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Bio-photosensor: Cyanobacterial photosystem I coupled with transistor via molecular wire

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Abstract

We report on the first successful output of electrons directly from photosystem I (PSI) of thermophilic cyanobacteria to the gate of a field-effect transistor (FET) by bypassing electron flow via a newly designed molecular wire, i.e., artificial vitamin K_1, and a gold nanoparticle; in short, this newly manufactured photosensor employs a bio-functional unit as the core of the device. Photo-electrons generated by the irradiation of molecular complexes composed of reconstituted PSI on the gate were found to control the FET. This PSI-bio-photosensor can be used to interpret gradation in images. This PSI-FET system is moreover sufficiently stable for use exceeding a period of 1 year.

Keywords: Cyanobacterial photosystem I; Gold nanoparticle; Molecular wire; Field-effect transistor; Bio-photosensor

1. Introduction

Photosynthesis is among the most impressive phenomena on earth, not only because it has given rise to the world as we know it, but also because it has provided abundant inspiration for major scientific inquiry into clean and inexhaustible solar energy [1,2], water splitting [3,4], carbon dioxide and nitrogen fixation [5,6], and most importantly, the almost 100%-efficient photo-electric conversion systems involved in the primary process of photosynthesis [7,8]. This ultimate system developed over a period of the four billion years of the evolution cycle. Photosynthesis has fascinated a large number of scientists, who have expended much effort to imitate this process; however, the artificial induction of functional biosystems has been rare [9]. In spite of the difficulty of such an approach, the use of the photosynthetic protein complexes that regulate photosynthesis appears to be reasonable for the investigation of photosynthetic bio-systems.

A large number of trials have been conducted to date involving the application of such biological systems to

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electronic devices. For example, in a few studies, chloroplasts were spread on an SnO_2 electrode and were examined as photoelectrochemical cells [10,11]. Recently, the chloroplast has been investigated in terms of how the orientation of proteins strongly affects the transfer of bionic electrons to an electrode [12–14]. The high performance of PSI is the result of its well-designed spatial configuration (position, direction, etc.); however, no investigations using the PSI photonic device in this context have been reported to date. In this paper, we discuss the first successful direct coupling between functional bionic components (PSI) to artificial electronic devices (FET) via a molecular electric wire designed at the molecular order (Fig. 1); in addition, the output of electrons from PSI to FET is demonstrated with the aim of obtaining a PSI-bio-photosensor capable of interpreting the gradation in an image.

2. Materials and methods

2.1. Materials

Thermophilic cyanobacteria *Thermosynechococcus elongatus* strain BP1 was used as an origin of photosystem I complex (PSI). All chemical reagents were obtained from commercial sources and used without additional purification. FET chips (No. 001314) with an Si_3N_4–Ta_2O_5 thin layer-covered gate were purchased from BAS Inc.

2.2. Characterization

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500 instrument at room temperature. Chemical shifts in ppm were referenced to tetramethylsilane (0.00 ppm) as an internal standard. EI-MS measurements were recorded on a Shimadzu GCMS-QP5000A. FAB-MS spectra were recorded on a JMS SX-102 mass spectrometer (JEOL). Elemental analysis of the products was performed on a Yanaco MT-6 C, H, N corder at the Elemental Analysis Center of the University of Tokyo. Quartz crystal microbalance (QCM) measurements were carried out with a Hokuto HQ-101B QCM controller.

2.3. Isolation of PSI

The cultivation, isolation, and purification of PSI were carried out according to well-known procedures reported in the literature [15].

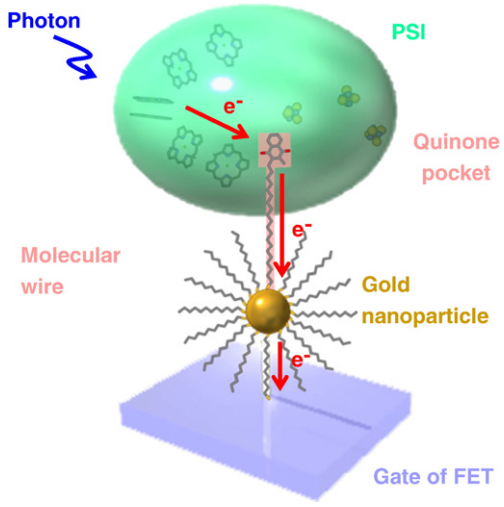

Fig. 1. The concept of the bio-photosensor made of PSI coupled with transistor via molecular wire.

2.4. Synthesis of molecular wire and surfactant

2-(15-Bromopentadecyl)-3-methyl-1,4-naphthoquinone, 1-[15-(3-methyl-1,4-naphtoquionon-2-yl)]pentadecyl disulfide ($(NQC_{15}S)_2$), 1-[15-(3-methyl-1,4-naphtoquionon-2-yl)]pentadecyl thiolate-protected gold nanoparticles ($NQC_{15}S$-AuNP) [16], 1-bromo-12-phenoxydodecane, and (12-phenoxydodecyl)triethylammonium bromide were newly synthesized according to the procedures shown in Scheme 1. The details of the reaction conditions and characterization are described in Supplementary Information.

2.5. Reconstitution of PSI with molecular wires

Purified PSI samples were washed with pure water six times to remove the detergents from the surface of PSI. Next, samples were dried up by lyophilizer (Tokyo Rikakikai FD-1000) for 2 days. To remove VK_1 from PSI, the dry samples were suspended in 50% water-saturated diethyl ether (1 mg dried PSI / 5 mL diethyl ether) for 10 min at 4 °C, then diethyl ether was removed by centrifugation. This treatment was repeated twice. The VK_1-free PSI was re-suspended in 20 mM MES-buffer containing (12-phenoxydodecyl)triethylammonium bromide (PSI:(12-phenoxydodecyl)triethylammonium bromide = 1:300). To reconstitute PSI, $NQC_{15}S$-AuNP was added to the PSI solution (PSI:$NQC_{15}S$-AuNP = 1:1) and gently stirred for 1 day at 4 °C. Excess $NQC_{15}S$-AuNP was removed by five times ultrafiltration using centrifugal filter (Millipore Amicon ultrafree-MC 100,000NMWL) and pure reconstituted PSI, $NQC_{15}S$-AuNP@PSI, was obtained.

2.6. PSI photoactivity measurements

A modified double beam spectrophotometer (Hitachi Model 557) was used to determine the formation of cation of reaction center chlorophyll a in PSI ($P700^+$) under actinic blue light irradiation. Broad band actinic blue light (25 Wm^{-2}) was obtained by the combination of a 30 W tungsten lamp and 10 mm path 20% $CuSO_4$ water solution. PSI sample solution was contained in a disposable polystyrene cuvette having 10 mm measuring light (701 nm) path and 3 mm actinic blue light path. To eliminate contamination of actinic light to a photo-multiplier, an interference filter transmitted 701 nm light (Optical Coatings Japan) was put on the surface of photo-multiplier.

2.7. TEM measurements

The TEM images of the intact PSI and $NQC_{15}S$-AuNP@PSI were recorded at 75 kV using a Hitachi H-7000 system, and the $NQC_{15}S$-AuNP image was obtained at 200 kV using a Hitachi HF-2000 system. The solutions of native and modified PSI molecules were dropped on the carbon-coated copper grids. The samples were not subjected to staining.

2.8. Photocurrent measurements

A self-assembled monolayer (SAM) of 1,4-benzenedimethanethiol was prepared on the surface of the gold electrode by immersing an Au-mica plate which had been annealed by hydrogen frame just before use in an ethanol solution of 10 mM 1,4-benzenedimethanethiol. Then, $NQC_{15}S$-AuNP@PSI was immobilized on the SAM via Au-S bond by immersing the SAM-modified gold electrode in a buffer solution d containing the reconstituted PSI for 24 h.

Photocurrent measurements were carried out with the electrochemical cell equipped with an Ag/AgCl reference electrode and a Pt counter electrode in the presence of 250 mM sodium L-ascorbate (NaAs) as a sacrificial reagent, 2.5 mM 2,6-dichloroindophenol sodium hydrate (DCIP) as a mediator, and 100 mM $NaClO_4$ in the MES-NaOH (pH 6.4) buffer aqueous solution. The $NQC_{15}S$-AuNP@PSI-immobilized Au-mica electrode was irradiated with a monochromatic light from an Asahi Spectra LAX100 Xe lamp, passed through an optical filter (Asahi Spectra, $\Delta\lambda = \pm 6.5$ nm). The light intensity was 3.3 mW at 680 nm, and the irradiation area was 0.16 cm^2. With controlling the electrode potential by a FUSO HECS318C potentiostat, the current responses with the light irradiation were measured and recorded as the photocurrent.