【Grant-in-Aid for Scientific Research(S)】
Biological Sciences (Biology)

Title of Project： Studies on the oxygen-evolving reaction mechanism of photosystem II at an atomic resolution

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Research Area：Structural Biological Chemistry
Keyword：X-ray crystallography, Photosynthesis, Oxygen evolution, Enzymatic reaction Artificial photosynthesis

【Purpose and Background of the Research】

In natural photosynthesis, photosystem II (PSII) performs light-induced electron transfer and water-splitting reactions, which lead to the formation of molecular oxygen. PSII from thermophilic cyanobacteria consists of seventeen membrane-spanning subunits, three hydrophilic, peripheral subunits, and many cofactors with a total molecular weight of 700 kDa for a dimer. X-ray crystal structures of PSII have been reported at 3.8-2.9 Å resolutions for PSII, which provide arrangement of protein subunits and most of the cofactors involved in the electron transfer reactions. However, the detailed structure of Mn_4Ca-clulster, the catalytic center of light-induced oxygen evolution, has not been resolved. We have improved the resolution and diffraction quality of PSII crystals significantly, and succeeded in solving the crystal structure of PSII from *T. vulcanus* at a resolution of 1.9 Å as shown in Figure 1. Electron density distributions for each of the five metal ions in the Mn_4Ca-cluster are clearly separated, allowing us to locate the individual metal ions and all of the ligands to the metal cluster unambiguously. This work was highly evaluated and selected in the breakthrough of the year, 2011, *Science*.

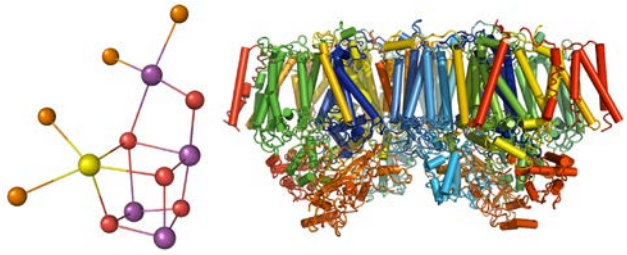

Figure 1　Mn4Ca cluster and PSII dimer

The light-induced water oxidation is catalyzed by the Mn_4Ca-cluster, changing its Si-states (with i=0-4) in the Kok cycle upon extraction of each electron by the PSII reaction center. When 4 electrons and 4 protons are extracted from 2 molecules of water, 1 molecule of di-oxygen is formed. In order to elucidate the water oxidation mechanism of PSII, crystallographic analyses for all Si-states are inevitable. At present, however, we have only the precise structure of the Mn_4Ca-cluster at the S1-state.

【Research Methods】

In order to obtain structural information for the S0-state, we will analyze the crystal structures of iodine-substituted PSII, herbicide complexes, and PsbM deletion mutant at an atomic resolution. The S2-state will be realized by laser light and resolved its structure also by X-ray crystallography.

【Expected Research Achievements and Scientific Significance】

The experimental proposals mentioned above are highly challenging, and if the structures of S0 and S2 states in the Kok cycle are uncovered, the real water oxidation mechanism proposed will provide important information to design water oxidation catalysts inevitable to realize artificial photosynthesis for a sustainable world on our planet.

【Publications Relevant to the Project】

・Umena, Y., Kawakami, K., Shen, J.-R., Kamiya, N., Crystal structure of oxygen- evolving photosystem II at a resolution of 1.9 Å, Nature, 473(7345), 55-60 (2011).
・Kamiya, N. and Shen, J-R., Crystal Structure of oxygene-evolving photosystem II from Thermosynechococcus vulcanus at 3.7 Å resolution, Proc. Natl. Acad. Sci. USA 100, 98-103(2003).

【Term of Project】 FY2012-2016

【Budget Allocation】 167,400 Thousand Yen

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