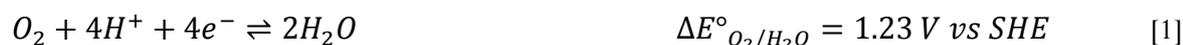


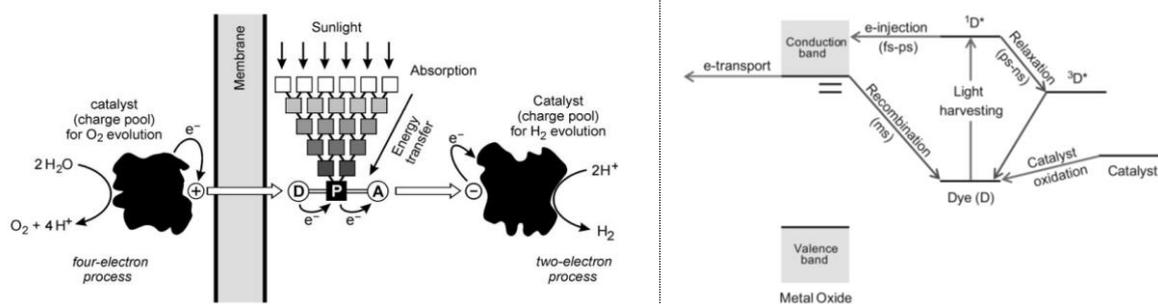
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# Summary

Since the industrial revolution the demand for energy has increased rapidly, mostly due to the development of new technologies accompanied with an increase in the global population and an increased standard of living. Up to now, the majority of this demand has been supplied by the combustion of fossil fuels. However, fossil fuels are limited sources of energy. In addition, CO<sub>2</sub> is released upon combustion of fossil fuels, which is undesirable as it is a significant contributor to the greenhouse effect. Of primary concern is that the use of fossil fuels as an energy resource and a chemical feedstock to drive the growing modern economy is unsustainable. A sustainable, carbon neutral and cost effective route for the production of fuels to drive the modern economy is one of the biggest endeavors of mankind. Hydrogen gas is an ideal candidate to serve as a carbon neutral fuel, hence the interest in the development of a hydrogen based economy. If produced from renewable feedstocks, the use of hydrogen is considered to be sustainable and non-polluting. To realize this, technologies have to be developed for the conversion of solar energy to hydrogen, using H<sub>2</sub>O as a renewable feedstock. This thesis treats the development of a relatively new technology based on the concepts of artificial photosynthesis for the production of hydrogen. In *chapter 1* the fundamental principles of such an artificial leaf are discussed and the contribution it could make to sustainable energy applications. These principles involve the use of molecular components which are immobilized onto semi-conducting metal oxide (M<sub>x</sub>O<sub>y</sub>) electrodes. Part of the components consist of molecular sensitizers, used to capture the solar radiation. Co-immobilized on the M<sub>x</sub>O<sub>y</sub> substrate are molecular water oxidation catalysts (WOCs) or proton reduction catalysts (PRCs) which are driven by the sensitizers and catalyze the half-reactions accompanied with the splitting of H<sub>2</sub>O depicted in equation 1 and 2 respectively. The introductory chapter discusses the role of the catalysts in an artificial photosynthetic device in terms of energy efficiency as they lower the overpotential needed to drive both half-reactions. Lowering the overpotential results in an increase in the overall solar to hydrogen conversion efficiency of the artificial photosynthetic device.



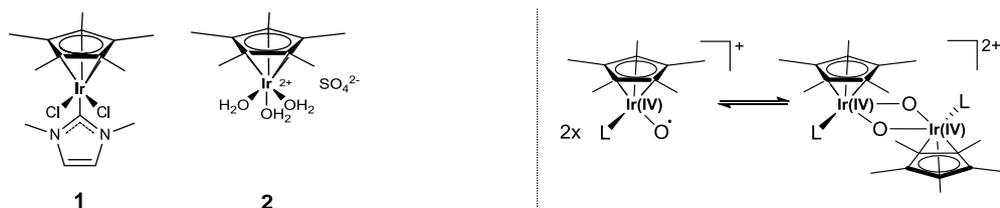
Another factor that affects the efficiency of an artificial photosynthetic device is the quantum yield of photo-generated charge-carriers into the M<sub>x</sub>O<sub>y</sub> valence and conduction bands after the absorption of solar light by the surface-immobilized molecular sensitizers. Overall, the efficient transport of photo-generated charge-carriers through the M<sub>x</sub>O<sub>y</sub> material is necessary as it prevents undesired recombination pathways of photo-injected electrons or holes with surface-



**Figure 7.1** (left) The molecular components for the construction of an artificial leaf. (right) Energy diagram depicting the desired electron flow of photo-injected electrons and undesired recombination pathways.

immobilized sensitizers, inhibiting the activation of the respective co-immobilized catalyst (figure 7.1). The oxidation of  $\text{H}_2\text{O}$  (equation 1) is considered to be the bottleneck when compared to the proton reduction half-reaction (equation 2) as this four electron process is kinetically more difficult. Therefore the focus will be on the application of molecular water oxidation catalysts, immobilized onto sensitized  $\text{M}_x\text{O}_y$  photoanodes for the photodriven  $\text{H}_2\text{O}$  oxidation half-reaction. To select a suitable water oxidation catalyst, detailed understanding of the catalytically active species that facilitates the oxidation of  $\text{H}_2\text{O}$  is required as this determines the rate at which the catalytic cycle is completed. Structural integrity of the catalytic precursor is key for strategies that involve the functionalization of the molecular complex for electrode surface anchoring or the covalent attachment of suitable molecular sensitizers (*chapter 3*). Related to this, the nature of the catalytically active species is of importance as it determines the required oxidation potential for a molecular sensitizer in the construction of photoanodes based on molecular components that catalyze the oxidation of  $\text{H}_2\text{O}$ .

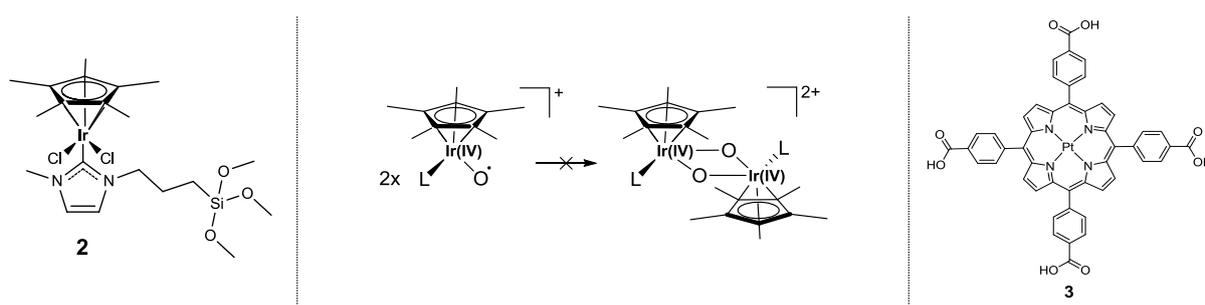
Central to the developments discussed in this thesis is the use of a simple and fast N-heterocyclic carbene ligated water oxidation catalyst reported by our group in 2011 (complex **1**, figure 7.2). This complex has two coordination sites available for  $\text{H}_2\text{O}$  to coordinate after displacement of the chloride anions under aqueous conditions. To get insight in the exact nature of the catalytically active species for compound **1**, in comparison to similar  $\text{IrCp}^*\text{LX}_2$  water oxidation catalysts, careful analysis in the changes of the  $\text{Ce}^{4+}$  consumption rate were studied in *chapter 2* using stopped-flow UV-VIS spectroscopy when the catalyst is used in the  $\text{Ce}^{4+}$ -driven oxidation of  $\text{H}_2\text{O}$ .



**Figure 7.2** (left) NHC  $\text{IrCp}^*\text{Cl}_2$  **1** and  $\text{IrCp}^*(\text{H}_2\text{O})_3$  **2** water oxidation catalysts. (right) Postulated *in-situ* dimer formation for NHC complex **1** ( $\text{L} = \text{NHC}$ ) and tris-aqua complex **2** ( $\text{L} = \text{H}_2\text{O}$ ).

Importantly, the obtained catalytic data is analyzed using reaction progress kinetic analysis (RPKA), which is a methodology developed by Blackmond and thus far has not been applied for the interpretation of kinetic data related to water oxidation catalysis. The methodology allows to observe distinct changes in the  $Ce^{4+}$  consumption rate during the reaction progress as a result of the influence of the chelating ligand around the iridium metal center. Based on the results obtained with this methodology it is concluded that with respect to iridium based molecular water oxidation catalysts, the formation of *bis- $\mu$ -oxo* bridged species is a crucial step in the process that converts the catalytic precursor to a catalytically active state that shows high TOFs with respect to the catalytic oxidation of  $H_2O$ . It is assumed that the formation of such species facilitate the formation of oxygen through kinetically accessible faster pathways which is reflected in higher observed TOFs. Detailed studies of novel molecular  $IrCp^*LX_2$  catalytic precursors therefore is important as the results in the current study show that the ligand determines if the formation of *bis- $\mu$ -oxo* bridged species, leading to fast catalytically active species, is accessible.

In *chapter 3*, it is demonstrated that important differences in the catalytic activity are observed after modification of the N-heterocyclic carbene ligand with a trimethoxysilane functional group. It is demonstrated from the kinetic profile that the trimethoxysilane group hinders the formation of *bis- $\mu$ -oxo* bridged species which was demonstrated to be important for the unmodified catalytic precursor **1** in the  $Ce^{4+}$  driven catalytic oxidation of  $H_2O$  (figure 7.3). As a consequence relatively high potentials are required for the electrocatalytic formation of  $O_2$  using the modified NHC  $IrCp^*Cl_2$  **2** dissolved in a phosphate buffer solution. Probably because also in this case the formation of *bis- $\mu$ -oxo* bridged species is hindered. As dinuclear complexes are not accessible it is assumed that complex **2** follows a *WNA* catalytic pathway and the formation of high-valent  $Ir^{5+}(=O)$  oxo species is necessary for the electrocatalytic oxidation of  $H_2O$ .

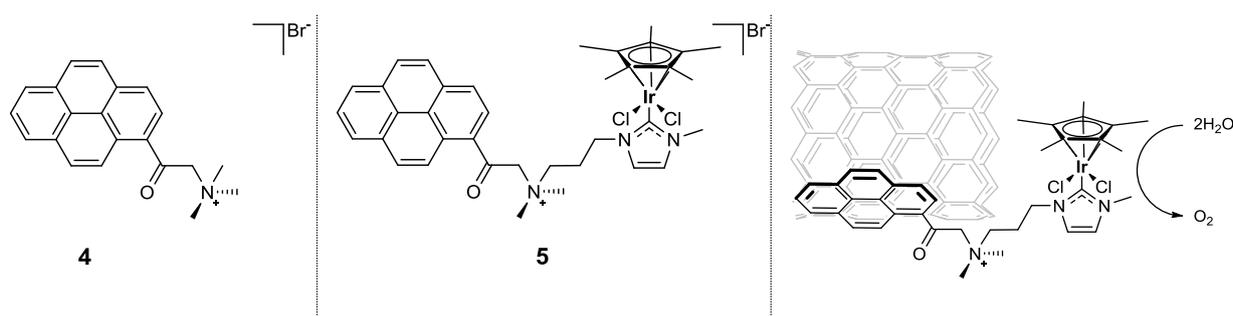


**Figure 7.3** (left) Trimethoxysilane modified NHC  $IrCp^*Cl_2$  **2**. (right) Pt(II)-porphyrin sensitizer **3**.

Following the strategy to prepare photoanodes based on molecular components, discussed in *chapter 1*, the successful anchoring of the modified NHC  $IrCp^*Cl_2$  catalytic precursor **2** onto FTO/ $TiO_2$  based electrodes is demonstrated. In addition, it is demonstrated that catalytic precursor **2** can be co-immobilized with a Pt(II)-porphyrin molecular sensitizer **3** (right panel in figure 7.3) onto FTO/ $TiO_2$ . The photoanodes show higher photocurrent densities in comparison to photoanodes functionalized with either catalytic precursors **2** or Pt(II)-porphyrin

**3** which is ascribed to photooxidation of  $\text{IrCp}^*\text{Cl}_2$  **2** by the Pt(II)-porphyrin sensitizer. When evaluated alongside Bodipy and Sn(II)-porphyrin based molecular sensitizers, only Pt(II)-porphyrin sensitizer **3** shows suitable properties in terms of electron injection into the  $\text{TiO}_2$  conduction band, the oxidation potential and photo-stability. However, the molecular sensitizer proves to be insufficient for the overall photodriven catalytic oxidation of  $\text{H}_2\text{O}$ . Presumably, the oxidation potential of **3** is insufficient to generate the  $\text{Ir}^{5+}(=\text{O})$  oxidation state of surface-immobilized precursor **2**, required for the electrocatalytic oxidation of  $\text{H}_2\text{O}$  to occur.

In *chapter 4* an alternative strategy is reported to immobilize an iridium based water oxidation catalyst onto FTO electrodes which is evaluated for the electrocatalytic oxidation of  $\text{H}_2\text{O}$ . The strategy is based on non-covalent  $\pi$ - $\pi$  interactions between a pyrene functionalized NHC  $\text{IrCp}^*\text{Cl}_2$  water oxidation catalyst (complex **5** in figure 7.4) and the sidewalls of multi-walled carbon nanotubes. The water soluble cationic pyrene compound **4** has been reported to form stable dispersions of MWCNTs in aqueous solutions and it was found that these properties are retained for the novel compound **5**, as MWCNT/**5** assemblies are readily formed under neutral and acidic conditions. In addition, the MWCNT/**5** assembly shows activity in the  $\text{Ce}^{4+}$  driven oxidation of  $\text{H}_2\text{O}$ . These combined properties validated the preparation of MWCNT/WOC composed anodes based on iridium used for the electrocatalytic oxidation of  $\text{H}_2\text{O}$ .

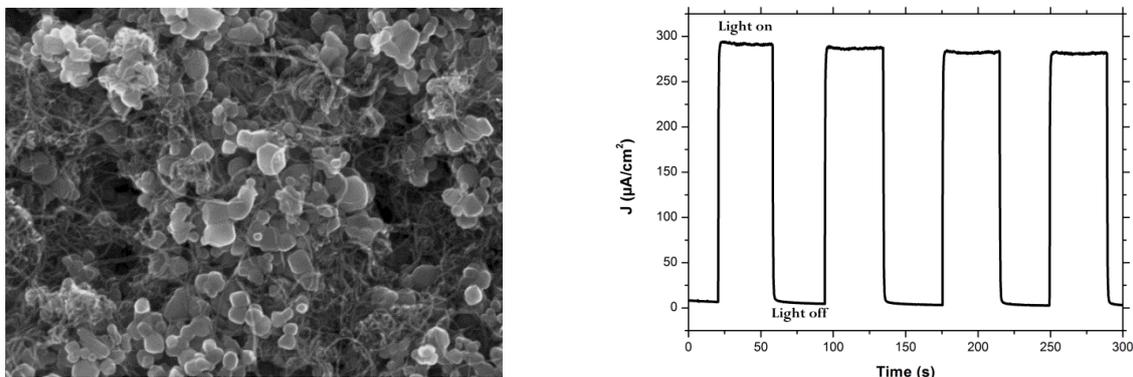


**Figure 7.4** (left) pyrene acetyl ammonium bromide **4** (middle) pyrene functionalized NHC  $\text{IrCp}^*\text{Cl}_2$  **5** (right) non-covalent surface anchoring to the sidewalls of multi-walled carbon nanotubes.

Deposition of the MWCNT/**5** assembly onto FTO surfaces leads to increased current densities when the anode is used as a working electrode with respect to the electrocatalytic oxidation of  $\text{H}_2\text{O}$ . At higher anodic polarizations initially high current densities were achieved, however, these currents prove to be non-sustainable due to delamination and degradation of the FTO/MWCNT/ $\text{Pyr}^+$  anode. The immobilization strategy is limited to applications below 1.4 V vs NHE as oxidation of the pyrene backbone is evident at higher potentials.

Activation of  $\text{M}_x\text{O}_y$ -immobilized catalysts can be inhibited by electron-hole recombination pathways (figure 7.1). To prevent these undesired recombination pathways, in *chapter 5* a method is proposed to increase the transport efficiency of photo-generated charge-carriers through semiconducting  $\text{M}_x\text{O}_y$  materials. As discussed in *chapter 3*, FTO/ $\text{TiO}_2$  electrodes are the most commonly applied substrates to immobilize molecular water oxidation catalysts and molecular sensitizers for the construction of photoanodes used for the (photo)electrocatalytic oxidation of  $\text{H}_2\text{O}$ . In *chapter 5* a novel procedure is introduced to integrate MWCNTs into

TiO<sub>2</sub>, NiO or SnO<sub>2</sub> materials, based on the use of sodium 1-pyrene sulphate. It is demonstrated that the novel FTO/MWCNT/TiO<sub>2</sub> composite anode surface remains photoresponsive upon illumination with light using a 300 nm longpass filter in basic and acidic buffer solutions (figure 7.5). In addition, it is demonstrated that the surface can be functionalized with the same molecular components studied in *chapter 3*.



**Figure 7.5** (left) Scanning electron micrograph images of FTO/MWCNT/TiO<sub>2</sub> composite surface (right) Illumination of FTO/MWCNT/TiO<sub>2</sub> in N<sub>2</sub> saturated 1 M KOH.

Electron transfer from surface-immobilized molecular compounds to the MWCNT/TiO<sub>2</sub> composite surface was demonstrated and the immobilized catalytic precursor **2** electrocatalytically oxidizes H<sub>2</sub>O. The results obtained using the described strategy opens perspectives to develop novel materials for the (photo)electrocatalytic oxidation of H<sub>2</sub>O based on molecular composed FTO/MWCNT/M<sub>x</sub>O<sub>y</sub> composite (photo)anodes. In *chapter 6* a strategy is proposed as an initial step to the development of artificial leaf configurations based on microfluidic type devices using oxidized porous silicon side-walls. The anchoring of compound **2** in the pores of oxidized porous silicon substrates is demonstrated, showing the importance of the control in pore diameter upon preparation of the surface porosity, with respect to the accessible specific surface area upon immobilization of the catalytic precursor.

The development and understanding of the (photo)catalytic oxidation of H<sub>2</sub>O using iridium based compounds remains a complicated challenge. The research described in this thesis contributes to the elucidation of this mechanism by carefully comparing the reaction progress of IrCp\* WOCs and translates the findings to the development of novel photoanodes based on IrCp\* WOCs for the photodriven oxidation of H<sub>2</sub>O. It clearly demonstrates the consequences of ligand functionalization and immobilisation on critical properties such as reaction rate and the potential at which oxidation occurs. To reduce the required oxidation potential, it is proposed that IrCp\* catalytic precursors should be anchored to the FTO/TiO<sub>2</sub> surface as *bis-μ-oxo* bridged dimeric species as this is assumed to be a prerequisite for the (photo)electrocatalytic oxidation of H<sub>2</sub>O to occur at moderate overpotentials. The system as described in this thesis is a novel example of a molecularly composed photoanode using an iridium based water oxidation catalyst. In the context of artificial photosynthetic device design based on molecular iridium compounds, this is an important step.