Futurum
Tsukuba Science Journal

Bioelectrochemical Photodiode Using Hot-Spring Microalgae Showing Ultraviolet Optical Rotation and Energy Generation

Bio-Photodiode

Kyoka Komaba, Hiromasa Goto*

Department of Material science, Faculty of Pure and Applied Sciences,
University of Tsukuba, Tsukuba Ibaraki 305-8573, Japan.
*Correspondence: gotoh@ims.tsukuba.ac.jp

ABSTRACT

In this research, we prepared a simple-form photodiode with *Cyanidium caldarium* having photosystem II, an extreme environmental organism. *Cyanidium caldarium* is spontaneously deposited on a glass electrode in the form of a biofilm. The algae-coated electrode functions as an electron provider as a cathode in the biological electrochemical photodiode system, which is assembled in the laboratory. Hot-spring water can serve as an electrolyte solution with conductivity as well as a culture fluid for the algae. The ionic exchange layer is not required in the biological cell. This paper reports the ultraviolet right optical rotation of *Cyanidium caldarium* and its energy generation function.

Keywords: *Cyanidium caldarium*, photodiode, hot springs, photosynthesis, microalgae

Introduction

One of the most important issues for our future is the development of new energy generation [1] and energy storage. From the viewpoint of bioapplications and environmental issues, biophotovoltaic systems [2–5] and biofuel cells [6,7] have been developed. Further, the efficient metals absorption function of algae living in sulfuric hot springs may contribute a solution to the rare earth depletion problem for high technologies [8].

In this research, we prepared a bioelectrochemical photodiode with *Cyanidium caldarium* as an extreme environment organism, which habits on the rock in hot-spring water under the condition of pH < 5 and swiftly running water at ca. 30 °C–55 °C. Figure 1 depicts a circularly polarized differential interference contrast optical microscopy (C-DIM) image. *Cyanidium caldarium* shows green color derived from chlorophyll *a* having Mg in the center to conduct photosynthesis. Previously, Zn-type chlorophyll has been found in *Acidiphilium rubrum*, showing pink in color [9].

First, the properties of *Cyanidium caldarium* sampled in Kusatsu (Gumma, Japan) were evaluated by Fourier transform infrared (FT-IR) absorption, ultraviolet–visible (UV–vis) optical absorption, circular dichroism (CD), and optical rotatory dispersion (ORD) spectroscopy measurements.

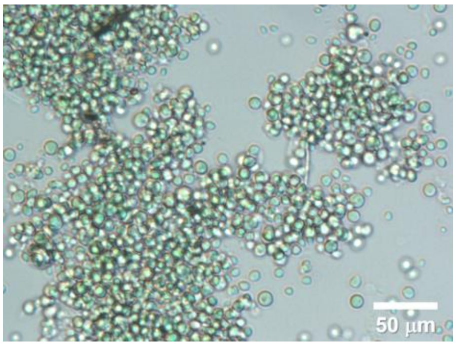

Figure 1. Circularly polarized differential interference contrast optical microscopy (C-DIM) image of *Cyanidium caldarium*.

The ORD determined that *Cyanidium caldarium* has an ultraviolet range optical rotation function. Next, we prepared an electrochemical photodiode using *Cyanidium caldarium*.

As shown in Figure 2, the algae bio-photodiode can be expressed by a photoelectrical symbol.

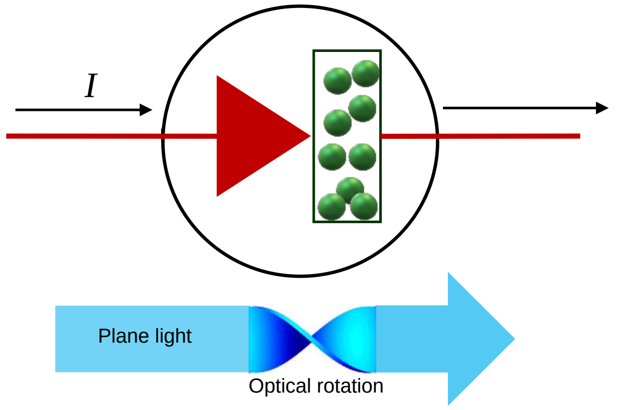

Figure 2. Photoelectrical symbol of the algae bio-photodiode.

Experimental

Materials

Cyanidium caldarium and spring water were sampled in Kusatsu hot spring. Kusatsu spring water shows ca. 4.8 mS/cm. The pH value at 25 °C was 2.1.

Instruments

The FT-IR absorption spectrum for the dry form of *Cyanidium caldarium* was obtained with an FT/IR-4600 (JASCO, Tokyo) using the KBr method. An Eclipse LV100 high-resolution polarizing microscope was used for optical microscopy observations (Nikon, Tokyo). UV–vis optical absorption spectra were recorded on a V-630 UV–vis spectrophotometer (JASCO). A J-720 spectropolarimeter (JASCO) with an ORD unit and an artifact detection/correction unit (JASCO) was used to measure the CD and the ORD (JASCO). Electrical conductivity measurements for the hot-spring water were performed with a CG-201 PL TOA electrode and a conductivity meter model CM-20E (TOA Electronics Ltd). Electrical measurement for the algae-based diode was carried out with a digital electrometer R8252 ADVANTEST (Tokyo). Indium-tin-oxide (ITO) coated glass electrodes were submerged into the hot-spring water containing living *Cyanidium caldarium*. As a substrate, *Cyanidium caldarium* was naturally deposited on the ITO to form the algae-coated electrode in the form of biofilms.

Setup for biological photodiode

Figure 3 depicts the preparation of the biological photodiode system. First, five pieces of the *Cyanidium caldarium* coated ITO glass electrode as the cathode (5 cm × 5 cm) were placed in a beaker with Kusatsu spring water as an electrolyte solution. Another ITO as an anode was set in the beaker.

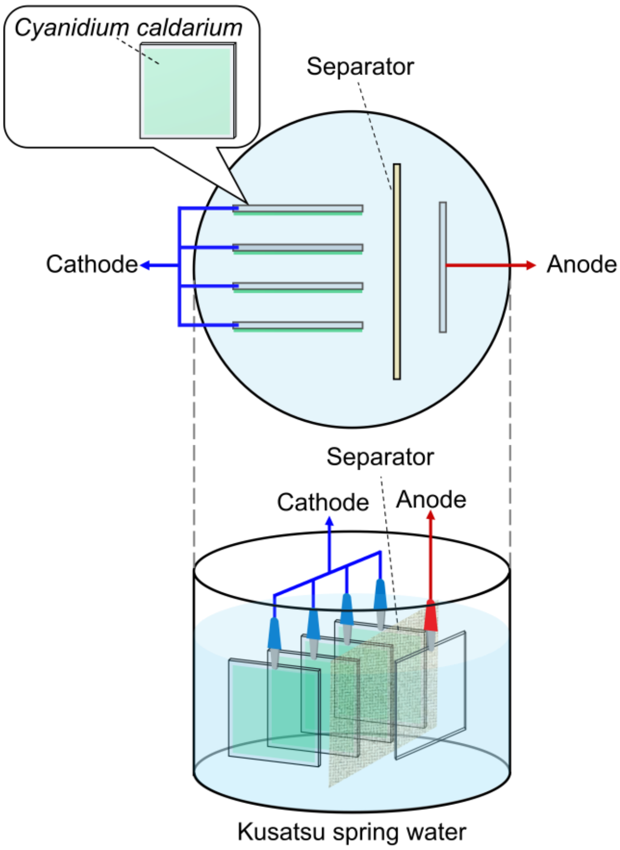

Figure 3. Bio-electrochemical photodiode system.

Results and discussion

Cyanidium caldarium

IR spectroscopy

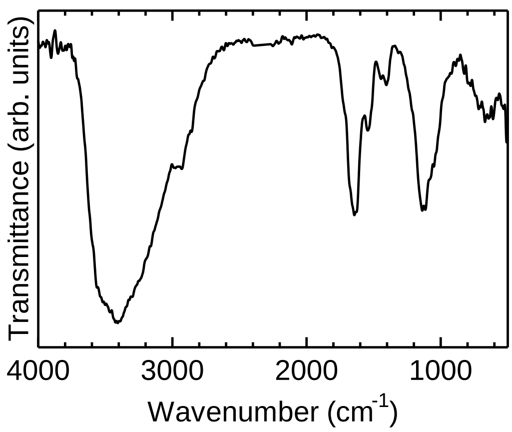

Figure 4. Infra-red (IR) spectrum of dried *Cyanidium caldarium*.

Table 1. Assignment of IR signals (ν: stretching vibration, δ: vending vibration).

	ν_{OH}	ν_{CH}	$\nu_{C=O}$	ν_{CN}	δ_{OH}	δ_{CH}
			(cm^{-1})			
Cyanidium caldarium	3425	2946	1647	1543	1404	1137

The IR measurement results of *Cyanidium caldarium* dried under vacuum are displayed in Figure 4. Table 1 summarizes the assignment of the IR signals. Microalgae consist of proteins, cellulose, saccharides, and minerals. The signals derived from OH vibration were observed at 3425 and 1404 cm^{-1} due to saccharide elements. The signals derived from C=O and CN vibrations were shown at 1647 and 1543 cm^{-1}, respectively. This result indicates that *Cyanidium caldarium* has proteins.

UV–vis spectroscopy

Figure 5 shows the result of the UV–vis optical absorption spectrum of *Cyanidium caldarium* in Kusatsu spring water. The photosystem II complex, which is involved in the photolysis of water, is associated with absorption bands at 633 and 683 nm. Here, *Cyanidium caldarium* absorbs solar energy to transfer electrons and electrolyze water to produce oxygen.

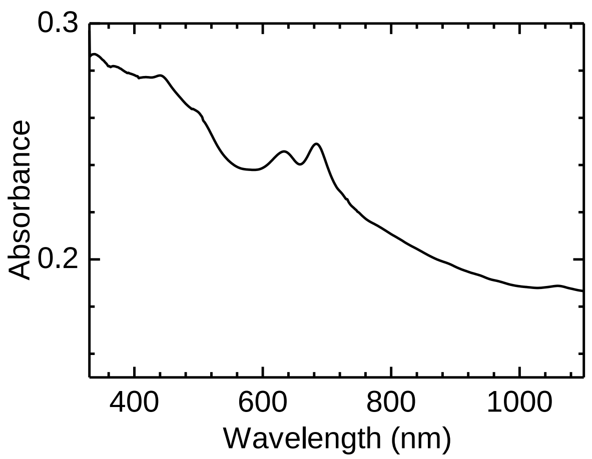

Figure 5. UV–vis optical absorption spectrum of *Cyanidium caldarium*.

CD and ORD spectroscopies

Figure 6 shows the CD and the ORD spectroscopy measurement results of *Cyanidium caldarium* in Kusatsu spring water. This finding indicates that *Cyanidium caldarium* absorbs circularly polarized light and has right (clockwise) optical rotation of ultraviolet (~300 nm) light function as a natural rotation of light.

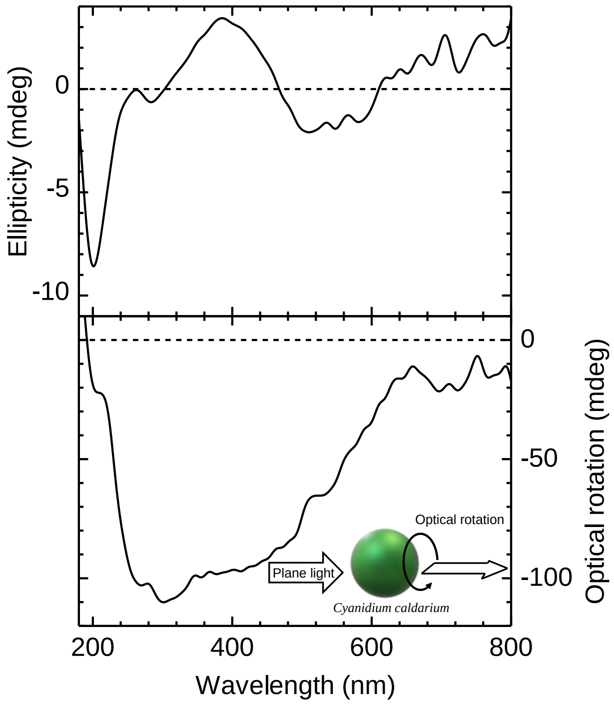

Figure 6. Circular dichroism **(**CD) and optical rotatory dispersion (ORD) spectra of *Cyanidium caldarium* in Kusatsu spring water.

Photodiode

For 100 h at 25 °C, the photodiode generated a current of ca. 10 mA/m^2, 0.08 V indicating the photosynthesis of *Cyanidium caldarium* yields electricity (Figure 7).

To date, bio-solar cells has been developed [10,11]. Recently, continuous supply power for six months to microprocessors from biophotovoltaic systems using a cyanobacteria on an aluminum electrode was reported [12].

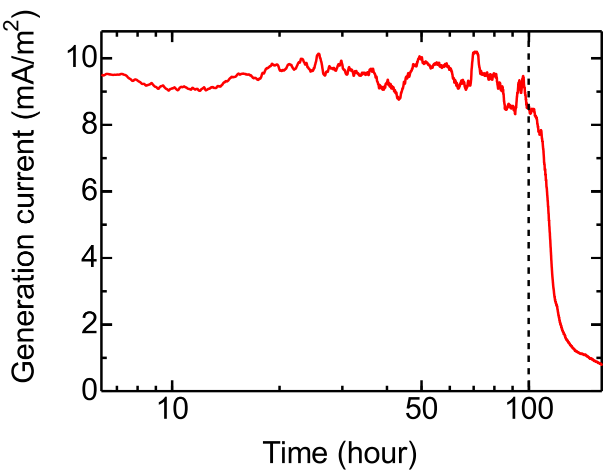

Figure 7. Generation current from photodiode as a function of time.

Higher current generation and longer life of the *Cyanidium caldarium*-based cell are expected with a higher water temperature (optimal temperature, 45 °C) [13,14] and circulation similar to that of the hot-spring water environment.

Conclusions

The photoelectrochemical diode has been developed using *Cyanidium caldarium* as an extreme environment organism living in high temperature and strong acid conditions. The diode preparation is simple because no ion-exchange membrane is required, and spontaneous deposition of biofilms on the artificial electrode, which functions as a cathode, is employed. Electrical current flows in one direction from anode to cathode with an injection of an electron from the *Cyanidium caldarium* biofilm on the ITO. Furthermore, we found that *Cyanidium caldarium* performs an ultraviolet region optical rotator. Following inorganic and organic semiconductors, the application of biological systems is a new technology for optoelectronics.

Acknowledgement

We would like to thank the Glass Workshop, University of Tsukuba.

References

[1] Watanabe, H.; Li, D.; Nakagawa, Y.; Tomishige, K.; Kaya, K.; Watanabe, M. M. *Appl. Energy* **2014**, *132*, 475–484.

[2] Lee, H.; Choi, S.; *Lab. Chip*, **2015**,*15*, 391–398.

[3] Bombelli, P.; Iyer. D. M. R.; Covshoff, S.; McCormick, A, J.; Yunus, K.; Hibberd, J. M.; Fisher, A, C.; Howe, C, *J. App. Microbiol. Biotechnol*. **2012**, *97*, 429–438.

[4] Yagishita, T.; Sawayama, S.; Tsukahara, K.; Ogi, T. *Sol. Energy*. **1997**, 61, 347–353.

[5] Morales, M.; Hélias, Arnaud.; Bernard, O. *Biotech. Biofuel*. **2019**, *12*, 239.

[6] Shitanda, I.; Fujimura, Y.; Takarada, T.; Suzuki, R.; Aikawa, T.; Itagaki, M.; Tsujimura, S. *ACS Sens*. **2021**, *6*, 3409–3415.

[7] Amao, Y.; Fujimura, M.; Miyazaki, M.; Tadokoro, A.; Nakamura, M.; Shuto N. *New J. Chem*. **2018**, *42*, 9269–9280.

[8] Minoda, A.; Sawada, H.; Suzuki, S.; Miyashita, S.; Inagaki, K.; Yamamoto, T.; Tsuzuki, M. *Appl. Microbiol. Biotechnol.* **2015**, *99*, 1513–1519.

[9] Kobayash, M.; Akiyama, M.; Yamamura, M.; Kise, K.; Takaich, S.; Watanabe, T.; Shimada, K.; Iwaki, M.; Itoh, S.; Ishida, N.; Koizum, M.; Kan, H.; Waka, N. Structural Determination of the Novel Zn-Containing Bacteriochlorophyll in Acidiphilium Rubrum, *Photomed. Photobio*., **1998**, *20*, 75–80.

[10] Torimura, M.; Miki, A.; Wadano, A.; Kano, K.; Ikeda, T. *J. Electroanal. Chem*., **2001**, *496*, 21–28.

[11] Kaneko, M., Mol. Cat. Ener. Conv., eds. T. Okada and M. Kaneko (Springer, Berlin, 2009) p. 199–215.

[12] Bombelli, P.; Savanth, A.; Scarampi, A.; Rowden, S. J. L.; Green, D. H.; Erbe, A.; Årstøl, E.; Jevremovic, I. Hohmann-Marriott, M. F.; Trasatti, S. P.; Ozer, E.; Howe, C. J. *Energy Env. Sci.*, **2022**, *15*, 2529–2536.

[13] Darley, W. M. *Algal Biology: A Physiological Approach*. Blackwell Scientific Publications, 1982. Basic Microbiology series Vol. 9.

[14] Eisele, L. E.; Bakhru, S. H.; Liu, X.; MacColl, R.; Edwards, M. R. *Biochim. Biophys. Acta – Bioenerg*. **2000**, *1456*, 99–107.

ORCID

Hiromasa Goto: 0000-0003-4276-735X

Citation
Komaba, K.; Goto, H. *Futurum-Tsukuba Sci. J*., **2022**, *5*, 75–78.