

In Situ Scanning Tunneling Microscopy Study of the Effect of Iron Octaethylporphyrin Adlayer on the Electrocatalytic Reduction of O₂ on Au(111)

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The adlayer of 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine iron(III) chloride (FeOEP) was prepared by immersing Au(111) substrate in a benzene solution containing FeOEP molecules, and it was investigated by cyclic voltammetry (CV) and in situ scanning tunneling microscopy (STM) to examine the effect of the adlayer on the electrocatalytic activity for the reduction of O₂ in 0.1 M HClO₄. Voltammetric results indicated that the FeOEP-modified Au(111) electrode enhanced the two-step, four-electron reduction of O₂ to H₂O. In situ STM images revealed the highly ordered adlayer of FeOEP on the reconstructed Au(111) surface during the first electrochemical reduction of O₂ to H₂O₂. When the electrode potential was scanned to the potential region where H₂O₂ was reduced further to H₂O, the STM image became unclear because of the high mobility of FeOEP molecules on the terrace. The result in the present study suggests that the mobility of FeOEP on the Au surface is an important factor affecting the overall four-electron reduction of O₂.

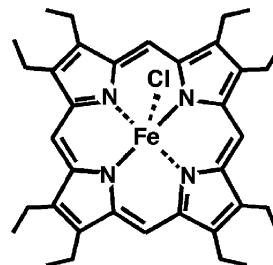
Introduction

The formation and characterization of ordered adlayers of porphyrin molecules at electrolyte–electrode interfaces are important in both fundamental and applied fields. Porphyrins are of great interest in such diverse fields as biology,¹ photosynthesis,¹ electrocatalysis,^{2,3} and molecular devices.⁴ Especially, thin films of porphyrins and their derivatives have been intensively studied because of the interest in electrocatalytic reactions, such as the reduction of O₂, for developing efficient fuel cells.^{2,3,5–11} For the electrocatalytic reduction of O₂, the reactivity has been investigated on graphite electrodes modified with various porphyrin and phthalocyanine derivatives.^{2,3,7–11} However, not much attention has been paid so far to the adlayer structure of those porphyrins, and the relationship between the adlayer structure and the electrocatalytic activity is still unclear.

We recently succeeded in spontaneously forming highly ordered molecular arrays of water-insoluble 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine cobalt(II) (CoTPP),¹² cobalt(II) phthalocyanine (CoPc),¹³ cobalt(II) porphine (CoP),¹⁴ and 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine cobalt(II) (CoOEP)¹⁴ on a Au(111) surface by immersing Au(111) in benzene solutions containing those molecules. Although those adlayers were stable even at potentials near the H₂ evolution potential, the electrochemical reduction of O₂ revealed not the four-electron reduction but the two-electron reduction of O₂ which proceeded only to H₂O₂ with the transfer of two electrons, not to H₂O with the transfer of four electrons.

In the present study, to achieve the four-electron reduction of O₂ to H₂O, we selected 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine iron(III) chloride (FeOEP, see Chart 1) and

CHART 1: Chemical Formula of 2,3,7,8,12,13,17,18-Octaethyl-21*H*,23*H*-porphine Iron(III) Chloride (FeOEP)



prepared highly ordered self-organized adlayers of FeOEP on Au(111). The electrochemical reduction of O₂ on the FeOEP-modified Au(111) electrode was examined, and the relationship between the adlayer structure and the electrocatalytic activity of the self-organized FeOEP layer for the reduction of O₂ was clarified by in situ scanning tunneling microscopy (STM) measurements.

Experimental Section

FeOEP and 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine cobalt(II) (CoOEP) were purchased from Aldrich, and used without further purification. Benzene was obtained from Kanto Chemical Co. (Spectroscopy Grade). H₂O₂ was obtained from Kanto Chemical Co. The electrolyte solution was prepared with HClO₄ (Cica-Merck) and ultrapure water (Milli-Q SP-TOC; ≥ 18.2 MΩ cm).

The Au(111) single-crystal electrodes were prepared by the Clavilier method.¹⁵ The FeOEP adlayer was formed by immersing a Au(111) electrode into a roughly 10–100 μM FeOEP–benzene solution for 7–20 s after first annealing it in a hydrogen flame and quenching in ultrapure water saturated with hydrogen.^{12–14,16} The FeOEP-adsorbed Au(111) electrode

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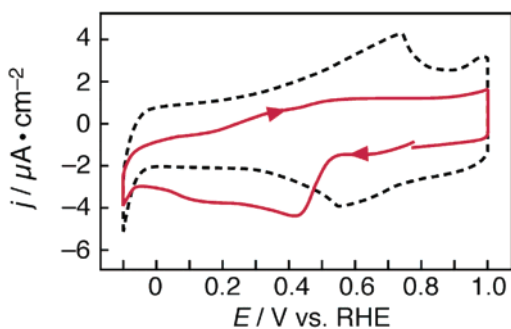


Figure 1. Cyclic voltammograms of bare Au(111) (dashed line) and FeOEP-modified Au(111) (solid line) electrodes in 0.1 M HClO₄ under a N₂ atmosphere. The potential scan rate was 50 mV s⁻¹.

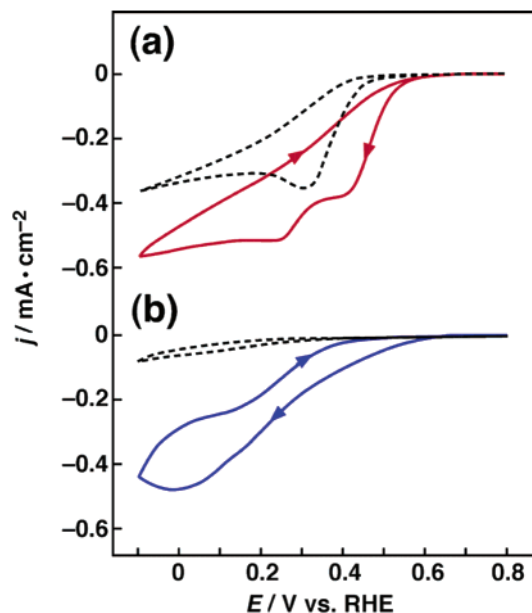


Figure 2. Cyclic voltammograms of CoOEP-modified (dashed line) and FeOEP-modified (solid line) Au(111) electrodes in 0.1 M HClO₄ in an O₂ atmosphere (a) and in the presence of 10 mM H₂O₂ (b), respectively. The potential scan rate was 50 mV s⁻¹.

was then rinsed with ultrapure water, and it was transferred into an electrochemical cell for both voltammetric and STM measurements to prevent contamination.

Cyclic voltammetry (CV) was carried out at 20 °C using a potentiostat (HOKUTO HAB-151, Tokyo) and the hanging meniscus method in a three-compartment electrochemical cell in either a N₂ or O₂ atmosphere. Electrochemical STM measurements were performed by using a Nanoscope E (Digital Instruments, Santa Barbara, CA) with tungsten tips etched in 1 M KOH. To minimize residual faradic current, the tungsten tip was coated with nail polish. STM images were recorded in the constant-current mode with a high-resolution scanner (HD-051). All potentials are referred to the reversible hydrogen electrode (RHE).

Results and Discussion

Voltammetry. Cyclic voltammetry of FeOEP-modified Au(111) electrodes was performed in 0.1 M HClO₄ under a N₂ atmosphere. As shown in Figure 1, the CV for the bare Au(111) electrode (dotted line) in the double-layer potential region was the same as that reported previously, which shows that a well-defined Au(111) surface was exposed to the HClO₄ solution.^{14,16,17} The solid line in Figure 1 is the CV obtained on the first scan for the FeOEP-modified Au(111) electrode. The

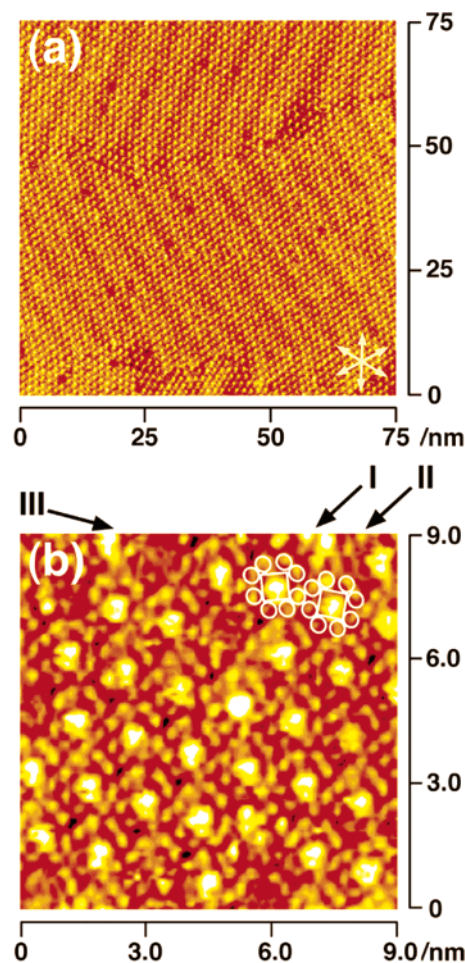


Figure 3. Large-scale (75 × 75 nm²) (a) and high-resolution (9 × 9 nm²) (b) STM images of the FeOEP adlayer formed on a Au(111) surface in 0.1 M HClO₄ acquired at 0.85 V vs RHE. The potential of the tip and the tunneling currents were 0.35 V and 1.5 nA (a) and 1.25 nA (b), respectively. The set of three arrows indicates the close-packed directions of the Au(111) substrate.

open circuit potential (OCP) of the FeOEP-modified Au(111) electrode was around 0.7–0.8 V versus RHE, and the potential scan was made in the negative direction from the OCP. The effect of the adsorption of FeOEP was clearly observed in the double-layer charging current. The decrease in the double-layer charging current suggests that the Au(111) surface is covered with hydrophobic FeOEP molecules. As can be seen in Figure 1, a reductive peak was seen at 0.42 V during the cathodic scan. This is attributed to the reduction of Fe(III) to Fe(II), because this potential is in close agreement with the redox potentials observed with the graphite electrode modified with iron porphyrins.^{7,8} The cathodic current commencing at -0.05 V is due to the H₂ evolution reaction. In contrast, broader peaks appeared in the potential range between 0.2 and 0.7 V during the anodic scan, suggesting that the reoxidation process of FeOEP molecules is slow. Similar voltammograms were obtained with CoTPP,¹² CoP,¹⁴ and CoOEP.¹⁴

On the FeOEP adlayer on the Au(111) surface, the O₂ reduction was examined in 0.1 M HClO₄ saturated with O₂. As can be seen in Figure 2a, a clear difference in electrocatalytic activity exists between the CoOEP-modified and FeOEP-modified Au(111) electrodes. On the CoOEP-adsorbed Au(111) electrode (dotted line), the catalytic current of O₂ commenced at about 0.5 V during the cathodic scan, and a clear reduction peak was observed at 0.32 V as described in our recent paper.¹⁴ At potentials more negative than 0.3 V, the reductive current

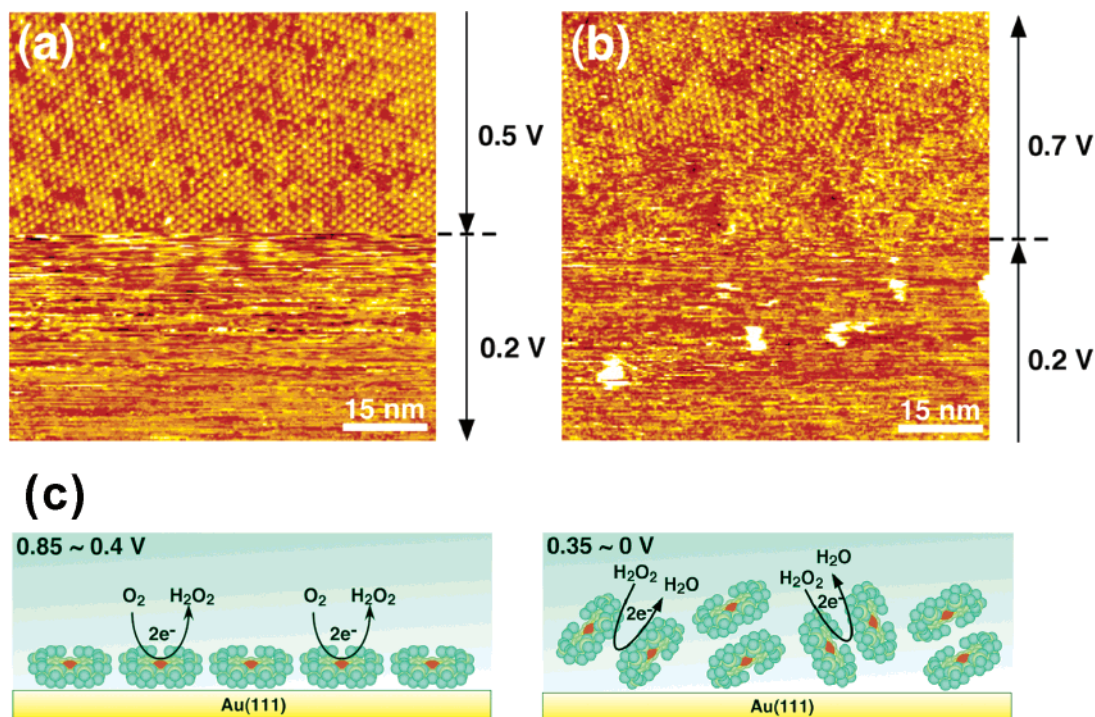


Figure 4. Composite STM images of the FeOEP adlayer on a Au(111) surface in 0.1 M HClO_4 acquired at 0.2 V, after stepping the potential from 0.5 V (a) and returning to 0.7 V (b), respectively. The potential of the tip and the tunneling current were 0.45 V and 1.5 nA, respectively. (c) Proposed models for the FeOEP adlayer on Au(111) surface in 0.1 M HClO_4 .

remained almost constant because of the process being limited by the diffusion of O_2 . It was estimated from the current density (ca. 0.4 mA cm^{-2}) that the two-electron reduction of O_2 to H_2O_2 occurred on the CoOEP-modified Au(111) electrode. On the other hand, the CV profile of FeOEP-modified Au(111) electrode (solid line, Figure 2a) was quite different from that of CoOEP (dotted line). On the FeOEP-adsorbed Au(111) electrode, the catalytic current of O_2 commenced at about 0.6 V during the cathodic scan, and two electrocatalytic reduction peaks were observed clearly at 0.45 and 0.25 V. From the current density, it can be roughly estimated that the two-step four-electron reduction of O_2 to H_2O occurred at the FeOEP-modified Au(111) electrode. We next examined the electrochemical reduction of H_2O_2 at both the CoOEP-modified and the FeOEP-modified Au(111) electrodes. In this case, the difference in electrochemical activity between the CoOEP-modified and FeOEP-modified Au(111) electrodes was very clearly observed as shown in Figure 2b. While no peak was seen at the CoOEP-modified Au(111) electrode, a reductive peak appeared at 0 V at the FeOEP-modified Au(111) electrode. The observed current density shows that two electrons passed at 0 V, that is, the electrochemical reduction of H_2O_2 to H_2O took place on the FeOEP-modified Au(111) electrode.

In Situ STM. To investigate the adlayer structure of FeOEP on Au(111) electrode, in situ STM was performed in the present study. Figure 3 shows typical STM images of an FeOEP adlayer on Au(111) acquired at 0.85 V in 0.1 M HClO_4 . Ordered domains were found on the atomically flat terrace, and individual molecules were recognized even in the large area of $75 \times 75 \text{ nm}^2$. Modulation is seen as rows on the surface in Figure 3a. Careful inspection of the Au(111) surface reveals that rows in Figure 3a are separated with a spacing ranging from about 6.8 to 9.2 nm on the terrace. The difference in height is only about 0.06 nm, which is much smaller than the height of the atomic step. These results reveal that the transformation of underlying Au atoms from (1×1) to $(\sqrt{3} \times 22)$, the so-called reconstruc-

tion, was caused by the adsorption of FeOEP. The reason for the reconstruction being induced by the adsorption of FeOEP is not clear, but the following mechanism may be proposed: the adsorbed FeOEP induces a negative charge on the Au(111) surface to shift the potential of zero charge (E_{pzc}) of the FeOEP-modified Au(111) to a value more positive than that of bare Au(111) (0.24 V vs SCE) in 0.01 M HClO_4 .¹⁸ The reconstruction of Au(111) surfaces has been shown to be induced also by the adsorption of CoTPP, CuTPP, and CoOEP as reported in our recent papers.^{12–14} To obtain structural details of the FeOEP adlayer, high-resolution STM images were also acquired at 0.85 V. Figure 3b shows a typical high-resolution STM image acquired in an area of $9 \times 9 \text{ nm}^2$, revealing the internal molecular structure and the molecular orientation in the ordered domain. By careful inspection, two different orientations can be seen for FeOEP molecules in molecular rows, that is, FeOEP molecules in the molecular row marked by arrow I are rotated by about 15° with respect to those in the row marked II. Each FeOEP molecule can be recognized as a bright center spot with eight additional spots at the corners. The center in each FeOEP molecule was observed as the brightest spot. At this potential, the central Fe ion is in the state of Fe(III) because of the coordination with Cl^- anion, that is, the d_{z^2} orbital should be empty. The reason why the center of the FeOEP appears as a bright spot is not clear, but one possibility is that chloride might act as a new tunneling pathway, which could increase the tunneling current at the central position of Fe(III)Cl. Careful inspection of Figure 3b also allows one to distinguish two different orientations of FeOEP molecules in the molecular rows, that is, the orientation of each FeOEP molecule in the molecular row marked I is different by about 15° from that in the row marked II. Each FeOEP molecule can be recognized as a square with eight additional spots at the corners corresponding to eight ethyl groups. It is clear that FeOEP molecules possess alternately different orientations in molecular rows I and II. The intermolecular distance along row I or II was found to be 1.67 ± 0.07

nm. The intermolecular distance along row III was 1.45 ± 0.05 nm. The packing arrangement and the brightness at the center spot of FeOEP are identical to those of CoOEP on Au(111) as described in our recent paper.¹⁴

To investigate the stability of the FeOEP adlayer on the Au(111) surface in 0.1 M HClO₄, the dependency of the adlayer structure on potential was examined. Highly ordered adlayers of FeOEP were consistently observed in the potential region between 0.9 and 0.4 V. Composite STM images were recorded by stepping the electrode potential as shown in Figure 4a. When the electrode potential was stepped from 0.5 to 0.2 V in the middle of scanning, the STM image became unclear. The adlayer of FeOEP immediately disappeared as shown in the lower part of Figure 4a. No electrochemically induced reconstruction of Au(111) was observed at this potential, suggesting that FeOEP molecules did not desorb from the Au surface but became highly mobile on the surface. Two min later, the electrode potential was returned to 0.7 V from 0.2 V. An identical structure was again formed on the terrace as shown in the upper portion of Figure 4b. In the potential region between 0.4 and 0 V, a face-to-face dimer of FeOEP molecules might have formed near the Au surface because of the high mobility of the adsorbed FeOEP molecules, as illustrated in the proposed model in Figure 4c. As described in our previous paper, a highly ordered adlayer of CoOEP was consistently observed in the potential region between 0 and 0.95 V.¹⁴ Although further investigation is needed, the observed effect of potential switching clearly demonstrates that the stability of MOEP adlayer on Au(111) depends on the center metal ion. The stability of adlayers on the electrode surface might be one of the important factors controlling the electrochemical activity for the reduction of O₂.

Conclusion

By immersing a Au(111) substrate into a benzene solution containing FeOEP, we succeeded in preparing ordered adlayers of FeOEP on the Au(111) surface. A highly ordered adlayer of FeOEP was spontaneously formed on the reconstructed Au-

(111) surface. In situ STM images revealed that the electrochemical reduction of O₂ to H₂O₂ was enhanced on the highly ordered adlayers of the FeOEP-modified Au(111) electrode, whereas the electrochemical reduction of H₂O₂ to H₂O took place at negative potentials where FeOEP molecules are highly mobile on the Au(111) surface.

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