Application News

No. A621

Spectrophotometric Analysis

Determination of Photoreaction Quantum Yield and Direct Observation of Intermediate in Photocatalytic Reaction

Global warming and energy problems are critical issues for realizing a sustainable society. Artificial photosynthesis has attracted attention as a method with the potential to solve, at a single stroke, these serious problems that may threaten the survival of humankind. High efficiency photoenergy conversion reactions are required in research on artificial photosynthesis, and the photoreaction quantum yield*1 is a performance indicator that makes it possible to judge the level of reaction efficiency quantitatively. The number of photons absorbed by a sample, which is necessary for calculation of the photoreaction quantum yield, can be obtained by a simple procedure by using the Lightway™ photoreaction quantum yield evaluation system developed recently by Shimadzu.

This article introduces an example of measurement of the photoreaction quantum yield of carbon dioxide (CO_2) reduction and direct observation of the intermediate by a Ru-Re supramolecular complex photocatalyst using the Shimadzu Lightway*2 photoreaction quantum yield evaluation system.

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*1 "Photoreaction quantum yield" is defined as the number of product molecules / number of absorbed photons.

*2 The Lightway photoreaction quantum yield evaluation system was developed by Shimadzu Corporation under the supervision of Prof. Osamu Ishitani and Assistant Prof. Yusuke Tamaki of the Dept. of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology.

Lightway Photoreaction Quantum Yield Evaluation System

Fig. 1 and Fig. 2 show the appearance of Lightway and a schematic diagram of its system configuration, respectively. Lightway consists of two optical systems (photoreaction irradiation light system and absorption spectrum measurement system), which are arranged orthogonally.

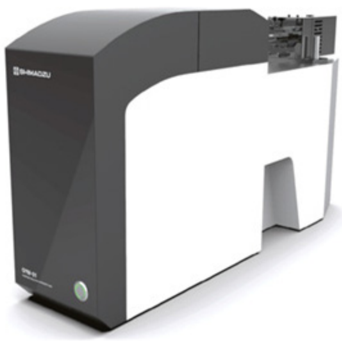

Fig. 1 Appearance of Lightway™ Photoreaction Quantum Yield Evaluation System (Appearance of System with Iris-S LED Light Source (CELL System Co., Ltd.))

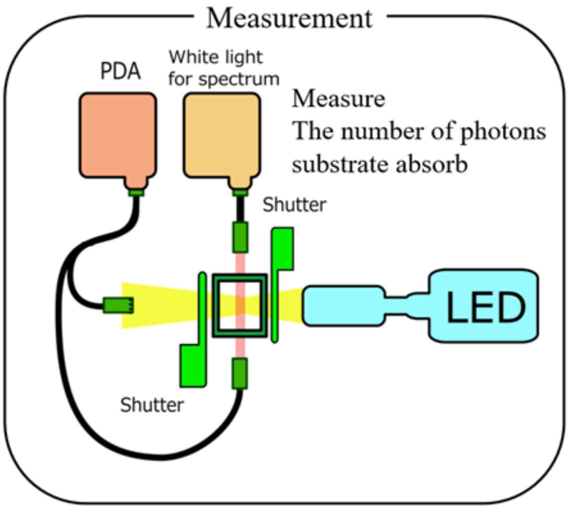

Fig. 2 Schematic Diagram of System Configuration

An LED light source is used in the photoreaction irradiation light system, supporting stable long-term measurement. The irradiation intensity (number of irradiated photons) can be set arbitrarily. Because the irradiation light source is calibrated by a built-in Shimadzu spectrophotometer and a NIST (National Institute of Standards and Technology) -traceable actinometer with a controlled absolute light intensity, calibration of the irradiated light with a chemical actinometer is not necessary.

The absorption spectrum measurement system makes it possible to measure the wavelength range from 250 to 800 nm with a minimum time interval of 0.1 s. A xenon flash lamp is used as the light source of the measurement system, and the sample spectrum in this wavelength range is detected with a photo diode array (PDA).

A stirrer is provided at the bottom of the cell holder, making it possible to stir the sample during measurement of the photoreaction. An optional water flow system for adjustment of the sample temperature is also available, and enables sample measurement while maintaining a constant sample solution temperature.

Lightway can measure the changes in the absorption spectrum of the sample while irradiating light on the sample, and automatically calculates the number of absorbed photons from the number of irradiated photons and the absorption spectrum.

Photocatalytic Reaction Using Ru-Re Supramolecular Complex Photocatalyst

1. Determination of Photoreaction Quantum Yield of CO_2 Reduction Reaction

The photoreaction quantum yield of the CO_2 reduction reaction in the presence of the Ru-Re supramolecular complex photocatalyst (see Fig. 3) was measured. Table 1 shows the measurement conditions. The absorption spectrum and the number of absorbed photons were measured simultaneously. The carbon monoxide (CO) formed by this photocatalytic reaction was measured quantitively by a gas chromatograph. As a result, the graph shown in Fig. 4, in which the amount of CO formation is plotted against the number of absorbed photons, was obtained. The slope in Fig. 4 corresponds to the photoreaction quantum yield. In this experiment, the product quantum yield of CO by the photocatalytic reaction φ_{CO} = 40 %.

Table 1 Measurement Conditions

Measurement interval	: 30 s
Measurement time	: 10/20/30/40 min
Irradiated wavelength	: 470 nm
Set irradiated photon number	: 17×10^{-9} einstein • s^{-1}

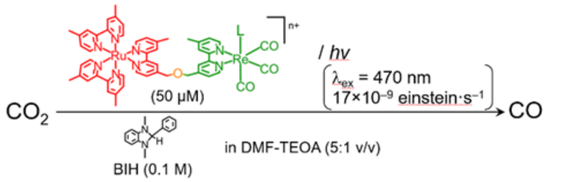

Fig. 3 Ru-Re Supramolecular Complex Photocatalyst

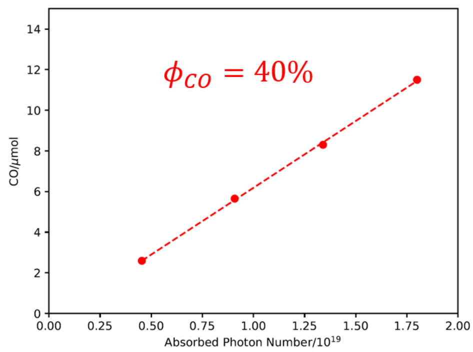

Fig. 4 Relationship of CO Formation and Absorbed Photon Number

2. Direct Observation of Intermediate

Next, we attempted direct observation of the intermediate in the photoreduction reaction of CO_2 using the Ru-Re supramolecular complex photocatalyst. The measurement conditions were the same as those in Table 1. Fig. 5 shows the time-dependent change of the absorption spectrum measured during the photocatalytic reaction, and Fig. 6 shows the difference spectrum when the absorption spectrum at the start of the measurement is defined as the base point. From Figs. 5 and 6, it can be understood that new absorption was observed at around 550 nm, and this is the spectrum of an intermediate. From a comparison with the reported data, it could be determined that this intermediate is a one-electron reduced species in which the Ru-Re supramolecular complex photocatalyst was reduced by a photoelectron-transfer reaction.

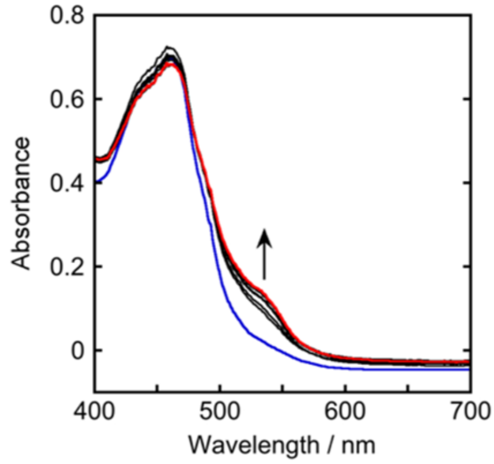

Fig. 5 Time-Dependent Change of Absorption Spectrum

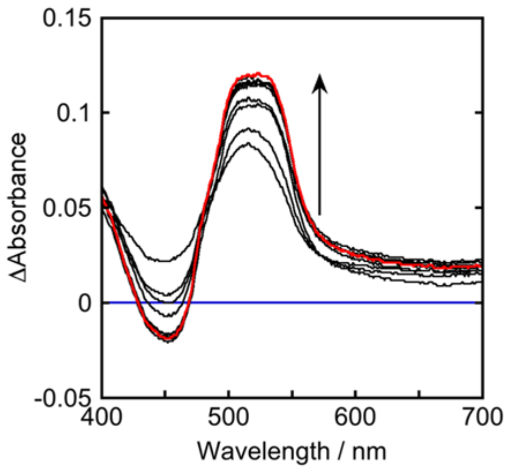

Fig. 6 Difference Spectrum of Time-Dependent Change of Absorption Spectrum

Conclusion

A photocatalytic reaction by a Ru-Re supramolecular complex photocatalyst was observed using the Shimadzu Lightway photoreaction quantum yield evaluation system. The photoreaction quantum yield by reduction of CO_2 to CO by the Ru-Re supramolecular complex photocatalyst was determined to be 40%. The time-dependent change of the absorption spectrum revealed the existence of a one-electron reduced species of the Ru-Re supramolecular complex photocatalyst as an intermediate in the reduction process.

<Acknowledgement>
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