—Communication—

Voltammetric Behavior of Self-assembled Monolayers of Novel Nickel (II/III) Pentaazamacrocyclic Complex on Gold Electrode and Electrocatalytic Oxidation of Hydrogen Peroxide

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1 INTRODUCTION

Surface-modified electrodes continue to be of interest for both fundamental and practical reasons¹⁾. Among the many different chemical strategies that could be used to prepare such modified electrodes, monolayer self-assembly method is a most promising tool for constructing stable, well-defined monolayers on electrode surfaces with atomic resolution²⁾. Reports on the monolayer-immobilization of several redox-active molecules on gold electrodes have appeared through this technique¹⁾. Tetraazamacrocyclic complexes of transition metals have been proved to be effective electrocatalysts in the reduction of carbon dioxide, nitrate, nitrous oxide, oxygen and oxidation of hydrogen peroxide, cystine, glucose etc³⁾. Especially the usually unstable oxidation states of transition metal ions (Ni(III), Ni(I), Co(III), Co(I), etc.) can be stabilized by complexing with polyazamacrocycles and the accession of those oxidation states can be modulated over a wide range³⁾. To introduce the monolayer of redox active nickel (II) complex on the electrode

surface, we newly synthesized a bispentaazamacrocyclic dinickel(II) complex, **1** (see Fig.1). The complex **1** was self-assembled with a coadsorbate, diphenyl disulfide, onto the gold electrode. In this short communication, we report the cyclic voltammetry of the self-assembly of **1** and its electrocatalytic activity towards hydrogen peroxide oxidation.

2 EXPERIMENTAL

The gold electrodes were prepared by sealing an annealed 1.0 mm diameter gold wire in an insulating poly(chlorotrifluoroethylene). After polishing the exposed gold surface with alumina powder (1.0 and 0.06 μ m), the electrodes were briefly etched in a 1:3:4 (in volume) mixture of conc. HNO₃/conc. HCl/water prior to immersion in a methanol solution containing a mixture of 0.15 mM complex **1** and 0.03 mM diphenyl disulfide. Electrodes were remained in the coating solution for at least 15 h and rinsed with methanol and water. Electrochemical measurements were performed in a two-compartment three-electrode cell, using a computer-controlled electrochemical measuring system (BAS, 100B/W). An NaCl saturated Ag/AgCl electrode was used as the reference electrode and a platinum wire as the counter electrode.

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Fig. 1 Typical cyclic voltammograms of the self-assembly of **1** on gold electrode in 0.1 M solution of H_2SO_4 (—) and HNO_3 (---). Potential scan rate: 500 mV s^{-1} .

3 RESULTS AND DISCUSSION

3.1 Electrochemistry of the self-assembly of **1**

Figure 1 shows the cyclic voltammograms of the self-assembly of **1** observed in 0.1 M aqueous solutions of H_2SO_4 and HNO_3 . In both the supporting electrolyte solutions, the cyclic voltammetric behavior is clearly that of a surface-confined species undergoing reversible oxidation-reduction, as indicated by the symmetrical and reversible redox waves and small peak splitting ($\Delta E_p < 20 \text{ mV}$) between the anodic and cathodic peak potentials. The anodic and cathodic peak currents (i_p^a and i_p^c) are proportional to potential scan rate ranging from 0.1 to 2 Vs^{-1} and the ratio of i_p^a to i_p^c at a given scan rate is unity. Integration of the current peak yielded $6.9 \times 10^{-11} \text{ mol cm}^{-2}$ as the surface coverage of the electroactive nickel complex, indicating that the distance between two nickel centers is ca. $16 \text{ \AA}$. The formal potential E^0 (estimated as the average of the anodic and cathodic peak potentials) for the redox reaction of the immobilized nickel

Fig. 2 Cyclic voltammograms of the self-assembly of **1** (a, a', b, b') and bare gold electrode (c, c') in the presence (b, b', c, c') and absence (a, a') of $10 \text{ mM H}_2\text{O}_2$. Electrolyte: $0.1 \text{ M Na}_2\text{SO}_4$ (pH 3)(a, b, c); 0.1 M NaNO_3 (pH 3)(a', b', c'). Potential scan rate: 500 mV s^{-1} (a, b, c); 100 mV s^{-1} (a', b', c'). S: $0.4 \text{ } \mu\text{A}$ (a, b, c); $0.25 \text{ } \mu\text{A}$ (a'); $1 \text{ } \mu\text{A}$ (b', c').

complex is more positive (0.84 V) in 0.1 M HNO_3 than that (0.60 V) in $0.1 \text{ M H}_2\text{SO}_4$. The change of the formal potential was reversible when the self-assembly electrode was moved between H_2SO_4 and HNO_3 environments. The observed trend of anion-controlled shift in the formal potential of Ni(II/III) redox couple may be due to the difference in coordinating tendency of SO_4^{2-} and NO_3^- anions⁴⁾, i.e., the oxidation of Ni(II) to Ni(III) is more favourable in H_2SO_4 than in HNO_3 .

3.2 Electrocatalytic oxidation of H_2O_2

The electrocatalytic activity of the self-assembly towards the oxidation of H_2O_2 was investigated. Figure 2 shows the cyclic voltammograms of the self-assembly in an aqueous 0.1

M NaNO_3 (pH = 3) solution in the presence and absence of 10 mM H_2O_2 . In the presence of H_2O_2 , an enormous increase in the anodic peak current was observed with the disappearance of the cathodic peak (Fig. 2b'). The coincidence of the oxidation of H_2O_2 with that of the Ni(II) complex as well as the disappearance of the Ni (III) reduction peak clearly indicate that the electrooxidized Ni(III) complex participates directly in the electrocatalytic oxidation of H_2O_2 . At a bare gold electrode the oxidation peak of H_2O_2 could not be observed when probed in the same potential region (Fig.2c'). Similarly the oxidation of H_2O_2 at the self-assembly electrode was pursued in an aqueous 0.1 M Na_2SO_4 (pH = 3) solution with or without H_2O_2 (Fig. 2). In the presence of H_2O_2 , the cyclic voltammogram at the self- assembly electrode (Fig. 2b) resembles that observed at a bare gold electrode (Fig. 2c), except that a capacitive current is largely decreased at the former electrode. Thus, no electrocatalysis of the self- assembly of **1** for H_2O_2 oxidation was actually observed in Na_2SO_4 solution.

In conclusion, we can demonstrate that the formal potential of the self-assembly of **1** and its electrocatalytic activity for the oxidation of H_2O_2 greatly depend on the supporting electrolyte anion.

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