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Nanostructure of Functionalized Electrodes for Protein Electrochemistry

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Preparation of a suitable electrode/solution interface, at which rapid electron transfer reaction of metalloprotein takes place, is important not only for studying biological functions of metalloproteins using conventional electrochemical techniques but also for applying biological functions to design various bioelectrochemical systems [1,2]. In recent years, functional electrodes using single crystal electrode surfaces have been examined extensively, and surface structures and surface functions of the modified electrodes became clear at the molecular level [3-9].

In the present paper, surface functions of modified electrodes for the rapid electron transfer of cytochrome c have been examined by using new surface modifiers [10].

For cytochrome c electrochemistry, indium oxide (In2O3) and so-called electron transfer promoter (such as bis(4-pyridyl)disulfide, 4,4'-PySSPy and 4-mercaptopyridine, 4-PySH) modified electrodes are effective to obtain a well-defined voltammogram [1,2] The STM image of the 4-PySH modified Au(111) electrode showed the rectangular unit cell of a *p*(5 x √3R-30˚) structure with an interaction of two neighboring 4-PySH [5-8]. On the other hand, the 2-PySH modified Au(111) electrode showed a *p* (4 x √7R-19.1˚ or 40.9˚) structure with no dimer formation, suggesting that 2-PySH adsorbed at both thiolate S and pyridine N atoms [6]. On a 2-PySH modified electrode, poor electrochemical response of cytochrome c was seen as was on a thiophenol modified electrode. Similar disulfide formation for 4-PySH (*p* (√2R-45˚ x 5R-53.1˚)) and adsorption at both thiolate S and pyridine N atoms for 2-PySH ((√2 x 3√2) R-45˚) were also observed, respectively, on 4-PySH and 2-PySH modified Au(100) electrodes, where 2-PySH modified Au(100) electrode showed no electrochemical response [9].

2-Mercaptopyrazine (2-PyZSH) and 2-mercaptoquinoxaline (or 2-mercaptobenzo-pyrazine, 2-MQ) modified Au(111) electrodes gave well-defined cyclic voltammograms of cytochrome c like the cases of 4-mercaptipyridine (4-PySH) and 3-mercapto-pyridine. The STM images of the surface of 3-PySH modified Au(111) electrodes suggested a (6 x √3R-30˚) structure. The STM images of 2-PySH and 2-PyZSH modified surfaces were similar to each other, suggesting 2-PySH and 2-PyZSH adsorbed at both thiolate S and pyridine (or pyrazine) N atoms with pyridine (or pyrazine) ring being perpendicular to the electrode surface. The 2-PyZSH modified surface has another pyrazine N atom faced to the solution, through which cytochome c can interact, and the double layer capacitance data of the electrode gave more hydrophilic nature than the 2-PySH modified surface. On the other hand, although 2-MQ was suggested to adsorb on the electrode in a similar manner to 2-PySH and 2-PyZSH to give N atom at the solution side, the 2-MQ modified surface showed less hydrophilicity than the 2-PySH modified surface due to the quinoxaline ring.

These results clearly reveal that the pyridine and pyrazine N atoms faced to the solution (rather than the hydrophlicity of the electrode surface) are important for the rapid electron transfer of cytochrome c on these modified electrodes.

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