

Mechanism of photosynthetic water-splitting revealed by an X-ray free electron laser

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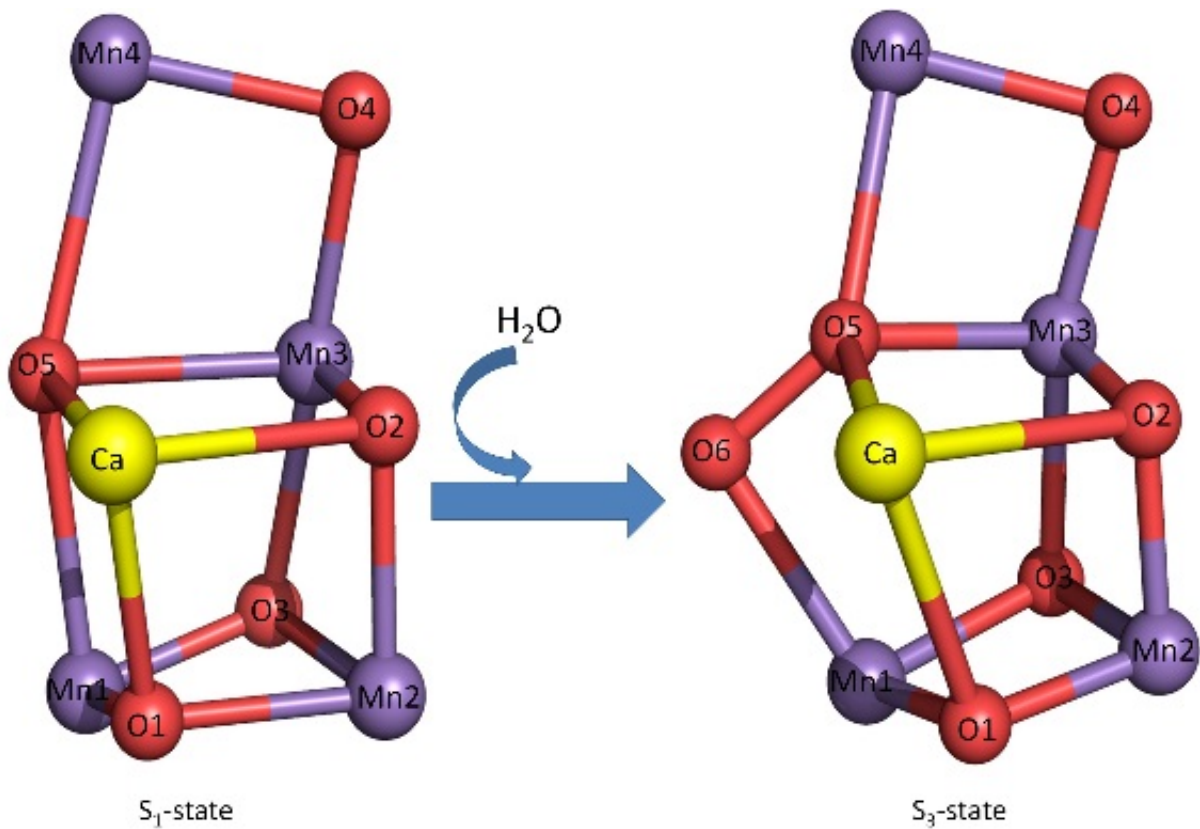


Figure 1: Structural changes of the Mn₄CaO₅-cluster induced by two flashes of illumination. S₁-state: without illumination; S₃-state: after two flashes of illumination. Credit: Okayama University

Photosystem II (PSII) is a huge membrane-protein complex that

catalyzes light-induced water-splitting, leading to the generation of protons and molecular oxygen. This reaction converts light-energy from the sun into chemical energy that is required to sustain almost all living activities on Earth. The water-splitting reaction is catalyzed by a Mn_4CaO_5 -cluster embedded within the protein matrix of PSII, and proceeds through five intermediate states called S_i-states. The structures of PSII and the Mn_4CaO_5 -cluster have been resolved with atomic resolution, however, mechanisms governing water-splitting are unclear due to the lack of intermediate structures of the enzyme.

Now, Michihiro Suga, Fusamichi Akita, Jian-Ren Shen at Okayama University, and colleagues at institutes including Kyoto University, RIKEN, have clarified and resolved the structure of the Mn_4CaO_5 -cluster at S₃-state—an intermediate state that exists immediately before the formation of molecular [oxygen](#), generated by two flashes of optical illumination. They employed a pump-probe method where two laser flashes were used to pump the enzyme to the intermediate state, and the X-ray diffraction data were collected by a serial-femtosecond crystallography method using femtosecond X-ray free electron lasers (XFEL) at SACLA, Japan.

The results showed the insertion of a new oxygen atom (water molecule) close to an already existing oxo-oxygen termed O₅, enabling the formation of [molecular oxygen](#) between O₅ and the newly inserted oxygen atom (O₆). This clearly demonstrated the mechanism governing the [water-splitting reaction](#) catalyzed by PSII, and provided a blueprint for design and synthesis of efficient artificial catalysts that in the future could be utilized in artificial photosynthesis to produce clean and renewable energy from the sun.

More information: Michihiro Suga et al. Light-induced structural changes and the site of O=O bond formation in PSII caught by XFEL, *Nature* (2017). [DOI: 10.1038/nature21400](https://doi.org/10.1038/nature21400)

Provided by Okayama University

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