

Supplementary Information

Photocatalytic Alginate Fuel cells for Energy Production and Refinery of Macroalgae

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1. Fabrication procedure of TiO₂-modified anodes

The following steps are further detail of the anode fabrication procedure.

1. Carbon sheets were cut and washed repeatedly by agitation in ultrapure water and ethanol. The washed substrates were then dried overnight at 60°C to remove remaining droplets.

2. Prior to TiO₂ deposition, the substrates were pressed flat and treated with ultraviolet light and ozone (O₃) for 30 minutes using a UV/ozone treatment setup (ASUMI-GIKEN ASM1101N) to increase their surface hydrophilicity and improve their interaction with the methanol-dispersed TiO₂.
3. TiO₂ particles were dispersed in methanol (Wako, reagent grade) to a concentration of 5 mg/mL and thoroughly agitated by ultrasonication for 30 minutes prior to deposition.
4. The UV/O₃-treated carbon sheet substrates were placed on a hot plate, and the TiO₂ dispersion was pipetted onto the substrate surface multiple times until the desired TiO₂ loading was achieved. The substrates were left for 5 minutes between successive TiO₂ drops to allow the methanol to evaporate.
5. The substrates were annealed in an oven (Shimadzu, MPN-310) for 400°C for 2 hours, then left overnight to cool to room temperature naturally prior to use.

2. Output voltage measurement over 24 hour operation

The fuel cell voltage was measured continuously over a period of 24 hours through the following steps.

1. The assembled fuel cell was connected to a voltage recorder via an external circuit.
2. In either the presence or absence of artificial solar irradiation, the system was left stationary for five minutes to let the open-circuit voltage stabilize.
3. A resistance decade box was connected between the fuel cell and voltage recorder. The resistance was set to 3.3kΩ, which gave the maximum power density in experiments from the previous section. Continuous recording of the cell voltage was initiated as soon as the resistance was incorporated into the external circuit, with the recorded

values sent to a laptop connected to the voltage recorder. The sampling rate was set to 0.1 Hz (one value recorded every ten seconds, for a total of 8640 readings over 24 hours).

3. HPLC analysis of alginate solutions

The configuration of the HPLC system used in this study is shown in Fig. S1. All units besides the reservoir, column and desktop were purchased from Shimadzu Inc. The system consists of a peristaltic pump (LC-10AS) driving the mobile phase from a reservoir, through a degasser unit (DGU-20A) to remove any dissolved gases and into the column (Shodex OHPak SB802.5), whose temperature is maintained by the column oven (CTO-10A). Samples are injected into the system externally using a microsyringe just prior to the column. After liquid flows through the column, it is sent through two detectors. The former, a UV detector (SPD-10A), is similar to a spectrophotometer, in which the flowing liquid is irradiated with ultraviolet light of a single wavelength, and its absorbance is measured. The latter (RID-10A) compares the refractive index of the liquid flowing through a sample optical cell within the detector with that of a liquid contained in a reference cell adjacent to the sample cell. Due to the order in which the sample flows through the detectors, if a species produces a detectable signal in both detectors, its retention time as observed by the UV detector will be slightly earlier than that on the refractive index detector. A desktop computer, connected to the equipment through a communication bus module (CBM-20A), is used to adjust various equipment parameters, operate the system and display experimental results. The various experimental conditions and equipment parameters used in the following analyses are given in Table S1.

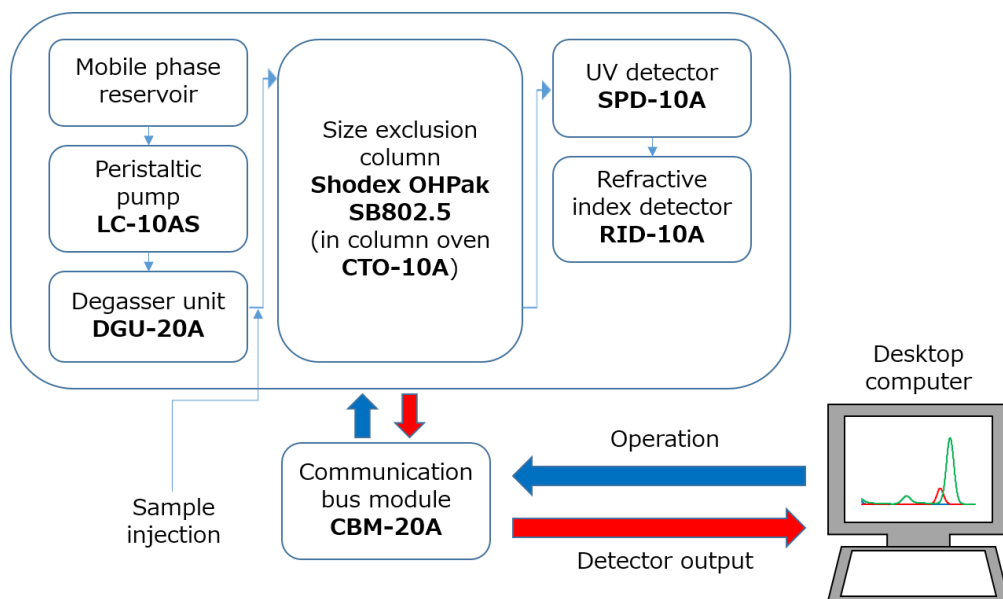


Fig. S1 Schematic of HPLC system used in this study.

Table S1 Experimental conditions and equipment parameters used for HPLC measurements.

Mobile phase	0.2M phosphate buffer
Mobile phase flow rate	0.5 mL / min
Sample injection volume	20 μ L
Column oven temperature	35°C
detection wavelength	260 nm

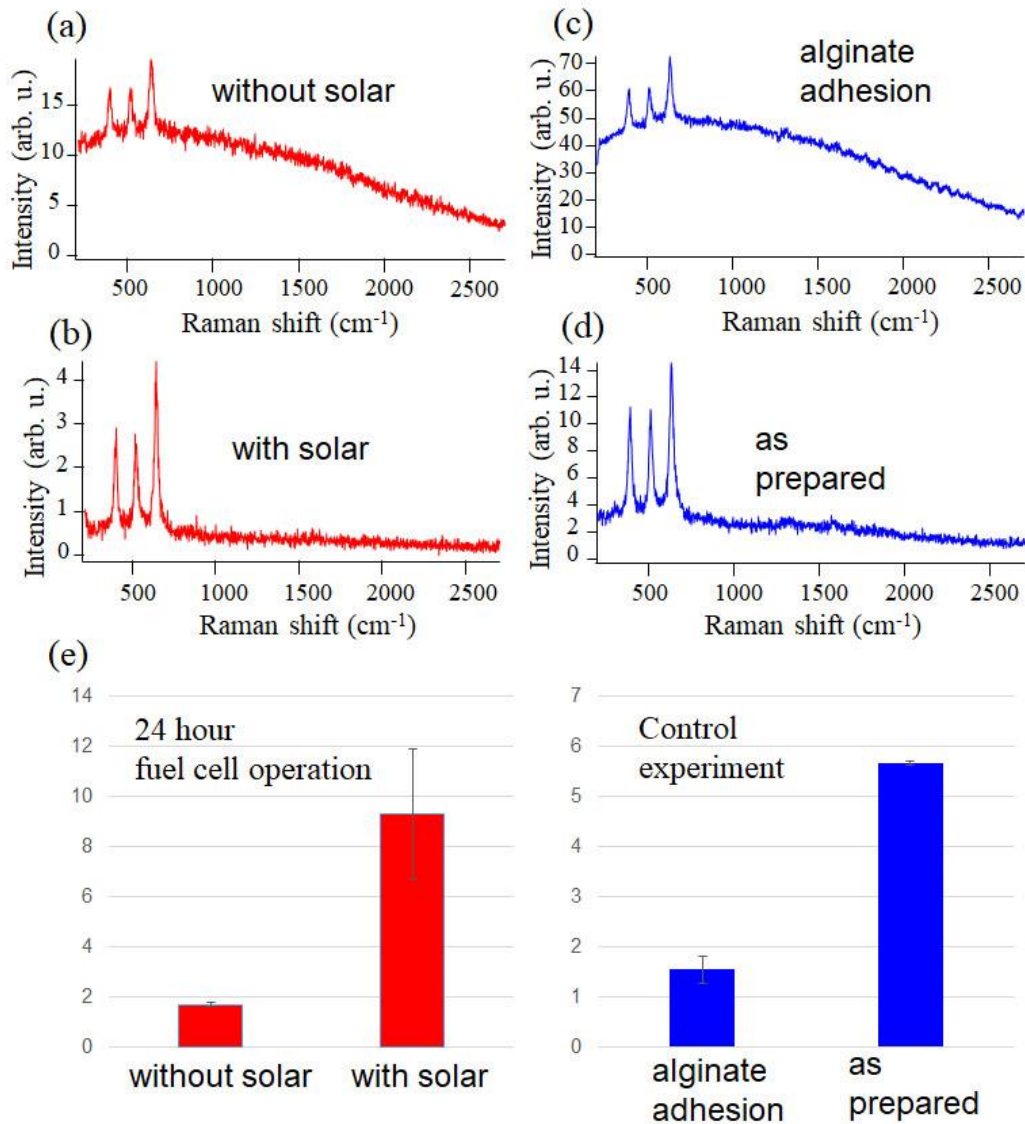


Fig. S2 (a, b) Raman spectra of TiO₂/C electrodes after 24 hour cell operation without (a) and with (b) solar illumination. (c, d) Raman spectra of TiO₂/C electrodes after (c) and before (d) alginate adhesion. (e) Intensity ratios of Raman band at 638 cm⁻¹ to broad emission intensity at 1000 cm⁻¹.

4. Evaluation of the self-cleaning effect of TiO₂/C electrodes

Fig. 4 in the main text indicates that the output of the alginate fuel cell decreased to near 0 V without solar illumination, whereas it kept a certain level over the 24-h operation under solar illumination. These results could be attributed to the photocatalytic self-

cleaning effect of TiO₂ toward the alginate adsorption. We evaluate this point by Raman spectroscopy. A laser beam (PD-LD, SLM-632.8-FS; wavelength 632.8 nm, power 1.4 mW at the sample plane) was focused on an electrode surface via an objective lens (magnification 10x, N.A. 0.12). Raman scattering spectra were measured with a spectrometer (SR303i with DU970N, Andor). Fig. S2 (a) and (b) show Raman spectra of TiO₂/C electrodes after 24 hour cell operation without and with solar illumination, respectively. Clear three peaks correspond to Raman bands of anatase phase of TiO₂. The Raman spectra of the electrode without solar illumination (Fig. S2a) has a distinct broad emission. On the other hand, the contribution of the background emission is quite low and three Raman bands of anatase phase were observed clearly in the case of the solar irradiated electrode (Fig. S2b). It is likely that the broad emission could be attributed to the alginate adsorbed on an electrode surface. Thus we performed Raman spectral measurements of a TiO₂/C electrode, on which alginate was pasted intentionally. This alginate-coated electrode was prepared by dropping a 10 μL of the alginate/NaOH solution on a TiO₂/C electrode and drying solvent. Raman spectrum of an alginate-coated electrode (Fig. S2c) shows anatase Raman bands with a broad background emission, which is similar with that of the electrode after 24 hour cell operation without solar irradiation (Fig. S2a). This broad emission band was not distinct in the original electrode (before the alginate adsorption). These results indicates that the intensity ratio of anatase Raman band to broad emission represents the degree of the alginate adsorption, as shown in Fig. S2e. Thus Raman spectral analysis demonstrates the self-cleaning effect of TiO₂/C electrodes during the alginate fuel cell operation under the solar irradiation.