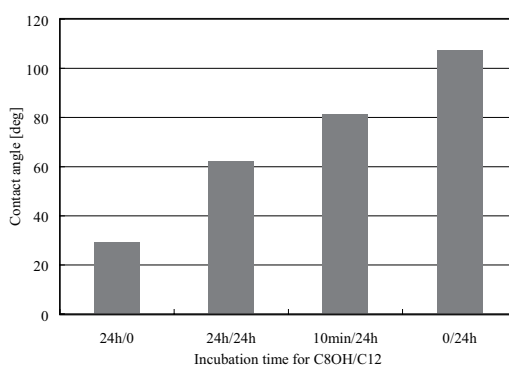


Fig. 7. Contact angles of C8OH- C_n ($n = 12, 16$) mixed SAMs. Surfaces were prepared by a C8OH- C_n replacement method.

and a smaller imaginary value (Z'') at low frequencies. The increment in the imaginary part of impedance was caused by a large surface electrical capacitance, which was brought about by a thinner electrical double layer formed by ions in solution.

3.3 Odor response

The specificity of odorant adsorption onto the fabricated mixed SAMs was evaluated by QCM measurement. The C10- C_n mixed SAM surfaces, which were obtained by the replacement method, had different specificities to ethanol and phenethyl alcohol, however, the response magnitudes did not correspond to the sizes of odor molecules (data not shown).

Many odor molecules have electrical dipoles and hydrophobic parts in their structure; therefore, a hydrophobic nanospace and an electrical dipole buried inside a nanopore are essential for the odor sensor surface. Thus, we used the incubation time of C8OH/ C_n = 10 min/24 h, because a smaller ratio of C8OH might lead to a smaller nanospace. Figure 8 shows the time course of QCM responses, that is, typical responses to two different concentrations of ethanol and phenethyl alcohol. The compositions of SAMs used were mercaptoalcohol, alkane thiols, and their mixed SAMs. A fast response to ethanol and a slow response and recovery to phenethyl alcohol were observed. SAMs containing C8OH had a relatively fast response to phenethyl alcohol.

Figure 9 shows a summary of the responses to ethanol and phenethyl alcohol of SAMs. The amount of odorant adsorption was calculated from frequency changes using the Sauerbrey equation.⁽⁸⁾ The responses of mixed SAMs to ethanol were about the same, whereas those of C8OH-C16 to phenethyl alcohol were smaller than those of C8OH-C12. The distance from the SAM surface to the buried hydroxyl terminal of C8OH of C8OH-C16 might be larger than that of C8OH-C12. Hydroxyl groups of alcohol might interact with the hydroxyl terminal of C8OH via a hydrogen bond; therefore, a longer distance may prevent the adsorption of OH group of phenethyl alcohol onto the OH

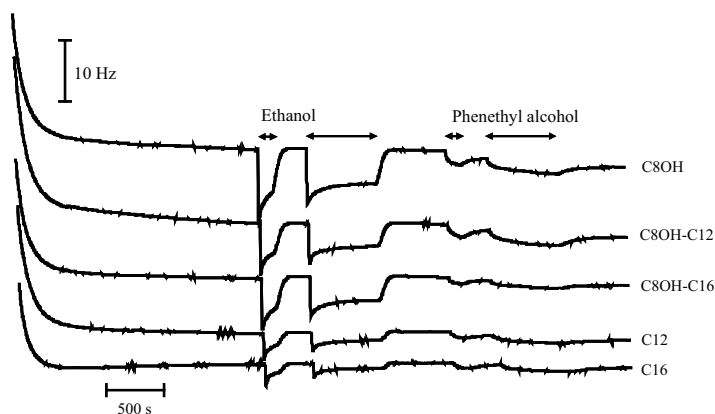


Fig. 8. QCM response curves of mixed SAMs.

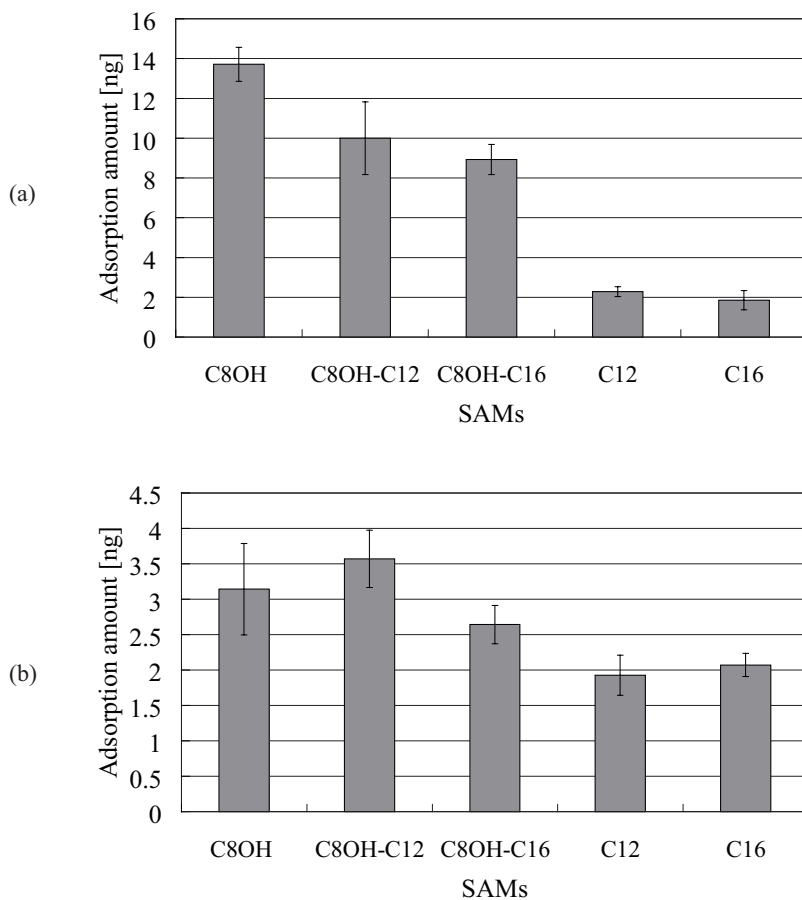


Fig. 9. Amounts of (a) ethanol and (b) phenethyl alcohol adsorbed onto the mixed SAMs measured by QCM responses. The area of the QCM surface was 0.39 cm². Vertical bars denote standard deviations.

group of C8OH, where phenyl groups cannot penetrate nanospaces easily. It is suggested that unspecific adsorption occurred in the case of phenethyl alcohol because all SAMs responded to phenethyl alcohol in spite of the different hydrophobicities of the surfaces. In contrast, the magnitudes of response to ethanol were larger in the case of SAMs with hydrophilic surfaces. Consequently, the substructure constructed of a OH group and a certain hydrophobic chain can be measured using the present mixed SAMs.

4. Conclusion

A fabrication method for SAMs with nanospaces was examined by various surface analyses. The surface properties of SAMs could be controlled for both competitive and replacement methods. The mixed SAMs obtained were evaluated and confirmed to have different responses to odorants using QCM measurement. A nanoscale structure is necessary for odor sensors, and the present nanospaces of mixed SAMs are a good candidate for the odor sensor surface. However, more detailed surface analysis is required, particularly of the nanospace size for fabricating surfaces more specific to various odorants. Furthermore, sensitive detection methods are indispensable. QCM was used in this study; however, its mass sensitive transducer is not adequate for the analysis of the present monolayer surface because of its low sensitivity. QCM also has a problem with its ability to distinguish unspecific adsorption. It is important to install a high-performance detector that can provide molecular information on the adsorbed odor molecules^(9,10) and use a gas-preconditioning method that can filter various odorants in the odor sensor system.

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