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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 Mn4CaO5-cluster1,2 of Photosystem II (PSII) through a linear four oxidation intermediates of Si-state cycle (Si, i = 0-4). The catalyst becomes a Mn4CaO6-cluster in the S3-state by incorporation of additional oxygen O6 nearby a unique central oxo-bridge O53, 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 Mn4CaO5-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, peroxo, oxyl/oxo, and oxyl/hydroxo. By altering the O5-O6 distance and examining the residual densities in the Fobs- Fcal 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.

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References

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