Adsorption Kinetics and Thermodynamics of 2-Aminoethanethiol onto a Polycrystalline Gold Electrode Determined by Cyclic Voltammetry of Reductive Desorption

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ABSTRACT

The reductive desorption of 2-aminoethanethiol (AET) monolayers formed on a polycrystalline gold electrode has been studied using cyclic voltammetry. Three cathodic peaks were observed and they were assigned to reductive desorption from each small domain of Au(111), (100), and (110) over the polycrystalline surface. The kinetics of adsorption were likely under the condition where the kinetic control and the diffusion control were balanced over the concentration range 5–50 μM (M = mol dm⁻³), whereas it was described by the kinetic control model at 100 μM. The thermodynamics of adsorption was well-described by the Langmuir isotherm. The saturation surface coverage was found to be 5.3 × 10⁻¹⁰ mol cm⁻², which suggested that AET adsorbed lying flat on a polycrystalline gold electrode.

1. Introduction

Molecular design of electrode surfaces has extensively been investigated since 1980s due to its ability to alter the nature of electrode surfaces and to give new functions. One of the most attractive and widely used techniques to modify the electrodes is self-assembly of alkanethiols on electrodes, because they can form stable monolayers (self-assembled monolayers, SAMs) with highly ordered structure and their preparation is facile. Therefore, they have been used for various applications such as chemical and biological sensors, barrier films, drug delivery, and biofuel cell.

Adsorption kinetics of long-chain alkanethiols onto Au(111) surfaces have been studied in detail. The initial step was described well by diffusion-controlled Langmuir adsorption. The second step was called as a surface crystallization process, where the disordered alkyl chains formed a two-dimensional crystal. The adsorption steps of long-chain alkanethiols leads to a well-ordered SAMs, especially on a single-crystalline Au(111) surface. The adsorbed monolayer has been reported to have (√3 × √3)R30° structure where the alkyl chains are tilted at an angle of 30° from the normal to the Au(111) surface.

Cyclic voltammetry of the reductive desorption of the thiol-modified gold electrode has been employed to evaluate the state of the SAMs such as surface coverage, orientation, stability, and adsorption energy. At negative potential the following reductive reaction (1) takes place

\[ R - S - Au + e^- \rightarrow R - S^- + Au \] (1)

The potential of reductive desorption depends on the nature of thiol, such as chain length and head group repulsion. The more stable SAMs of thiols exhibit more negative desorption potentials.

In most researches on alkanethiol SAMs, single-crystalline Au(111) substrates have been employed because it is easy to evaluate the state of SAMs and to understand surface process. However, it has been reported that the structure and stability of SAMs depend on the surface crystallographic orientation and surface condition of substrates. On the other hand, there have been only a few reports on detailed adsorption characteristics of SAMs on a polycrystalline gold electrode because its surface roughness makes an understanding of the surface process difficult. Rough surfaces, however, have advantages for particular practical applications such as electrocatalysis and sensing. Thus, it is important to study the adsorption properties of SAMs on a polycrystalline gold electrode in detail.

A variety of functional groups can form SAMs and the terminal groups play an important role to determine the properties of the monolayers such as wettability and ionization. 2-aminoethanethiol (AET) has a short alkyl chain and forms SAM on a gold electrode, providing an amino group-functionalized surface. In addition to control hydrophobic property of the electrode surface, the SAMs of AET have been extensively used as an anchor to introduce various bioactive and electroactive materials on gold electrodes, because amino groups can covalently attach them to the substrate. Since the SAM of AET allows an electron tunneling through it by minimizing the distance between the modified functional molecules and the gold substrate, it has been a suitable anchor to attach electroactive materials to gold substrates. However, AET forms disordered SAM in which adsorbed thiol lies due to weak intermolecular interaction arising from short alkyl chain length. This gives rise to low orientation of the functional materials further introduced. It has been reported that the SAM of AET forms (7 × √3) structure when a single-crystalline Au(111) electrode was immersed in millimolar AET solution at 50°C for 30 min. However, there has not been a report on adsorption properties of the AET on a polycrystalline gold electrode. For the modification of a gold substrate with functional molecules via AET, polycrystalline gold electrodes have widely been used because of the simplicity of preparation and the advantage of large roughness factor as mentioned above. Therefore, it is important to investigate the adsorption properties of AET onto a polycrystalline gold electrode in detail.

In the present paper we aim to evaluate kinetics and thermodynamics of AET adsorption onto a polycrystalline gold electrode using cyclic voltammetry of the reductive desorption in alkaline solution. The study of AET adsorption onto an electrode is expected to provide fundamental insights of adsorption systems of thiols with short alkyl chains and fundamental groups.
2. Experimental

AET was purchased from Wako Pure Chemical Industries and used as received. Sulfuric acid (high special grade, Wako Pure Chemical Industries), ethanol (guaranteed reagent, Wako Pure Chemical Industries), and potassium hydroxide (BioXtra, Aldrich) were used without further purification. Water was purified with Millipore (Direct-Q® 3 UV).

A polycrystalline gold disk electrode (1.6 mm in diameter, 0.02 cm², BAS) or single-crystalline gold electrode was used as the working electrode. A Ag/AgCl with double-junction (Inter Chemi Ltd.) and a coiled Pt wire were used as a reference and a counter electrode, respectively. The polycrystalline gold disk electrode was polished with 0.05 µm alumina suspension (Refine Tec Ltd.), rinsed with water, and sonicated in water for 3 min with an ultrasonic bath (UT-1055, Sharp). It was then electrochemically cleaned in a 0.1 M (M = mol dm⁻³) sulfuric acid, by applying potentials of +1.5 and −0.1 V vs. Ag/AgCl for 30 s each, and repeating the potential cycles between those values at 5 V s⁻¹ until the cyclic voltammetry of a clean polycrystalline gold electrode was obtained. The electrochemical cleaning was carried out with a lab-made three compartments cell. A 0.1 M sulfuric acid aqueous solution was degassed with nitrogen gas for 10 min before use, and it was flowed over the solution during experiments. A real surface area of the polycrystalline gold electrode was calculated from the charge of monomolecular gold oxide layers in the cyclic voltammetry of a clean polycrystalline gold electrode. The single-crystalline gold electrode was prepared with high purity single-crystal mica sheets (© 14 mm², Nilaco) by the vapor flame-annealing with a hydrogen flame for 2 min before use. The formation of Au(111) terraces was confirmed by cyclic voltammetry in a 0.1 M sulfuric acid aqueous solution.

The polycrystalline gold electrode or single-crystalline gold electrode was then immersed into an ethanol solution (20 mL) containing AET to form a monolayer of the AET on the electrode surface. After the electrode was taken out from the AET solution, it was carefully rinsed with ethanol and water, and then transferred to a cylindrical electrochemical cell containing a 0.1 M potassium hydroxide solution. The surface coverage (Γ) of the adsorbed AET on the gold electrode was estimated from an integration of the reductive desorption peak in the cyclic voltammogram measured in a 0.1 M potassium hydroxide solution at 10 mV s⁻¹. The 0.1 M potassium hydroxide solution was degassed with nitrogen gas for 30 min before use, and it was flowed over the solution during experiments. All electrochemical measurements were performed with a potentiostat (HZ-5000, Hokuto Denko). All measurements were performed at room temperature (25 ± 1°C).

3. Thermodynamics and Kinetics of Adsorption

Monolayer formation by self-assembly can be assumed as the competition reaction of adsorbate molecules, solvent, and ions in solution for binding sites on the surface of substrate.²²–²⁴ Such a situation can be expressed as

\[ \Delta A_{\text{ads}} + S_{\text{ads}} = A_{\text{ads}} + S_{\text{sol}} \]  

where \( \Delta A_{\text{ads}} \) represents the adsorbate molecules in solution, \( S_{\text{ads}} \) is the solvent and/or ions adsorbed on the substrate, \( A_{\text{ads}} \) represents the adsorbate molecules adsorbed on the substrate and \( S_{\text{sol}} \) is the solvent and/or ions displaced into the solution by the adsorbate. The amount of molecules adsorbed on the substrate will depend on the concentration of adsorbate in solution, \( A_{\text{ads}} \). The equilibrium relationship between the bulk solution concentration of adsorbate (\( \Gamma_0 \)) and \( \Gamma \) of adsorbate molecules is represented by an adsorption isotherm. Several types of isotherms have been proposed²⁵ and the differences among them depend on the type of interactions between adsorbates. The simplest isotherm is the Langmuir isotherm, which describes the adsorption when the adsorbate interaction is only due to its size. The Langmuir isotherm is described by

\[ \frac{\theta}{1 - \theta} = \beta C_\lambda^* \]  

where \( \theta \) is the fractional coverage (\( \Gamma_0/\Gamma_\lambda^* \)) of the surface (\( \Gamma_\lambda^* \) is the surface coverage of \( A_{\text{ads}} \) at time \( t \) and \( \Gamma_\lambda^* \) is the saturation coverage) and \( \beta \) is the adsorption coefficient. The adsorption free energy (\( \Delta G_f \)) can be determined using

\[ \Delta G_f = -RT \ln(C_\lambda \beta) \]  

where \( C_\lambda \) is the concentration of solvent.

If attraction or repulsion interaction between adsorbates is taken into account, an exponential term is added to the Langmuir isotherm. One of the simpler isotherms that takes into account such interactions is the Frumkin adsorption isotherm.²³,²⁴,²⁶ The Frumkin isotherm is expressed as

\[ \frac{\theta}{1 - \theta} \exp(-2g\theta) = \beta C_\lambda^* \]  

where \( g \) represents the interaction parameter which takes into account interactions between adsorbates. When no interactions exist between adsorbates (\( g \) equals zero), the Frumkin isotherm is reduced to the Langmuir isotherm (Eq. (3)). Positive \( g \) represents attractive force, whereas negative \( g \) represents repulsive interaction.

In order to explain the kinetics of adsorption, assuming an adsorption equilibrium, two general models can be used. The first model includes kinetic (activation) control of the system, whereas the other includes fast adsorption with mass transport or diffusion control.²⁷ The detailed theory of these models has been previously described.²²,²⁴ Briefly, the kinetic control model under Langmuirian adsorption conditions can be written as

\[ \Gamma_t = \Gamma_0 (1 - \exp(-k_t \Gamma_\lambda^*)) \]  

where \( \Gamma_t \) is the surface coverage at a given bulk concentration and \( k_t \) is the rate constant of adsorption. In this equation, as \( \Gamma_\lambda^* \) increases, \( \Gamma_t \) will increase until \( \Gamma_t \) is reached. Therefore until this concentration is reached, \( \Gamma_t \) will be controlled by the bulk concentration.

The second model, fast adsorption with mass transport or diffusion control, assumes semiinfinite linear diffusion of a species in solution to a stationary plane with Langmuirian adsorption at boundary, and it can be expressed as

\[ \frac{\Gamma_t}{\Gamma_0} = K \left( \frac{C_\lambda^*}{D t} \right)^{1/2} \]  

where \( D \) is the diffusion coefficient of the adsorbate and \( K \) is a constant (2π⁻¹/₂).

4. Results and Discussion

4.1 The reductive desorption potentials

Figure 1 shows a typical cyclic voltammogram in a 0.1 M potassium hydroxide solution for a polycrystalline gold electrode which was immersed in a 100 µM AET solution for 3 h. On the first
Scan, three cathodic peaks were observed at ≈0.63, 0.80, and 1.0 V, but they disappeared on the successive second scan. This result clearly indicates that three cathodic peaks on the first scan can be attributed to the reductive desorption of AET.

Ohsaka et al. have previously reported the reductive desorption of cysteine and 4-mercaptobenzoic acid layers adsorbed on polycrystalline gold and single-crystalline Au(111), Au(100), and Au(110) electrodes. In that report, when cysteine and 4-mercaptobenzoic acid adsorbed on single-crystalline Au(111), Au(100), and Au(110) electrodes, each reductive desorption peak appeared at different potential in the order of (111) > (100) > (110). When they adsorbed on the polycrystalline gold electrode, three cathodic peaks were observed and their potentials were found to be in good agreement with those obtained at the single-crystalline Au(111), Au(100), and Au(110) electrodes. In addition, Yang et al. have demonstrated that the potentials at which reductive desorption of the nonanethiol-modified single-crystalline gold electrode occurs correlate with the potential of zero charge of the bare single-crystalline gold electrodes.

A surface of polycrystalline is known to consist of a certain distribution of the three low index faces with a large number of kinks and steps. In fact in the CV of a reductive desorption of AET SAM at a single-crystalline Au(111) electrode, a reductive desorption peak was obtained at ≈0.63 V. This value is consistent with that for the polycrystalline gold electrode, indicating that the peak can be attributed to the desorption reaction of AET from Au(111) face over the polycrystalline gold surface.

Based on those results and the previous reports, it is indicated that three cathodic peaks at ≈0.63, 0.80, and 1.0 V in this work correspond to reductive desorption from each small domain of Au(111), (100), and (110) over the surface. Furthermore, it is also suggested that the stabilities of AET monolayers formed on Au(111), (100), and (110) faces on the polycrystalline gold increases in the order of (111) < (100) < (110) faces.

4.2 Kinetics of adsorption

Figure 2 shows the time-dependence of the \( \Gamma \) obtained for a polycrystalline gold electrode immersed in 5–100 µM AET ethanol solution. Here, the \( \Gamma \) was calculated using a base line, which was drawn taking into account a double layer charging current of the desorption CV and a CV of a bare polycrystalline gold electrode in a 0.1 M potassium hydroxide solution. A typical example of a base line is shown as a curve g in Fig. 1. Since a small shoulder at ca. ≈1.1 V on the desorption CV (Fig. 1a) also existed on CV of the bare gold electrode (Fig. 1f), the charge in this shoulder was eliminated from the calculation of the \( \Gamma \). Figure 2 shows a trend that the \( \Gamma \) increases with the immersion time at all concentrations examined. The curves in Fig. 2 were obtained using a least-square best fit of the experimental data using Eq. (6) with \( \Gamma_0 \) and \( k_1 \) as the adjustable parameters. As can be seen at all solution concentrations, agreement of the data to the fits implies that the kinetic control model would be applicable. At 5–20 µM of AET the \( \Gamma \) reached equilibrium within ca. 30 min. At concentrations above 35 µM the kinetics of adsorption were quite fast so that the \( \Gamma \) reached equilibrium within ca. 5 min. We believe that the time range where \( \Gamma \) rapidly increases with time corresponds to the initial fast step of the adsorption, and the time range where \( \Gamma \) becomes nearly constant corresponds to the second slow step. The times taken to reach equilibrium for the adsorption of 2-mercaptoethanol on a gold electrode have been reported to be 3 min, 30 s, and 10 s at concentrations of 2, 20, and 200 µM, respectively. These are shorter than the time in this study, indicating that the functional group affects the adsorption kinetics of alkanethiols on a gold surface. Table 1 summarizes \( \Gamma_0 \) and \( k_1 \) obtained from an analysis of the data in Fig. 2 using Eq. (6). It is revealed that the \( \Gamma_0 \) increases with the bulk solution concentration of AET over the concentration range 5–35 µM and becomes virtually constant at concentrations higher than 35 µM. This is the anticipated result assuming that Eq. (2) describes the adsorption equilibrium process and that the kinetics of adsorption follow the kinetic control model. The situation can qualitatively be explained as follows. The concentration near the electrode reaches the bulk concentration after adequate time to allow

**Figure 1.** Typical cyclic voltammograms of a polycrystalline gold electrode, which was immersed in a 100 µM AET ethanol solution for 3 h, at (a) 1st, (b) 2nd, (c) 3rd, (d) 4th, (e) 5th cycle, and of (f) a bare polycrystalline gold electrode in a 0.1 M potassium hydroxide solution. A typical base line to calculate \( \Gamma \) was shown as a curve g. Scan rate was 10 mV s\(^{-1}\).

**Figure 2.** Adsorption kinetics at (A) 5, (B) 10, (C) 20, (D) 35, (E) 50, and (F) 100 µM AET on a polycrystalline gold electrode in ethanol solution.
Table 1. Thermodynamic and kinetic parameters for AET from the analysis of Fig. 2.

| C_A (µM) | \( \Gamma_\ell (10^{-10} \text{mol cm}^{-2}) \) | k_f (10^2 \text{M}^{-1} \text{s}^{-1}) |
|----------|---------------------------------|-------------------------------|
| 5        | 4.0                             | 3.6                           |
| 10       | 4.9                             | 4.1                           |
| 20       | 5.1                             | 12                            |
| 35       | 5.4                             | 9.6                           |
| 50       | 5.2                             | 6.1                           |
| 100      | 4.8                             | 9.9                           |

Table 2. Diffusion coefficients (D) for AET from the analysis of Fig. 3. Values in parenthesis were calculated using the slopes of two points.

| C_A (µM) | D (10^{-6} \text{cm}^2 \text{s}^{-1}) |
|----------|-------------------------------------|
| 5        | 4                                   |
| 10       | 3                                   |
| 20       | (5)                                 |
| 35       | (2)                                 |
| 50       | (1)                                 |
| 100      | (0.5)                               |

Figure 3. Variation of normalized surface coverage \( (\Gamma_\ell / \Gamma_\ell^*) \) as function of \( t^{1/2} \) at (A) 5, (B) 10, (C) 20, (D) 35, (E) 50, and (F) 100 µM AET ethanol solution using the data in Fig. 2.

The time scale less than 1 min is too short to carry out CV measurements immediately after immersing the electrode in the solution. The values of D over the concentration range 20–50 µM appeared to be appropriate as species in aqueous solution. However, the value obtained at 100 µM is rather unphysical because that is 1 order of magnitude smaller than the typical value. Thus the kinetics of the adsorption might also be described by the diffusion control model over the concentration range 20–50 µM and by the kinetic control at 100 µM.

On the other hand, as mentioned above, a good correlation was evident between the experimental data and fitting with Eq. (6) at all concentrations examined (Fig. 2), indicating that the system would be under the kinetic control. Thus, in conclusion of the kinetics, at the present stage, the kinetics of adsorption were under the condition where the kinetic control and the diffusion control were balanced over the concentration range 5–50 µM, whereas it was described by the kinetic control model at 100 µM. Since it is difficult to differentiate between two models over the concentration range 5–50 µM, we need to investigate the details of each model more closely in future.

4.3 Thermodynamics of adsorption

The values of \( \Gamma_\ell \) calculated with Eq. (6) in the kinetics section of the adsorption are plotted in Fig. 4 against the concentration of AET in the solution. Before determining the Langmuir or Frumkin isotherm better describes this AET system, values for \( \Gamma_\ell \) and \( \beta \) must be determined. Those values were obtained using a least-square best fit of the experimental data to the Langmuir isotherm’s parameters. The curve A is the best fit of the experimental data to the Langmuir isotherm (Eq. (3)) with \( \Gamma_\ell^* \) and \( \beta \) as the adjustable parameters. The values of \( \Gamma_\ell \) and \( \beta \) were calculated to be \( 5.3 \times 10^{-10} \text{mol cm}^{-2} \) and \( 7.6 \times 10^3 \text{L mol}^{-1} \), respectively. It has been reported that for AET densely adsorbed on a single-crystalline Au(111) surface \( \Gamma \) was...
6.6 \times 10^{-10} \text{ mol cm}^{-2} \text{ and its SAM formed } (7 \times \sqrt{3}) \text{ structure.}^{20} 
The \Gamma_c \text{ in this study appeared to be smaller than that value.}^{20} \text{ Further, it has been reported that AET adsorbed on a silver surface can form}
trans conformer with a free amino group faced away or gauche conformer with the amino group close to the metal surface.\text{21} 
Therefore, it would be possible that AET adsorbed lying flat on a polycrystalline gold electrode. Another possibility is that the \Gamma_c \text{ differs depending on the crystallographic face of gold.}

The value of \beta \text{ was used to calculate the } \Delta G^\circ \text{ with Eq. (4). The calculated value of } \Delta G^\circ \text{ was } -41 \text{ kJ mol}^{-1}, \text{ which is larger than that}
for the adsorption of bist(2-hydroxyethyl) disulfide onto a polycrystalline gold electrode (\approx 38 \text{ kJ mol}^{-1}).\text{20} \text{ Therefore, it is}
suggested that AET strongly adsorbs onto a polycrystalline gold electrode.

The Frumkin isotherm (Eq. (5)) was calculated varying the g \text{ until a best fit to the experimental data was obtained (curve B in}
Fig. 4). The values used for \Gamma_c \text{ and } \beta \text{ were those obtained from the fit to the Langmuir isotherm (curve A in Fig. 4). The value of } g \text{ was found to be 0.03, suggesting the presence of a weak attractive}
interaction between the adsorbates molecules. Possible contribution to the attractive forces is the van der Waals interaction between the
adsorbed AET. However, since } g \text{ is negligibly small,\text{22} likely due to small alkyl chain length, we conclude that the adsorption of AET is}
well-described by the Langmuir isotherm.

5. Conclusions

This report investigates the reductive desorption of AET monolayers on a polycrystalline gold electrode. Three cathodic peaks were observed at \approx 0.63, -0.80, \text{ and } -1.0 \text{ V} \text{ and they were assigned to reductive desorption from each small domain of Au(111), (100), and (110) over the surface. Furthermore, it was also}
stable that the stabilities of AET monolayers formed on Au(111), (100), and (110) faces on the polycrystalline gold increases in the order of (111) < (100) < (110) faces. The adsorption kinetics of AET onto a polycrystalline gold electrode were likely under the
condition where the kinetic control and the diffusion control were balanced over the concentration range 5–50 \mu M \text{ of AET. On the}
other hand, the adsorption kinetic was described by the kinetic control model at 100 \mu M. The values of adsorption rate constant were 3.6 \times 10^{-2}–12 \times 10^{2} \text{ M}^{-1} \text{ s}^{-1}, \text{ indicating that the adsorption rate of AET on a polycrystalline gold electrode is not very fast probably}
because of the interaction between amino groups of AETs. The values of the equilibrium coverage increased with the bulk concentration of AET. The adsorption thermodynamics was represented by the Langmuir isotherm as the interaction parameter of the Frumkin isotherm was found to be 0.03, indicating small interaction between the adsorbate molecules. The saturation surface coverage was found to be 5.3 \times 10^{-10} \text{ mol cm}^{-2}, which suggested that AET adsorbed lying flat on a polycrystalline gold electrode. Another possibility is that the surface coverage differs depending on the crystallographic face of gold. The free energy of the adsorption was calculated to be } -41 \text{ kJ mol}^{-1}, \text{ indicating strongly adsorption force. In order to evaluate the adsorption characteristics of AET on each faces of polycrystalline gold electrode in detail, further work will include an investigation into the adsorption using single-crystalline gold electrodes.}

References

1. R. W. Murray, Molecular Design of Electrode Surfaces, John Wiley and Sons, New York, NY, (1992).
2. A. Ulman, Chem. Rev., 96, 1533 (1996).
3. S. Xu, S. J. N. Cruchon-Dupeyrat, J. C. Garno, G.-Y. Liu, G. K. Jennings, T.-H. Yong, and P. E. Laibinis, J. Chem. Phys., 108, 5002 (1998).
4. A. Chou, P. K. G. Eggers, M. N. Paddon-Row, and J. J. Gooding, J. Phys. Chem. C, 113, 3203 (2009).
5. C. Berggren, P. Stählsandke, J. Brunndell, and G. Johansson, Electroanal., 11, 156 (1999).
6. G. Mani, D. M. Johnson, D. Marton, M. D. Feldman, D. Patel, A. A. Ayon, and C. M. Agrawal, Biomaterials, 29, 4561 (2008).
7. E. H. Yu and K. Scott, Energies, 3, 23 (2010).
8. C. D. Bain, E. B. Troughton, Y.-T. Tao, J. Evall, G. M. Whitesides, and R. G. Nuzzo, J. Am. Chem. Soc., 131, 321 (1989).
9. N. Camillone, I. C. E. D. Chidsey, P. Eisenberger, P. Fenter, J. Li, K. S. Liang, G.-Y. Liu, and G. Scrocco, J. Phys. Chem., 99, 744 (1995).
10. N. Camillone, I. C. E. D. Chidsey, G.-Y. Liu, and G. Scrocco, J. Chem. Phys., 98, 4234 (1993).
11. C. A. Alves, E. L. Smith, and M. D. Porter, J. Am. Chem. Soc., 114, 1222 (1992).
12. K. Arihara, T. Ariga, N. Takashima, K. Arihara, T. Okajima, F. Kimamura, K. Tokuda, and T. Ohnaka, Phys. Chem. Chem. Phys., 5, 3758 (2003).
13. M. S. El-Deab and T. Ohnaka, Electrochim. Acta, 49, 2189 (2004).
14. T. Kakiuchi, H. Usui, D. Hobara, and M. Yamamoto, Langmuir, 18, 5231 (2002).
15. D.-F. Yang, C. P. Wilde, and M. Morin, Langmuir, 12, 6570 (1996).
16. T. Kakiuchi and D. Hobara, Bunseki Kagaku, 51, 1089 (2002). [in Japanese]
17. O. Dannenberger, M. Buck, and M. Grunze, J. Phys. Chem., 103, 2202 (1999).
18. F. Mukae, H. Takehara, and K. Takada, Bull. Chem. Soc. Jpn., 69, 2461 (1996).
19. N. Hisanumatu, T. Iida, T. Yasa, K. Takada, and A. Yuchi, Sens. Actuators, B, 203, 289 (2014).
20. M. Kawasaki, T. Sato, and T. Yoshimoto, Langmuir, 16, 5409 (2000).
21. S. Trasatti and O. A. Petriu, J. Electroanal. Chem., 327, 353 (1992).
22. J. D. Tirado, D. Acevedo, R. L. Bretz, and H. D. Abruña, Langmuir, 10, 1971 (1994).
23. D. Acevedo, R. L. Bretz, J. D. Tirado, and H. D. Abruña, Langmuir, 10, 1300 (1994).
24. K. Naito, H. Iezaki, T. Yasa, and K. Takada, J. Electrochem. Soc., 165, H455 (2018).
25. S. Trasatti, J. Electroanal. Chem., 53, 335 (1974).
26. J. O’M Bockris, A. K. N. Reddy, and M. Gamboa-Aldeco, Modern Electrochemistry Second Edition Fundamentals of Electrochemistry, Khawer Academic/ Plenum Publishers, New York, NY, p. 919 (2000).
27. W. H. Reinmuth, J. Phys. Chem., 50, 473 (1946).
28. C. L. Perdriel, A. J. Arvia, and M. Ipohorski, J. Electroanal. Chem., 215, 317 (1986).
29. L. L. Rouhana, M. D. Moussallem, and J. B. Schlenoff, J. Am. Chem. Soc., 133, 16080 (2011).
30. D. S. Karpovich and G. J. Blanchard, J. Electrochem. Soc., 131, 3758 (2003).
31. A. Kudelski and W. Hill, Langmuir, 15, 3162 (1999).
32. K. Takada, D. J. Díaz, H. D. Abruña, I. Cuadrado, C. Casado, B. Alonso, M. Morán, and J. Losada, J. Am. Chem. Soc., 119, 10763 (1997).