

Effect of Iron Octaethylporphyrin Adlayer on the Electrochemical Reduction of O₂ on Au(111) Electrode

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Porphyryns are of great interest in such diversified fields as biology, photosynthesis, electrocatalysis, and molecular devices. Formation and characterization of ordered adlayers of porphyrin molecules at electrolyte-electrode interfaces are important in both fundamental and application fields. Especially, thin films of porphyryns and their derivatives have been intensively studied for the interest in electrocatalytic reactions, such as the reduction of O₂ for developing efficient fuel cells.^{1,2} However, not much attention has been paid so far to the adlayer structure of those porphyryns, and the relationship between the adlayer structure and the electrocatalytic activity is still unclear.

In the present study, adlayers of 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine iron(III) chloride (FeOEP) and cobalt(II) (CoOEP) were prepared by immersing Au(111) substrate in a benzene solution containing either FeOEP or CoOEP molecules, and they were 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, whereas the CoOEP-modified Au(111) electrode indicated only two-electron reduction of O₂ to H₂O₂ (see Fig. 1a).³ In situ STM images revealed the highly-ordered adlayer of FeOEP on reconstructed Au(111) surface during the electrochemical reduction of O₂ to H₂O₂ (see Fig. 2). To investigate the stability of FeOEP adlayer on 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. When the electrode potential was scanned to the potential region where H₂O₂ was reduced further to H₂O, the STM image became unclear due to the high mobility of FeOEP molecules on the terrace. 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 Fig. 3b. In the potential region between 0.4 and 0 V, a face-to-face dimer of FeOEP molecule might have formed near the Au surface because of the high mobility of the adsorbed FeOEP molecules, as illustrated in the proposed model in Fig. 3c. On the contrary, highly-ordered adlayer of CoOEP was also found on Au(111), and it was stable in the potential range between 0 and 0.9 V. 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 O₂.⁴

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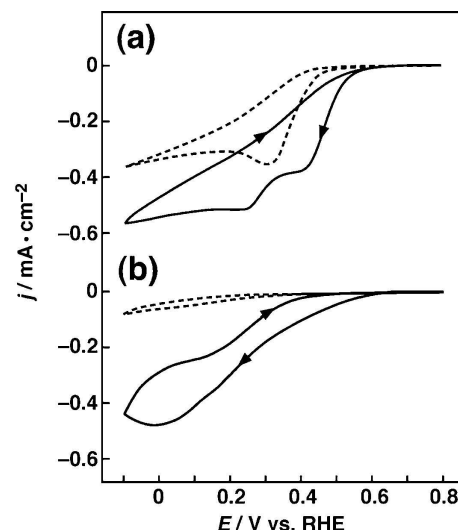


Figure 1 Cyclic voltammograms of CoOEP- (dashed line) and FeOEP- (solid line) modified Au(111) electrodes in 0.1 M HClO₄ in O₂ atmosphere (a) and in the presence of 10 mM H₂O₂ (b), respectively. The potential scan rate was 50 mV s⁻¹.

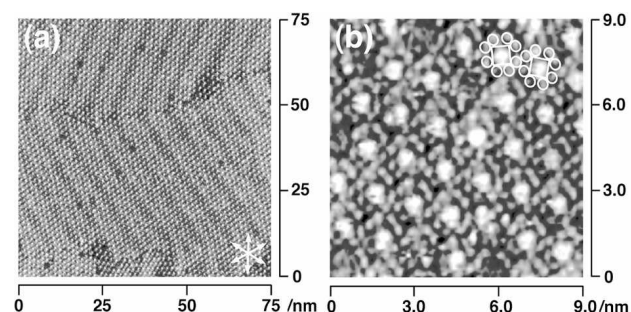


Figure 2 Large-scale (75 × 75 nm²) (a) and high-resolution (9 × 9 nm²) (b) STM images of the FeOEP adlayer formed on Au(111) surface in 0.1 M HClO₄ acquired at 0.85 V vs. RHE. Potential of the tip and tunneling currents were 0.35 V and 1.5 nA (a) and 1.25 nA (b), respectively.

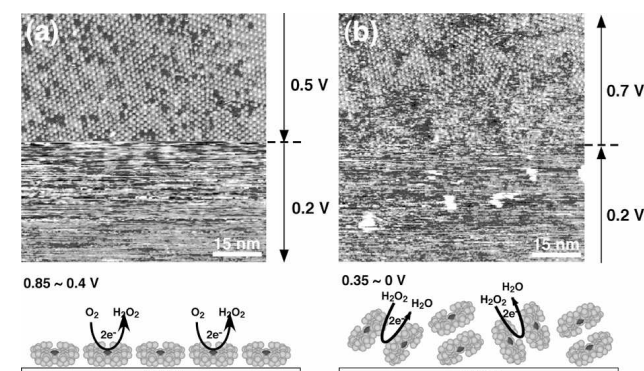


Figure 3 Composite STM images of the FeOEP adlayer on Au(111) surface in 0.1 M HClO₄ acquired at 0.25 V, after stepping the potential from (a) 0.4 V and returning to (b) 0.7 V, respectively. Potential of the tip and tunneling current were 0.45 V and 1.5 nA, respectively. (c) Proposed models for the FeOEP adlayer on Au(111) surface in 0.1 M HClO₄.