Electrochemical Detection of Manzeb Using Reductive Desorption from Au(111) and Au(100)

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ABSTRACT

Electrochemical detection of ethylenebis(dithiocarbamic acid) manganese zinc complex (Manzeb), a widely used insecticide, by reductive desorption from Au(111) and Au(100) has been studied. Dithiocarbamate groups containing adlayer were formed on gold single-crystal electrodes by immersing into a Manzeb aqueous solution. The electrochemical responses and the adsorption amounts were evaluated based on the reductive desorption of sulfur species from the gold surface in alkaline solution. The detection limit for Manzeb depended on the modification time and the crystallographic orientation of gold. The limits of detection were 500 nM and 100 nM when a Au(111) electrode and a Au(100) electrode were used, respectively. The surface-enhanced infrared absorption spectra of Manzeb on a Au thin film electrode in its monolayer state showed that Manzeb was adsorbed on the substrate via the dithiocarbamate moiety and the long axis of ethylenebis(dithiocarbamate) dianion was almost perpendicular to the surface.

Keywords : Au Single-crystal Electrode, Reductive Desorption, Ethylenebis(dithiocarbamate)

1. Introduction

Ethylene bisdithiocarbamates (EBDCs), such as Manzeb, Maneb, and Zineb (Fig. 1), are widely used in Japan and all over the world as insecticidal fungicides for vegetables and fruit trees because they are inexpensive and less phytotoxic. The amount of production and import per year for Manzeb, Maneb, and Zineb in our country are as high as 6,555, 1,046, and 416 ton, respectively.1 Since EBDCs are widely used in large amounts and there is wide interest in their existence and persistence in the environment, the necessity to investigate environmental pollution by EBDCs has been frequently pointed out. In addition, Manzeb, Maneb, and Zineb have been suspected of having endocrine disrupting action, which has increased the necessity of environmental monitoring.2

Since EBDCs are thermally unstable, gas chromatography (GC) or GC/mass spectroscopy (MS), widely used for monitoring trace chemical substances in the environment, cannot be used for their analysis. Therefore, some other methods have been developed, using its oxidation product,3,4 its methyl iodide derivative,5-7 and high-performance liquid chromatography (HPLC),8 however, these methods require special treatments for improving sensitivity.

Herein we report a new method for the electrochemical detection of Manzeb based on dithiocarbamates. It is well known that gold has strong interactions with thiol and/or disulfide groups. Therefore, dithiocarbamate compounds are expected to strongly adsorb onto a gold electrode surface, forming self-assembled monolayers (SAMs). SAMs have been studied for application in both fundamental surface chemistry9-14 and applied surface science.15,16 Particularly, the cyclic voltammogram of SAM-modified electrodes in alkaline solution shows a reductive desorption wave;17 thus, the reductive desorption method can be applied for electrochemical sensing.18-21 The surface concentration of the adsorbed molecules was quantified by measuring the charge consumed for the reduction of these molecules.

In this study, we used Au(111) and Au(100) electrodes. Au(111) is a commonly used substrate, and the resultant organic monolayers have been characterized. Au(100) shows a different atomic arrangement from Au(111), thus producing SAMs that are more stable toward electrochemical reductive desorption.22 Therefore, we prepared a Manzeb adlayer on Au(111) and Au(100) substrates, and compared the detection limit and adsorption properties of Manzeb using reductive desorption. The measurement process is quite simple: we can detect Manzeb by dipping the electrode into a test solution for 30 min and recording the voltammograms.

Figure 1. Chemical structures of (a) ethylenebis(dithiocarbamic acid) manganese zinc complex (Manzeb), (b) ethylenebis(dithiocarbamic acid) manganese complex (Maneb), and (c) ethylenebis(dithiocarbamic acid) zinc complex (Zineb).
2. Experimental

Manzeb was used as-received from Wako Pure Chemicals. All other chemicals are of G.R. grade and were used as received. All the solutions were prepared using ultrapure water purified by a Millipore Milli-Q (Advantage) system. Au(111) and Au(100) single-crystal electrodes were prepared from a high-purity Au wire of diameter 0.8 mm (99.999%; Tanaka Kikinzoku Kogyo K.K.) by Claviler’s method.21 Prior to each experiment, the single-crystal electrode was annealed for 30 s in a hydrogen flame and quenched in Milli-Q water saturated with hydrogen gas. The modified electrode was prepared by immersing a freshly annealed Au(100) or Au(111) single-crystal electrode in an aqueous or alkaline (1 mM KOH) Manzeb solution. The concentration of the modifier in the solution was varied from 0.01 µM to 50 µM, and the modification time was varied from 1 min to 3 h. The modified Au single-crystal electrode surface was thoroughly washed with Milli-Q water, and the electrode was finally transferred to the electrochemical cell. Electrochemical reductive desorption of the modifier from the single-crystal electrodes was carried out in 0.1 M KOH solution at a scan rate of 50 mV s⁻¹ at 25°C, using a 621E (ALS/HCI Instruments) electrochemical analyzer. A Pt wire was used as the counter electrode, and Ag/AgCl (sat. KCl) reference electrodes were used for linear sweep voltammetry (LSV) and cyclic voltammetry (CV) studies.

An Agilent Carry-600 FT-IR spectrometer equipped with an MCT detector and a single-reflection accessory was used to record the spectra. The spectrometer was operated in the rapid-scanning mode with a resolution of 4 cm⁻¹. Thin-film Au substrates for surface-enhanced infrared absorption spectroscopy (SEIRAS) were prepared according to reported procedures.22,23 The prepared Au film substrates are not single-crystal but polycrystalline in nature and have relatively strong enhancement factors for SEIRAS.

3. Results and Discussion

3.1 Reductive desorption of Manzeb adlayer from Au(111)

Figures 2(a-d) show the LSV profiles of a Manzeb-modified Au(111) electrode, prepared by immersing the bare electrode in 50 µM Manzeb solution containing 0.1 M KOH for 1, 3, 10, and 30 min, respectively, in a 0.1 M KOH solution. No increase in reduction current was observed for longer modification time, suggesting that Manzeb forms a monolayer on Au(111) under the immersion conditions. The reductive peak potential was observed at −0.92 V vs. Ag/AgCl (sat. KCl). Since no reductive wave was observed in the potential region for Mn²⁺ or Zn²⁺ solution (1 mM) containing 0.1 M KOH at a bare Au(111) electrode, this wave was attributed to the adsorbed Manzeb molecule. It was shown that Manzeb was detected with relatively high sensitivity by reductive desorption. The reduction peak current and the charge for reductive desorption depended on the immersion time and Manzeb concentration during treatment. In the second LSV scan of the Manzeb-modified electrode, the reduction peak corresponding to the Manzeb was not detected completely (data not shown), implying that the Manzeb adlayer can be electrochemically desorbed from the Au surface in an alkaline solution. Since the Manzeb molecule contains dithiocarbamate moieties, the reductive desorption probably requires two electrons per molecule, based on an assumption that one Manzeb molecule was adsorbed onto the Au(111) surface via two sulfur atoms and not four. The electronic charge consumed by the reductive desorption of Manzeb-modified electrode under the conditions shown in Fig. 2(d) in 0.1 M KOH solution was calculated to be 110 µC cm⁻² (obtained by integrating the reduction current of LSV over the potential range from −0.7 V to 1.05 V), leading to a surface excess of $(5.8 \pm 0.5) \times 10^{-10}$ mol cm⁻² if two-electron reduction takes place as per the following equation:

\[
\text{Manzeb-Au} + 2e^- → \text{Manzeb}^{2-} + \text{Au}
\]

As we have reported previously, the surface excess of pyridine ethanethiol (PyC₅S₂)-modified Au(111) was calculated to be $5.4 \times 10^{-10}$ mol cm⁻².24 Kakiuchi et al. reported the voltammetric properties of the reductive desorption of alkanethiol SAMs from a gold surface.26 The closely packed decanethiol SAM on Au(111) showed a very sharp desorption peak with a full-width at half-maximum (FWHM) of 20 mV. In this case, the reduction peak charge is greater than what is expected from the surface structure of the alkanethiol SAM on Au(111). Using a Padé approximant expression, combined with the semi-infinite linear diffusion of adsorbed species, they explained the discrepancy between the adsorbed amount of an alkanethiol calculated from the peak charge and the amount expected from the closely packed structure on Au(111) by the effect of the double-layer charging current. On the other hand, we have no information on the adlayer structure of Manzeb on Au(111), including whether the Manzeb forms highly ordered close-packed monolayer. Here, the cross-sectional area of Manzeb is almost equal to that of PyC₅S₂, assuming perpendicular orientation to the electrode surface of the dithiocarbamate group of Manzeb and the thiolate group of PyC₅S₂. Therefore, if the Manzeb molecules form a close-packed SAM on Au(111), the surface excesses of Manzeb and PyC₅S₂ should be almost equal, suggesting the formation of a closely packed Manzeb adlayer under these experimental conditions. The effect of double-layer charging current should be considered.26 However, the surface excess of Manzeb was obtained from the reduction peak charge assuming only two-electron reduction.

3.2 Reductive desorption of Manzeb-adlayer from Au(100)

Figures 3(a and b) show the LSV profiles of a Manzeb-modified Au(100) electrode prepared by immersing the bare electrode in 10 and 50 µM Manzeb solution, respectively, for 30 min in 0.1 M KOH solution. For the Manzeb adlayer on Au(111), only one reduction peak was observed for their LSV profiles, independent of the modifier concentration and modification time. In contrast to Au(111), depending on the concentration and modification time of the modifier, multiple reduction peaks were observed at −0.61, −0.80, −0.89, and −0.96 V for curve (a), and −0.63, −0.88, and −0.98 V for curve (b) vs. Ag/AgCl (sat. KCl) under the modification conditions. Thus far, the structural details of the Manzeb molecule on Au(100) have not been studied, but we speculate that the structure of the adsorbed Manzeb molecule on Au(100) is different from that on Au(111). Au(111) and Au(100) have hexagonal and square lattices, respectively. The distances

![Figure 2](image-url)
the Manzeb adlayer prepared under different conditions. Each point represented the averaged value obtained from results obtained from three repeated experiments. For the Au(111) electrode, the Manzeb adlayer showed only one reduction peak, from which the charge was calculated. On the other hand, since several reduction peaks were observed in the LSV profiles of the Manzeb adlayer on the Au(100) electrode, the charge used here was obtained from the sum of the charges calculated from the different peaks. The reductive charge increased upon increasing immersion time up to 30 min. Further increase in immersion time did not improve sensitivity. When the Au(111) electrode was immersed in 10 µM Manzeb aqueous solution, a clear reduction wave was observed; no reduction waves were observed for 1 µM Manzeb aqueous solution (Fig. 4(a)). On the other hand, when Manzeb was modified in an alkaline solution (0.1 M KOH), the detection limit reached 500 nM (Fig. 4(b)).

No reduction waves were observed upon immersing Au(100) electrode in 1 µM Manzeb aqueous solution for 30 min (Fig. 4(c)). The detection limit was improved by using an alkaline solution of Manzeb. It is thought that the anionic form of dithiocarbamic acid (RSS⁻) generated by alkaline hydrolysis of Manzeb adsorbs strongly to the electrode surface. The lowest detection limit with the Au(100) electrode was 100 nM of Manzeb, after 30 min immersion in an alkaline solution.

3.4 Adlayer structure of Manzeb

Vibrational spectroscopy was performed to confirm that Manzeb molecules orient vertically on the Au electrode. To elucidate the structure of the Manzeb monolayer or submonolayer on a single-crystal substrate, vibrational spectroscopy must be conducted using a single crystal as substrate. Thus far, to the best of our knowledge, it is very difficult to record infrared spectra of a submonolayer or a monolayer on a single-crystal substrate. Surface-enhanced infrared absorption spectroscopy (SEIRAS) can generate IR spectra of a monolayer or submonolayer on a substrate, although SEIRA-active substrate is required. The Au thin film electrode prepared herein is not a single crystal, but is SEIRA-active and rich in Au(111) surface. For the reductive desorption of Manzeb adlayer, there is almost no difference between the Au thin film and the Au(111) electrode. Therefore, we decided to use SEIRAS and a Au thin film electrode to investigate the structure of the Manzeb monolayer.

It is useful to refer to theoretical calculations for assigning IR spectra peaks to the normal vibration modes. In preliminary X-ray photoelectron spectroscopic measurements, metals like Mn and Zn were not detected, suggesting that the Manzeb was adsorbed on the Au(111) electrode as the dianionic form of ethylenebis(dithiocarbamate). Therefore, calculations were performed on the dianionic form of Manzeb. Density functional theory calculations were performed using Gaussian 09 with B3LYP/6-311G(d,p) basis set on a personal computer. After the dianion structure was optimized and checked, the frequencies were calculated. Table 1 shows the calculated frequencies and the assignments of the vibrational modes for the dianion obtained, without considering the interactions between the dianion and the substrate.

Figure 5(a) shows the FT-IR spectrum of Manzeb dispersed in KBr. Four sharp strong bands are observed at 1483, 1351, 1062, and 994 cm⁻¹, corresponding to the symmetric N–H bending associated with C–N stretching mode, the symmetric C–H bending mode, the N–H bending associated with C–H bending mode, and the asymmetric C–S stretching associated with N–H bending mode, respectively; these are in good agreement with the corresponding calculated frequencies of 1525.9, 1355.6, 1072.1, and 975.2.0 cm⁻¹ (Table 1).

Figure 5(b) shows the SEIRA spectrum of Manzeb adlayer on Au/mica substrate. This SEIRA spectrum was quite different from that obtained for Manzeb dispersed in KBr in the peak intensity ratios. A relatively strong band was observed at 1300–1500 cm⁻¹; however, the band around 1000 cm⁻¹ is quite weak. The direction of the vibrational modes of 1525.9 and 1355.9 cm⁻¹ (calculated wavenumber) are almost parallel to the long axis of the ethylenebis(dithiocarbamate) dianion shown in Fig. 6(a). On the other hand, those of 1072.1 and 975.2 cm⁻¹ are almost perpendicular to the long axis. These results strongly indicate that the ethylenebis(dithiocarbamate)···
calculations for ethylenebis(dithiocarbamate) dianion form.

Table 1. Vibration frequencies (cm⁻¹) obtained by Gaussian DFT calculations for ethylenebis(dithiocarbamate) dianion form.

| Mode number | Wavenumber /cm⁻¹ | Vibration mode                                                                 | Strength/A.U. |
|-------------|------------------|-------------------------------------------------------------------------------|---------------|
| 1           | 975.2            | Asymmetric C–S stretching associated with NH bending                          | 664.07        |
| 2           | 1072.1           | N–H bending associated with C–H bending                                      | 152.5         |
| 3           | 1261.1           | Asymmetric C–H bending associated with C–N stretching                          | 154.43        |
| 4           | 1310.3           | Symmetric C–H bending and N–H bending                                        | 231.7         |
| 5           | 1355.6           | Symmetric C–H bending                                                         | 77.55         |
| 6           | 1525.9           | Symmetric N–H bending associated with C–N stretching                          | 545.7         |
| 7           | 3070             | Asymmetric C–H stretching                                                     | 77.7          |
| 8           | 3622             | Asymmetric N–H stretching                                                     | 39.6          |

Figure 6. (a) Optimized model of ethylenebis(dithiocarbamate) dianion. Here, the direction of the arrow defined the long axis of the dianion. (b) Schematic illustration of ethylenebis(dithiocarbamate) dianion adlayer on Au(111) substrate. The ethylenebis(dithiocarbamate) dianion adsors on the substrate via the dithiocarbamate moiety.