VII-C Electrochemical Analysis of Biological Functions of Metalloproteins and their Mutated Molecules and its Applications to Coordination Chemistry for Catalysis

Using surface-functionalized electrodes, biological functions and bioelectrochemical properties of metalloproteins and their mutated and redox-center modified molecules have been analyzed electrochemically to develop new bioelectrocatalytic systems and bioelectro-functional devices.

Surface structures and properties of functional modified electrodes have also been examined at molecular level using STM, electrochemical and other spectroscopic techniques.

VII-C-1 Effects of Alkyl Chain as a Spacer on Electrochemical Reaction and SEIRA Spectra for Self-Assembled Monolayer Having Anthraquinone Redox Center

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[*Electrochemistry* **69**, 980 (2001)]

Self-assembled monolayers (SAMs) of 1-mercapto-anthraquinone (AQSC0), bis(3-(1-anthraquinonylthio)-propyl)disulfide (AQSC3) and bis(6-(1-anthra-quinononylthio)hexyl)disulfide (AQSC6), on a gold electrode were investigated by cyclic voltammetry and surface enhanced infrared absorption spectroscopy (SEIRAS). A redox wave was observed for all the anthraquinone (AQ) derivatives and the redox potential shifted *ca.* –60 mV/pH in the pH region from 1 to 7. The peak separation of the voltammograms depended on the spacer length of the AQ derivatives, and the heterogeneous electron transfer rates of AQSC0, AQSC3 and AQSC6 at pH 1 were 7.5, 2.3×10^{-1}, and 3.1×10^{-3} s^{-1}, respectively. For the SEIRA spectra of AQSC0 and AQSC3, the C=O stretching and C–C stretching bands of AQ ring were clearly observed, suggesting that the AQ ring plane is perpendicular or tilted to the electrode surface. The SEIRA signal of the AQ derivatives decreased with an increase in the alkyl chain length, indicating taht the AQSC3 and AQSC6 molecules were adsorbed on the electrode not by the sulfide S atoms but by the thiolate S atoms.

VII-C-2 Analysis of Biological Functions of Metalloproteins Using Biocompatible Modified Electrodes

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[*Anal. Sci.* **17**, 1355 (2001)]

Recent developments on bioelectroanalytical chemistry of metalloproteins have been discussed for the following subjects. 1) Surface structures for the rapid electron transfer of metalloproteins (in particular for cytochrome *c*) have been discussed and 3-mercapto-pyridine has been shown as a new surface modifier for cytochrome c electrochemistry. 2) Biological functions and electron transfer kinetics of myoglobin have been analyzed by comparing electrochemical properties of native molecule with those of artificially designed molecules. For electron transfer kinetics, the re-organization energy due to the structural change at the redox center during electron transfer reaction has been shown to play an important role. 3) Use of ferredoxin as an electron-donating mediator, bioelectrocatalytic reactions have been demonstrated. These results suggest that electrochemical techniques using functional electrodes are useful for analysis and use of biological functions of metalloproteins.

VII-C-3 Interfacial Structures of Self-Assembled Monolayers of 2-Pyridinethiol on Au(111) Studied by In Situ Tunneling Microscopy

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[*Anal. Sci.* **17**, 1383 (2001)]

In situ Scanning Tunneling Microscope (STM) operating under electrochemical condition was used to study self-assembled monolayers of 2-pyridinethiol (2-PySH) on Au(111) in perchloric acid solution. Each molecule appeared as two spots, presumably originated from adsorption through S and N atoms of 2-pyridinethiolate with a vertical orientation on the Au(111) surface. The ordered 2-pyridinethiolate monolayers exhibited a p (4 × $\sqrt{7}$R–40.9°) structure, which was constructed by alternative arrangements of two types of molecular rows with differently rotated molecules. In situ STM also revealed that the monolayer consisted of molecularly ordered domains with the p (4 × $\sqrt{7}$R–40.9°) structure, its mirror structure defined as p (4 × $\sqrt{7}$R–19.1°), and their rotational structures. Detailed interfacial structures and molecularly ordered domains of 2-pyridinethiolate monolayer have been elcidated by in situ STM imaging in aqueous solution.

VII-C-4 NADP$^+$ Sensor on Chrorella Ferredoxin/Ferredoxin-NADP$^+$-Reductase Modified Indium Oxides

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[*Chem. Sens.* **17**, 92 (2001)]

Chlorella ferredoxin (ChFd) was immobilized electrostatically with the aid of cationic polypeptides such as poly-L-lysine (PLL) or poly-L-ornithine onto indium oxide electrodes. Clear redox waves of the immobilized ChFd was observed. In the presence of ferredoxin-$NADP^+$-reductase (FNR) and $NADP^+$, $NADP^+$ was reduced to NADPH electrocatalytically at the modified electrode. Also, both ChFd and FNR were immobilized on the electrode, and the prepared ChFd/FNR modified electrode was applied to the $NADP^+$ sensor.

VII-C-5 Surface pKa of Amine-Terminated Self-Assembled Monolayers Evaluated by Direct Observation of Counter Anion by FT-Surface Enhanced Raman Spectroscopy

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[*Chem. Lett.* 80 (2002)]

The acid-base reaction of aminothanethol (2-AT) and 6-amino-1hexanethiol (6AT) self-assembled monolayers (SAMs) on a gold electrode was monitored by fourier-transform surface enhanced Raman spectroscopy (FT-SERS). A band attributed to counter anion, such as ClO_4^- or NO_3^- for NH_3^+ , was clearly observed during protonation of the amino group of 2AT or 6AT. The nband intensity decreased with increasing solution pH. The surface pKa's of 2AT and 6AT SAMs on a gold electrode at 0 V *vs.* Ag/AgCl (saturated KCl) were 5.0 ± 0.2 and 3.8 ± 0.3, as evaluated from the intensity-pH curve.

VII-C-6 Ion Selectivity for Electrode Reactions on Functionalized Monolayer Modified Electrode

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[*Chem. Sens.* **18**, 133 (2002)]

Electrode reactions of various ionic species on pyridine-, pyrimidine-, benzene- and related thiolate modified Au(111) and Au(100) single crystal surfaces were carried out. Clear selectivity of the electrode reaction for a given ionic species depending on the modified surface was seen. Charge of the ionic species was not so important. In particular, on the benzenethiolate modified electrode surface, the electrode reaction of ferri-/ferro- redox couple in acidic solution was clearly inhibited, but no inhibition was observed for the electrode reaction of ferri-/ferro-cyanide redox couple. On the other hand, by increasing the number of –SH group in the benzene ring (1,4-dithiol < 1,3,5 trithiol < 1,2,4,5 tetrathiol), ferri-/ferro redox couple showed an increased enhancement of the electrochemical responses, but ferri-/ferro-cyanide redox couple showed an inhibition on the electrode reaction. On the bases of the properties of the modified electrode surfaces obtained by STM image, impedance analysis, contact angle and other data, the surface hyrophilicity (or hydration/dehydration of the ionic species) of the modified electrodes was concluded to play an important role on the electrode reaction of ferri-/ferro- redox couple.

VII-C-7 In-Situ STM Observation of Coronene Epitaxial Adlayers on Au(111) Surfaces Prepared by the Transfer of Langmuir Films

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[*Thin Solid Films* **409**, 206 (2002)]

A highly ordered epitaxial adlayer of coronene on an Au(111) surface was prepared by a wet process technique, which consisted of the simple transfer of Langmuir films. The structure and dependence on potential of the adlayer were then investigated by in situ scanning tunneling microscopy (STM). The adlayer processed a (4×4)-Au(111) superlattice structure, and each coronene molecule was visualized as an individual hexagon on high-resolution STM images. The multilayer portion was present without any potential control, probably due to the excess generated by the transfer. The adsorption behavior of coronene, including the formation of the multilayers, showed dependence on the potential. A flawless adlayer without the presence of any multilayers was achieved by the application of nagative potential, in which the multilayer-substrate interaction was adequately weakened.

VII-C-8 New Route to Protoporphyrins III and XIII from Common Starting Pyrroles

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[*Tetrahedron Lett.* **43**, 3109 (2002)]

A new approach to protoporphyrins III (2') and XIII (3') has been developed based on a single set of starting materials, namely, 2,4-dimethyl-3-(2-chloroethyl)-carbethoxypyrrole (4) and 3,3'-di(2-methoxycarbonyl-ethyl)-4,4'-dimethyldipyrromethane-5,5'dicarboxylic acid (5) for both targets. The biladiene route was adopted for the preparation of 2' (five steps, 18% overall yield) while the coupling of two pyrromethenes was used to synthesize 3' (four steps, 11% overall yield).