In silico study of reaction mechanisms and design principles for water oxidation catalysts

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Chapter 1:

Introduction

1.1 Natural and artificial photosynthesis

Photosynthesis is the physical-chemical process by which plants, algae and some bacteria convert the solar energy into chemical energy, through the synthesis of organic compounds. In these organisms, the photosynthetic processes lead to the release of molecular oxygen and the removal of carbon dioxide from the atmosphere that is used to synthesize carbohydrates. Photosynthesis provides the energy and reduced carbon required for the survival of virtually all life on our planet, as well as the molecular oxygen necessary for the survival of oxygen consuming organisms [1-3].

1.1.1 Photosystem II

Photosystem II (PSII) is a multi-subunit protein complex embedded in the thylakoid membranes of higher plants, algae and cyanobacteria. It uses solar energy to catalyze a series of electron transfer reactions resulting in the splitting of water into molecular oxygen, protons and electrons. These reactions dissipate power on a scale of ~100 TW, being responsible for the production of atmospheric oxygen and indirectly for almost all the biomass on the planet [4].

Despite its importance, the catalytic properties of PSII have never been reproduced in any artificial system. Understanding its unique chemistry is not only important in its own right, but could have implications for the development of systems that allow us to obtain a clean source of chemical energy, reproducing the natural reaction.

The photosystem II complex is composed of more than fifteen polypeptides and at least nine different redox components that have been shown to undergo light-induced electron transfer [5]. However, only five of these redox components are known to be involved in transferring electrons from H_2O to the plastoquinone pool, and one of them is the water oxidizing tetra-manganese cluster from the oxygen evolving complex (OEC).

Photosystem II is the only known protein complex that can oxidize water, resulting in the release of molecular oxygen into the atmosphere. Despite years of research, the molecular events that lead to water oxidation are still a matter of current investigations. Energetically, water is a poor electron donor. The oxidation-reduction midpoint potential of water is +0.82 V (pH 7). In photosystem II this reaction is driven by the oxidized chlorophyll *a* in the reaction center, $P680^+$, which has a midpoint potential estimated to be +1.2 V at pH 7). Water oxidation requires two molecules of water and involves four sequential turnovers of the reaction centre. This was shown by an experiment demonstrating that oxygen release by photosystem II occurs with a four flash dependence [6, 7]. Each photochemical reaction creates an

oxidant that removes one electron from the system, resulting in a net reaction that involves the release of one oxygen molecule, the deposition of four protons into the inner water phase, and the transfer of four electrons to the Q_B-site, producing two reduced plastoquinone molecules [8-10].

1.1.2 Oxygen Evolving Complex

The photosynthetic oxygen evolution occurs at a specialized site of PSII called the oxygen-evolving complex (OEC) [5, 11]. To couple the single-electron photochemistry of the PSII reaction centre to the four-electron oxidation of two water molecules to molecular oxygen, the OEC cycles through five intermediate states, denoted S_i, where the index *i* indicates the number of positive charges accumulated at the OEC and runs from 0 to 4. The S_4 state decays spontaneously back to the S_0 state, releasing an oxygen molecule. The catalytic centre of the OEC is a Mn_3O_4Ca cubane with a fourth manganese atom outside the cube. The detailed structure of the OEC has been matter of debate during the last decade, with the most accepted structures being the Ferreira and the Loll model [12, 13]. However, more recently a higher resolution structure has been obtained from X-Ray data by Umena et al. [14]. Moreover, there is increasing converging evidence that the four oxidizing equivalents are not accumulated, instead they are used throughout the S-state cycle to extract electrons and protons from two

water molecules bound to the MnCa cluster in the S_0 state. In addition, it is known that calcium and chloride ions are required to perform the water-oxidation catalysis and it is thought that their location is close to the MnCa cluster [5].

The radical states formed during the reaction on the substrate water intermediates are stabilized by increasing the oxidation state of the MnCa cluster. During each step of the S_0-S_4 cycle one proton and one electron are released, the system remains electroneutral, and no coulombic restriction is imposed to the system by the increase of the oxidation state of the manganese atoms. However, there is considerable discussion about the mechanistic details of this reaction [15-17].

1.1.3 Artificial photosynthesis

The aim of the artificial photosynthesis research is to obtain an "artificial leaf", a device able to perform the same hydrolysis reaction as in the natural system in order to obtain hydrogen using water as the raw material.

This device needs to have different modules to mimic and perform the various stages of the photochemistry as in the photosynthetic organisms. An antenna system is needed for efficient light harvesting. A charge separator complex is crucial to stabilize the radicals formed upon photoinduced electron transfer and to delay the charge recombination. A robust and efficient catalyst is also necessary to

perform the water oxidation cycle. Moreover, the complete device, the artificial leaf, must be self-healing in order to reduce the possible light damage along the whole process [18].

During the last two decades, important scientific progress has been obtained in the field of light harvesting units and charge separation systems [19-21]. However, one of the bottlenecks in artificial photosynthetic research is the chemical design of a synthetic water splitting catalyst able to perform the multi electron oxidation reaction at high turnover number and frequency, with moderate overpotential and high current density.

1.2 Water oxidation catalysts (WOC)

The natural PSII system has been the inspiration and the starting point for many researchers in developing a catalytic structure for efficient water oxidation. The search of a molecular catalyst capable to generate oxygen from the oxidation of two water molecules has been very active already in the eighties and nineties with the study and synthesis of several biomimetic catalysts, mainly with two manganese centres linked by oxygen bridges [22-25]. Also ruthenium has been used extensively as metallic centre in similar catalyst architectures [25, 26].

During the last decade a large effort has been devoted in the synthesis of catalysts with different kind and number of metallic centres and different ligands [27]. The most explored catalysts are the ones based on ruthenium [28, 29], cobalt [30-32] and iridium [33-35], and during the last years also iron has been explored as a possible metallic centre [36]. DFT calculations have been also performed to clarify the underlying reaction mechanism in some of these catalysts [34, 35, 37-39]. Available computational chemistry tools have reached a predictive power which is good enough to allow not only the understanding of reaction mechanisms in existing catalysts, but even the important and crucial landmark of assisting in the design of new catalysts.

An effective water oxidation catalyst must be capable of water oxidation at a potential minimally above the thermodynamic value, with a high turnover frequency and able to run during hundred thousands of cycles. However, these are characteristics needed only from an efficiency point of view. For a good catalyst it is also necessary to use an abundant material. A catalyst based on a rare and expensive metal might represent a problem when moving into a large scale production.

Nowadays, the catalysts with the best performance are based on ruthenium or iridium. However, these two metals are extremely rare, leading to an economical and availability problem. This is the reason why the search for other catalysts based on more abundant metals has been a hot topic during the last years. In Figure **1.1** it is possible to

observe that ruthenium is around four orders of magnitude less abundant than cobalt, and six to eight orders of magnitude less abundant than manganese and iron, respectively. Iridium is still less abundant than ruthenium. At this point is clear that a compromise between efficiency and availability is crucial in order to find the most appropriate catalysts for the water oxidation reaction.

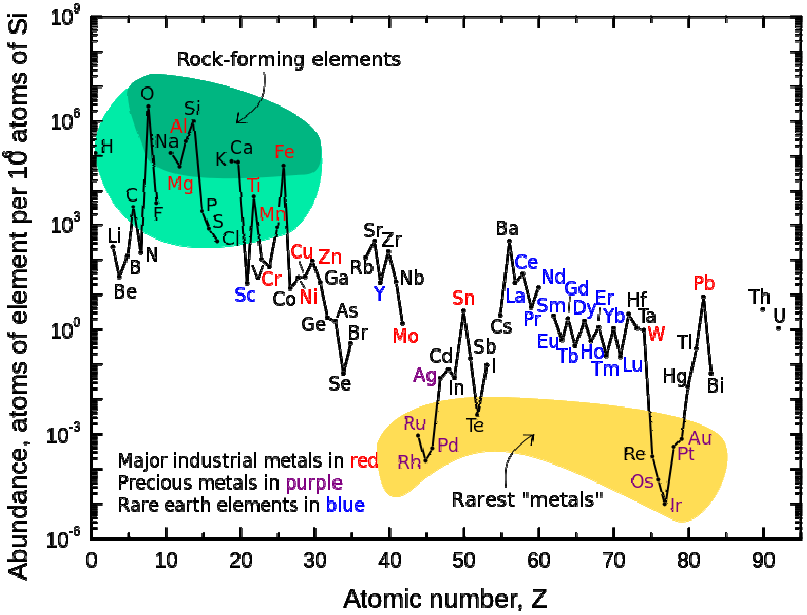

Figure 1.1. Relative abundance of elements in the Earth's upper crust. Not shown: Noble Gases, Tc(43), Pm(61), and all elements after Bi(83), except for Th(90) and U(92).

1.3 Aim and scope of this thesis

Throughout the last decades the water oxidation process has been extensively investigated. However, open questions remain on the reaction mechanism and the possible intermediates in the catalytic cycle. Indeed, different catalysts can function through different reaction routes. Some of them work in a proton-coupled electron transfer (PCET) pathway, while other catalysts have a non-PCET behaviour.

Some of these problems lie in the very short lifetime of intermediates, which makes it difficult to characterize them experimentally. Within this context, DFT calculations represent a very useful tool. In fact quantum-mechanical computational tools allow exploring and analyzing the possible intermediates and study and compare different reaction pathways in order to find the energetically most likely one. In the same way the thermodynamics of the catalytic cycle and the kinetics of the reaction coordinates can be analyzed.

The specific aim of this thesis is the study of different catalysts and reaction pathways to find clues about the mechanism of the reaction and develop guiding principles for the design of efficient water oxidation complexes.

Chapter **2** gives a general overview of the theoretical methods and approximations used throughout this thesis. In chapter **3** a mechanistic

study of one of the first Mn based catalysts, the $[H_2O(terpy)Mn(O)_2Mn(terpy)OH_2]^{3+}$ complex, is presented. The novelty of this work is the use of *ab initio* molecular dynamics simulations tools to include dynamics and explicit solvent effects. Moreover, methods used to simulate rare events are here employed to explore the reaction pathway and allow crossing the activation energy barrier within the typical *ab initio* molecular dynamics time scale. A structural rearrangement and a new intermediate complex are found which can explain degradation processes observed in experimental work. In chapter **4**, the mechanism for the oxygen-oxygen bond formation of mono-nuclear ruthenium based catalysts is studied with computational tools based on DFT similarly to those used in the previous chapter. One important finding in this work is that the explicit inclusion of the water environment is crucial to properly characterize the reaction pathway. Indeed the solvent is not a simple spectator but participates in the reaction as proton acceptor to facilitate the formation of the intermediate hydroperoxo complex and to perform the complete oxygen bond formation reaction. Thereafter, in chapter **5**, the thermodynamics of the complete S_0-S_4 cycle is analyzed and compared for mono-metallic catalysts of the same family as the one analyzed in chapter **4**. Here we modify *in silico* the metallic centre and the aromatic ring ligand to explore their effect on the thermodynamic cycle and on the resulting overpotential. This work aims to identify important common denominators and guiding principles in the design of water

oxidation catalysts. Finally, in chapter **6**, a general overview of the main conclusions obtained in this thesis is given. In this chapter is also presented a brief introduction to the current and future research, as well the new techniques that can be put into practice to improve the understanding of this catalytic reaction.

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