

Ferredoxin 자기조립박막의 분자 다이오드 특성

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Molecular Diode Characteristic of Ferredoxin Self-assembly Film

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INTRODUCTION

In the initial process of photosynthesis, a biological electron transfer system, photoelectric conversion occurs and then long-range electron transfer takes place very efficiently in one direction through the biomolecules[1]. The specific energy and electron transfer takes place on a molecular scale due to the redox potential difference as well as the electron transfer property of functional molecules, especially the electron acceptor, sensitizer and electron donor[2]. In recent years, various artificial molecular photodiode have been fabricated by mimicking the electron transport function of biological photosynthesis[3]. In our previous study, the MIM structured device was fabricated with the hetero films consisting of electron transfer proteins. In this study, the molecular scale diode effect of ferredoxin self-assembly monolayer onto the Au substrate was investigated by STM/I-V measurement. Surface morphology of ferredoxin monolayer was observed by the high resolution STM. The molecular scale diode using ferredoxin self-assembly monolayer is presented as a model system for the nanoelectronic device based on the biomimesis.

EXPERIMENTAL&METHODS

The ferredoxin extracted from Spinach was purchased from Sigma Chemical Company (St. Louis, USA). The ferredoxin was dissolved into the deionized water with pH 7.0 and degassed by the nitrogen gas. Concentration of the ferredoxin solution was 10mM. To fabricate the self-assembly monolayer, functional -SH group was inserted into the ferredoxin molecules by using the bridging molecule SPDP [4].

Pretreated Au substrate was immersed into the 10mM modified ferredoxin solution for 1min, and then rinsed with the Tris-HCl buffer solution and deionized water to remove the salts remaining on the ferredoxin surfaces. Finally, the ferredoxin/Au structured self-assembly monolayer was constructed. Structure of the prepared monolayer of ferredoxin was schematically illustrated in figure 1.



Figure 1. Schematically Structure of Ferredoxin Self-assembly Monolayer

Current-voltage (I-V) measuring unit (SMU Model 236, Keithley, USA) was used as a bias source and current measurement for the ferredoxin self-assembly monolayer. Conducting Au STM tip ($\Psi=1\text{mm}$, Sigma Chemical Co., USA) was used as a top electrode for the conductivity measurement. Electrical resistance between STM tip and Au substrate was more than $10\text{ M}\Omega$ in 0 V . Current and resistance were measured when the STM tip is moved toward the sample surface. Set point for the STM tip approaching was 0.5 nA and scan range for the conductivity measurement was $1\sim 1\text{ V}$. The topography of ferredoxin self-assembly monolayer was obtained by STM (Auto Probe CP, Park Scientific Instruments, USA). In all experiments, STM was operated in constant height mode at ambient condition. Typical set point, servo gain, and scan rate were 0.5 nA , $3\sim 5$, and 3Hz , respectively.

RESULTS&DISCUSSION

To construct the molecular scale electronic device with functional protein films, the formation of arrayed molecular film of the protein has been considered as one of the most important factors dominantly affecting the device performance. The ferredoxin film formation is done by Self-Assembly technique by the SPDP methods. Self-Assembly technique using the -SH functional group of molecules provided a high degree of density without loss of activity. Surface morphology of the ferredoxin Self-Assembly monolayer was shown in figure 2.

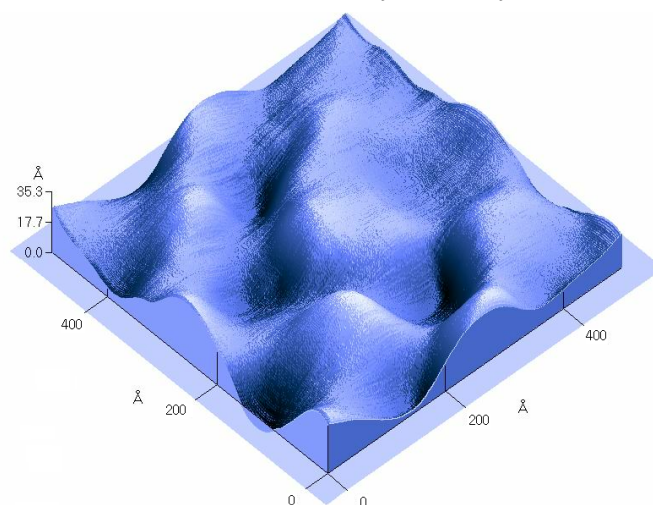


Figure 2. STM Surface Morphology of Ferredoxin Self-assembly Monolayer

As shown in figure 2, size of the adsorbed ferredoxin molecules was about 50~80Å and height was about 30Å. It is indicated that the ferredoxin molecules were well aggregate the spherical type cluster before monolayer formation. The arrayed head groups of the ferredoxin molecules were shown with bright spot and partially the holes were shown with dark spot, which might be the non-bonded Au part. On the whole the ferredoxin molecules were successfully adsorbed onto the Au substrate and construct the self-assembled monolayer.

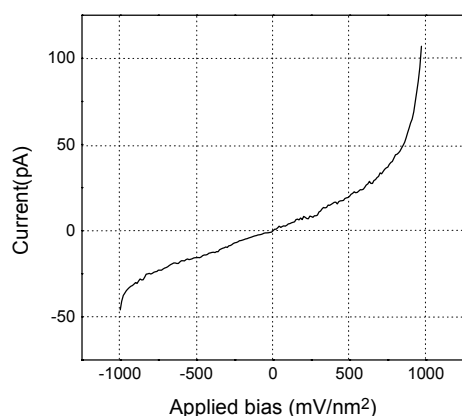


Figure 3. Photoelectric Characteristics of Ferredoxin Self-assembly monolayer;
 (a) rectifying property or diode effect,
 (b) Conductivity between the Au tip/ferredoxin monolayer/Au substrate

The molecular scale electronic property of functional protein monolayer based on the electron transport in the biological photosynthesis process was investigated. The metal tip/protein layer/metal substrate structured molecular electronic device was fabricated by the ferredoxin self-assembly monolayer. By approaching the conducting Au STM tip onto the ferredoxin monolayer surface, electron transfer characteristic of metal/insulator/metal structure was obtained in ambient condition. In Figure 3(a), the rectifying property or diode effect were observed from the measurement of current-voltage characteristic. When a forward bias was applied in range of 0 ~ +1V, the current was generated with the appropriate bias voltage. On the other hand, the current was less generated in the backward environment in range of 0 ~ -1V. When +1V of forward bias was applied to the ferredoxin self-assembled monolayer, the current flow was generated with 100pA. Otherwise, when -1V of reverse bias was applied, the current flow was -50pA. Unsymmetrical property of the current-voltage, which called rectification of diode, is due to the electron transport pathway of the Au-ferredoxin-Au structure. Work function effect between Au substrate and STM tip was subtracted from the data. Conductivity between the Au tip/ferredoxin monolayer/Au substrate was determined as shown in figure 3(b). In the ohmic region (between -0.1 ~ +0.1V) the resistance of the ferredoxin monolayer was maximum and the conductivity in 0 ~ +1V is generally higher than

in 0 ~ -1V. This result indicated that the current flow in forward bias is more than that in backward bias. Thus it can be concluded that the rectified property of the proposed molecular diode function was verified and thus the proposed molecular array mimicking photosynthesis can be usefully applied as the molecular scale diode and memory device.

The molecular scale electronic device composed of functional protein based on the electron transport in the biological photosynthesis process was investigated. The metal tip/protein layer/metal substrate structured molecular electronic device was fabricated with the self-assembly monolayer consisting of the -SH group inserted ferredoxin. Based on the topologies by STM, the monolayer of ferredoxin onto the Au substrate was verified. The directional flow of current occurred efficiently in the proposed molecular device. The diode characteristic of the proposed device was verified by the current-voltage measurement. Thus the proposed molecular electronic device composed of electron transfer protein could be applied as a molecular scale diode.

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