Unraveling the mechanism of water oxidation catalyzed by non-heme iron complexes

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Water oxidation (WO) reaction has a central biological relevance in photosynthesis, the most important process by which green plants obtain and store energy.[1] This reaction has been identified as one of the bottlenecks for the development of artificial photosynthesis schemes.[2] Since water is abundant and its oxidation produces O_2 as by product, light-driven oxidation of water is arguably the most attractive source of electrons to be used in multi-ton scale. Therefore, WO may be ideally coupled with very important reduction reactions such as generation of H_2 or the reduction of CO_2.

Fundamental understanding of metal catalysed WO mechanisms at molecular scale is essential for its development. As a result, major efforts have been devoted into experimental and theoretical mechanistic studies of homogeneous systems based on first row transition metals manganese,[3] cobalt[4] and iron.[5] The last can be seen as a particularly attractive metal for designing oxidation catalysts because it is abundant, environmentally benign, and inexpensive. With this consideration in mind, we recently reported a family of non-heme iron catalysts for water oxidation, which yield the highest turnover number described so far for any homogeneous WOC based on a 1st row transition metal.[5a,6]

In order to understand how these iron catalyst work, we have carried DFT calculations to i) propose a viable catalytic cycle consistent with our experimental results for the mechanism of chemically driven (Ce^{IV}) O_2 generation from water and ii) to unravel the role of the ligand of the non-heme iron catalyst in the water oxidation reaction activity.[7]

Computational studies supported by experimental results will permit to understand which factors make feasible the WO process. Then, this information could be used as a guide to synthetize more efficient iron based WO catalysts.

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