Communications

Electrocatalytic Behavior of Self-assembled Monolayer of a Novel Tetraazamacrocyclic Copper(II) Complex in Ascorbate Oxidation

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Self-assembled monolayers (SAMs)[1] of alkanethiols on gold have been used as a powerful method to prepare a chemical interface which is stable and structurally well-defined monolayer with a controllable thickness and desirable function. These characteristics of a SAM make them ideal model systems to study both fundamental and practical issues such as catalysis, electro-optic devices, sensors, corrosion, lubrication, adhesion, molecular recognition, and electron/energy transfer.[2,3] In particular, a SAM can offer specific properties and selectivity to the chemical interface if a terminal group of the SAM is redox active for the functions of the monolayer-modified electrode surface.

The transition metal complexes of macrocyclic ligands have been extensively investigated in solution because they are very useful in design and development for anion recognition recepter[4] as well as effective electrocatalyst.[5] In addition, they play an important role in biological process catalyzing the dismutation of a toxic superoxide radical (O_2^-) to hydrogen peroxide and water.[6] However, there have been only a few studies on the SAMs of transition metal-macrocyclic ligand complex. Ohsaka *et al.*[7] reported an electro-catalytic oxidation of hydrogen peroxide using SAM of Ni(II)-pentaazamacrocyclic complex on gold. Bilewitz and co-workers[8] studied the role of SAM of a Cu(II)-tetraaza-macrocyclic complex in ascorbate oxidation catalysis. With a view to developing new type of dismutase mimic and catalase active site containing transition metal ion, we have synthesized a novel tetraazamacrocyclic ligand **L** (shown in Figure 1) which can not only complex with a transition metal(II) ion in solution but also contains long alkylthiol as a head group for anchoring the electroactive macrocyclic complex to the gold electrode surface.

In this communication, we report elecctrocatalytic behavior of the SAM consisted of Cu(II) complex of the ligand **L** in oxidation of ascorbic acid. There are considerable interests for this type of copper(II) complexes because of development of an effective superoxide dismutase mimic and in their immobilization on electrode in order to obtain new catalytically active interface. First of all, the electroactive Cu(II) complex of **L** (abbreviated as CuL) has been easily

synthesized in situ by dropping 5 mM $CuCl_2$ methanol solution into 1 mM **L** in methanol. In order to find out the ratio of metal to ligand in the CuL complex formation reaction, the absorbance of CuL was monitored and the complex showed an absorbance maximum at 600 nm. In the spectroscopic titration, the absorbance was increased up to the equivalent point and then was not changed to the continuous addition of Cu(II) solution. We have observed the stoichiometric equivalents of Cu^{2+} cation and **L** at the equivalent point. This exactly indicates that Cu(II) complexes of 1 : 1 Cu(II) : **L** are produced in the titration reaction. In order to modify gold electrode with the SAM of CuL, a clean keyhole-shaped Au thin film electrode was immersed for 12 h in the methanolic mixture solution containing the same equivalents of $CuCl_2$ and **L** (1 mM) after the solution was stirred for a few minutes. As an alternative to prepare the SAM of CuL on gold, we have tried to make coordination of Cu^{2+} into the macrocyclic ring of **L** which has been already covalently immobilized onto the gold surface via Au-thiolate bond. From cyclic voltam-metric measurement, this method was found to be not effective to obtain a full coverage of Cu^{2+}-complexation at the interface of SAM of **L**. It might be due to compact two-
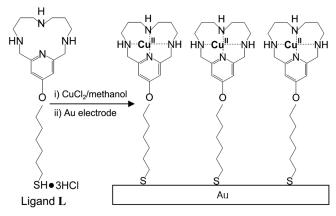

Figure 1. Molecular structure of the ligand **L** and formation of the electroactive self-assembled monolayer consisted of Cu(II) complex of **L** on Gold thin film electrode.
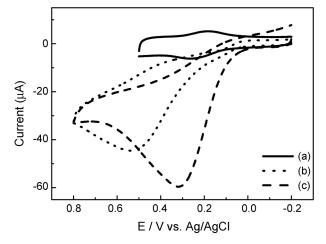
Figure 2. Typical cyclic voltammograms of (a) Au electrode modified with SAM of CuL complex in 0.1 M phosphate buffer (pH 7.01), (b) bare Au electrode and (c) Au electrode modified with SAM of CuL complex in 0.1 M phosphate buffer solution (pH 7.01) containing 1.0 mM ascorbic acid. All scan rates were 100 mV/s.

dimensional structure as well as hydrophobicity of the SAM. Figure 2a shows a typical cyclic voltammogram (CV) for the spontaneously adsorbed SAM of a novel CuL complex on gold electrode in 0.1 M phosphate buffer (pH 7.01). A pair of redox waves (ΔE_p = 68 mV) was observed corresponding to reversible reaction of $Cu^{2+/+}$ redox couple in the complex. As expected for the voltammetric behavior of the surface-attached redox centers,[9] the anodic and cathodic peak currents were linearly proportional to scan rate up to 0.5 $V \cdot s^{-1}$ and the current ratio was close to unity at the same scan rate (data not shown). To estimate the coverage of copper(II) redox centers on gold surface, the faradaic charges under the redox curve were integrated and averaged, and it gave surface coverage value of 1.64×10^{-10} mole cm^{-2} based on the surface roughness (*ca.* 1.4) of the gold substrate. This value is close to a full monolayer coverage of $1.41(\pm 0.02) \times 10^{-10}$ mole cm^{-2}, which was experimentally observed in the perpendicular orientation for SAM of Ni(II) tetraazamacrocyclic complex on gold electrode.[7] However, the assumption seems to be reasonable in that the ring size of CuL complex is slightly smaller than that of the Ni(II) complex. Figure 2b shows an irreversible oxidation curve observed at a bare Au electrode in 0.1 M phosphate buffer (pH 7.01) containing 1.0 mM ascorbic acid. However, the gold electrode modified with SAM of CuL presented the larger current due to the oxidation of ascorbic acid at the less positive potential of 0.31 V, shifted by 240 mV in the same solution (shown in Fig. 2c). These electrocatalytic characteristics can be explained by the electrostatic cooperativity of the positively charged CuL and the negatively charged ascorbate because ascorbic acid (pK_a = 4.17) is present in its anionic form at pH 7.01. Here, it is interesting to note that the peak potential of electrocatalytic maximum current (in Fig. 2c) is quite near the oxidation potential (in Fig. 2a) of CuL complex SAM on gold, an indicative of electron transfer mediation of the copper(II) complex. The reason for this phenomenon is based on the fact that the oxidation peak potential of

ascorbate at gold electrode modified with ligand **L** only is much more positive than that at bare Au electrode. At this time, the SAM of **L** on gold simply blocks electron transfer for oxidation of ascorbate ion. Currently, we are investigating the controllability of electrocatalytic behavior depending on pH, selective determination of dopamine in high concentration of ascorbic acid, and electrocatalysis of oxygen and hydrogen peroxide reduction on the electroactive SAM of CuL complex on gold.

Electrochemical measurements were carried out in a single compartment cell with Au thin film electrode as a working electrode, platinum counter electrode, and a Ag/AgCl (3 M KCl) as a reference electrode. Voltammetric experiments were performed with the use of a BAS 100B/W Potentiostat. The electrolyte solutions were prepared with deionized water purified to a resistivity of 18 MΩ/cm with a UHQ II system (Elga) and deaerated by purging with nitrogen gas. The Au thin film electrodes were prepared by sputtering Au target in the high vacuum (*ca.* 10^{-6} torr) onto microslide glass precoated with *ca.* 30 nm thick titanium film right below a mask of keyhole shape (diameter 5.0 mm, area 0.196 cm^2). The Au electrode was immersed for 30 s in a hot "pirhana" solution (3 : 1 mixture of concentrated H_2SO_4 and 30% H_2O_2). After copious rinsing with deionized water, the Au electrode was electrochemically cleaned by potential cycling in 0.5 M H_2SO_4 in the potential range of − 0.30 V and 1.5 V *vs.* Ag/AgCl(3 M KCl) until typical cyclic voltammogram of clean gold was obtained. After rinsing with deionized water, ethanol, and drying with nitrogen gas blowing, the thin film electrode was immersed in the ethanolic solution of 1 mM CuL complex for 12 h at room temperature. The complex solution was easily prepared in situ by dissolving each 1 equivalents of $CuCl_2$ and **L**, and 4 equivalents of triethylamine in ethanol.

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