Structural and functional parallels between the Mn_4CaO_5 water oxidation center in the Photosystem II protein complex and a synthetic manganese-oxide catalyst for artificial photosynthesis

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Oxidation of water molecule to protons, electrons and molecular oxygen is the reaction which is responsible for the formation of most of the oxygen in the atmosphere. The process of water oxidation is part of the oxygenic photosynthesis. It is catalyzed by a Mn4CaO5 cluster located in a transmembrane protein called Photosystem II in plants and cyanobacteria [1]. The same process is pivotal also for the sustainable production of non-fossil fuels and for that reason it has been extensively studied during the last decade. However, it is still not sufficiently well understood and this hampers the development of stable and efficient artificial catalysts which can mimic the function of the natural paragon in a large-scale technological systems.

Recently, using a simple electrochemical technique, we designed an efficient protocol to electrodeposit under benign conditions a Mn-based oxide catalyst on an electrode surface starting from an aqueous solution of a simple Mn salt [2]. As the resulting self-assembled material is non-crystalline, we used quasi in-situ X-ray absorption spectroscopy (XANES and EXAFS) to study the structure of the catalyst in its resting state and during the catalytic process at different anodic potentials.

The results show that the electrodeposited catalytically active material is amorphous Mn oxide which shares structural motifs with the water oxidation center of Photosystem II. Moreover this analogy between the native and synthetic catalysts extends over the structural changes during the water oxidation cycle. The detailed analysis of the data demonstrates that the potential-induced Mn oxidation state and structural changes astonishingly resemble those occurring in the natural photosynthetic cycle. This implies that the inorganic catalyst mimics the natural paragon not only structurally but also functionally and the understanding of both artificial and natural water oxidation processes can be mutually beneficial.

Figure 1. Manganese oxidation state changes detected by X-ray absorption spectroscopy in the inorganic Mn oxide catalysts (left) and in the Mn4CaO5 catalytic center in Photosystem II (right).

References:

[1] H. Dau, I.Zaharieva, M. Haumann, Curr. Op. Chem. Biol. 16, 3 (2011).

[2] I. Zaharieva, P. Chernev, M. Risch, K. Klingan, M. Kohlhoff, A. Fischer, H. Dau, Energy Environ. Sci. 5, 7081 (2012).

figure 1