

UNRAVELLING THE MECHANISM OF WATER OXIDATION CATALYZED BY NON-HEME IRON COMPLEXES

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Water oxidation (WO) reaction has a central relevance in photosynthesis, the most important process by which green plants obtain and store energy.^[1] WO has been identified as one of the bottlenecks for the development of artificial photosynthetic schemes.^[2] Since water is abundant and its oxidation produces O₂ 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 H₂ or the reduction of CO₂.

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 later 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 reported a family of non-heme iron catalysts for WO, which yield activities among the highest reported for any first-row transition-metal system thus far described.^[5a,c]

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}) O₂ generation from water and ii) to unravel the role of the ligand architecture in the water oxidation reaction activity.^[6] Computational studies supported by experimental data permit to understand which factors make feasible the WO process and guide the synthesis of more efficient iron based WO catalysts.

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