Functionalization of Gold Surfaces Using Benzene-Patterned Self-Assembled Monolayers for Surface-Polarization Controlling Method

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In order to improve the sensitivity of the surface-polarization controlling method to detect aromatic compounds which are hazardous chemicals, self-assembled monolayers (SAMs) in benzene were evaluated using cyclic voltammetry and electrochemical impedance spectroscopy. A cyclic voltammogram for the reductive desorption of SAMs adsorbed from a benzene solution containing 1-octanethiol (OT) suggested that OT adsorbed on Au surfaces competed with bulk benzene molecules. The results of electrochemical impedance spectroscopy also revealed the structure of SAMs with benzene holes. Furthermore, benzene can be specifically identified at less than 1 ppm using the benzene-patterned SAM.

1. Introduction

Aromatic compounds have been used or produced in various industries. These compounds including hazardous ones might adversely affect the water and atmosphere. The presently adopted methods for water monitoring such as gas chromatography and liquid chromatography, which provide the required sensitivity, are expensive in terms of cost of the apparatus, heavy maintenance and time consumption because of the analytical procedure. In order to monitor the safety of water continuously and widely, the develop-

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ment of a convenient and easy analysis technique has recently been required.

In this study, we proposed a quantitative and qualitative analysis for adsorbates on an electrode surface using electrochemical impedance spectroscopy (EIS) under electrode-potential sweep. On solid electrodes the impedance has a form which corresponds to a 'frequency-dependent' capacitance rather than an 'ideal' capacitance. This behaviour is usually called 'capacitance dispersion' or a constant phase element (CPE).[1] The origin of the capacitance dispersion can be attributed to the presence of atomic scale inhomogeneities of the electrode surface; 'surface disorder'[2] or specific anion adsorption.[3] Therefore, it is expected that unspecific adsorption of a comparatively large molecule like an aromatic compound has significantly influence on the CPE behavior.

A surface-polarization controlling method was proposed as a new impedance spectroscopy technique,[4,5] which measures electrochemical impedance attributed to the CPE behavior under a dynamically controlled electrode-potential. Chemical substances affect the electrode impedance by a weak and transitory adsorption onto the electrode surface. The adsorption modality varied by electrode potential is dependent on the characteristics of the chemical substances at the electrode solution interface. Therefore, analytes can be broadly identified by the CPE impedance-voltage curve, i.e., the electrode-potential dependencies of the impedance are correlated with the properties of chemicals adsorbed onto or which interact with the surface. The origin of the CPE behavior can be attributed to the presence of atomic scale inhomogeneities of the electrode surface or the adsorption, therefore this method is effective for high-affinity molecules to the electrode surface. In fact, impedance changes by bisphenol A, one of the endocrine disruptors, was confirmed at ppb order in our earlier study.[6,7] We also confirmed that quasi-mediators added in test solutions were useful for the identification of chemical substances.[7-9] However, such identifiable detection has not been realized at less than 1 ppm yet and it was necessary to modify the sensing materials, that is the working electrode, in order to improve the sensitivity.

In the present study, we used self-assembled monolayers (SAMs) as modifiers of the electrode. SAMs developed by 1-octanethiol (OT) adsorption which competed with benzene adsorption[10] were evaluated using cyclic voltammetry and the surface-polarization controlling method. The SAM obtained had many defect holes which might function as adsorption sites for aromatic compounds. The present sensor surface which has a potholed SAM of benzene size realizes simple molecular recognition such as that performed by the molecular imprinting method.[11]

2. Experiment

A gold surface was sputtered to a thickness of approximately 2000 Å onto silicon substrates which were precoated with a 200-Å-thick adhesion layer of titanium. The gold-coated silicon wafer was cut into the required size (1 cm × 2 cm). A cleaning procedure in ultrapure water with 30% and 25% NH_4 OH in proportions of 5:1:1 for 10 min at 80°C was employed to remove the organic contaminants before the substrates were immersed in the incubating solutions for SAMs.[12,13] These substrates, after rinsing in ethanol, were immersed in the 100 μM 1-octanethiol (OT) solution diluted by ethanol 99.5% or benzene

99.5% for 5 min, and then rinsed in ethanol and finally dried with nitrogen-gas flow.

A SAM-adsorbed gold substrate was mounted just beneath the bottom of a polypropy-lene-micropipette tip cell as shown in Fig. 1. A Pt wire (CE) and a Ag|AgCl|saturated KCl electrode (RE) were enclosed in the tip. Supporting electrolytes suctioned by a syringe touched the gold substrate through the tip hole whose diameter was 1 mm. Using the tip-cell, experiments could be performed at several spots over a gold substrate. All the experiments were performed under a nitrogen atmosphere.

Cyclic voltammograms for the reductive desorption were measured in the range between -0.2 V and 1.2 V at a constant sweep rate of 50 mV s^{-1} in deaerated 0.5 M KOH.

Electrochemical impedance measurements were performed in 0.1 M KCl. Impedance spectra from 10 Hz to 20 kHz were measured at 0 V, 0.5 V and -0.5 V, and then the electrode-potential dependencies of the impedance were estimated at 35 Hz while scanning from 0.5 V to -0.5 V in 0.05 V steps. Electrochemical impedance of the electrode is given by $Z = R_s + R_p + jX_p$. R_s is the solution resistance. Electrode capacitance, C_p, was estimated using the X_p *vs.* $1 / \omega$ plot.

The electrode potential scanning measurements were performed 5 times at different spots on the WE using 0.1 M KCl as the base measurement, and then impedance changes by benzene or bisphenol A (BPA) contained in 0.1 M KCl were measured at 5 other spots.

3.   Results and Discussion

3.1   *Coverage of benzene-patterned SAM by thiol compounds*

The coverage of Au electrode by thiol compounds could be confirmed by the reductive desorption of thiol molecules.[14] The desorption peak potentials depend on the chain
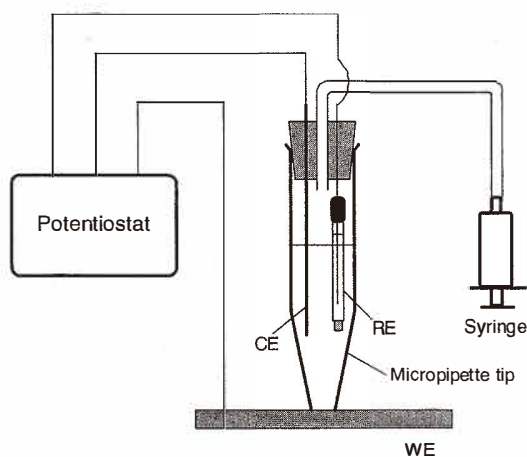

Fig. 1.   Micropipette tip cell.   WE: SAM-adsorbed gold substrate, RE: Ag|AgCl|saturated KCl electrode and CE: Pt wire.

length of alkanethiol. The peak potential shifts to a more negative value as the length of the alkyl chain increases. The desorption at a more negative potential indicates that alkanethiolate monolayers adsorbed on Au more strongly. The amount of adsorbed molecules can be estimated from the area under the desorption peaks, i.e., total charge involved in desorption reaction.

These measurements, stripping CV, were carried out for the electrodes, which were bare Au, potholed SAM and completely-covered SAM. The OT coverage of potholed SAM which was prepared by OT adsorption from benzene solution was confirmed by the CV for stripping.

Figure 2(a) shows a cyclic voltammogram for the reductive desorption of a SAM adsorbed from an ethanolic solution containing 100 μM OT. Two reductive desorption peaks appeared at -0.89 V and -1.13 V, although a single peak was observed for the desorption of OT at annealed Au/mica, atomically smooth terrace sites.[15,16] These peaks were desorption from terrace sites and step sites on nonannealed Au/Si.[17] Since the adsorbates at step sites bound more strongly than at terrace sites, the peaks appearing at -0.89 V and -1.13 V were due to the desorption current from terrace sites and step sites,
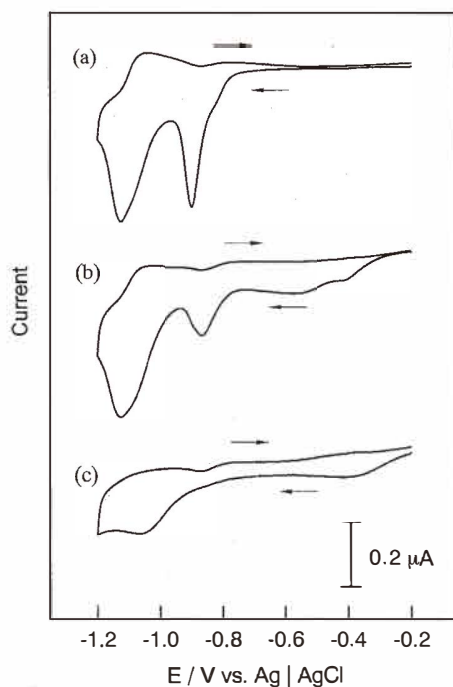

Fig. 2. Cyclic voltammograms for the reductive desorption of SAMs in 0.5 M KOH solution. (a) gold electrode modified with 100 μM OT in EtOH, (b) gold electrode modified with 100 μM OT in benzene and (c) bare gold electrode. Initial potential: -0.2 V, scan rate: 50 mV s^{-1}.

respectively. The total amount of adsorbed OT was 0.30 nmol cm^{-2}. In the present experiments, gold substrates were dipped into a dilute OT solution for a short period, 5 min. The total amount of adsorbed OT was approximately 30% of the result for a long period, 2–24 h.[1516] This result suggested that the OT molecules on Au surface formed an initial stripe structure[18] rather than ($\sqrt{3} \times \sqrt{3}$)$R30°$ overlayer structures. This short preparation time was adopted to attain a surface structure with benzene-hole. The amount of adsorbed OT on terrace sites that were revealed at a desorption current at –0.89 V was 0.09 nmol cm^{-2}. Figure 2(b) shows a cyclic voltammogram for the reductive desorption of a SAM adsorbed from a benzene solution containing 100 μM OT. Two desorption peaks were confirmed as in Fig. 2(a). The total amount of adsorbed OT was 0.24 nmol cm^{-2}. The amount of adsorbed OT on terrace sites in benzene solvents was 0.05 nmol cm^{-2}, which was less than that in ethanol. This amount suggests that 43% of Au terrace surfaces were not covered by OT molecules compared with fully covered OT SAM. Therefore the surface had many holes which were formed by competitive benzene adsorption on Au. Benzene strongly adsorbs on various metal surfaces by π orbital sharing,[19] and therefore the decrement of OT molecule adsorption from benzene solution suggests that OT adsorbed on Au surfaces competed with bulk benzene molecules. In other words, SAMs prepared in benzene, benzene patterned SAMs, had a potholed structure with holes due to benzene.

3.2 Impedance spectroscopy of SAMs electrode

Figure 3(a) shows the complex impedance plots of a bare Au electrode carried out at 0 V, 0.5 V and –0.5 V versus Ag|AgCl|saturated KCl in 0.1 M KCl. Since a redox reaction did not occur under these conditions, the locus of impedance showed a straight line with a constant phase angle α of CPE behavior which arose from the microscopic surface disorder of electrode surfaces.[2] On the other hand, the tilt angles of the line locus and frequency dependencies of impedance were affected by the electrode potential. Thus, in the surface-polarization controlling method, analytes were detected using the CPE impedance depending on the electrode potential.

Figure 3(b) shows the impedance plot for the benzene patterned SAM, as in Fig. 2(b). The locus of impedance on the benzene patterned SAM was larger than that of bare Au, that is, the interfacial capacitance was smaller than that of bare Au. However, a tilted locus denotes that the interfacial impedance of the benzene-patterned SAM contained the CPE impedance. In contrast, the impedance of completely-adsorbed SAMs in Fig. 3(c) was much larger and exhibited purely capacitive behavior. These results suggest that the total double layer capacitance measured on the benzene-patterned SAM can be assumed to be a parallel combination of two capacitors, $C_{\text{total}} = C_{\text{h}} + C_{\text{m}}$, where C_{h} is the capacitance at benzene holes and C_{m} is the capacitance across the monolayer itself, where C_{m} is much smaller than C_{h} due to the thickness of electrical double layers.

3.3 Responses to aromatic compounds

The benzene-patterned SAM was evaluated by measuring benzene and BPA using the surface-polarization controlling method. Relative changes of R_{p} and C_{p} were calculated by $(R_{\text{p}} - R_0)/ R_0$ and $(C_{\text{p}} - C_0)/ C_0$, where $R_{\bullet}$ and C_0 are impedance in 0.1 M KCl base solution and R_0 and C_0 are the averages of $R_{\bullet}$ and C_0, respectively.
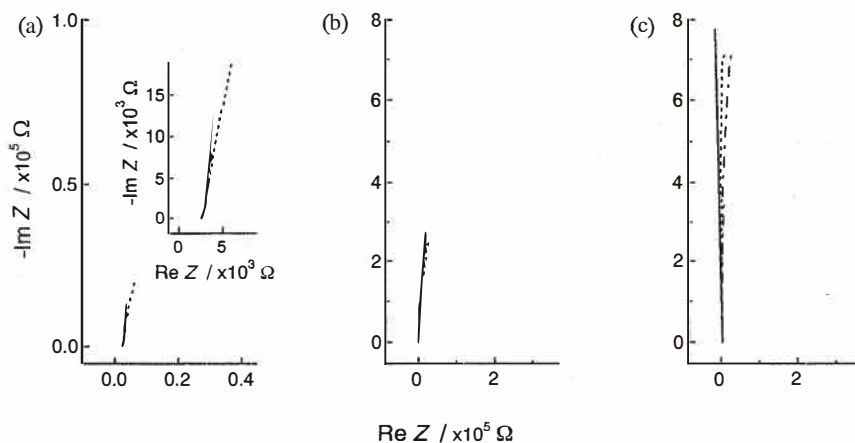
Fig. 3.   Complex plane impedance plots at 0 V (straight line), 0.5 V (dotted line) and –0.5 V (dashed line) vs. Ag|AgCl|sat'd KCl. (a) bare gold electrode, (b) gold electrode modified with 100 μM OT in benzene and (c) gold electrode modified with 100 μM OT in EtOH. Frequency range used: 20 kHz to 10 Hz at 15 points.

Figure 4 shows $(R_p - R_0)/R_0$ and $(C_p - C_0)/C_0$ in 0.1, 1 and 10 ppm benzene. In the case of bare Au, relative changes of impedance were less dependent on the concentration of benzene. As the concentration of benzene increased, $(R_p - R_0)/R_0$ once increased then decreased and peak potentials shifted significantly. $(C_p - C_0)/C_0$ curves also changed with concentration. These results suggest that the adsorbing orientation of benzene to the Au surface had varied. It was reported that benzene or aromatic compounds adsorbed on metal surfaces with a perpendicular orientation at low concentrations and with a flat orientation at high concentrations.[20] On the other hand, relative changes of impedance depended on the concentration of benzene in the case of the benzene-patterned SAM. As the concentration of benzene increased, $(R_p - R_0)/R_0$ increased and $(C_p - C_0)/C_0$ decreased. The increment of $(R_p - R_0)/R_0$ indicates that the domain of the Au surface which was not covered with SAMs was more inhomogeneous than that brought about by benzene molecules' adsorption onto the surface and makes the surface more disordered. The decrement of $(C_p - C_0)/C_0$ indicates that C_h, the capacitance at benzene-holes, decreased since C_m, the capacitance across the monolayer itself, was not changed largely by benzene or BPA (Fig. 5). These results suggest that benzene adsorbed in benzene-holes of the SAMs. The present benzene-patterned SAM had different response characteristics from both the bare Au and the completely-covered OT electrode. Therefore, holes which formed by competing adsorption of benzene appeared to function as specific responding sites.

Figure 6 shows $(R_p - R_0)/R_0$ and $(C_p - C_0)/C_0$ at 0.01, 0.1 and 1 ppm BPA. Relative impedance changes with BPA concentration at the benzene-patterned SAM were similar to those of bare Au, although the dependencies of electrode potential were somewhat different. $(R_p - R_0)/R_0$ increased abruptly in 1 ppm. $(C_p - C_0)/C_0$ in 0.1 ppm was similar to
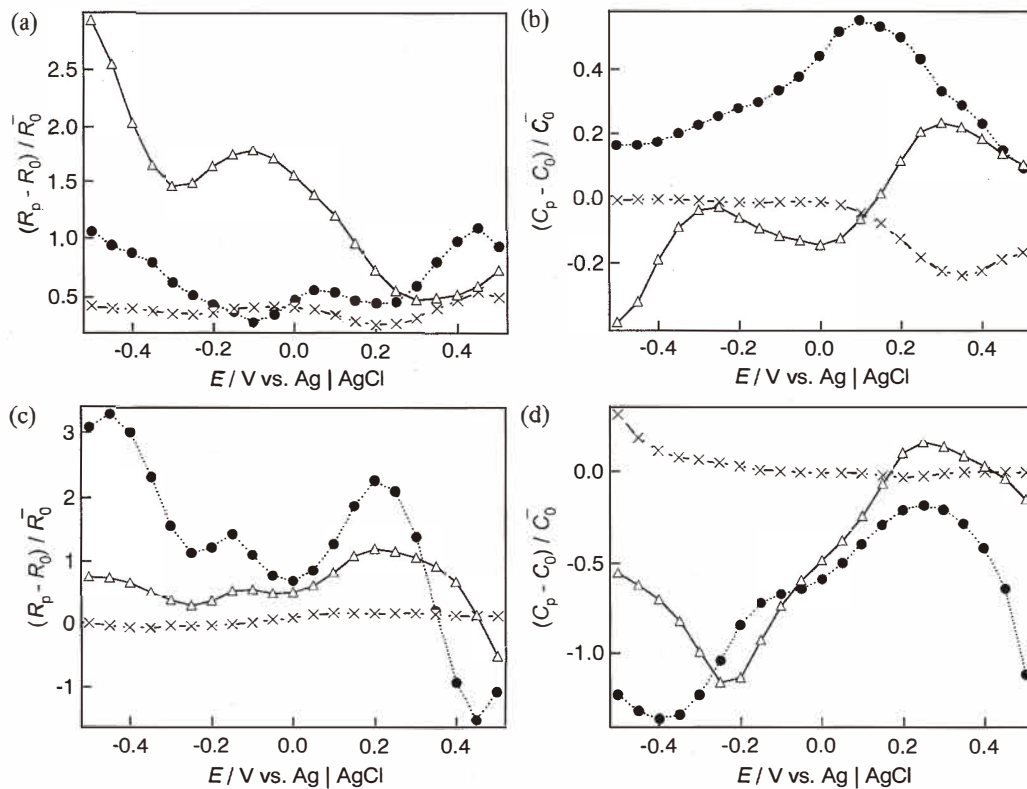
Fig. 4.   Relative changes of Rp and relative changes of Cp. (a) and (b): bare Au, (c) and (d): benzene-patterned SAM. Crosses denote 0.1 ppm benzene, open triangles denote 1 ppm benzene and filled circles denote 10 ppm benzene.
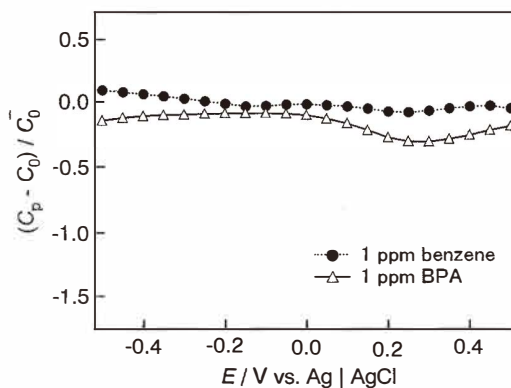

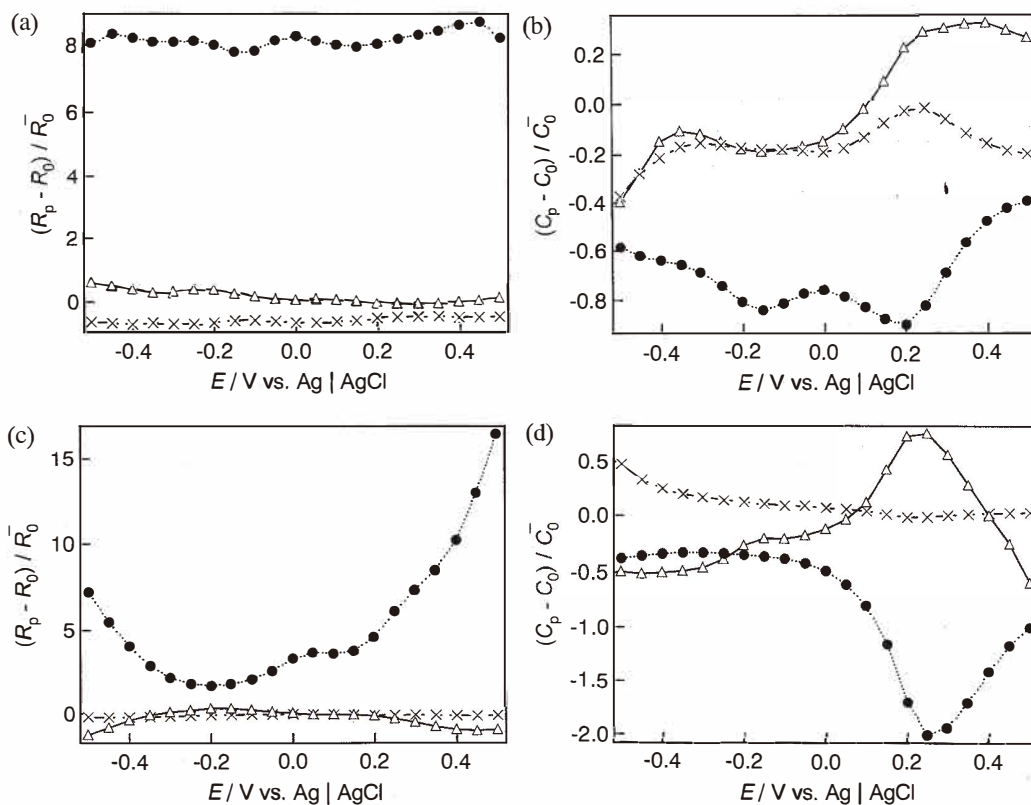Fig. 5.   Relative changes of completely-covered OT SAM by benzene and BPA.

Fig. 6.   Relative changes of Rp and relative changes of Cp. (a) and (b): bare Au, (c) and (d): benzene-patterned SAM. Crosses denote 0.01 ppm BPA, open triangles denote 0.1 ppm BPA and filled circles denote 1 ppm BPA.

that of 1 ppm benzene at bare Au, and then the capacitance decreased in 1 ppm. This suggests that BPA began adsorbing onto the Au surface at less than 0.1 ppm and covered it fully at 1 ppm. In the benzene-patterned SAM, BPA molecules adsorbed on benzene-hole sites of SAMs or another bare sites. However, BPA molecules might less closely fit in the benzene-hole sites than benzene molecules, and the specificity of the electrode to BPA seemed to be inferior to benzene responses.

Figure 7 shows averages of absolute values of $(C_p - C_0)/C_0$ over electrode potential for benzene and BPA. Total C_p changes of benzene responses for the benzene-patterned SAM were much larger than those of bare Au as compared with the case of BPA. This means that benzene can be specifically identified at less than 1 ppm using the benzene-patterned SAM. It was difficult to detect less than 10 ppm benzene applying previous methods using bare Au surfaces, however the modified Au electrode is effective for selective and highly sensitive detection of benzene.
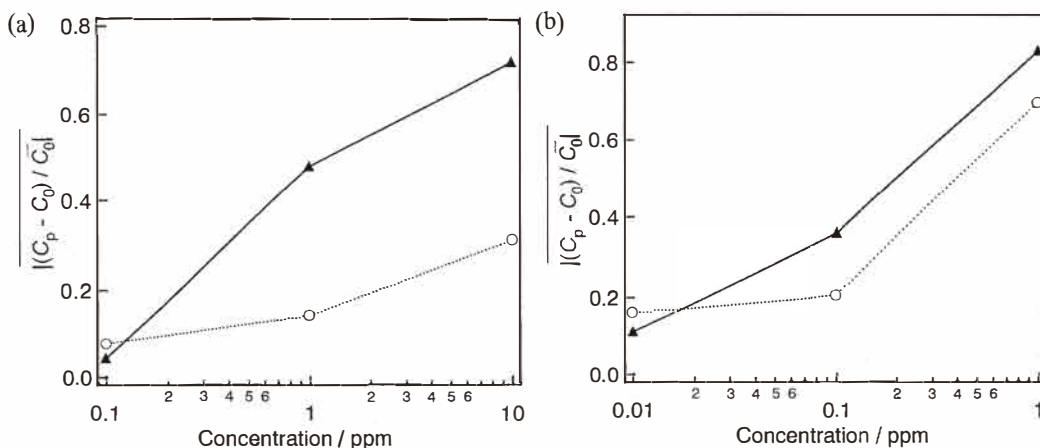
Fig. 7. Average responses of electrode capacitance for (a) benzene and (b) BPA. Filled triangles denote benzene-patterned SAM Au and opened circles denote bare Au.

4.   Conclusion

Using cyclic voltammetry and the surface-polarization controlling method, we confirmed a SAM of OT with holes which formed by competing adsorption of benzene. Since the holes functioned as specific benzene responding sites, benzene was specifically identified at less than 1 ppm. This modification method for electrodes has advanced sensitive and selective measurement by the surface-polarization controlling method.

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