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Local Photoswitching Effects of Cytochrome *c*/Viologen/GFP Hetero-Thin Film

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Abstract

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. The metal/insulator/metal structured device consisting of GFP, viologen, cytochrome *c* hetero-thin film was presented based on the biomimesis. GFP, viologen, and cytochrome *c* was used as an electron sensitizer, a mediator, and an electron acceptor. Cytochrome *c* molecules and viologen molecules were deposited by Langmuir-Blodgett (LB) technique, and GFP molecules were adsorbed by self-assembly method (SAM). Surface morphology of hetero-thin film was analyzed by scanning tunneling microscopy (STM). Local photoswitching effects of a proposed photodiode were verified by current-voltage measurements using hybrid STM/I-V measurement system.

Introduction

Bioelectronics and molecular electronics are a breakthrough with great potential for generating new concepts and technologies for the development of electronic devices. The concept in the development of new functional bioelectronic devices can be inspired from the biological systems such as an electron transfer chain or photosynthetic reaction center. By mimicking the organization of functional molecules in the biological electron transfer system, an artificial bioelectronic device can be realized. 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 the functional molecules, especially the electron acceptor, electron relay, sensitizer, and electron donor.[1] Various artificial photodiodes have been fabricated by mimicking the electron transport function of biological photosynthesis.

In this study, local photoswitching function of cytochrome *c*/viologen/GFP hetro-thin film was investigated using hybrid STM/I-V measurement system.[2,3] The directional flow of photocurrent through their redox potential difference occurred efficiently in the proposed molecular device. Local photoswitching effects of the proposed system was verified and thus the proposed molecular system composed of biomolecules could be

applied as biomolecular photodiode with nano scale.

Materials and Methods

N-allyl-N'-[3-propylamido-N",N"-di(n-octadecyl)]-4,4'-bipyridium dibromide (viologen) was synthesized, and green fluorescent protein(rEGFP) was purchased from CLONTECH CO(Palo Alto, California, USA), and cytochrome *c* (extracted from horse heart, type VI) was purchased from Sigma Chemical Company(St. Louis, USA). Other miscellaneous reagents were purchased from Sigma Chemical Company and used without further purification.

Cytochrome *c* was deposited onto gold substrate by LB technique using a circular langmuir trough (type 2022, Nima Tech, England), and the viologen was deposited onto cytochrome *c* LB film by same technique. The self-assembly (SA) monolayer of GFP was constructed by dipping the hetero LB film (viologen LB film deposited onto cytochrome *c* LB film) into the GFP solution. The surface morphology of cytochrome *c* LB film onto the gold substrate and cytchrome *c*/viologen/GFP hetero-thin film were analyzed using STM (AutoProbe CP, PSI, USA). The STM microtopographic images were obtained at a constant-current mode, set point I=0.4 nA, sample bias V=0.9 mV. Photocurrent was measured by hybrid STM/I-V measurement system. The schematic illustration of the method of hybrid STM/I-V measurement was shown in Figure 1.

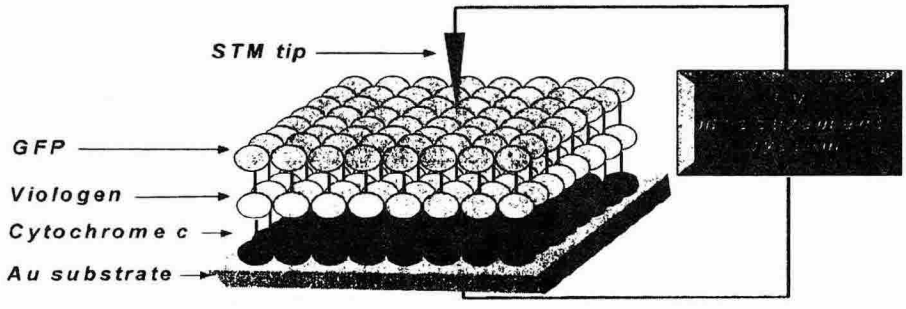
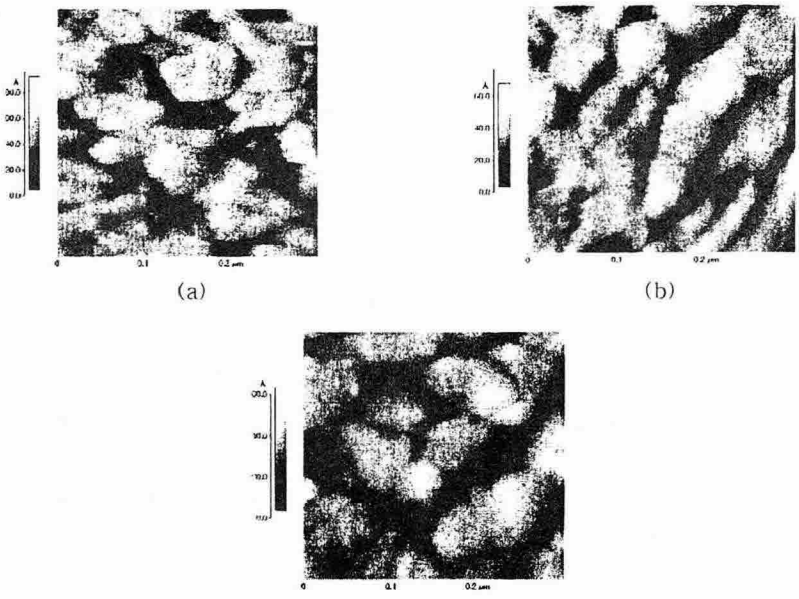


Figure 1. The schematic illustration of the method of hybrid STM/I-V measurement

Results and Discussion

Figure 2(a) shows STM images of cytochrome *c* LB films onto the gold substrate. Cytochrome *c* LB film deposited onto the gold substrate is uniform. Film height is about 60~90 Å, and protein aggregation size is about 0.05㎛~0.1㎛. Viologen molecules deposited onto the cytochrome c LB film is shown in Figure 2(b). Viologen molecules aggregated onto cytochrome *c* LB film. As shown in Figure 2(c), the spherical types of aggregation of GFP molecules was observed. It is intimated that GFP molecules were partially adsorbed onto the viologen/cytochrome *c* hetero LB film surface. The

aggregation size and height of cytochrome *c*/viologen /GFP hetero-thin film were about 50~600Å, 0.05μm~0.15μm, respectively.



(a) (b)

(c)

Figure 2. STM images of scan size 0.3μm×0.3μm ; (a), cytochrome *c* LB film onto the gold substrate ; (b), viologen LB film onto cytochrome *c* LB film ; (c), cytochrome *c*/viologen/GFP hetero-thin film onto the gold substrate

The local photoswitching response of cytochrome *c*/viologen/GFP hetero-thin film is shown in Figure 3. When a forward bias was applied in accordance with the energy level profile of the MIM device, a photocurrent was generated. With repeated step illumination, a reproducible photocurrent was generated. Under illumination, the photocurrent of the thin film was observed. However, in the dark state, amount of current was less than that in the illuminated state. This result indicates that the photoswitching function of the bio-photodiode was achieved. In the proposed bio-photodiode, the photoinduced unidirectional flow of electrons could be achieved due to the redox potential difference as well as the electronic coupling between the functional molecules. It was also observed that the photocurrent intensity was dependent on the external bias voltage. Higher photocurrents were generated as the external bias voltage increased.

From these results, it can be concluded that the photoswithching effects using scheme of the substrate/hetero-thin film/STM tip were verified and the proposed molecular array mimicking photosynthetic reaction center can be usefully applied as a model

system for the development of the biomolecular photodiode.

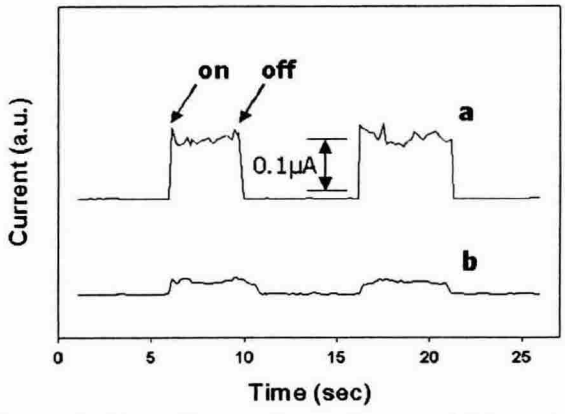


Figure 3. Local photoswitching effects of cytochrome c/viologen/GFP hetero-thin film onto the gold substrate ; (a), bias voltage : 1V ; (b), bias voltage : 0V

The biomolecular device composed of functional proteins based on the electron transport in the biological photosynthesis process was investigated. The hetero-type films consisted of GFP, viologen and cytochrome *c* which were used as a sensitizer, an electron mediator and an electron acceptor, respectively. Based on the topologies by STM measurement, the deposition of cytochrome *c*/viologen/GFP hetero-thin film was verified. And local photoswitching effects of the proposed system was verified by I-V measurements. Thus the proposed molecular system composed of biomolecules could be applied as biomolecular photodiode with nano scale.

References

[1] M. Fujihira, "Organic Thin films and Surfaces: Direction for The Nineties"(1995), Thin Films, 20, 239-277

[2] Supriyo Datta, Weidong Tian et al., "Current-Voltage Characteristics of Self-Assembled Monolayers by Scanning Tunneling Microscopyz"(1997), Physical review letters, 79(13), 2530-2533

[3] S.Boussaad, L. Dziri, R. Arechabaleta et al., "Electron-Transfer Properties of Cytochrome c Langmuir-Blodgett Films and Interactions of Cytochrome *c* with Lipids"(1998), Langmuir, 14, 6215-6219