Electrochemical Characteristics of Ferredoxin Self-Assembled Monolayers on Au Substrate for Molecular-Memory Application

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Abstract

Self-assembled monolayers of *spinach* ferredoxin immobilized to Au substrate were investigated. Ferredoxin was immobilized onto the chemically modified Au surface. Au surface were modified to NH^{3+} by the 4-aminothiphenol and then modified by N-succinimidyl-3-[2-pyridyldithio]propionate for the ferredoxin immobilization. To verify the electrochemical activity of immobilized ferredoxin molecules, cyclic-voltammetry was measured. Finally, to verify the memory application, reduction potential was applied to ferredoxin molecules as for the write function, and then current transients observed from the reduced ferredoxin layers were measured for the read function of memory applications.

Introduction

Molecules that might be suitable for use in molecular electronic devices have recently been the subjects of much attention[1]. Current approaches for the molecular electronic devices are based on the development of molecular-scale switches, which can be used as for the logic and memory device[1]. Because the basic paradigm for electronic information storage is retention of charge in a capacitor, the most straightforward approach to molecular scale memory would store charge at the molecular level[2]. Another, more fundamental, approach would utilize the oxidation states of individual molecules to store charge[3]. This technique has the advantage that multiple oxidation-reduction states within one molecule can be addressed to access multibit.

Redox-active biomolecules have charged states at various potential. Application of a reducing potential causes the biomolecules to obtain electrons, resulting in a negatively

charged monolayer. When an oxidizing potential is applied, electron-transfer returns the molecules to the neutral state[4].

In this study, molecular memory effect of self-assembled monolayers of *spinach* ferredoxin were investigated by applying the reduction potential as a write function and measuring the stored reducing charge as a read function. Ferredoxin was immobilized onto the chemically modified Au surface. Au surface were modified to NH^{3+} by the 4-aminothiphenol (4-ATP) and then secondary modified by N-succinimidyl-3-[2- pyridyldithio]propionate (SPDP) to ferredoxin immobilization. To verify the electrochemical activity of immobilized ferredoxin molecules, cyclic-voltammetry(CV) of ferredoxin layer was measured. Finally, to verify the memory application, reduction potential was applied to ferredoxin molecules as for the write function, and then the current transients observed from the reduced ferredoxin layers were measured for the read function of memory applications.

Materials and Methods

Ferredoxin was dissolved in Tris-HCl buffer solution at pH 7.0 to 10mM and degassed with nitrogen gas. 4-ATP and SPDP were dissolved in Ethanol to 10mM and 1mM at the nitrogen atmosphere glove box, respectively. The substrate used for the ferredoxin immobilization was Au coated glass of size 1x1cm.

The prepared Au substrate was immersed into the 4-ATP solution for 24hrs, and then rinsed with absolute ethanol and deionized water before drying under in a nitrogen atmosphere. The prepared 4-ATP layer was immersed into the SPDP solution for 12hr, and then the SPDP modified 4-ATP layer was rinsed with ethanol and deionized water. The hetero-layer composed of 4-ATP/SPDP was then soaked in the ferredoxin solution for 1hrs, and rinsed with Tris-HCl buffer solution and deionized water to remove the salts remaining on the ferredoxin surface, to produce the final ferredoxin/SPDP/4-ATP structured hetero-layer. Since the ferredoxin surface have four Cystein group, it can be chemically bonded to the SPDP. The structure of the prepared hetero-layer composed of ferredoxin/SPDP/4-ATP is illustrated schematically in Fig. 1 (left).

All electrical property of ferredoxin layer was obtained using potentiostat (CHI-660, CHI, USA). 10㎛ carbon SECM probe was used as the working electrode. Pt wire

and Ag/AgCl was used as the counter and reference electrode. Fig.1 (right) shows the schematic illustration for the electrical property measurement. To investigate the memory application, oxidation-reduction potential, open curcuit potential (OCP), and retention current of reduced ferredoxin were obtained from CV, OCP-time dependence, and amperometric i-t measurement.

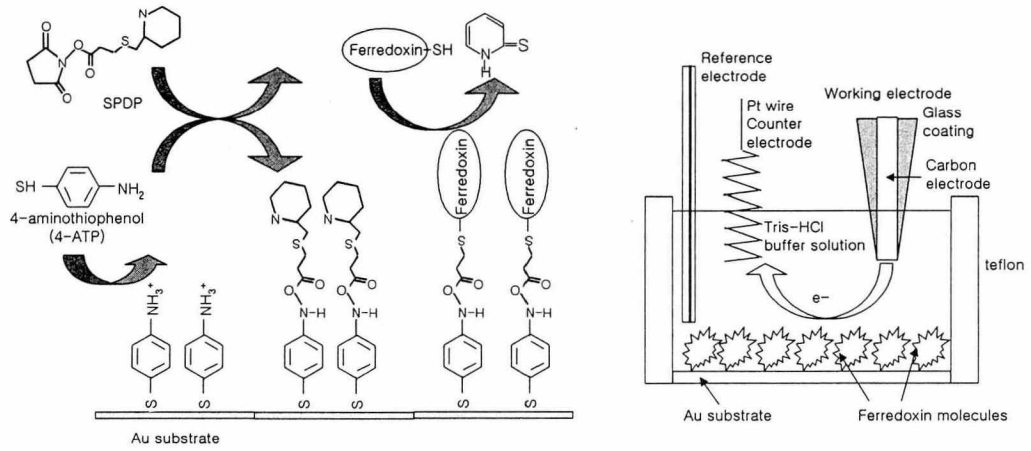

Figure 1. Schematic illustrations of (left) Ferredoxin imobilization and (right) electrochemical property measurement.

Results and discussions

In Fig. 2(left), the oxidation and reduction potentials of immobilized ferredoxin were highly negative at -470 mV and -610 mV, respectively. The -540 mV value for the midpoint potential determined by CV indicates the redox-potential of the immobilized ferredoxin. It is shown that the ferredoxin molecules were successfully immobilized onto the Au surface and the redox activity of immobilized ferredoxin was preserved through reduction-oxidation.

The neutral state OCP value is around -220mV (data was not shown). In this study, the OCP value could use the read function by applying the OCP value to the reduced ferredoxin layer. Charge is stored (written) to the ferredoxin layer via application of potential step as a reducing potential (-610mV). This experiment is conventionally known as chronoamperometry. As shown in fig.2 (right), the potential step from -580 to -640mV reduced the ferredoxin layer. Thus, the charge density of reduced state

ferredoxin is higher than neutral state. In order to read the charge in the reduced ferredoxin, it can be accomplished with a technique that amperometric i-t measurement. The charge stored in the reduced ferredoxin layer can be read by applying the OCP value[1]. As shown in fig.3, reconnection of the electrode at the OCP when the ferredoxin is reduced immediately results in the flow of current that oxidize the reduced molecules. In fig.3, the current decreases (retention charge) from reduced state to neutral state of ferredoxin were clearly measured (read) by applying the OCP to reduced ferredoxin with the lapse of time. In this molecular memory, the charge retention time of reduced state is around 90sec. Thus, to preserve the reduced state (write), it is necessary to apply the reducing potential every 90sec.

From these results, it is concluded that the ferredoxin layer could be used as a molecular memory device by the reducing potential and current flow measurement.

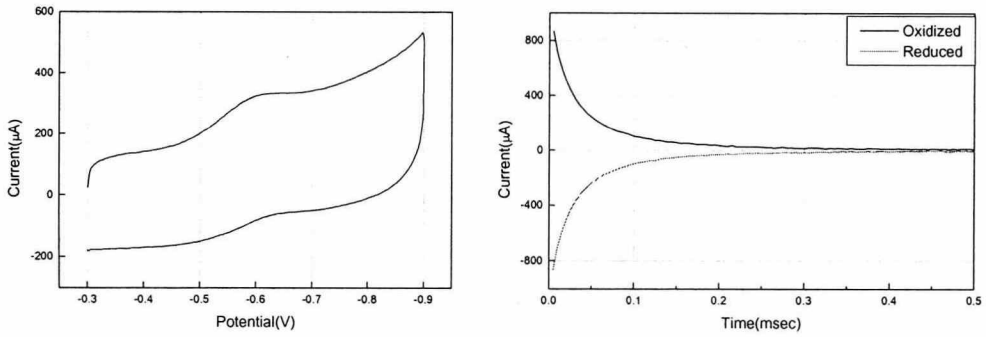

Fig.2 (left) Oxidation-reduction potential value of ferredoxin layer by CV measurement; (right) Current transient of the ferredoxin layer using a chronoamperometry.

Acknowledgements

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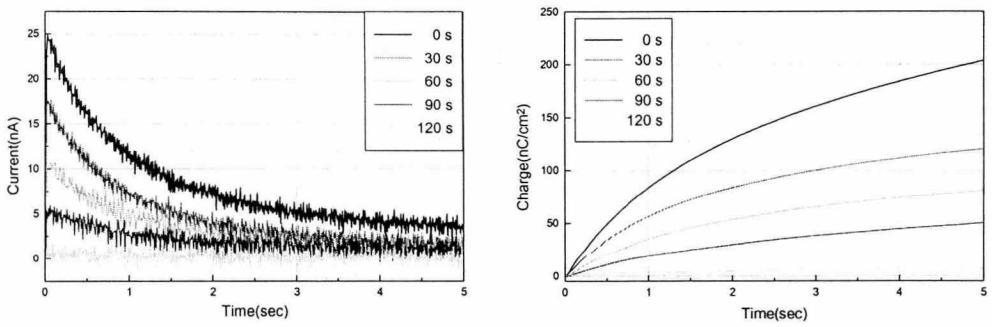

Fig.3 The charge retention of the reduced ferredoxin with the lapse of time. (left) Current decrease from the reduced ferredoxin; reconnection at the measured OCP of -220mV. (right) Charge density obtained by integrating the current decreases.

References

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