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Application News

Lightway™ Photoreaction Evaluation System / Nexis™ GC-2030 Gas Chromatograph

Evaluation of Iridium Complex-Based Photocatalytic Hydrogen Generation System for Artificial Photosynthesis Studies

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User Benefits

- Photoreaction quantum yield, which is essential for evaluating the efficiency of artificial photosynthesis, can be accurately measured.
- Hydrogen can be detected by gas chromatograph with thermal conductivity detector (TCD), using argon as carrier gas.

■ Introduction

In recent years, hydrogen energy has attracted interest as a way to achieve carbon neutrality because it burns without CO_2 emissions. In particular, studies are underway on so-called “green hydrogen” that does not emit CO_2 even during its manufacturing process. A promising method for the production of green hydrogen is to generate hydrogen through artificial photosynthesis using solar energy and a photocatalyst. However, this technique still has the challenges of increasing solar energy conversion efficiency and reducing manufacturing costs. One approach suggested as an effective way to solve those problems is to build an artificial photosynthesis system that utilizes the long wavelength light, which has the highest intensity of sunlight.

Photoreaction quantum yield, which refers to how efficiently photons are utilized, is commonly used as an index for the energy conversion efficiency of artificial photosynthesis systems. Calculating the photoreaction quantum yield requires determining the number of photons absorbed and the quantity of hydrogen generated. The former can be measured using Lightway photoreaction evaluation system and the latter using Nexis GC-2030 gas chromatograph.

This article describes the use of the Lightway and Nexis GC-2030 systems to evaluate a visible light-responsive photocatalytic hydrogen generation system that uses an iridium complex with coumarin ligands as a photosensitizer.

■ Photocatalytic Hydrogen Generation System Details and Measurement Conditions

The reagents used in the photocatalytic hydrogen generation system and their roles are indicated in Table 1 1).

Table 1 Roles and Concentrations of Reagents Used

Reagent	Purpose	Concentration	Structural Formula
Iridium Complex	Photosensitizer (PS)	8 µM	Fig. 1 (left)
Cobalt Complex	Water reduction catalyst	335 µM	Fig. 1 (right)
Sodium Ascorbate	Sacrificial reagent*1	0.1 M	–
CH_3CN-pH 4.5 Acetic Acid Buffer Solution	Solvent	–	–

*1 Sometimes used to evaluate hydrogen generation in basic research of artificial photosynthesis systems.

The structures of the respective complexes are shown in Fig. 1 and the reaction systems in Fig. 2.

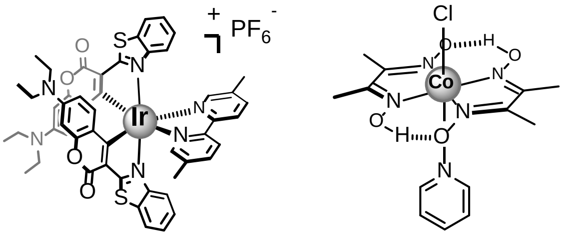

Fig. 1 Structural Formulas of Complexes
(Left: Iridium Complex; Right: Cobalt Complex)

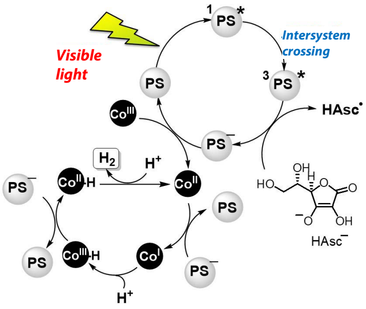

Fig. 2 Iridium Complex-Based Photocatalytic Hydrogen Generation System

The excited iridium complex photosensitizer (PS) obtains an electron from the ascorbate ion ($HAsc^-$) to decrease the charge state of the cobalt (Co) complex ($Co^{III} \rightarrow Co^{II}$). That Co complex serves as a catalyst that promotes hydrogen ion (H^+) reduction. Note that when oxygen coexists, part of the energy obtained from the photosensitizer is consumed to generate singlet oxygen. To prevent oxygen contamination, the samples were bubbled with inert gas (N_2) for 30 minutes before measurement.

The measurement conditions for the Lightway system used to measure the number of photons and the Nexis GC-2030 system used to quantitate how much hydrogen was generated are listed in Tables 2 and 3, respectively.

A long-necked cell with a septum was used for this analysis. After using the Lightway system to measure the number of absorbed photons, 200 µL of the headspace gas present in the long-necked cell is collected with a gas-tight syringe and injected into the Nexis GC-2030 system.

Table 2 Conditions for Measuring the Number of Photons Absorbed

Instrument:	Lightway
Measurement Interval:	5 sec
Measurement Time:	5/10/20 min
Measurement Wavelength:	460 nm
Number of Irradiation Photons:	9.00×10^{-8} einstein•s^{-1}

Table 3 Measurement Conditions for Gas Quantitation

Instrument:	Nexis GC-2030
Injection Port Unit:	SPL-2030
Detector:	TCD-2030
Column:	Micropacked ST 2 m × 1 mm I.D. (P/N: MP-01) (Input 250 m × 0.50 mm I.D. and df = 10 µm into software for flow calculation)
Injection Volume:	200 µL (gas-tight syringe)
Injection Port Temperature:	150 °C
Injection Mode:	Split (1:2)
Carrier Gas:	Ar, constant linear velocity mode (30 cm/s)
Purging Flowrate:	3 mL/min
Column Oven Temperature:	35 °C (2.2 min)
Detector Temperature:	260 °C
Detector Current:	30 mA
Make-up Gas:	Ar, 8 mL/min

If the baseline no longer stabilizes after repeated analyses, heat the column at a high temperature or use a heating program after each analysis to drive off contaminants out of the column.

■ Hydrogen Quantitation by Gas Chromatograph

TCD was used as the Nexis GC-2030 detector and argon as the carrier gas. TCD detects target compounds based on their difference in thermal conductivity from the carrier gas. Therefore, argon is commonly used as a carrier gas for hydrogen analysis due to its large difference in thermal conductivity compared with hydrogen. An example of a chromatogram obtained from this measurement is shown in Fig. 3. The peak of hydrogen was detected at a retention time of 0.5 minutes.

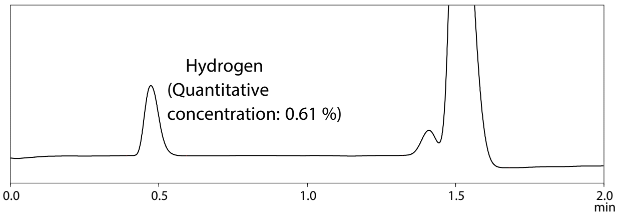

Fig. 3 Chromatogram of Sample Analysis Obtained with Gas Chromatograph

The calibration curve obtained by the analysis of the standard hydrogen gas samples is shown in Fig. 4.

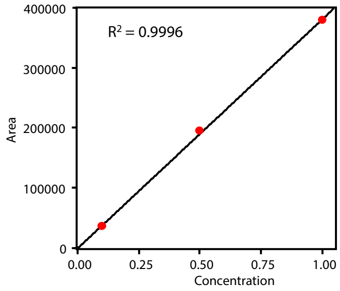

Fig. 4 Calibration Curve of Hydrogen (0.1 %, 0.5 %, 1 %)

The hydrogen concentration was determined by the calibration curve in Fig. 4. The volume of hydrogen generated was calculated based on the hydrogen concentration and the cell headspace volume. In addition, the hydrogen volume was converted to hydrogen mass assuming one mole of hydrogen per 22.4 L.

■ Calculation of Photoreaction Quantum Yield

Accurate quantum yield can be calculated from the number of absorbed photons measured by Lightway and the number of generated hydrogen molecules measured by Nexis GC-2030.

The relationship between the number of absorbed photons and the number of generated hydrogen molecules is shown in Fig. 5.

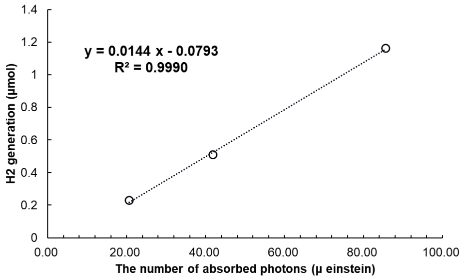

Fig. 5 Relationship between Number of Absorbed Photons and Number of Generated Hydrogen Molecules.

This confirms excellent linearity between the number of absorbed photons and the number of generated hydrogen molecules.

In this case, the following two formulas were used to calculate the quantum yield.

Φ_1 = Number of Hydrogen Generated
/ Number of Photons Absorbed … (1)
Φ_2 = Number of Electrons Used in Reaction
/ Number of Photons Absorbed …(2)

Equation (1) has a value equivalent to the slope in Fig. 5, which results in a calculation of $\Phi_1 = 1.44$ %. Assuming one photon is transferred per electron, two electrons are required to generate a hydrogen, resulting in a maximum quantum yield value of 50 % based on the definition in equation (1).

With equation (2), given that two electrons are used per molecule of hydrogen, the slope in Fig. 5 is doubled to result in a calculation of $\Phi_2 = 2.88$ %. That method results in a maximum quantum yield of 100 % for all photoreactions premised on one photon transfer per electron. When comparing quantum yield with previous researches, it is necessary to confirm which definition was used as the basis for calculating the yield.

In reference 2), the quantum yield of photocatalytically generated hydrogen was measured based on an iridium complex with a ligand bond other than the coumarin ligand. In that case, the calculation is reported as $\Phi_2 = 0.13$ % (446 nm), based on equation (2). A comparison showed that the method in this article produced far superior quantum yield, with about 22 times higher quantum yield than the method in reference 2).

■ Confirmation of Decrease in Photosensitizer Quantity

The decrease in the iridium complex photosensitizer quantity was confirmed based on the change in the absorption spectrum before and after the reaction. Absorption spectra obtained using the Lightway system before and after the reaction are shown in Fig. 6.

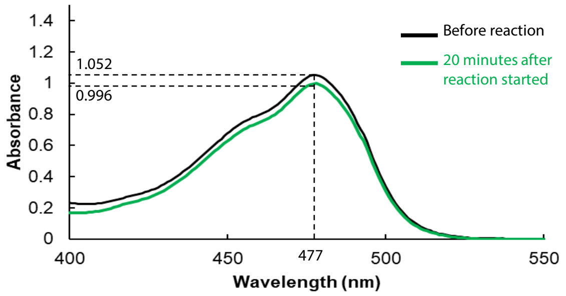

Fig. 6 Absorption Spectra of Iridium Complex Before and After Photocatalytic Hydrogen Generation Experiment

The absorbance at 477 nm, which is the peak from the iridium complex, was 1.052 before the reaction and 0.996 twenty minutes after the reaction. This indicates that absorbance decreased about 5 % during the reaction. Assuming that the decrease in absorbance is proportional to the decrease in iridium complex quantity, it can be inferred that the iridium complex quantity also decreased about 5 %.

■ Conclusion

This article describes using a Lightway photoreaction evaluation system and Nexis GC-2030 gas chromatograph to evaluate the efficiency of a visible light-responsive photocatalytic hydrogen generation system, which has attracted attention within the artificial photosynthesis research field for achieving carbon neutrality. The results confirmed excellent quantum yield performance compared with preceding studies. The method can also be used to estimate the decrease in quantity of photosensitizer based on the change in the absorption spectra before and after reactions.

References

1) S. Takizawa et. al., *Inorg. Chem.* 2016, 55, 8723–8735.
2) S. De. Kreijger et. al., *Inorg. Chem.* 2022, 61, 5245–5254

Acknowledgments

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