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Water Oxidation in Natural Photosynthesis

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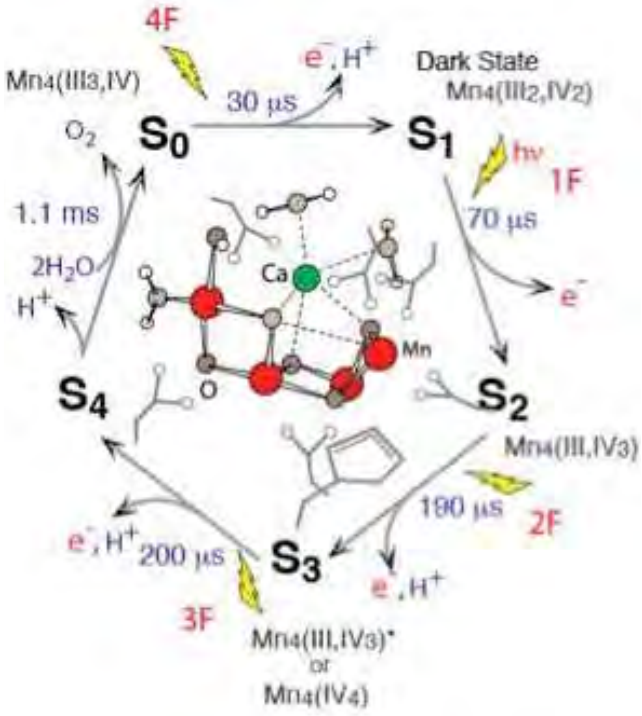
The photosynthetic water oxidation reaction is energetically demanding and mechanistically complex because of the difficulties in managing the four electron, four proton redox chemistry required for the evolution of molecular oxygen starting from two water molecules. The reaction takes place in Photosystem II (PS II), a multi-subunit membrane protein present in plants, algae, and cyanobacteria. This sunlight-driven reaction is catalyzed by an oxygen-evolving complex (OEC), that consists of an oxo-bridged four Mn and one Ca cluster. O2 is formed and released only after four oxidation equivalents are accumulated at the OEC. The structure of the Mn4CaO5 cluster has been studied by various spectroscopic and diffraction methods. The recent XRD study by Umena et al.[1] has shown the oxo-bridged Mn4Ca cluster structure at 1.9 Å resolution. Based on this high-resolution XRD structure, there have been efforts to obtain chemically optimized structures and structural changes of the Mn4CaO5 cluster during the catalytic cycle using spectroscopic parameters and theoretical approaches. EXAFS spectra of the PS II S states show that the structure of the Mn4CaO5 cluster changes during the catalytic cycle.[2] In particular, the short Mn-Mn distances change in the range of 2.7 to 2.9 Å. Such changes in oxygen-bridged Mn-Mn distances can reflect several chemical parameters; Mn oxidation state changes, protonation state changes of bridging oxygens, ligation modes (e.g. bidentate/monodentate), as well as fundamental changes in geometry. We have also used femtosecond X-ray spectroscopy and crystallography to study the catalytic process of the OEC.[3] The femtosecond X-ray pulses of the free-electron laser allows us to out-run X-ray damage at room temperature, and the time-evolution of the photo-induced reaction can be probed using a visible laser-pump followed by the X-ray-probe pulse. We will discuss a possible water oxidation mechanism based on these results.

[1] *Y. Umena, K. Kawakami, J.-R. Shen, et al., Nature 473, 55-65 (2011),* ***[2]*** *C. Glöeckner, J. Kern, M. Broser, et al., J. Biol. Chem. Online (2013),* ***[3]*** *J. Kern, R. Alonso-Mori, V. Yachandra, et al. Science, 340, 491-495 (2013)*



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