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Self-assembled monolayer of thiolated heme derivatives was formed on gold surface. The thickness of the formed monolayer and the kinetics of this adsorption were studied by surface plasmon resonance spectroscopy. This monolayer was characterized by an electrochemical method.

Keywords: heme derivatives; gold; self-assembled monolayer; surface plasmon resonance spectroscopy; cyclic voltammograms; electroreflectance

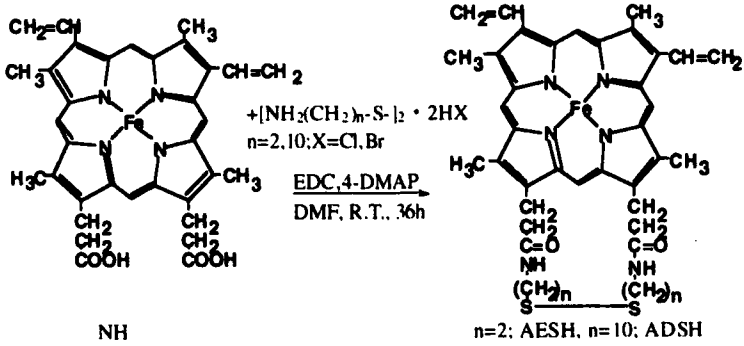
INTRODUCTION

Self-assembled monolayers (SAMs) of organosulfur compounds on metal surfaces have been widely studied because of their extensive applications in molecular technologies.[1] Thiols and disulfides covalently adsorb on gold (Au) surfaces through a S-Au linkage. Heme,

which contains iron bound to the pyrrole rings, is well known as a prosthetic group of many proteins such as hemoglobin, myoglobin, and b-type cytochromes for the specific biological action. Forming a SAM of heme on Au is applicable to devices such as electrochemical biosensors and bioelectonics. Here we discuss the direct adsorption of thiolated heme derivatives on Au, on the basis of the adsorption kinetics and electrochemical (EC) investigation of their SAM.

EXPERIMENTAL

Heme (iron protoporphyrin IX), NH, was reacted with eirther 2,2'-dithio-bis[ethylamine] or 10,10'-dithio-bis[decylamine] to produce its derivatives, AESH and ADSH, as shown in Scheme 1. 50 μM of heme derivatives in ethanol was exposed to the evaporated Au on either LaSFN9 for Surface plasmon resonance spectroscopy (SPS) or mica for EC. SPS was carried out using homemade equipment, and the adsorption kinetics and the optical thickness were observed.[2] Cyclic voltammograms (CVs) and electroreflectance (ER) spectra of heme derivatives adsorbed on Au were measured in a deaerated aqueous



SCHEME 1 Synthetic route of heme derivatives and structures.

solution containing 30 mM phosphate (pH 7) at 20 ± 3 °C, using a homemade three-electrode cell. The potential was referred to a Ag | AgCl | saturated KCl electrode. The instrumentation for ER measurements was described previously.[3,4]

RESULTS AND DISCUSSION

Figure 1 shows the adsorption kinetics for heme derivatives. All the samples show steep slope at the beginning of the adsorption. AESH and ADSH reached the plateau regions in thickness, whereas NH didn't reach the saturation even after 24 hours, showing that AESH and ADSH are able to form monolayer but NH forms aggregates.

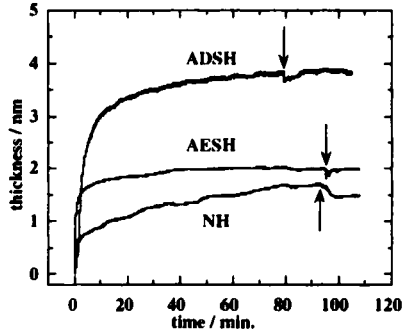


FIGURE 1 Adsorption kinetics of heme derivatives from ethanol on Au surface. Arrow shows the start of rinsing.

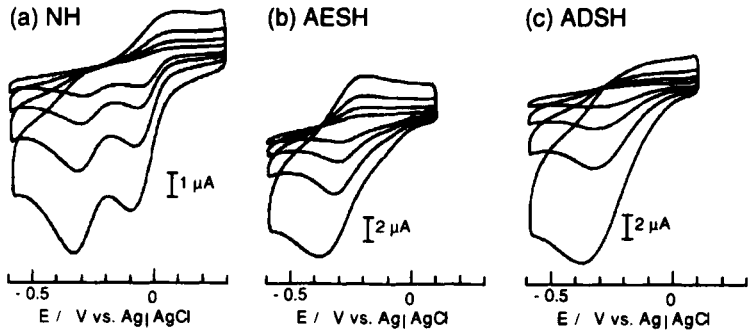


FIGURE 2 Cyclic voltammograms of heme derivatives adsorbed on Au in 30 mM phosphate buffer: scan rate, 20, 50, 100, 200 mV s^{-1}; initial potential, + 0.1 V for AESH and ADSH, + 0.3 V for NH.

Figure 2 shows CVs for NH, AESH, and ADSH. Only one peak appeared around –0.3 V for heme derivatives, whereas two peaks were observed at –0.05 and –0.3 V for NH. The cathodic peak current was proportional to the sweep rate for all CVs, revealing that the redox response arises from the surface-confined species. The area of cathodic peak tends to be larger than that of anodic peak. This reflects a contribution of the catalytic reduction current of dioxygen remained in buffer.

Figure 3 represents the real part of the ER signal for AESH on Au electrodes measured at the peak potential of the corresponding CV. The similarity of the ER spectrum to a difference absorption spectrum of NH in solution, except the shift in the ER peaks about 20 nm toward longer wavelength, confirms that the redox response originates from the adsorbed heme derivatives on Au. The electron transfer rate constant, k_{ET} was estimated to be ca. 600 s^{-1} for AESH adsorbed on Au from the frequency dependence of ER response.[4]

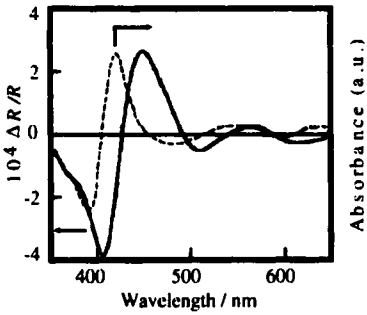


FIGURE 3 ER spectrum of AESH adsorbed on Au: Edc, - 0.3 V, freguency, 8 Hz, modulation amplitude, 50 mV. The dotted line shows a difference absorption spectrum between the reduced and oxidized forms of NH.

References

[1] A. Ulman, *Chem. Rev.*, **96**, 1533 (1996).
[2] W. Knoll, *MRS Bull*, **7**, 29 (1991).
[3] T. Sagara, S. Igarashi, H. Sato, K. Niki, *Langmuir*, **7**, 1005 (1991).
[4] Z. Q. Feng, T. Sagara, K. Niki, *Anal.Chem.*, **67**, 3564 (1995).