Electrochemical tuning of metabolisms of photosynthetic microbes

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Extracellular electron transfer (EET) involves the direct or indirect interaction of intracellular redox-active species with extracellular solid materials including electrodes[1]. EET is currently being applied towards the electrochemical cultivation of microbes, which gain energy by the exchange of electrons generated during respiration with extracellular electrodes. In particular, this cultivation method has been successfully applied for electricity production from waste biomass in microbial fuel cells and carbon dioxide fixation. Another interesting aspect of EET via extracellular electrodes is to regulate intracellular redox state (IRS). As the IRS is determined by the balance between inflow and outflow of electrons, it can be precisely regulated by electrochemical tuning of the EET process (Figure 1).

Photosynthetic microbes are able to synthesis organic compounds from CO_2 by using light energy, and have attracted a lot of attentions for production of useful organic compounds and biofuels. The rate-limiting factor of the photosynthesis in photosynthetic bacteria is known to be CO2-fixation process (Calvin cycle). Especially, the activity of RuBisCO, which is CO_2-fixing enzyme, is much lower compared with general enzymes. By improving the expression level or the activity of RuBisCO, total activity of the photosynthesis is expected to be improved. It is known that photosynthetic bacteria can sense environmental factors (e.g. light intensity and O_2 concentration) through the redox state of the electron transport chain in the cells, and regulate the expression levels of photosynthetic genes including a gene encoding RuBisCO depending on the redox state. In this study, it was attempted that the redox state of the electron transport chain in *Rhodopseudomonas palustris* cells were interfered by electrochemical cultivation with the aim being put on enhancing the expression level of RuBisCO toward the improvement of the CO_2-fixating ability.

For electrochemical cultivation, three-electrode system (Ag/AgCl/ KCl(sat) reference, glassy carbon working, and Pt counter electrodes) was used. PMF polymer (Figure 2) developed by our group[2] was added as a biocompatible mediator to electrically connect bacterial cells and the extracellular electrode. All the incubation and measurement were taken in a 30 °C incubator. The electrode potential was set at +0.1 V or + 0.4 V vs. SHE where the PMF is electrochemically reduced or oxidized state, respectively. It was shown that expressions of genes encoding RuBisCO were successfully regulated by electrode potential (Figure 3), affecting the CO_2 fixation ability (Figure 4). We also revealed for another photosynthetic microbe, *Synechococcus elongates* PCC7942 cells, that not only metabolism but also circadian clock can be electrochemically regulated in the presence of PMF mediators.

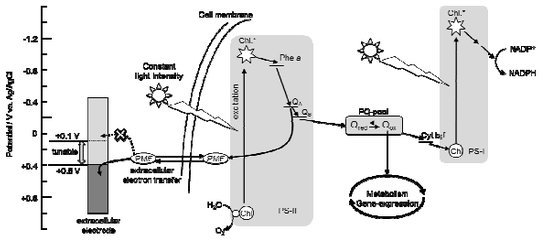

Figure 1. Concept of the present work

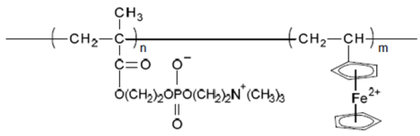

Figure 2. Molecular structure of PMF polymer.

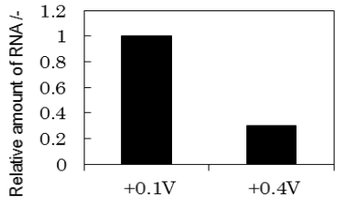

Figure 3. Relative amount of mRNA *cbbS*, a gene encoding an enzyme related to RuBisCO synthesis at two different applied potentials.

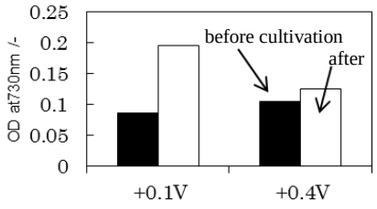

Figure 4. OD value at 730 nm representing cell concentration before and after electrochemical cultivation at two different potentials.

[1] B. E. Logan, K. Rabaey, *Science* 2012, **337**, 686.
[2] K. Nishio, et al., *ChemPhysChem* 2013, in press.