Preparation of a New Self-assembled Polyamide Film Containing Disulfide Bonds on a Gold Surface

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1 INTRODUCTION

The self-assembly of organic molecules including sulfur atom, such as thiol, disulfide, on a gold surface is one of the attractive phenomena to prepare a monolayer film modified electrode¹⁾. This method is simple and alternative to Langmuir-Blodgett technique. Many investigations on basic characterization of the monolayer film modified electrodes and their applications have been reported²⁾. However, few polymeric analogs to modify a gold or other metal surfaces have been prepared³⁻⁵⁾. In this paper we report a preparation of a new polyamide that have disulfide bonds in its main chain, poly[imino(3,3'-dithiodipropionyl)-imino(2,2'-dithiodiethyl)], polyamide (I), (Scheme I). Furthermore, specific interaction between iodine and the polymer is also suggested by electrochemical and infrared measurements for the modified electrodes.

Scheme I. Structure of polyamide(I).

2 EXPERIMENTAL

Polyamide(I) was prepared by condensation of 3,3'-dithiodipropionic acid and cystamine with interfacial polymerization technique. The diacid was converted to the acid dichloride by heating for 90 min under reflux with excess thionyl chloride. The cystamine aqueous solution (24 mmol/100 ml) containing NaOH (96 mmol) was added to the acid dichloride/CCl₄ solution (24 mmol/100 ml). The polymer was purified by reprecipitation of polyamide(I)/formic acid solution from methanol (Total yield 73%). Structure of polyamide(I) was confirmed with IR, ¹H-, and ¹³C-NMR measure-

ments. IR(cm⁻¹)1644 (amide I), 1545.5 (amide II), ¹H NMR(δ, ppm) 3.91 (4H, -CH₂-CONH-), 3.11(8H, -CH₂-S), 2.99 (4H, -CH₂NHCO-), ¹³C NMR(δ, ppm) 179.2, 41.3, 41.1, 36.4, 32.9.

Hydroxymethylferrocene and N, N-dimethylaminomethylferrocene methiodide were prepared according to the literature⁶⁾.

Preparation of the polymer modified electrode was performed as in the following procedure: a gold sputtered glass plate (0.5 cm x 1.0 cm) was dipped into a 10 mmol dm⁻³ polyamide(I)/formic acid solution for 24 h at room temperature (20-25 °C) and washed with formic acid and water (purified by a Milli-Q purifying system) repeatedly. The modified electrode was used within 24 h after preparation. Electrochemical measurements were performed at 25 °C in a conventional three-electrode cell consisting of a working electrode (a gold sputtered glass plate or polymer modified electrode, surface area 0.5 cm²), a Pt electrode as the counter electrode (surface area 12.5 cm²), and a saturated calomel electrode (SCE) as the reference electrode. All solutions for electrochemical measurements were purged with Ar gas for 30 min prior to use.

3 RESULTS AND DISCUSSION

Modification of polyamide(I) on a gold substrate was confirmed by FTIR reflection adsorption spectroscopy (RAS). The peaks at 1644 and 1545.5 cm⁻¹ attributed to amide I and amide II band ⁷⁾ in the polyamide(I) were clearly observed in the RAS spectrum of the polyamide(I) modified electrode.

The cyclic voltammogram for polyamide (I) modified electrode in 0.2 mol dm⁻³ Na₂SO₄ aqueous solution showed the capacitive current and no obvious peaks in the range between -0.2 and 0.6 V. Furthermore the peak height and the shape of the cyclic voltammogram for polyamide(I) modified electrode in

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aqueous solution containing $0.2 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ and 1 mmol dm^{-3} hydroxymethylferrocene was similar to those for a bare electrode (observed redox response at 0.219 V and 0.160 V). Thus the polyamide(I) on the electrode did not prevent electron transfer between the electrode and the redox species in the bulk solution. It suggests that the coated film on the electrode is very thin. Figure 1 shows the cyclic voltammograms for a polyamide(I) modified electrode and a bare gold electrode in aqueous solution containing $0.2 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ and 1 mmol dm^{-3} N,N-dimethylaminomethylferrocene methiodide. In anodic scan the shape and the height of the peak in the voltammogram for the modified electrode are same as those for the bare electrode. In cathodic scan the bare electrode shows two peaks (P_{C1} at 0.430 V and P_{C2} at 0.360 V). The modified electrode shows two peaks (P_{C1} at 0.430 V and P_{C2}' at 0.385 V and one shoulder peak (P_{C3} about 0.360 V). According to the literature ^{8, 9}, P_{C1} corresponds to the reduction current of iodine produced by oxidation of iodide ion and P_{C2} and P_{C3} are attributed to the reduction of ferrocenium to ferrocene. Decrease of P_{C1} and increase of P_{C2}' are observed for the polyamide(I) modified electrode. The variation in the quantity of electricity for P_{C1} ($\Delta Q_{P_{C1}} = 176 \mu\text{C cm}^{-2}$) is nearly equal to that for P_{C2}' ($\Delta Q_{P_{C2}'} = 136 \mu\text{C cm}^{-2}$). It suggests that the reduction potential of iodine shifts more negative and overlaps the reduction peak of ferrocenium ion. The potential shift indicates the stabilization of iodine on the polyamide(I) modified electrode. Interaction between iodine and polyamide(I) is confirmed by the infrared spectrum of polyamide(I) treated with iodine vapor. The peak of amide I and amide II shifted to lower wavenumber, (amide I, from 1644 cm^{-1} to 1636 cm^{-1} , amide II, from 1545.5 cm^{-1} to 1538.8 cm^{-1}) after the iodine-dope treatment. This suggests the complex formation between polyamide(I) and iodine, $-\text{C}=\text{O}\cdots\text{I}_2$ and/or $\text{HN}\cdots\text{I}_2$. Formation of similar polyamide-iodine complex has been observed¹⁰). Therefore, P_{C2} is attributed to the reduction current of the iodine adsorbed by the polyamide(I) molecules on the electrode. Detail investigation of the modified electrode is now in progress.

Fig. 1 Cyclic voltammograms for a bare gold electrode (broken line) and polyamide(I) modified electrode (solid line) in aqueous solution containing $0.2 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ and 1 mmol dm^{-3} N,N-dimethylaminomethylferrocene methiodide. Scan rate 5 mV s^{-1} .

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