

Development of artificial leaf device for solar fuel production

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Introduction

Recently, solar fuels such as hydrogen gas from water and methanol from carbon dioxide reduction based on the artificial photosynthesis have received considerable attention.¹⁾ The photosynthesis proteins are well-organized into thylakoid membrane in natural leaf. Thus, the photosynthesis reaction proceeds in the thylakoid membrane device. In natural leaf, glucose and oxygen are produced from CO₂ and water with solar energy. To mimetic the leaf "Artificial leaf" for solar fuel such as hydrogen gas from water and methanol production from CO₂, the components such as a photosensitizer, an electron carrier molecule and a catalyst are immobilized on the surface of suitable substrate.

In this work, two kinds of artificial leaf devices for solar fuel production are developed. One is the artificial leaf device consisting of chlorophyll derivative chlorin-e₆ (Chl-e₆), viologen (electron carrier) and platinum nano-particle onto silica-gel based substrate for solar hydrogen production. The other is solar synthesis of formic acid from CO₂, which is consisted of chlorin-e₆, viologen and formate dehydrogenase (FDH) onto silica-gel based substrate.²⁾ Here, the device for hydrogen production is described.

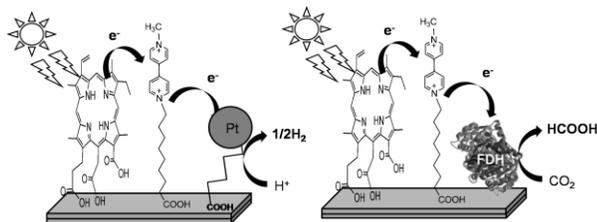


Figure 1. Outline of artificial leaf for solar fuel production. The left side is the artificial leaf device for solar hydrogen production and the right side is the device for formic acid production from CO₂.

Experimental

The procedure of artificial leaf device was prepared as follows. Silica-gel based TLC plate (1.4 × 2.8 cm) was dipped into 10 mM HCl aqueous solution for 30 min and then the plate was washed with distilled water for several times. The HCl-treated TLC plate was dried in desiccator.

To immobilize the Chl-e₆ and 1-carboxylundecanoyl-1'-methyl-4,4'-bipyridinium bromide, iodide (CH₃V(CH₂)₉COOH) onto HCl-treated TLC plate, the plate was dipped into methanol solution containing Chl-e₆ (6 μM) and CH₃V(CH₂)₉COOH (300 μM) for 68 h at 25 °C. To remove physically adsorbed Chl-e₆ and CH₃V(CH₂)₉COOH, the device was washed with methanol. The amount of Chl-e₆ and CH₃V(CH₂)₉COOH immobilized onto Au-coated device were estimated using a spectrophotometer (Multispec-1500 Shimadzu) according to previous reported method.

Finally, platinum nano-particle was immobilized onto the device. The device was methanol solution containing 12-dodecanethiol for 24 h at 25 °C and then dipped into the Bis-Tris buffer solution (pH 7) containing platinum nano-particle for 24 h at 4 °C and then the was washed with Bis-Tris buffer solution (pH 7). This was defined as Chl-V- Pt-device.

The reaction system was consisted of Chl-V- Pt-device, glass slide substrate and the reaction vessel made from silicone with an internal volume of 3 ml.

Results and Discussion

First, photoreduction of viologen moiety onto Chl -V device (without platinum nano-particle) was attempted with visible-light irradiation (100 mW cm⁻², Solar simulator YSS-40, Yamashita Denso). To prevent degradation of Chl-e₆ and CH₃VCH₂COOH onto device by near UV light, wavelengths of less than 390 nm were blocked with a cut-off filter (SCF-50S-39L Sigma Koki). The reduced viologen moiety was measured with a diffusion refractive spectroscopy. When the sample solution containing NADPH (20 mM) was introduced in the reaction system using cassette tube pump (SMP-23 EYELA) and irradiated from the glass slide substrate side, the color of surface of Chl -V device was changed to blue with irradiation, indicating the reduction of viologen moiety onto the plate. By using diffusion refractive spectroscopy measurement, the refraction band with 550-625 nm attributed to the reduced viologen increased with increasing irradiation time. These results indicated that viologen moiety onto the plate was reduced with the photosensitization of neighboring Chl-e₆ onto the device.

As the photoreduction of viologen moiety onto the Chl -V device was accomplished, photoinduced hydrogen production with Chl-V- Pt-device was attempted. The sample solution containing NADPH (20 mM) was circulated in the reaction system using cassette tube pump with visible light irradiation (100 mW cm⁻²). The amount of hydrogen produced was measured with a gas chromatograph. Figure 2 shows the time dependence of hydrogen produced using the Chl-V-Pt-device. Hydrogen production was observed and was increased with increasing irradiation time.

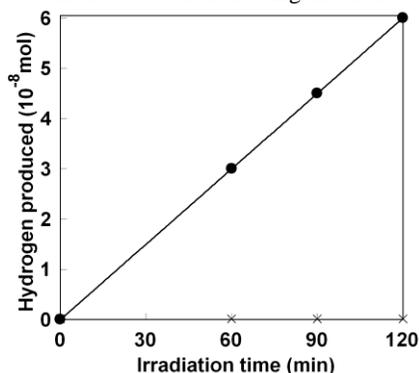


Figure 2. Time dependence of hydrogen production using Chl-V-Pt-device with visible light irradiation (100 mW cm⁻²). X: dark condition.

After 2 h irradiation, 6.0 × 10⁻⁸ mol of hydrogen was produced. On the other hand, no hydrogen production observed in dark condition. The amount of Chl-e₆ molecules onto the device was estimated to be 32 nmol (device size: 1.4 × 2.8 cm; the amount of Chl-e₆ onto device: 8.0 nmol cm⁻²). The produced hydrogen was 6.0 × 10⁻⁸ mol after 2 h irradiation. The turn over number of Chl-e₆ molecules onto the device was estimated to be 187.5 times per hour.

References

- (1) Amao, Y. *ChemCatChem*, **2011**, 3, 458.
- (2) Amao, Y., Shuto, N., Furuno, K., Obata, A., Fuchino, Y., Uemura, K., Kajino, T., Sekito, T., Iwai, S., Miyamoto, M., Matsuda, M. *Faraday Discussion*, **2012**, in press.