Electrochemical Atrazine Detection Using Au(111) Electrode Modified with Self-assembled Monolayer of Mercaptoquinone

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Self-assembled monolayers (SAM) of mercaptohydroquinone (MHQ) were constructed on a Au(111) surface. Redox charge due to hydroquinone/benzoquinone reaction of the MHQ SAM modified Au(111) electrodes was dependent on the concentration of atrazine contained in an electrolyte solution, indicating that the MHQ SAM modified Au(111) electrode functioned as an atrazine sensor.

Atrazine, which is a herbicide and acts as an endocrine-disrupting chemical, can cause gonadal abnormalities in living things.[1–3] Although use of atrazine has been restricted in many countries, atrazine still remaines in many areas due to its chemical stability. Mass analysis, gas chromatography, and ELISA (enzyme-linked immunosorbent assay) have been generally used for atrazine detection, however, the equipment is too large to be mobile and detection times are long. Except for them, several immunosensors for atrazine were also reported[4–6] but these methods are not suitable for atrazine detection because of their chemical unstability. Thus, a rapid and durable detection system for atrazine would be desirable. Electrochemical sensors are quick detection systems and can be portable because they are often very small. Organic layer modified electrodes are more durable than immune sensors which use biomolecules.

Self-assembled monolayers of alkylthiols on gold have been extensively studied because of their high density, regular orientation, and high stability, and have been applied to various fields such as sensors, corrosion inhibition, wetting control, and biomolecular and molecular electronic devices.[7–9] Electrochemical properties of gold electrodes modified with SAMs of mercaptoquinone derivatives and their surface orientation have also been reported by many research groups.[10–16] Since atrazine acts to hinder electron transfer at a quinone portion in natural photosynthetic systems,[17–19] it is expected that a SAM of mercaptohydroquinone (MHQ) could function as a atrazine sensor.

In this paper, we investigated the atrazine concentration dependence of electrochemical properties of a Au(111) electrode modified with a SAM of MHQ. The present results indicate that the MHQ SAM modified gold electrode can act as an atrazine sensor.

MHQ was synthesized using previously reported procedures.[13,20] MHQ SAM was prepared on a Au(111) surface by dipping the Au(111) substrate into an ethanol solution containing 1 mM MHQ for more than 1 h, after annealing and quenching the Au(111) substrate. Before the electrochemical measurements, the potential of the MHQ SAM modified Au(111) electrode was kept at 0 V more than 5 min. Cyclic voltammograms (CVs) were measured in 0.1 M aqueous HCl electrolyte solution (pH 1.0) containing atrazine at various concentration.

Figure 1a shows the CVs of a Au(111) electrode modified with MHQ SAM. Around 0.4 V (vs. Ag/AgCl), anodic and

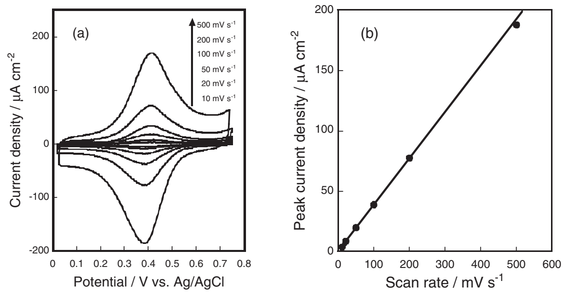

Figure 1. (a) CVs of the Au(111) electrodes modified with the SAMs of MHQ measured in 0.1 M HCl solution with various scan rates. (b) Relationship between scan rate and peak current density.

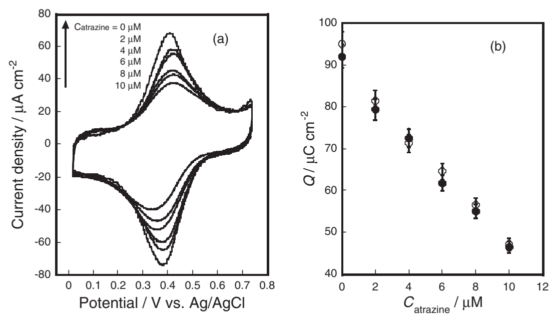

Figure 2. (a) CVs of the Au(111) electrodes modified with the SAMs of MHQ SAM measured in 0.1 M HCl solution containing various atrazine concentration, C_{atrazine}, with a scan rate of 200 mV s^{-1}. (b) Relationship between C_{atrazine} and integrated peak charge, Q. Anodic and cathodic charge present closed and open circles, respectively.

cathodic current peaks due to the hydroquinone/benzoquinone redox reaction with 2 protons and 2 electrons were observed. Peak current is proportional to scan rate (Figure 1b), showing that the redox reaction of these current peaks should correspond to the redox reaction of a quinone site in the MHQ SAM chemisorbed onto the Au(111) surface. Based on the integrated charge values of these current peaks, we can calculate the surface coverage to be ca. 3.0×10^{14} molecules cm^{-2}, which is almost the same value as those reported before.[11,13–15] From this surface coverage value, molecular area can be estimated to be 33 $Å^2$, suggesting that the aromatic ring of the MHQ molecule is oriented perpendicular to the Au(111) surface.[16]

Figure 2 shows the CVs of a Au(111) electrode modified with a MHQ measured in 0.1 M HCl solution containing atrazine at various concentration with a scan rate of 200 mV s^{-1}. Although anodic and cathodic peaks corresponding to the hydroquinone/benzoquinone redox reaction were observed in solution at all atrazine concentrations, C_{atrazine}, the higher the atrazine

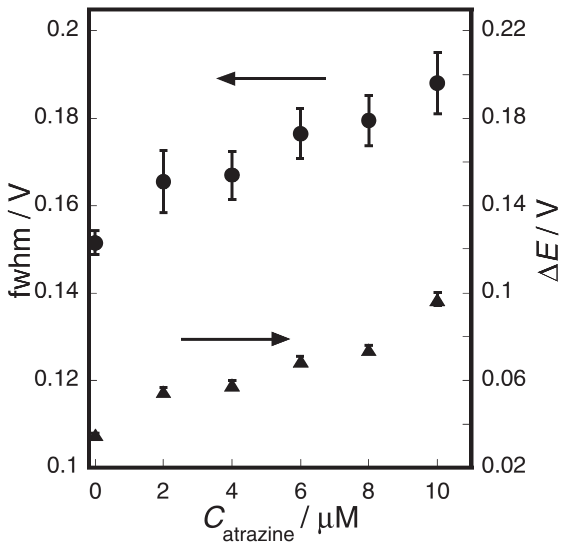

Figure 3. Fwhm (closed circles) and peak separation, ΔE, (closed triangles) as a function of $C_{atrazine}$.

concentration, the smaller the integrated peak charge, Q. This result indicated that the adsorbed atrazine at the quinone site of the MHQ SAM blocks electron transfer and/or proton transfer. Also, fwhm (full width of half maximum) values of current peaks and peak separation (ΔE) became larger with increasing atrazine concentration (Figure 3), showing that orientation of the MHQ molecules in the SAM becomes more random and electron transfer becomes slower when atrazine is adsorbed onto the MHQ SAM. These results of $C_{atrazine}$ dependence are consistent with previous reports.[17–19]

When the redox reaction of all MHQ on which atrazine is adsorbed is avoided, coverage of adsorbed atrazine, θ, can be defined as below;

$$\theta = \{Q(0) - Q(x)\}/Q(0) \quad (1)$$

where $Q(0)$ and $Q(x)$ are integrated charge of the redox peak measured in electrolyte solution without atrazine and with x μM atrazine, respectively. Figure 4 shows the relationship between the reciprocal of θ as a function of the reciprocal of $C_{atrazine}$. A linear relationship was obtained with a y intercept of 1, as clearly shown in Figure 4, indicating that the atrazine adsorption onto the MHQ SAM should be Langmuir type (eq 2).

$$1/\theta = 1 + (1/kC_{atrazine}) \quad (2)$$

where k is adsorption coefficient. A value of k can be calculated from the slope of the linear line in Figure 4 to be $1.8\,M^{-1}$. This value is relatively small because hydroxy groups of MHQ may be oriented perpendicular to the surface in which case atrazine cannot be adsorbed well by hydrogen bonding. Concentration dependence of the simazine, one of the triazine compounds, showed almost the same feature as atrazine, indicating that selectivity of the present system is not good, as compared with those of immunosensors.[4–6] Attempts of increasings of k value and of selectivity are now under investigation.

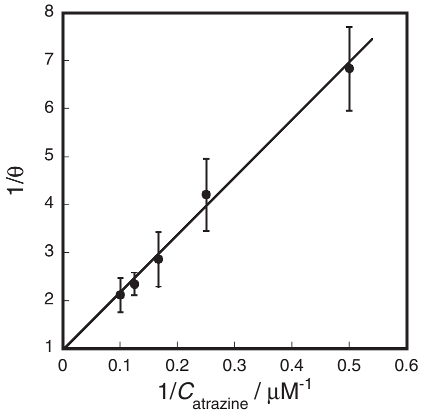

Figure 4. Langmuir plot of a reciprocal of θ as a function of a reciprocal of $C_{atrazine}$.

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