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Electron Transfer Mediated by Photosynthetic Reaction Center Proteins Between Two Chemical-Modified Metal Electrodes

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Photosynthetic reaction center (RC) proteins in photosynthetic bacteria are very interesting from the viewpoint of natural supramolecular electric devices. One of key factors for the enhancement in currents of RC protein devices is the achievement of low electron-injection barrier between proteins and metal electrodes. In this study, the electron transfer mediated by RC proteins between two gold electrodes modified with various self assemble monolayer (SAM) materials, was measured by use of conductive atomic force microscopy (CAFM). We found that, when both the Au(111) metal substrate and the gold-coated cantilever were modified with 2-mercaptopyridine, CAFM currents were especially enhanced.

Keywords: AFM; biodevice; photosynthesis; reaction center; *Rhodobacter sphaeroides*

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INTRODUCTION

Photosynthetic reaction centers (RC) in photosynthetic bacteria are natural supramolecular photoelectric conversion devices that are quite significant for the light energy conversion in biosystem. The initial reaction in RC is the light-induced charge separation of $(BChl)_2$ (Fig. 1a). Following the charge separation, transfer of an electron from the $(BChl)_2$ to the BPhl occurs within picoseconds. This process is characterized by high quantum efficiency and minimal side reactions. From the viewpoint of solid-state electronics, the remarkable features of RC proteins are (a) ultrahigh-speed electron tunneling transfer without energy dispersion, (b) single molecule, (c) lower production cost, (d) nanometer size (5–10 nm), (e) current rectification and (f) anisotropic distribution of surface hydrophilicity and charge. Greenbaum *et al*. have reported that electron transport vector adsorbed on electrode, i.e., orientation of RC proteins, was controllable by the chemical modification of the metal electrode as the results of scanning tunneling microscope (STM) measurements [1]. While, the performance of organic electronic devices depends in a very direct way on the charge carrier injection efficiency at metal/organic interfaces [2]. Thus the key factors for the enhancement in currents of RC protein devices are not only orientation of RC proteins but also lowering of electron-injection barrier between proteins and metal electrodes. In

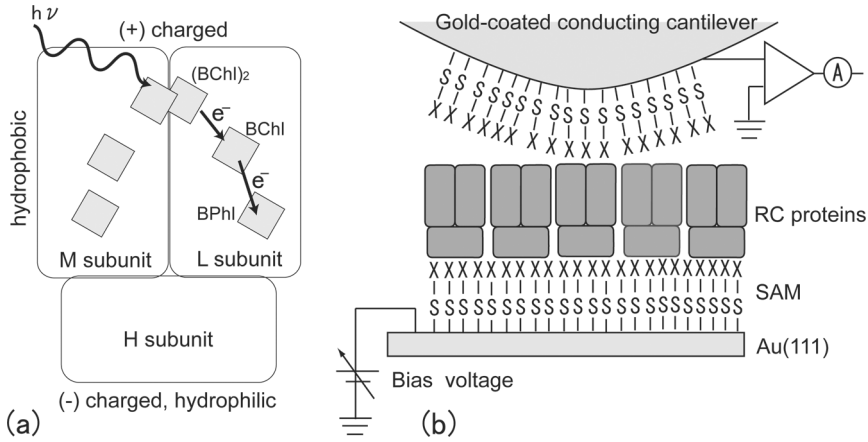

FIGURE 1 (a): Illustration of the structure and the electron pathway of an RC from *Rhodobacter sphaeroides* undergoing light-excitation. (b) CAFM applied for RC proteins between two chemical-modified gold electrodes. The chemical structures of X-S are presented at Figure 2.

this study, the electron transfer mediated by RC proteins between two gold electrodes modified with various self assemble monolayer (SAM) was measured by use of conductive atomic force microscopy (CAFM) *I-V* to find how to enhance and stabilize the current (Fig. 1b). In CAFM *I-V* measurement, the tip always contacts the sample surface with constant applied force of cantilever while voltage sweeping.

EXPERIMENTAL

Preparation of Immobilization of RC Proteins on Chemical-Modified Au(111) Substrate

The RC proteins were isolated from the purple bacterium *Rhodobacter sphaeroides* [3]. X-ray structure of this protein is refined to sub-nm resolution by several groups [4]. The concentration of the solubilized RC proteins was about 1 mM. Au(111) substrates with wide atomically flat terraces are prepared by vacuum evaporation of gold onto freshly cleaved mica substrates [5]. After Hydrogen flame annealing and immediate quenching into pure water, the Au(111) substrates were dried with nitrogen and immersed in 1 mM solution of mercaptoacetic acid ($HSCH_2COOH$, MA), 2-mercaptoethanol ($HSCH_2CH_2OH$, 2ME), 2-mercaptopyridine (C_5H_5NS, 2MP), 4-mercaptopyridine (C_5H_5NS, 4MP), or thiocyanuric acid ($C_3H_3N_3S_3$, TA) respectively for 2 h (Fig. 2). Electrodes modified with SAM of electron-transfer promoters, 2-MP or 4-MP are well known [6]. TA is effective for immobilization of RC proteins [7]. The surface hydrophilicity of SAM on Au(111) substrate is in the order of 2ME (high hydrophilic) > MA > 2MP > 4MP (low hydrophilic) > TA (hydrophobic) [8]. Modification with MA is to form negative-charged surface. The surface of 2MP and 4MP SAM is slightly negative. After chemical surface modification, they were rinsed thoroughly with ethanol and dried with nitrogen. The chemical modified Au(111) substrates were incubated in a RC protein solution

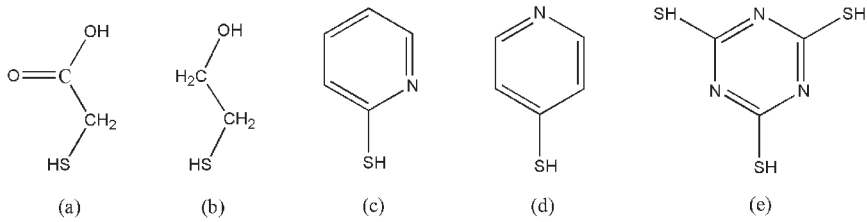

FIGURE 2 Chemical structures of SAM materials. (a) MA, (b) 2ME, (c) 2MP, (d) 4MP, and (e) TA.

for 10 min. After being rinsed thoroughly with distilled water, they were dried with nitrogen.

AFM Imaging and CAFM I-V Measurement

AFM images were recorded with SPI-3800 controller and SPA-300HV unit (SII Nanotechnology, Japan). SiN cantilevers with a spring constant of 0.09 N/m were used. Au/Cr-coated SiN cantilevers (OLYMPUS) with a spring constant of 0.025 N/m and typical tip radius of 40 nm were used as gold-coated ones. Thus we estimated that CAFM current pass through several ten RC proteins. Gold-coated cantilevers were immersed in SAM solution for 2 h to obtain the chemical-modified conductive cantilevers. A ramp bias voltage with a typical sweeping time of 100 ms was applied between the conductive tip and the lower Au(111) substrate. Current was monitored with a highly sensitive current-voltage amplifier connected to a conductive tip. The AFM imaging and CAFM *I-V* measurement were carried out in vacuum (5×10^{-5} Pa) at room temperature. Typical applied force of cantilever was 1 nN. Each CAFM *I-V* characteristics were obtained by averaging of 40 scans.

RESULTS AND DISCUSSION

Densely-packed RC proteins on MA, 2ME, 2MP or 4MP-modified Au(111) substrates show almost similar AFM images of 1 μm scan with the surface roughness of 4–5 nm (<7–10 nm: the size of a RC molecule) (Fig. 3a). However many large aggregations of RC proteins were observed on TA-modified Au(111) substrate with rather higher roughness of 7–8 nm (Fig. 3b). CAFM *I-V* characteristic of the RC proteins on 4MP-modified Au(111) substrate with bare gold-coated cantilever shows slightly current rectification behavior but no rectification on MA-modified one (Fig. 4a). In the case of 2ME modification, clear rectification was observed (Fig. 4b). Thus 2ME-modification was significantly effective to orient RC molecules onto the substrate in a perpendicular position to Au(111) substrate without the denaturation. In the previous report, similar behavior of *I-V* characteristics of single RC protein isolated from the purple bacterium *Rhodospirillum rubrum*, on 2ME or MA-modified Au(111) substrates were also observed by using STM [9]. Strong negative charged end groups of MA might denature RC molecules. The CAFM current through RC proteins on TA-modified Au(111) substrates was larger than on 2-ME modified one but the rectification was not observed (Fig. 4b). TA modification may be effective for lowering injection barrier but not

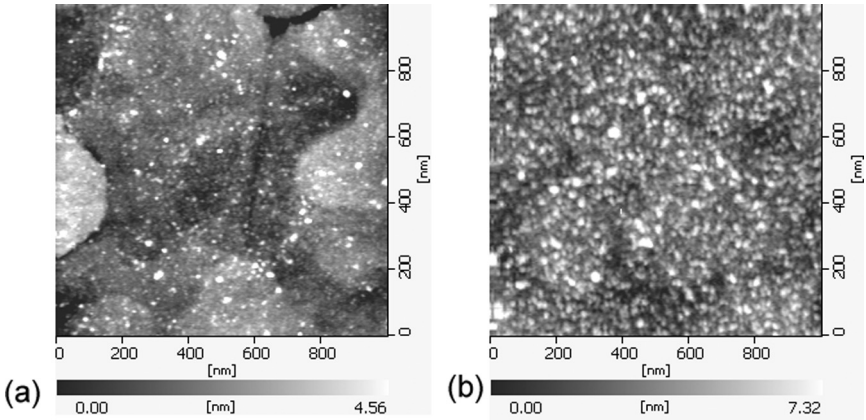

FIGURE 3 AFM images of RC proteins adsorbed on (a) 2ME (b) TA-modified Au(111) substrate.

for orientation of RC molecules. This is because hydrophobic surface of TA-modified Au(111) substrate causes aggregation of RC's without oriented structure (Fig. 3b). CAFM *I-V* characteristic of RC molecules on 2MP-modified Au(111) substrate shows clear current rectification with 3–4 times higher and stable current at 1 V than 2ME modification. Thus 2MP is useful for lowering injection barrier between RC proteins and Au(111), implying that the orientation and the

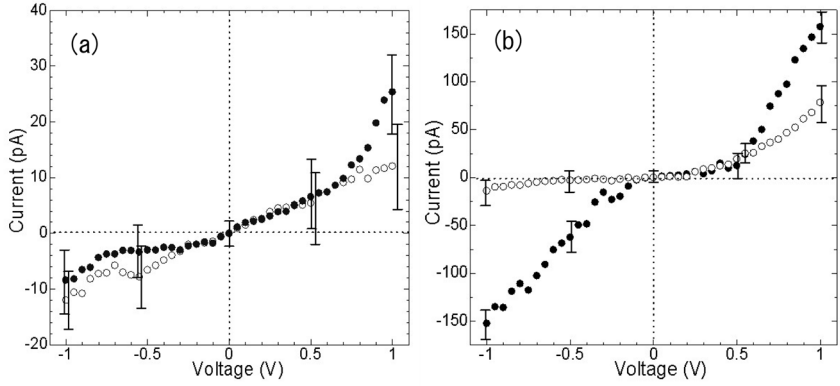

FIGURE 4 CAFM *I-V* characteristics of RC proteins adsorbed on (a) MA (circle), 4MP (dot), (b) 2ME (circle), TA (dot)-modified Au(111) substrate. The bare gold-coated cantilever was used. Error bars indicate the fluctuation of 40 scans.

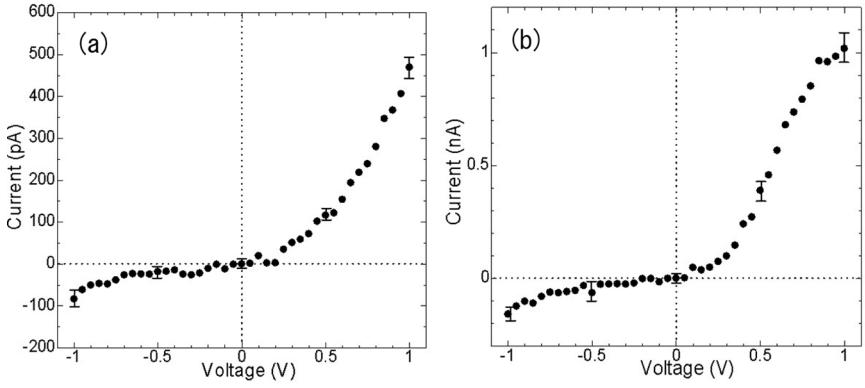

FIGURE 5 CAFM *I-V* characteristics of RC proteins (a) on 2MP-modified Au(111) substrate with bare gold-coated cantilever, (b) sandwiched by 2MP-modified Au(111) substrate and 2MP-modified gold-coated cantilever.

functionality of RC proteins were preserved. Remarkable enhancement of current was observed from RC molecules sandwiched by 2MP-modified Au(111) substrate and 2MP-modified gold-coated cantilever as shown in Figure 1b and 5b. This result implies that 2MP has crucial role for lowering injection between RC proteins and gold. In conclusion, these results show that SAM modification of both metal electrodes connected to RC proteins is effective to enhance the current from RC proteins.

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