

Light-harvesting complex promoted TiO₂:Rh-LHCII photocatalyst to reduce CO₂ into hydrocarbons

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Abstract

The global warming was caused by gases CO₂, N₂O, CH₄, PFCs and CFCs. Especially CO₂ contributes the most Greenhouse effect. This study focused on transforming CO₂ into valuable hydrocarbons. TiO₂ doped with rhodium by sol-gel method was chosen as candidate photocatalyst, TiO₂:Rh, to reduce carbon dioxide. In order to enhance the light absorption, a light-harvesting complex (LHCII) extracted from spinach was used to attach on the surface of the photocatalyst. The LHCII comprises 42 Chlorophylls which are the green pigments of plants that absorb blue and red light for photosynthesis[1]. Methanol, acetaldehyde or methyl formate was produced from aqueous CO₂ solution in a stirred batch reactor. Either TiO₂:Rh or TiO₂:Rh-LHCII photocatalyst was suspended in the reactor for comparison. The results indicated that the LHCII could really promote the transforming carbon dioxide. The products, such as CO, acetaldehyde and methyl formate were generated from the reduction of CO₂. The yield of acetaldehyde with TiO₂:Rh-LHCII was near ten times higher than that with TiO₂:Rh, and the methyl formate product was four times enhancement with LHCII modified photocatalyst. In the control tests, in which CO₂ was replaced by N₂, indicated that all hydrocarbons were converted from CO₂ reduction. LHCII was a stable material that could boost the efficiency in reducing CO₂.

Keywords: CO₂ reduction; Photocatalysis;
Light-harvesting complex; TiO₂:Rh-LHCII; Renewable.
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1 Introduction

Nature has evolved an organic complex which is used in natural photosynthesis similarly to a dye in photocatalysis. This is the Light Harvesting Complex II (LHCII). It consists of many pigments that are organized in such a way as to allow for optimized light use and light energy transfer. In this paper we describe the use of this complex to develop a novel hybrid dye-sensitized TiO₂ catalyst.

LHCII is a hydrophobic molecule, located in the thylakoid membrane of chloroplasts. It functions by absorbing solar energy in the form of photons and passing them on to the photosystem II (PSII) reaction center, which is a special pair of chlorophyll *a* molecules that can perform charge separation by absorbing a red light photon. In this paper, we will discuss the effects of attaching LHCII to the catalyst for the purpose of increasing the amount of light being used by the catalyst and allowing utilization of visible light.

LHCII is found in plants as a trimer, which is also its most stable form. One LHCII trimer contains 42 chlorophylls, which are the green pigments of plants that absorb blue and red light. There are two types of chlorophylls in the LHCII, chlorophyll *a* and *b* (Chla and Chlb respectively), with overlapping absorption spectra, showed as Figure 1. Chla and Chlb are positioned in an ordered fashion within the complex. Indeed, it has been suggested that there are individual binding sites for each type of chlorophyll within the LHCII. Chla absorbs at slightly longer wavelengths in the red and this allows the photon energy to travel “downwards” from Chlb to Chla, towards the reaction center. To this end, the chlorophylls

are positioned very close to each other, so that the energy can pass from one to the other by resonance transfer. A detailed review of light harvesting and its regulation in plants can be found in Ruban et al. [2]. A description of photosynthesis and the photosynthetic machinery can be found in Lawlor [3].

In vivo, LHCII is very stable. From studies in desiccation tolerant mosses, Proctor et al. conclude that the photosynthetic machinery is largely intact following desiccation, as recovery is rapid and therefore independent of protein synthesis, while Oliver et al. say especially about PSII that it requires little repair to begin photosynthesis following rehydration. Additionally, Liu et al. showed that it immobilized onto a metal surface and be stable for hours, giving support to its stability in vitro [4].

In plants, LHCII provides excitation energy to the reaction center causing the separation of an electron-hole pair. As in the artificial system, the hole is used for water oxidation, in the oxygen evolving complex, while the electron is used for carbon reduction. The excitation energy is passed on to the reaction center through resonance transfer, while charge transfer is not thought to occur in this step in vivo.

After adsorbing LHCII on to the catalyst surface we find that there is a functional relationship between them, as will be demonstrated in this paper. This raises the question of how it works in the artificial system, namely is it energy transfer or is it charge transfer. There have been accounts of charge transfer through the pigment matrix in dried chloroplasts, as mentioned in Lawlor [3], and in fact, initially it was thought that the chloroplast may function as a semiconductor, an idea that was later abandoned. On the other hand, it has been shown, using reaction-centerless mutants, that in vivo charge separation occurs in the reaction centers and not the LHCII. These two points together suggest that either mechanism is possible; especially since the preparation of our hybrid LHCII-catalyst involves a drying step. Additionally we do not know how the interaction with the catalyst surface will affect the properties of LHCII and it could be that this will make charge separation possible.

Regarding the energy transfer hypothesis, resonance transfer works by radiationless excitation transfer between

chromophores with overlapping absorption and emission bands. This means that we need upconversion to occur in order to have emission in the UV, where the catalysts absorb. Visible to UV upconversion has been reported using organic chromophores by Singh-Rachford & Castellano [5]. Further work is needed to confirm if this is possible in our system. Additionally, resonance transfer only works at distances of 1-10 nm.

2 Experiment

2.1 Material preparation

LHCII was isolated from spinach leaves by IEF of unstacked thylakoids as described in Ruban et al. [6]. For the preparation of the catalyst sample we used the sol-gel method adding Rhodium acetate as the Rh precursor. We mixed n-butanol, the metal precursor, Ti-butoxide and glacial acetic acid for 6 hours. Following the mixing, we dried the sample at 150°C (retained for 2 hours) and finally calcined it at 500°C (retained for 1.5 hours) in a Carbolite CWF 1100 Chamber Furnace. The sample was then manually crushed into powder using mortar and pestle for 20 min. The resulting sample was Rh-doped TiO₂ with a doping ratio of 0.02 wt%.

For the TiO₂:Rh-LHCII sample there was the additional step of mixing the catalyst in dilute LHCII solution for 2 hours at pH 5.3. The concentrations in the solution were 20 mg catalyst/mL, 25 mM 4-(2-Hydroxyethyl) piperazine-1-ethanesulfonic acid (HEPES), and 0.1 mg n-Dodecyl β -D-maltoside (β -DM)/mL. The chlorophyll concentration of the LHCII was 2.11 μ g/mL. We then centrifuged the mixture to form a pellet of the catalyst, removed the supernatant solution, and left the catalyst to dry in room temperature.

2.2 Stirred batch slurry reactor

Reducing CO₂ in the stirred batch slurry reactor had better efficiency than in the gas phase reactor. It was suggested that the catalyst, dispersed well in DI water, could utilize the light more efficiently. Before the photoreaction, 0.2 grams catalyst were dispersed in the slurry reactor and helium was used to purge the reactor for one hour, to drive out the organic compounds dissolved in the solution. 3 μ L of the slurry was extracted by syringe and

injected into the GC for analysis. After checking there were no organic compounds in the reactor, it was purged with CO₂ for thirty minutes to saturate the water with CO₂. To enhance the solubility of CO₂ in water, the outlet pressure of the CO₂ cylinder was adjusted to 1.1 bar. The distance between reactor and light source was kept at 30 cm and the lamp was turned on. The sample was analyzed by GC every hour to observe the change of the products over time. A 3 μ L sample was taken by liquid syringe and injected into the GC. After the CO signal appeared, the sample was purged out to avoid high concentration CO₂ being carried into the methanizer, which would poison the nickel catalyst. The sample being carried into methanizer was kept after purging out CO₂, to observe other products which would be identified by different concentration standard solutions. After the reaction, the catalyst was recycled and analyzed to detect any changes to its surface.

3 Results

3.1 Photoreduction of carbon dioxide

The efficiency of the catalysts used in reducing carbon dioxide was measured in a liquid phase reactor. Measurements were taken using the GC at every hour. The results are shown in Figure 2. CO could be detected after the first hour of the reaction with both of the catalysts. Acetaldehyde also could be observed in the reaction. In addition to CO and acetaldehyde, there was a small amount of methyl formate produced by reducing carbon dioxide with the two catalysts. The yield received from CO₂ reduction which was the average yield of repeated experiment. The yield of the products was within 5% error.

3.2 In-situ FT-IR

In-situ FT-IR analysis was used to realize the mechanism of photo reaction. The TiO₂:Rh- LHCII catalyst and the small reactor was purged by helium for one hour. After that, the CO₂, H₂ and Ar mix gas flowed into the reactor for 40 minute and turn off the two valves to ensure the reaction in batch system. The ratio of CO₂:H₂ : Ar = 2:1:1. Turned on the light for in-situ FT-IR analysis and recorded the spectrum every twenty minute. Figure3 showed the TiO₂:Rh-LHCII catalyst had additional two peaks at 2924 cm⁻¹ and 2852 cm⁻¹ comparing to TiO₂:Rh

which were CH₂ stretching of proteins. Peak at 2355 cm⁻¹ was assigned to CO₂ in the atmosphere and peak at 1618-1627 cm⁻¹ was indicated to be adsorbed, unassociated H₂O [7]. Before the photo reaction, the ratio of mixture gas CO₂:H₂ : Ar = 2:1:1 purged into the reactor for 40 minutes to let the gas adsorb on the surface of catalyst, and there were some characteristic peaks marked by red words. The peak appeared at 1554 cm⁻¹ was assigned to CO stretching of CO₃ group [8]. Characteristic peak appeared at 1430 cm⁻¹ was indicated to be $\nu_s(\text{HCO}_3)$ [9]. Opened the light source (400-500nm) for photo reaction, and recorded the spectrum which showed as the Figure 4. The peaks at 1716 cm⁻¹ (C=O) and 1352 cm⁻¹ (CH) were assigned to acetaldehyde. Two peaks at 1311 and 1357 cm⁻¹ were $\nu_{as}(\text{OCO})$ of CO₃. Four peaks at 1593, 1568, 1559 and 1542 cm⁻¹ were assigned to formate species on titania. The peak at 1505 and 1390 cm⁻¹ was assigned to CH₂ bending vibration of formaldehyde. 1459 and 1048 cm⁻¹ were assigned to methoxy group doubly bridged on the TiO₂. 1474 and 1340 cm⁻¹ were assigned to methanol gas (CH₃) adsorbed on the catalyst. 1188 cm⁻¹ was assigned to formic acid region.

4 Discussion

In the study, we want to compare the efficiency of reducing CO₂ with TiO₂:Rh and TiO₂:Rh-LHCII catalysts. The LHCII can absorb visible light very efficiently and so it was postulated that it would boost the light utilization of the catalyst. Therefore it was expect that TiO₂:Rh-LHCII should exhibit better photoactivity than TiO₂:Rh.

According to our results, the major products were CO, acetaldehyde and methylformate. CO appears first in the reactor, which supports the hypothesis that the organic products come from the reduction of CO₂ instead of the degradation of LHCII. The yield of acetaldehyde with TiO₂:Rh-LHCII was about ten times the yield with TiO₂:Rh catalyst. The yield of methyl formate with TiO₂:Rh-LHCII was also increased to four times the yield with TiO₂:Rh. Here was one point brought up that there was no formic acid and methanol detected by GC which was the source of methyl formate. Two explanations were given as follows: One reason was that methoxy and formate group anchored on the surface of catalyst as the intermediate and the two compounds reacted to form the methyl formate before

releasing. The other one was due to the GC detection limit, the yield of methanol and formic acid was below detection limit. It could be observed from the result of photo reaction that the selectivity of acetaldehyde was much higher than methyl formate which also could be proved by in-situ FT-IR analysis. In FT-IR result, the increase of acetaldehyde was more obviously than methyl formate which was correspond to the result from GC. According to thermodynamic view, the free energy of methanol was higher than that of acetaldehyde, and less methanol produced lead to less methyl formate produced which might be the reason that the selectivity of acetaldehyde was much higher than methyl formate. It can additionally be observed from the experiment that the amount of products in the reactor decreased after 4-5 hours of the reaction. According to the study of Tseng et al., this is because the reverse reaction occurred and part of the product was degraded by the catalyst.

5. Conclusion

TiO₂:Rh-LHCII catalysts in reducing CO₂ allowed us to confirm that the LHCII material enhances photoreduction. The result showed an increase of ten times for acetaldehyde and four times for methyl formate when comparing TiO₂:Rh-LHCII to TiO₂:Rh. The author also compared the efficiency of the catalyst to other groups' studies, showed as Table 1. It could be confirmed that LHCII is truly helpful for reducing carbon dioxide.

6 References

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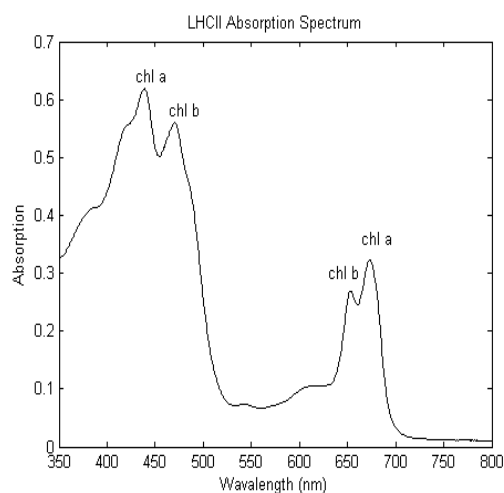


Figure 1 LHCII absorption spectra

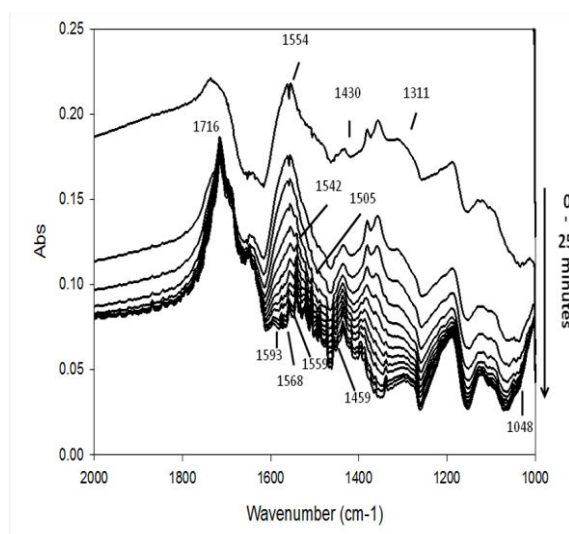


Figure 4 In-situ FTIR analysis of CO₂ reduction

With TiO₂:Rh- LHCII

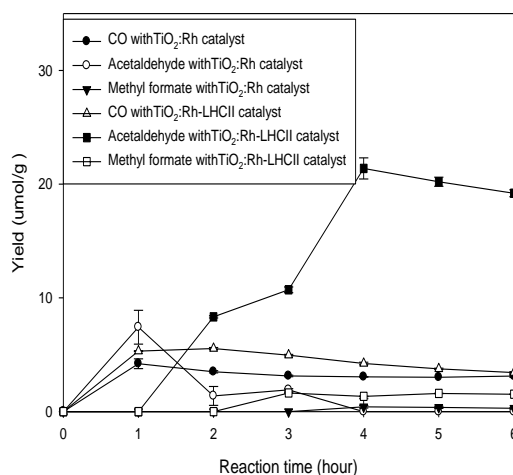


Figure 2 yield of CO₂ photo reduction by TiO₂:Rh and TiO₂:Rh- LHCII

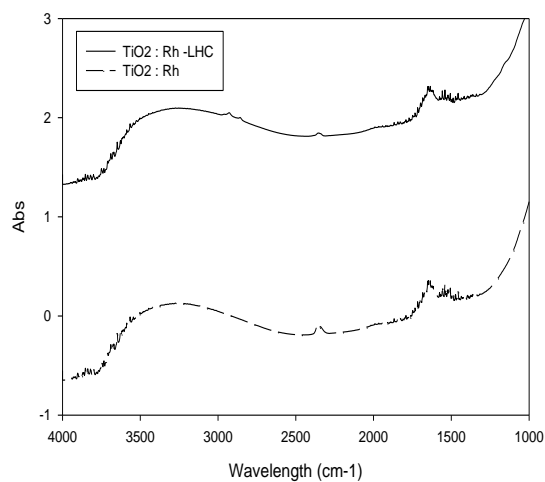


Figure 3 IR spectra of TiO₂:Rh and TiO₂:Rh- LHCII

T able 1: Performance comparison in photo reduction of CO₂

groups	Zhang	Varghese	Our research
Light source	450W Xe lamp (visible light)	AM1.5 sunlight	300W Xe light
catalyst	Iodine doped TiO ₂	Cu/ nanotube TiO ₂	TiO ₂ :Rh modified with LHCII
Major product	CO	CO, CH ₄	CO Acetaldehyde Methyl formate
Quantum efficiency	0.0086%	0.0266%	0.0411 %