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Photoreduction Behaviors of Microperoxidase-11 Adsorbed on the Roughened Silver Electrodes

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Abstract: It was found that microperoxidase-11 (MP-11) can undergo photoreduction at the bare roughened silver electrode. No photoreduction happens at the roughened silver electrode modified with mercaptoundecanoic carboxylic acid/poly-lysine. The photoreduction mechanism is discussed.

Keywords: Microperoxidase, polylysine, modified electrode, photoreduction.

MP-11 is an undecapeptide obtained from pepsin digestion of cytochrome C. It is considered a model for c-type cytochromes. MP-11 retains amino acid residues 11-21 of cytochrome C. Among the residues, Cys-14 and Cys-17 are bonded to the heme C vinyl groups and His-18 serves as a proximal fifth ligand to the Fe atom. It is considered a peroxidase because its activity is similar to that of peroxidases in several ways. It was reported that MP-11 can undergo the quasi-reversible electrochemical reaction at metal electrodes. In this paper, electrochemical reactions and photoreduction of MP-11 at the bare and modified roughened silver electrodes were compared.

The roughened silver electrodes were prepared using an oxidation and reduction cycle procedure[1]. Then, the electrode was immersed in 1 mmol/L alkanethiol solution for 2 h to form the self-assembled monolayer (SAM) of alkanethiol on the electrode surfaces. After rinsing with ethanol and water to remove excess alkanethiol, the electrode were soaked in 1 mmol/L poly-lysine for 1 h to form a poly-lysine layer on the SAM of alkanethiol. MP-11 was adsorbed on the bare roughened or modified silver electrode by exposure to 0.5 mmol/L MP-11 in buffer solution for 30 min.

The cyclic voltammogram (CV) of MP-11 adsorbed at the bare roughened silver electrode shows a pair of peaks. Both cathodic and anodic peaks are located at -0.38V. When MP-11 was adsorbed on the surface of the roughened silver electrode modified with mercaptoundecanoic carboxylic acid/ poly-lysine, the CV shows a pair of cathodic and anodic peaks located at -0.42 and -0.35V, respectively (**Figure 1, Curve b**). It indicates that even the surface of the silver electrode was modified with the mercaptoundecanoic carboxylic acid/poly-lysine layers, the electrochemical reaction can still occur. However, the reversibility at the modified electrode is less than that at the bare electrode. Repetitive cycling shows that the peak current decreases slightly after

20 cycles, indicating that MP-11 is strongly adsorbed on the layer of poly-lysine through electrostatic interactions.

Figure 2 shows the comparison of the surface enhanced resonance Raman scattering (SERRS) spectra of MP-11 adsorbed on bare, C_3-, and C_{11}-alkanethiol/poly-lysine modified roughened silver electrodes under the open circuit condition. At bare roughened silver electrode, with irradiation at 413 nm, the intensity of the oxidation state sensitive band at 1373 cm^{-1} gradually decreases, while a new band at 1356 cm^{-1}, corresponding to the reduced form of MP-11, appears and becomes dominant after 30 min (**Figure 2, Spectrum a**). The results indicate that MP-11 adsorbed on the surface of the bare roughened silver electrode can be photoreduced. It is generally accepted that the free electron in a metal can be excited under the illumination of light. The excited electron may escape from the metal to outside. The escaped electron may be captured by an acceptor molecule, resulting in the reduction of the acceptor molecule. Therefore, in this case, the photoejection of free electrons from the roughened silver is considered to be responsible for the reduction of adsorbed MP-11 molecules. Following modification with alkanethiol and poly-lysine, no photoreduction of MP-11 was observed as shown in **Figure 2, Spectrum b and c**, indicating that the layers of alkanethiol and poly-lysine between silver and adsorbed MP-11 may effectively prevent adsorbed species from photoreduction. It demonstrated that the effective electron transfer distances for electrochemical reactions and photoreductions are different.

Figure 1. CVs of (a) mercaptoundeca-noic carboxylic acid/poly-lysine modified roughened silver electrode, (b) MP-11adsorbed on the modified electrode. electrode.

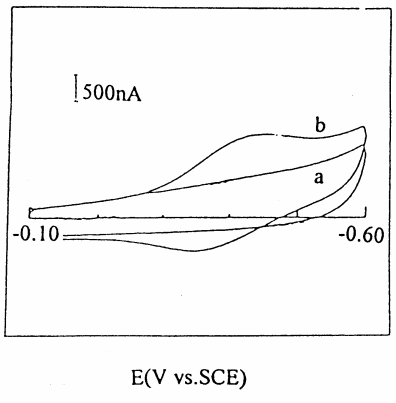
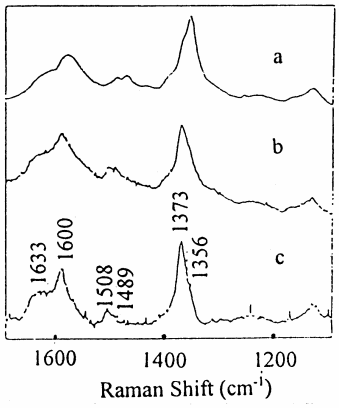


Figure 2. SERRS spectra of MP-11 adsorbed on (a) bare, (b) mercapto-propinoic acid/poly-lysine modified, (c) mercaptoundecanoic carboxylic acid/ poly-lysine modified roughened silver



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