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X-ray free electron lasers reveal the molecular mechanism for water oxidation in photosystem II

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Photosynthetic water oxidation is catalyzed by the Mn_4CaO_5 -cluster^{1,2} of Photosystem II (PSII) through a linear four oxidation intermediates of S_i-state cycle (S_i, i = 0-4). The catalyst becomes a Mn_4CaO_6 -cluster in the S₃-state by incorporation of additional oxygen O₆ nearby a unique central oxo-bridge O₅, supporting a dioxygen formation mechanism between O₅ and O₆. While insertion of the O₆ has gradually been accepted, the chemical structure of O₅ and O₆ remain controversial so that several possible mechanisms for the O=O bond formation have been under debate.

To reveal the molecular details in the water oxidation reaction, we analyzed the X-ray free laser (XFEL) structures of PSII in the S₁, S₂ and S₃ states by using fixed-target serial femtosecond crystallography with an XFEL provided by the SACLA⁴. In brief, single-shot diffraction images were collected in a fixed-data collection manner at a cryogenic temperature, in which PSII microcrystals were evenly sprayed on a mesh. Compared with serial femtosecond crystallography of PSII using a grease matrix as the injection medium at room temperature³, this method reduced the sample consumption by one order of magnitude and ensured low background images, allowing us to analyze multiple datasets at 2.15-Å resolutions.

No insertion of water was found in the S₂ state, but upon transition to the S₃ state, flipping of Glu-189 provides a space for incorporation of the additional oxygen O₆, and the Mn_4CaO_5 -cluster remains in the open-cubane form. To determine the exact chemical structure of the O₅ and O₆, we examined four possible chemical species; superoxo, peroxy, oxyl/oxo, and oxyl/hydroxo. By altering the O₅-O₆ distance and examining the residual densities in the F_{obs}-F_{cal} difference Fourier map, we found that a distance of 1.9 Å resulted in the weakest residual densities. This suggests an oxyl/oxo coupling mechanism for the O=O bond formation in OEC. Moreover, the flipping of the Glu-189 also induces van der Waals repulsion between the carbonyl oxygen of Glu-189 and Ala-411CP43, which is transmitted to a strictly conserved short loop of the CP43 subunit that restricts the size of the O₁-water channel. These structural changes in PSII between the different S-states reveal the mechanism of photosynthetic water oxidation by the cooperative action of substrate water access, proton release, and O=O bond formation.

Acknowledgments

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References

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