Efficiency, energetics and thermodynamic limits of photosynthetic water oxidation-from basic research to solar fuels.

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Soon exhausted oil resources as well as the global climate change have stimulated research aiming at the production of alternative fuels, ideally driven by solar energy. Any attractive scheme for production of solar fuels needs to involve the splitting of water into protons, energized electrons and dioxygen. In photosynthetic organisms, solar-energy conversion and catalysis of water splitting (or water oxidation) proceed in an impressive cofactor-protein complex denoted as photosystem II (PSII). The heart of biological water-oxidation is a protein-bound manganese-calcium complex working at technically unmatched efficiency. In an attempt to learn from nature, the natural paragon is intensely studied using advanced biophysical methods. Structural studies by X-ray spectroscopy with synchrotron radiation play a prominent role in this endeavor. Some secrets of biological water oxidation have been revealed recently, however pivotal questions have remained unanswered (for a more detailed account see (*1-4*)).

An overview is presented focusing on (i) the efficiency of solar energy usage in PSII, (ii) the interrelation between electron transfer and proton relocations, and (iii) the mechanism of water oxidation. Possibly also new results on water oxidation by synthetic manganese and cobalt oxides are presented and their future integration in synthetic nanostructured systems is considered.

1. Dau, H., and Haumann, M. (2006) Reaction cycle of photosynthetic water oxidation in plants and cyanobacteria (response letter), *Science 312*, 1471-1472.

2. Dau, H., and Haumann, M. (2008) The manganese complex of photosystem II in its reaction cycle - Basic framework and possible realization at the atomic level, *Coord. Chem. Rev. 252*, 273-295.

3. Dau, H., and Zaharieva, I. (2009) Principles, efficiency, and blueprint character of solar-energy conversion in photosynthetic water oxidation, *Acc Chem Res 42*, 1861-1870.

4. Dau, H., Limberg, C., Reier, T., Risch, M., Roggan, S., and Strasser, P. (2010) The mechanism of water oxidation: From Electrolysis via Homogeneous to Biological Catalysis, *ChemCatChem 2*, 724-761.