Hydrogen Production and Biofuel Cell by Light-harvesting Function of Zinc Chlorophyll-*a* Derivatives

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The photosynthesis is the most efficiency lighting-harvest system in nature. Two kind of photosynthetic proteins work as lighting-harvest (LH) and reaction center (RC) in the photosynthesis. In irradiation, the LH harvests solar energy and transfer the light energy to the RC. The RC accepts the energy from the LH and then transfers the electron to accepter such as quinone. Then, the system of harvest and transfer solar energy efficiency could develop by the function of both lighting-harvest and photon-conversion in photosynthesis.

The major pigment in the LH and the RC of higher plants and photosynthetic bacteria is chlorophyll-*a*. Mg ion has been known as the center metal of chlorophyll-*a* and bacteriochlorophyll-*a* until recently found a novel Zn-containing bacteriochlorophyll-*a* in an aerobic bacterium Acidiphilium rubrum growing at low pH (ca. 3) and confirmed its structure to be identical with that of bacteriochlorophyll-*a* esterifies with phytol. The reason why A. rubrum chose Zn has not been clarified yet. As is noted in the potential-pH relationship of Zn and Mg, Mg^{2+} is the stable form at neutral pH, while the region where Zn^{2+} is major form is limited to low pH. Under acidic condition, A. rubrum could include Zn as easily as Mg. Moreover, easy metalation of Mg chlorophyll-*a* and bacteriochlorophyll-*a* is known and hence more stable Zn-complexes are often used in the work on artificial photosynthesis. Thus, using Zn chlorophyll-*a* as a model of Zn bacteriochlorophyll-*a* is expected suitable for photoenergy conversion system such as H_2 evolution under acidic condition.

Recently, the utilization of the biomass contained in drainage as energy source has been much paid attention for production of clean energy. The H_2 evolved system will be developed by the combination of photoinduced water decomposition in visible region and the using hydrolysis of biomass resources such as sucrose and maltose for the photosynthesis mimetic process. In addition, photo-operated biofuel cell using biomass hydrolysis and the photo-induced electron transfer of H_2 evolution system, which based on the photosensitization of chlorophyll derivatives will be developed.

In this work, visible-light induced H_2 evolution from sucrose as the biomass using the photosensitization of Zn chlorophyll-*a*, which has the function of both the LH and the RC by visible light, was developed and the photoelectron conversion process in this H_2 evolution from sucrose was applied for biofuel cell by the photosensitization of Zn chlorin as chlorophyll derivative.

At first, Zn chlorophyll-*a* was prepared from Mg chlorophyll-*a* of *spirulina* and its optical properties were studied using spectroscopy.

Zn chlorophyll-*a* was synthesized by refluxing Mg chlorophyll-*a* with about 10 mol equiv of Zn acetate in 100 ml of methanol at 80 ºC for 5 h. The insertion of Zn ion into chlorophyll-*a* ring was measured by UV-vis spectroscopy. After the reaction, maximum absorption of chlorophyll-*a* was changed to red-shift region. Then methanol was removed by rotary evaporation and after the products were precipitated in water, the solution was performed by recrystallization. Zn chlorophyll-*a* was distributed 10 mmol dm^{-3} CTAB. Zn chlorin was also synthesized by refluxing chlorin with about 10 mol equiv of Zn acetate in the same ways.

The absorption bands of Zn chlorophyll-*a* were 421 nm attributed to Soret band and 662 nm attributed to Q-band. On the other hand, the bands of Mg chlorophyll-*a* were 433 nm attributed to Soret band and 668 nm attributed to Q-band. Thus, the absorption bands of both Zn and Mg chlorophyll-*a* has maximum in visible region. In comparison of the absorption spectra of Zn and Mg chlorophyll-*a*, a blue-shift in the absorption bands of Zn chlorophyll-*a* was observed.

The fluorescence emission peak of Zn and Mg chlorophyll-*a* were 664 and 668 nm, respectively. In comparison of the fluorescence emission peak of Zn and Mg chlorophyll-*a*, the blue-shift in the emission peak of Zn chlorophyll-*a* was observed as well as that in the absorption spectrum.

Next let us focus on the photostability of Zn chlorophyll-*a*. The Zn and Mg chlorophyll-*a* decomposition were proceeded by steady irradiation under various pH (4.0-8.0). Chlorophyll-*a* using center metal of both Zn and Mg was decomposed by change of pH against 60 min irradiation. However under various pH (4.0-8.0), the decomposition of Zn chlorophyll-*a* was suppressed compared with that of Mg chlorophyll-*a*. Thus, the stability of Zn chlorophyll-*a* by irradiation is superior to Mg chlorophyll-*a*.

In H_2 evolution system, the sample solution containing sucrose, invertase, NAD^+, GDH, chlorophyll-a (the center metal is Zn and Mg), methyl viologen and colloidal Pt was irradiated by visible light after 240 min irradiation. Amount of H_2 evolution using Zn chlorophyll-*a* was estimated to be 10.4 μmol.

Next let us forcus on biofuel cell based on electron transfer of hydrogen evolution process by chlorophyll-a derivative, Zn chlorin. The photovoltage and photocurrent of biofuel cell using Zn chlorin absorbed on TiO_2 film electrode were 415 mV and 9.0 μAcm^{-2}, respectively.

In conclusion, H_2 evolution system form sucrose as biomass using the photosensitizasion of Zn chlorophyll-*a* by visible light was developed. By visible light irradiation, the decomposition of Zn and Mg chlorophyll-*a* were 26 and 40 %, respectively under acidic conditions (pH 4.0). Thus, Zn chlorophyll-*a* was superior to Mg chlorophyll-*a* in photostability. Zn chlorophyll-*a* is suitable for photosensitizer in H_2 evolution system under lower pH conditions, which has much proton. The amount of H_2 evolution from sucrose using the photosensitization of Zn chlorophyll-*a* was estimated to be 10.4 μmol. Further research will be directed toward a photoinduced H_2 evolution system under acidic conditions using the photosensitization of Zn chlorophyll-*a*.

Visible light-operated biofuel cell using the combination by the photosensitization of Zn chlorin as a model of Zn chlorophyll-*a*, adsorbed on nanocrystalline TiO_2 film electrode and the electrochemical reduction from O_2 to H_2O of Pt electrode was developed.

Thus, the present biofuel cell using Zn chlorin adsorbed on nanocrystalline TiO_2 film electrode was operated in the wide visible region and was developed using electron transfer applied H_2 evolution from sucrose as biomass.