Research Highlights

Damage-free structure of photosystem II and the synthesis of model compounds for water-oxidation

Photosystem II (PSII) performs light-induced electron transfer reactions in photosynthesis, leading to the splitting of water into electrons, hydrogen ions, and oxygen, with which light energy from the sun is converted into chemical energy and molecular oxygen is produced to sustain all aerobic life on the earth. PSII is an extremely large membrane protein complex consisting of 20 subunits with a total molecular mass of 700 kDa for a dimer. The catalytic center for water-splitting is a Mn₄CaO₅-cluster organized as an asymmetric, distorted chair form embedded within the protein matrix of PSII.



Damage-free structure of the water-splitting catalyst $\mathsf{Mn}_4\mathsf{CaO}_{\text{s}}\text{-cluster}$ in photosystem II

The crystal structure of cyanobacterial PSII has previously been reported at a resolution of 1.9 Å using synchrotron radiation (SR) X-rays. However, due to the intense and continuous SR X-rays, the Mn_4CaO_5 -cluster has been suggested to suffer from radiation damage, leading to slight changes in the inter-atomic distances within the cluster.

Now, a joint team led by Jian-Ren Shen at Okayama University, and Masaki Yamamoto and Hedeo Ago at the RIKEN SPring-8 Center, has solved the damage-free crystal structure of PSII at 1.95 Å resolution using the femtosecond X-ray free electron laser (XFEL) provided by SACLA, an XFEL facility located within the same campus of SPring-8.

The research group prepared a large number of highly isomorphous, high quality, large sized PSII crystals, and used the femtosecond XFEL pulses to collect diffraction data from a fresh volume of the crystals after illumination by each pulse. In this way, completely damage-free diffraction data was collected, allowing the analysis of the structure by the "diffraction before destruction" approach.

The structure obtained revealed the precise inter-atomic distances within the Mn_4CaO_5 -cluster, enabling the mechanism of water-splitting to be examined in more detail. Based on the structure of the native Mn_4CaO_5 -cluster, a research team consisting of scientists from the Chinese Academy of Sciences, Free University Berlin (Germany), and Okayama University (Jian-Ren Shen) has succeeded in synthesizing an artificial compound resembling to a large extent the structure of the native Mn_4CaO_5 -cluster and exhibiting some distinctive characteristics of the native cluster.

These studies not only greatly advance our understanding of the mechanism of photosynthetic wateroxidation, but also are a large step forward towards the development of artificial photosynthesis that will ultimately provide us with a source of clean and renewable energy.

Reference1:

- Authors: Michihiro Suga¹, Fusamichi Akita¹, Kunio Hirata^{2,3}, Go Ueno², Hironori Murakami², Yoshiki Nakajima¹, Tetsuya Shimizu¹, Keitaro Yamashita², Masaki Yamamoto², Hideo Ago², Jian-Ren Shen¹
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- Department website: http://www.gnst.okayama-u.ac.jp/index_e.html
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Reference2:

- Authors: Chunxi Zhang¹, Changhui Chen², Hongxing Dong², Jian-Ren Shen³, Holger Dau⁴, Jingquan Zhao¹
- Title of original paper: A synthetic Mn4Ca-cluster mimicking the oxygen-evolving center of photosynthesis
- Journal, volume, pages and year: Science 348, 690 (2015).
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- Department website: http://www.gnst.okayama-u.ac.jp/index_e.html
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