

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-mercaptopropoxy)-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.

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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 electrocatalytic 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-mercaptopropoxy)-phenyl]-porphyrin (Co-TMPP) and cobalt-tetraphenylporphyrin (Co-TPP) axial attached with 4-mercaptopyrindine 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-mercaptopropoxy)-phenyl]-porphyrin (TMPP) was described as well [13]. Tetraphenylporphyrin (H₂TPP) and cobalt-tetraphenylporphyrin (Co-TPP) were prepared following the same procedure previously described [14]. 4-Mercaptopyrindine (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 H₂SO₄ and 30% H₂O₂). After copious rinsing with deionized water, the Au electrode was electrochemically cleaned by potential cycling in 0.5 M H₂SO₄ 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-mercaptopyrindine 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-mercaptopyrindine (10 mM) for 12 h. The prepared mercaptopyrindine 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-mercaptopyrindine 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-mercaptopropoxy)-phenyl]-porphyrin (Co-TMPP) thin films

The bare gold electrode was immersed in a 1 mM chloroform solution of tetra-*[p*-(3-mercaptopropoxy)-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.

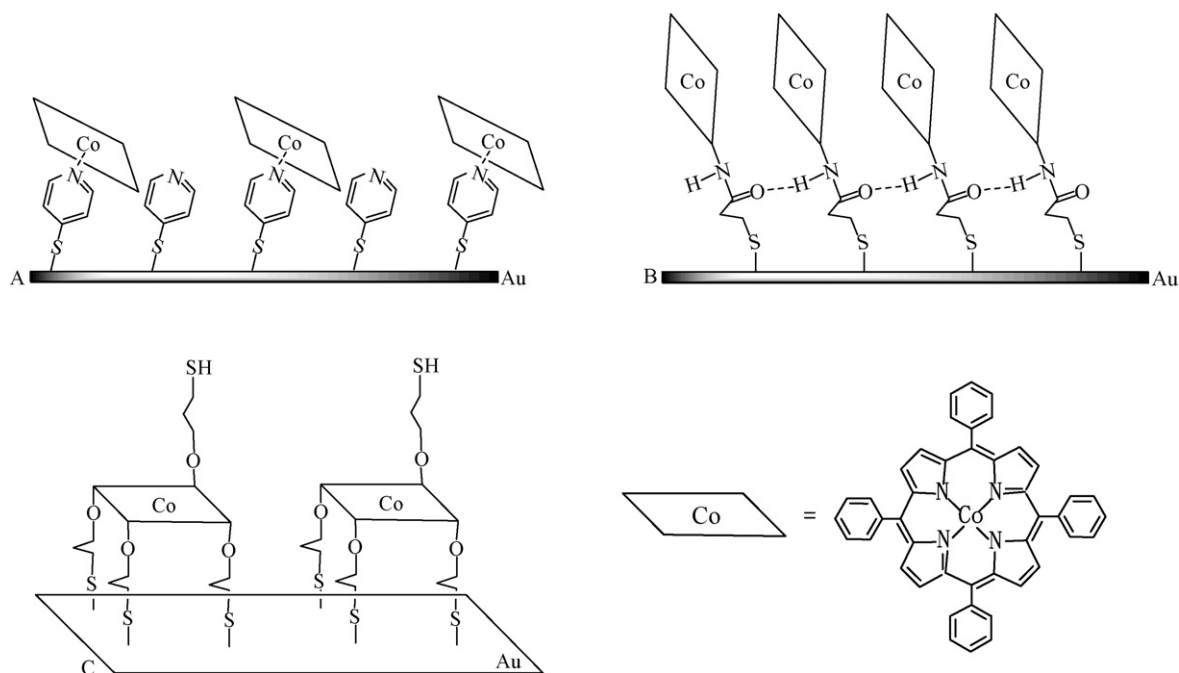
2.7. Electrochemistry measurements

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*-Bu₄NPF₆/CH₂Cl₂) 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].



Scheme 1. (A–C) The structure of three cobalt-porphyrin SAMs on the surface of gold electrode.

Fig. 2A showed a cyclic voltammogram of the Co-TPP-4MPY/SAMs in 0.1 M $n\text{-Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ at 50 mV s^{-1} where it was possible to observe a redox peak at 0.18 and 0.26 V that was assigned to the couple Co(III)/Co(II). We also observed the couple Co(III)/Co(II) at 0.14 and 0.24 V for Co-ATP-MPA/SAMs to catalyze dioxigen reduction in neutro solution

(0.1 M PBS, pH 7.0) (Fig. 2B). But, we could not observe the couple Co(III)/Co(II) of on the Co-TMPP/SAMs either in organic or in aqueous solution.

The presence of voltammetric peaks of the modified electrodes in Figs. 1 and 2, confirmed the immobilization of the

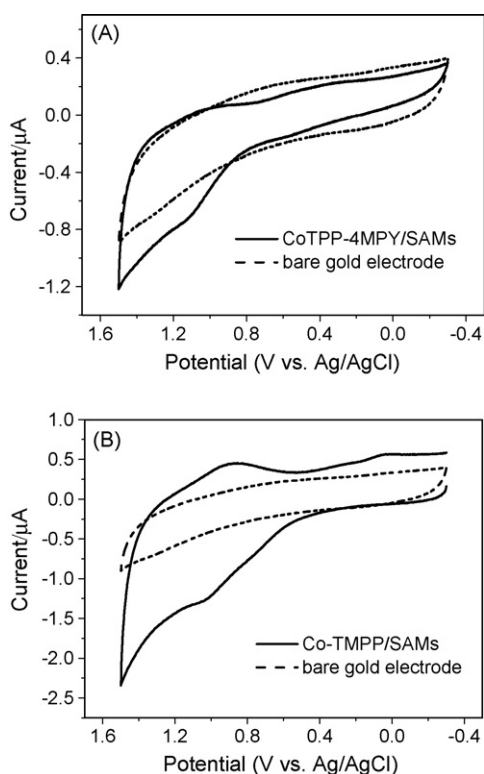


Fig. 1. Cyclic voltammograms of (A) bare gold and Co-TPP-4MPY/SAMs; (B) bare gold and Co-TMPP/SAMs in 0.1 M $\text{Bu}_4\text{NBF}_6/\text{CH}_2\text{Cl}_2$, 50 mV s^{-1} .

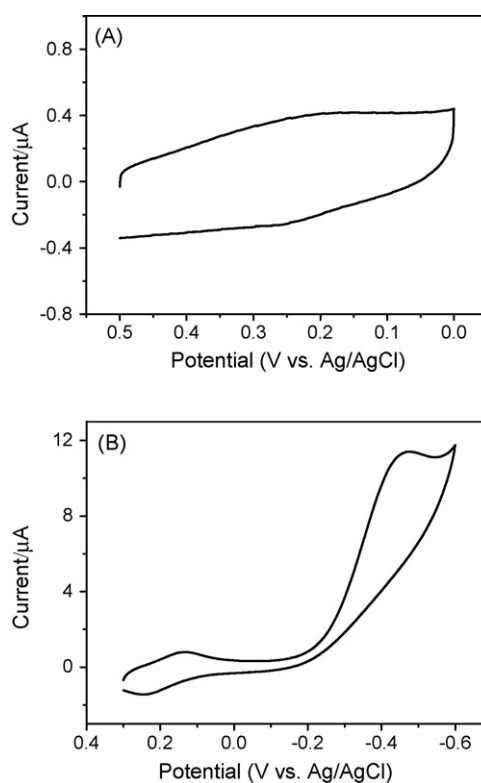


Fig. 2. Cyclic voltammograms of (A) Co-TPP-4MPY/SAMs in 0.1 M $\text{Bu}_4\text{NBF}_6/\text{CH}_2\text{Cl}_2$, 50 mV s^{-1} ; (B) Co-ATP-MPA/SAMs in 0.1 M PBS (0.1 M KCl, pH 7.0), 50 mV s^{-1} .

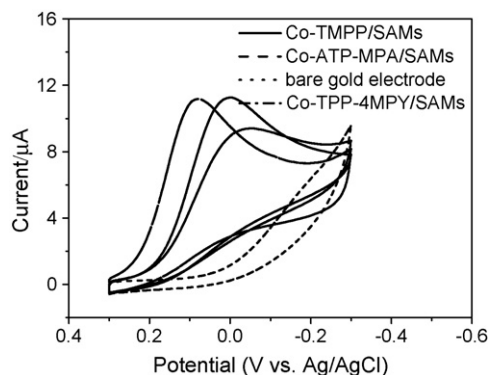


Fig. 3. Cyclic voltammograms in dioxygen-saturated 1 M HClO₄ for the reduction of molecular oxygen on various cobalt-porphyrin monolayers. 50 mV s⁻¹, initial potential +0.3 V.

cobalt-porphyrins. However, the peaks definition was not good enough to evaluate the electrode coverage by the passing charge during the potential scan. It was reported that the redox behavior of the metalloporphyrin itself in a monolayer usually gave unclear peaks in the cyclic voltammogram [3,17]. Moreover, published results of a series of free-base tetraphenylporphyrin SAMs [15] indicated that the oxidation processes of the porphyrin centre were too irreversible and ill-defined to estimate the surface coverage. The direct detection of the cobalt centre through its redox process was not possible to make either in organic or in aqueous solution.

As it was widely documented, alkythiol and disulphide SAMs could be reductively stripped from gold, in strong alkaline media and through the disruption of the S–Au bond. So, in this paper we could estimate the surface coverage of various porphyrins SAMs using a method reported by Weisshaar et al. [18]. Based on the relation $Q = nFA\Gamma$ (where Q is the total charge (C), A the electrode surface area (cm²), Γ the surface coverage (mol cm⁻²), n and F have their usual electrochemical meaning), the charge under a desorption wave was then used to provide a measure of the surface coverage of various porphyrins. The Γ values were 9.25×10^{-11} mol cm⁻² for Co-TMPP/SAMs, 3.10×10^{-10} mol cm⁻² for Co-ATP-MPA/SAMs and 6.15×10^{-11} mol cm⁻² for Co-TPP-4MPY/SAMs, which were consistent with those of the similar porphyrin SAMs reported previously [19–23].

3.2. Electrocatalytic reduction of dioxygen

3.2.1. Electrocatalytic reduction of dioxygen by cobalt-porphyrin self-assembled monolayer films

All of the cobalt-porphyrin monolayers prepared in this study were tested for the reduction of molecular oxygen. Compared with the bare Au electrode, the positive shift in the peak potential of the dioxygen reduction wave for the cobalt-porphyrin coated electrodes indicated that molecular films of cobalt-porphyrin catalyzed the reduction of dioxygen when in contact with 1 M HClO₄. The typical cyclic voltammograms taken in the oxygen saturated 1 M HClO₄ solution were shown in Fig. 3. As expected, the currents were higher when scan rate was increased and the peak shifted to more negative potentials and the peak cur-

rents increased linearly with the square root of the scan rate for the cobalt-porphyrin monolayers. The study suggested that the electrocatalytic processes were controlled by molecular oxygen diffusion in modified electrode [24]. For a typical irreversible reaction, the relationship between peak current and scan rate was as follows [12,25,26]:

$$i_p = 0.4958nFAC_0 \left(\frac{\alpha n_\alpha F}{RT} \right)^{1/2} \nu^{1/2} D_0^{1/2} \quad (1)$$

$$\Delta E_p = \frac{1.15RT}{\alpha n_\alpha F} \quad (2)$$

where n is the number of electrons transferred, A the surface area of the electrode (a surface area of 0.0355 cm² was employed), D_0 and C_0 the oxygen diffusion coefficient and the bulk concentration, respectively, ν the scan rate in V s⁻¹, α the transfer coefficient, n_α the apparent number of electrons transferred in the rate-determining step and ΔE_p is the peak potential change when the scan rate increases 10-fold. Other symbols have their usual significance. In the oxygen-saturated solution, $C_0 = 1.2$ mM and $D_0 = 1.7 \times 10^{-5}$ cm² s⁻¹, $D_0^{1/2}C_0$ was calculated as 4.95×10^{-9} mol^{-1/2} cm⁻² in the present experiment. The representative relationship between the scan rate and the reduction potential E_p was shown in Fig. 4 for Co-TPP-4MPY/SAMs. The potential shifts ΔE_p were determined to be 78, 75 and 55 mV for Co-TPP-4MPY, Co-TMPP and Co-ATP-MPA, respectively. The values of αn_α were calculated from Eq. (2), and replacing these values in Eq. (1), the number of electrons n for the reduction dioxygen could be calculated as 1.9 for Co-TPP-4MPY, 1.8 for Co-TMPP and 1.5 for Co-ATP-MPA. These facts concluded that under the catalysis of these single heterogenised metalloporphyrins, dioxygen, which reached the electrode by diffusion was mainly reduced through a two-electron process to H₂O₂. A catalytic mechanism of the electroreduction of dioxygen by cobalt-porphyrin SAMs was given in reaction [27]:

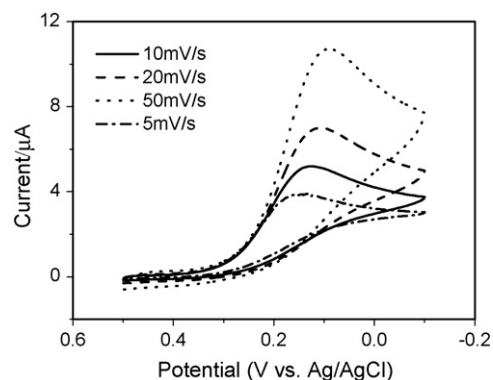
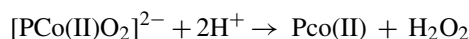
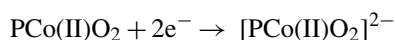
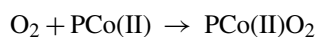


Fig. 4. Changes of i and E_p with the scan rate for the reduction of dioxygen on Co-TPP-4MPY/SAMs modified electrode with dioxygen-saturated 1 M HClO₄.

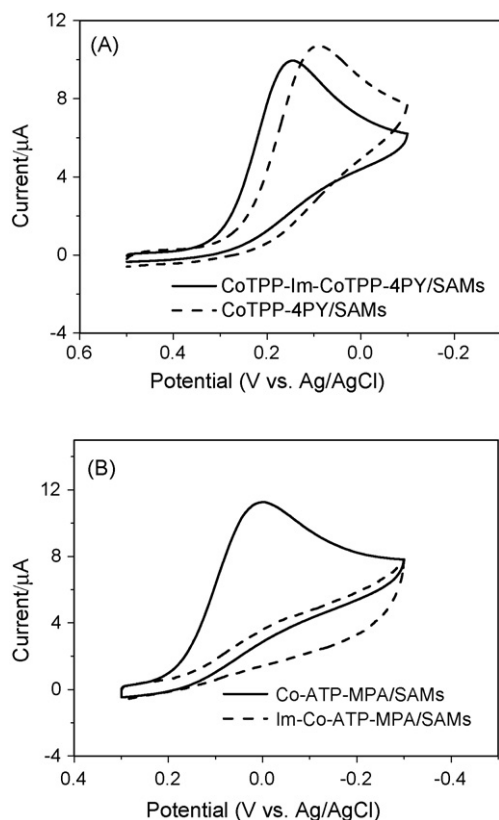


Fig. 5. Cyclic voltammograms in dioxygen-saturated 1 M HClO₄ for the reduction of molecular oxygen on (A) CoTPP-Im-CoTPP-4MPY/SAMs and Co-TPP-4MPY/SAMs; (B) Im-Co-ATP-MPA/SAMs and Co-ATP-MPA/SAMs. 50 mV s⁻¹.

3.2.2. Electrocatalytic reduction of dioxygen by cobalt-porphyrin self-assembled multilayer films

All of the cobalt-porphyrin films via axial attached Co-TPP to imidazole were also tested for the reduction of molecular oxygen and compared with the above three cobalt-porphyrin monolayer films. Further positive shift (Fig. 5A) in the peak potential of the dioxygen reduction wave for the CoTPP-Im-CoTPP-4MPY/SAMs, compared to the Co-TPP-4MPY/SAMs indicated that the catalytic molecular oxygen reduction ability of CoTPP-Im-CoTPP-4MPY films was higher. The peak potential position of CoTPP-Im-CoTPP/SAMs did not change compared with CoTPP/SAMs (not shown). But from Fig. 5B, it was shown that Im-Co-ATP-MPA/SAMs could not catalyze dioxygen reduction compared with Co-ATP-MPA/SAMs effectively. The representative relationship between the scan rate and the reduction potential E_p for CoTPP-Im-CoTPP-4MPY films was shown in Fig. 6 and based on the Eq. (1) and (2), we could calculate the number of electrons n for the reduction molecular oxygen as 2.8 for CoTPP-Im-CoTPP-4MPY/SAMs and 1.9 for CoTPP-Im-CoTPP/SAMs in 1 M HClO₄. The fact revealed that under the catalysis of CoTPP-Im-CoTPP-4MPY/SAMs, dioxygen reaching the electrode by diffusion was mainly reduced through two-electron and four-electron process to H₂O₂ and H₂O. The catalytic mechanism of the electroreduction of dioxygen by CoTPP-Im-CoTPP-4MPY/SAMs was also

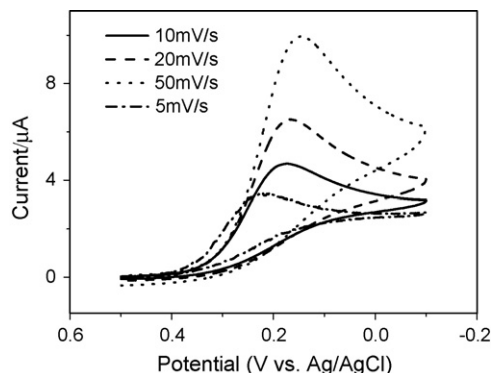
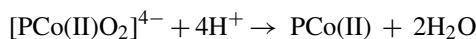
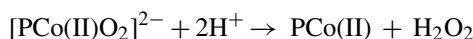
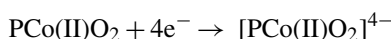
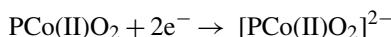
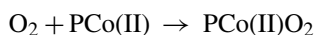


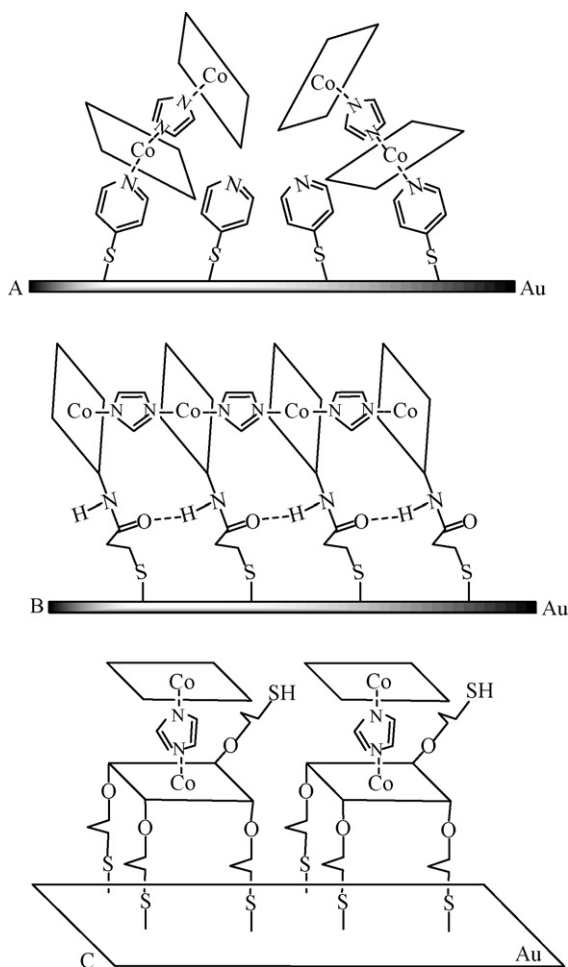
Fig. 6. Changes of i and E_p with the scan rate for the reduction of dioxygen on CoTPP-Im-CoTPP-4MPY/SAMs modified electrode with dioxygen-saturated 1 M HClO₄.

given in reaction [27]:



3.3. The orientation mode of the cobalt-porphyrins on the surface of gold

It has been shown [4,6] that catalytic activity of metal-porphyrin modified electrodes depended on the orientation of the molecules on the surface. Such structural control has been addressed in several papers in which the construction of monothiolated and tetrathiolated SAMs apparently resulted in perpendicular and coplanar orientation [6,22]. In fact, all forms of cobalt-porphyrin SAMs binding and catalyzing dioxygen reduction on gold were used in this study. Compared with the other two cobalt-porphyrin modified electrode films, Co-TPP-4MPY/SAMs was more effective and the catalytic efficiency for oxygen was higher ($n = 1.9$). There was no doubt that the orientation of porphyrin molecules was largely dependent on that of the pyridine molecule to the Au surface, namely, on the position of the nitrogen atom of the pyridine that coordinates to the central metal Co of the porphyrin core. The orientation of the pyridine ring with respect to the electrode surface reported by different research groups, however, was not unambiguous. Taniguchi et al. [28], based on their STM observation of 4-mercaptopyridine SAMs on Au(1 1 1), proposed that the pyridine ring was oriented almost vertical to the gold surface, and the molecular axis through the N and S atoms was normally tilted appreciably to the surface. The conclusion was in good agreement with other previous literature results for the SAMs of 4-mercaptopyridine [29–32] on Au or Ag surfaces. Furthermore, based on the surface coverage, Co-TPP-4MPY on the electrode was calculated by us



Scheme 2. (A–C) The structure of various cobalt-porphyrin films axial attached with imidazole on the surface of gold electrode.

to be $6.15 \times 10^{-11} \text{ mol cm}^{-2}$, the value of Co-TPP coverage was little lower than by Liu and co-workers ($8.17 \times 10^{-11} \text{ mol cm}^{-2}$) [28,33], but it was basically consistent with that of the little tilted parallel-oriented porphyrin film on metal surfaces. When combined imidazole axial with Co-TPP and Co-TPP-4MPY/SAMs to catalyse oxygen reduction, we could observe that the catalytic efficiency of CoTPP-Im-CoTPP-4MPY/SAMs for oxygen was higher ($n = 2.8$). Many research groups [34–38] have tested the catalysis of oxygen reduction for various structure of metalloporphyrin on electrode surface and found the efficiency of face to face metalloporphyrin structure was higher which could catalyse oxygen reduction to H_2O and electrons $n > 2.0$. The possible structure of CoTPP-Im-CoTPP-4MPY on gold was shown in Scheme 2A. So, we were able to gain some useful information considering the geometry of tetraphenylporphyrins and the N atom of the axial ligand [39]. The ligation of the Co atom of the porphyrin core with the N atom of pyridine indicated that the pyridine plane was not oriented parallel to the surface. The nitrogen atom of pyridine should be in a position that allowed access of the metalloporphyrin to it. The nearly flat orientation of the porphyrin in the present work suggested that both the pyridine plane and the axis through the N and S atoms was tilted, at least to some extent, to the Au surface.

The surface coverage was $3.10 \times 10^{-10} \text{ mol cm}^{-2}$ for Co-ATP-MPA/SAMs and corresponded to an area occupied by each molecule of 47 \AA^2 , and the hydrogen bond acted between N and O atoms among the chains indicated the metalloporphyrin molecules were well packed on the surface of electrode and the porphyrin ring oriented between the parallel or a perpendicular (30 \AA^2) position regarding the surface and the metalloporphyrin rings seemed to be overlapped. We could validate the hypothesis through catalysis oxygen reduction by axial ligand, namely imidazole. In this experiment, imidazole molecule could be axised to two Co atoms by Co–N bond. It was impossible to combine the other metal porphyrin, such as Co-TPP in the next step. From Fig. 5B, it was shown that Im-Co-ATP-MPA/SAMs could not catalyze oxygen reduction compared with Co-ATP-MPA/SAMs effectively. The possible mode for Im-Co-ATP-MPA/SAMs was shown in Scheme 2B.

The coverage of Co-TMPP/SAMs we estimated was similar to the value obtained by Murray and co-workers ($8.72 \times 10^{-11} \text{ mol cm}^{-2}$) [21,28], and corresponded to an area occupied by each molecule which was 159 \AA^2 . This value was little smaller for a flat (170 \AA^2) orientation of the molecules on the surface, which could be explained [14] by the presence of a well-packed layer. Murray and co-workers [21,40] presented a population of thiols not attached to the gold surface by XPS for Co(*o*-TMEPP). About 60–70% of the sulfur atoms in the monolayer were presented as gold-bound thiolates. This result, considering the Co(*o*-TMEPP) structure strongly suggested a preponderance of coplanar electrode-porphyrin binding. The catalytic position, namely cobalt atom, was axial possibly with N atoms of imidazole and axial with metalloporphyrin in the next step. The number of catalytic position for oxygen reduction has not changed. Therefore, we could draw a conclusion that the porphyrin ring of Co-TMPP was oriented parallel to the Au surface (Scheme 1B) and the possible mode for CoTPP-Im-Co-TMPP on the surface of gold was indicated in Scheme 2C.

4. Conclusion

In conclusion, we have prepared three cobalt-porphyrin-overlayered SAMs on gold and combined imidazole axial with CoTPP to investigate the orientation mode of porphyrin ring by catalytic oxygen reduction. Compared with the other two cobalt-porphyrins electrode films, the catalytic efficiency of molecular films of Co-TPP-4MPY for oxygen was higher ($n = 1.9$) and the reduction potential was more positive, in which the porphyrin molecules was little parallelly tilted oriented to the gold surface through the axis of N and Co atoms. The porphyrin ring of Co-TMPP was oriented parallel to the gold surface and the porphyrin ring of Co-ATP-MPA was little perpendicularly tilted to the electrode surface and parallel to each other for cobalt-porphyrin ring.

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