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Study of orientation mode of cobalt-porphyrin on the surface of gold electrode by electrocatalytic dioxygen reduction

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Abstract

Three orientation modes of self-assembled monolayers (SAMs) of cobalt-porphyrins on the surface of gold electrode have been prepared and tested in the electroreduction of dioxygen, such as cobalt-5-(4-aminophenyl)-10,15,20-triphenylporphyrin binding covalently to 3-mercaptopropionic acid pre-assembled on gold (Co-ATP-MPA); cobalt-tetra-[*p*-(3-mercaptopropyloxy)-phenyl]-porphyrin (Co-TMPP) and cobalt-tetraphenyl-porphyrin axially attached with 4-mercaptopyridine SAMs pre-assembled on gold (Co-TPP-4MPY). A cyclic voltammetric investigation was carried out in an attempt to elucidate the net reaction to the dioxygen reduction. These modes were all active in electrocatalytic reduction of dioxygen through a two-electron mechanism with hydrogen peroxide produced. By combining imidazole axial with Co-TPP and the above cobalt-porphyrin SAMs and together with by testing the multilayer cobalt-porphyrin films by reduction dioxygen, the study confirmed that the electrocatalytic properties of metalloporphyrin was directly related with the structure or orientation of porphyrin ring on the surface of the electrodes.

Keywords: Cobalt-porphyrins; Orientation mode on the gold surface; Self-assembled monolayers (SAMs); Electrocatalytic dioxygen reduction

1. Introduction

Based on remarkable progress in the study of the self-assembled monolayers (SAMs) of thiol, researchers are able to design and control electrode surface [1]. One of the most attractive applications of such surface would be its utilization as a model electrocatalyst because the true correlation between the surface structure and the electrocatalytic activity can be obtained only when the surface structure is well controlled. Among the many possible candidates for the electrocatalytical active center, porphyrin is the most attractive because of its well-known functions in biological and biomimetic systems [2]. From a structural viewpoint, the porphyrin is of particular interest because the orientation of the porphyrin ring can be controlled. For example, using the monothiolated and multithiolated porphyrins, perpendicularly and coplanarly oriented porphyrin monolayers can be constructed respectively.

Within the field of the self-assembled monolayers the most widely studied system is the chemisorption of thiols onto gold surfaces [3]. However, the direct immobilization of thiol terminated metalloporphyrin might bring some disadvantages. It has been reported [4] that the thiol can coordinate the central metal ion of the porphyrin, resulting in multilayer formation as well as blocking of the catalytic centre. Such coordination seems to be one of the reasons why the metal ions more commonly used in metalloporphyrins SAMs are the less coordinative. To solve this problem, several strategies have been reported for the preparation of metalloporphyrins, which involving more than one steps: (i) insertion of different metal ions into thiol-derivatised free-base porphyrin monolayers pre-assembled on gold [5]; (ii) preparation of SAMs containing imidazole-terminated adsorbates which are shown to bind covalently to a series of metalloporphyrins [6]; (iii) covalent attachment of metalloporphyrins to dimercaptoalkane-modified gold electrodes [7] and formation of a pyridinethiol SAMs followed by axial attachment of the metalloporphyrin [8–10].

In this paper, we have embarked on a program to explore porphyrin architectures in which the molecules oriented on the surface of the electrodes by electrochemistry were used. Three orientation of self-assembled monolayers of cobalt-porphyrins on the surface of gold electrodes have been tested in the electroreduction of dioxygen, such as cobalt-5-(4-aminophenyl)-

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10,15,20-triphenylporphyrin (Co-ATP) binding covalently to 3-mercaptopropionic acid pre-assembled on gold (Co-ATP-MPA); cobalt-tetra-[*p*-(3-mercaptopropyloxy)-phenyl]-porphyrin (Co-TMPP) and cobalt-tetraphenyl-porphyrin (Co-TPP) axial attached with 4-mercaptopyridine SAMs pre-assembled on gold (Co-TPP-4MPY).

2. Experimental

2.1. Chemicals

The synthesis of 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (ATP) and cobalt-5-(4-aminophenyl)-10,15,20-triphenylporphyrin (Co-ATP) were described in the previous literature [11,12] and the synthesis of tetra-[*p*-(3-mercaptopropyloxy)-phenyl]-porphyrin (TMPP) was described as well [13]. Tetraphenyl-porphyrin (H_2TPP) and cobalt-tetraphenyl-porphyrin (Co-TPP) were prepared following the same procedure previously described [14]. 4-Mercaptopyridine (4MPY) and 3-mercaptopropionic acid (MPA) were obtained from Fluka. While 1-ethyl-3-(3-dimethylamino-propyl)-carbodiimide (EDAC) and *N*-hydroxysuccinimide (NHS) were obtained from Sigma. Ethanol, chloroform, and other organic solvents used were spectroscopic grade. Water was dually distilled from an all-quartz still and nitrogen and oxygen of high purity were used for deaeration or aeration.

2.2. Preparation of substrates

Before each experiment, the surface of the gold electrode was first polished with alumina powder (diameter, 0.3 and 0.05 μm) and rinsed with pure water. Then this electrode was immersed for 3 min 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 −0.1 and 1.5 V versus Ag/AgCl until typical cyclic voltammogram of clean gold was obtained. Roughness factor for these Au electrodes was measured to be in the 1.13 ± 0.2 range and actual areas were obtained from the slope of the linear plot of cathodic current versus (scan rate)$^{1/2}$ for the reversible redox of $Fe(CN)_6^{3-/4-}$. After having been rinsed with distilled water and ethanol and having been dried, the electrode was begun to be modified.

2.3. Formation of a SAMs of 4-mercaptopyridine on gold and preparation of cobalt-porphyrin (Co-TPP-4MPY) thin films by axial coordination

Treated gold electrode was immersed into an ethanol solution of 4-mercaptopyridine (10 mM) for 12 h. The prepared mercaptopyridine SAMs on gold underwent 3 min sonication in ethanol before being used for reacting with the Co-TPP solution. Ligation of Co-TPP with the pyridine SAMs on gold was achieved by immersing the 4-mercaptopyridine SAMs on gold into a chloroform solution of Co-TPP (1 mM) for 72 h (Scheme 1A).

2.4. Preparation of cobalt-porphyrin (Co-ATP-MPA) thin films

The gold electrode were immersed immediately in a 10 mM solution of MPA in ethanol for 12 h. After being assembled, the electrodes were thoroughly rinsed with ethanol and water and dipped either in a 1 mg mL^{-1} EDAC–1 mg mL^{-1} NHS solution in 0.1 M PBS (pH 7.0) for 12 h, or a 1 mM Co(II)-5-(4-aminophenyl)-10,15,20-triphenylporphyrin in chloroform for about 12 h at 4 °C (Scheme 1B).

2.5. Preparation of cobalt-tetra-[p-(3-mercaptopropyloxy)-phenyl]-porphyrin (Co-TMPP) thin films

The bare gold electrode was immersed in a 1 mM chloroform solution of tetra-[*p*-(3-mercaptopropyloxy)-phenyl]-porphyrin (TMPP) for 48 h. Then, the modified electrode was removed from the solution and rinsed with chloroform and absolute ethanol and dried with high purity nitrogen for insertion of cobalt(II) ions into thiol-derivatised free-base porphyrin monolayers pre-assembled on gold [6] (Scheme 1C).

2.6. Preparation of cobalt-porphyrin films via axial attached Co-TPP with imidazole on the metalloporphyrin modified electrodes

The above cobalt-porphyrin modified electrodes were all rinsed thoroughly with chloroform, then immersed in an ethanol solution of imidazole (10 mM) for 24 h and 1 mM chloroform solution of Co-TPP for 48 h. The samples named CoTPP-Im-CoTPP-4MPY/SAMs, CoTPP-Im-CoTMPP/SAMs and Im-Co-ATP-MPA/SAMs were rinsed with chloroform, then ultrasonically treated in chloroform for 3 min. The freshly prepared samples were immediately used for electrochemical measurements.

2.7. Electrochemistry measurements

All electrochemical measurements were performed with a CH Instruments Electrochemical Workstation (CHI832, USA), using Ag/AgCl as the reference electrode, a platinum wire as the counter electrode, and the cobalt-porphyrin modified electrodes or bare gold electrode as the working electrode.

3. Results and discussion

3.1. Characterization of the cobalt-porphyrin monolayers

Cyclic voltammograms of the cobalt-porphyrin saturation-coverage SAMs were presented in Fig. 1, which was recorded in organic media (0.1 M *n*-Bu_4NPF_6/CH_2Cl_2) at 50 mV s^{-1}. The two observable redox processes, with oxidation peaks at 0.55 and 1.10 V and corresponding reduction ones at 0.35 and 0.96 V for Co-TPP-4MPY/SAMs (Fig. 1A), respectively. Only one pair of redox peak was at 0.84 and 1.02 V for Co-TMPP/SAMs (Fig. 1B) and 0.88, 1.05 V for Co-ATP-MPA/SAMs (not shown). These were all assigned to the redox of porphyrin core [3,15,16].