Water oxidation:
From biological photosynthesis
to amorphous transition metal oxides

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Water oxidation is pivotal in the 'ab-initio' synthesis of H_2 and carbon-based non-fossil fuels. In biological photosynthesis, water oxidation is efficiently catalyzed by a Mn_4CaO_5 cluster bound to the photosystem-II (PSII) pigment-protein complex of plants, alga and cyanobacteria. In recent years, synthetic catalysts based on amorphous oxides of first-row transition metals came into focus. Aside from the redox-active metal (Mn, Fe, Co, Ni), these oxides may contain additional redox-inert cations (K, Na, Ca, ..) and anions that could act as a proton acceptor (phosphate, borate, ..), as well as intercalated water molecules. We investigate these amorphous oxides using a combination of electrochemical and spectroscopic methods; synchrotron-based X-ray spectroscopy is the primary structural tool.

Starting with a summary of crucial mechanistic features of the biological catalyst, recent findings for amorphous oxides are described, suggesting surprising structural and functional analogies between the biological catalyst and the synthetic oxides. The location of catalytic sites is discussed and the question is raised whether surface amorphisation may be essential for catalysis by initially crystalline catalyst materials. A conceptual approach is outlined for description of the mode of water oxidation in the heterogeneous oxide catalysts with (some) molecular properties.