Functional Photo-electrochemical Devices for Solar Cells and Solar Fuels Based on Molecular Components

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Abstract
This thesis concerns the development and the study of molecular functional photo-electrochemical cells (PEC) for solar cells and solar fuels.

The first chapter gives a general introduction about photosynthesis, dye-sensitized solar cell and photo-electrochemical device for water splitting.

The second chapter describes a TiO$_2$-Co-catalyst electrode manufactured by a direct photo-deposition method. The electrode showed activity for electrochemical water oxidation in an electrochemical device.

In the third chapter, a photo-electrochemical cell (PEC) with two-electrodes for visible light driven water splitting has been successfully demonstrated. One electrode was a photo-anode, which assembled a ruthenium water oxidation catalyst (complex 1) into a dye-sensitized porous nanostructured TiO$_2$ electrode by employing a cation-exchange membrane (Nafion). The other electrode was platinum which was used as a passive cathode for proton reduction.

In the fourth chapter, an earth abundant metal complex with an anchoring group (cobalt complex 2) was synthesized and investigated as water oxidation catalyst. This complex was further applied into a photo-anode in a PEC. The photo-anode was assembled by co-sensitization of complex 2 to a dye-sensitized porous nanostructured TiO$_2$ electrode. The PEC device gave ca. 250 $\mu$A/cm$^2$ photo-current and 7.2 % IPCE without applying any bias voltage, which is much higher than the reported results in the sample type of PEC. Meanwhile, we have shown that the catalytic effect is not from free cobalt ions, CoO$_x$ film or nanoparticles formed in situ by using complex 2 in the device.

The last two chapters describe an optimization of the NiO films prepared in two steps rather than one step film and applied in p-type DSSCs. This optimized film could adsorb more dye (P1), leading to a significant light harvesting efficiency (LHE) and IPCE in DSSCs. We further combined this P1 sensitized photo-cathode with a hydrogen evolution catalyst (complex 3) and applied this photo-cathode into a PEC for visible light hydrogen evolution.

Keywords: artificial photosynthesis, dye sensitized solar cell, hydrogen generation catalyst, nickel oxide (NiO), titanium dioxide (TiO$_2$), water oxidation catalyst, water splitting
Abbreviations

A Absorbance
bpy 2,2’-bipyridine
c Concentration
CB Conduction band
COx Cobalt based catalyst (Co-based catalyst)
CV Cyclic voltammetry
DSSC Dye-sensitized solar cell
Dye* Excited state dye
Dye+ Oxidized state dye
Dye− Reduced state dye
E Energy levels
EDX Energy-dispersive X-ray spectroscopy
FTO Fluorine-doped tin oxide
GC Gas chromatography
HOMO Highest occupied molecular orbital
IPCE Incident photon to current conversion efficiency
Isc Short-circuit current
ITO Indium-doped tin oxide
Jsc Short-circuit current density
l Pathlength of the sample
LHE Light harvesting efficiency
LUMO Lowest unoccupied molecular orbital
MLCT Metal to ligand charge transfer
NHE Normal hydrogen electrode
NiO Nickel oxide
OEC Oxygen-evolving complex
PEC Photo-electrochemical cell
Pin The input of the illumination intensity
Pmax The maximum output power of the solar cell
PS I Photosystem I
PS II Photosystem II
Pt Platinum
SEM Scanning electron microscopy
TiO2 Titanium dioxide
TOF Turnover frequency
TON Turnover number
VB Valence band
 Voc Open-circuit voltage
$\text{ZnO}$  Zinc oxide
$\eta$  Power conversion efficiency of solar cell
$\varepsilon$  Molar extinction coefficient
List of Publications

This thesis is based on the following papers, referred to in the text by their Roman numerals I-VI:

I. **Double-Layered NiO Photocathodes for p-Type DSSCs with Record IPCE**
   
   Lin Li, Elizabeth A. Gibson, Peng Qin, Gerrit Boschloo, Mikhail Gorlov, Anders Hagfeldt and Licheng Sun
   

II. **A photoelectrochemical device for visible light driven water splitting by a molecular ruthenium catalyst assembled on dye-sensitized nanostructured TiO$_2$**
   
   Lin Li, Lele Duan, Yunhua Xu, Mikhail Gorlov, Anders Hagfeldt and Licheng Sun
   

III. **Visible light driven hydrogen production from a photo-active cathode based on a molecular catalyst and organic dye-sensitized p-type nanostructured NiO**
   
   Lin Li, Lele Duan, Fuyu Wen, Can Li, Mei Wang, Anders Hagfeldt and Licheng Sun
   

IV. **Electrochemical water oxidation by photo-deposited cobalt-based catalyst on a nano-structured TiO$_2$ electrode**
   
   Lin Li and Licheng Sun
   

V. **Electrocatalytic water splitting: A bi-functional water-soluble molecular Co-based complex for both catalytic water oxidation and hydrogen generation**
   
   Lin Li, Fusheng Li, Lele Duan, and Licheng Sun
   
   *manuscript*

VI. **A photoelectrochemical device for visible light driven water splitting with a molecular cobalt complex assembled on dye-sensitized porous nanocrystalline TiO$_2$ electrode**
   
   Lin Li, Peter William Lohse, Fusheng Li, Anders Hagfeldt and Licheng Sun
   
   *manuscript*
List of papers not included in this thesis:

VII. **Synthesis and mechanistic studies of organic chromophores with different energy levels for p-type dye-sensitized solar cells**
    Peng Qin, Joanna Wiberg, Elizabeth A. Gibson, Mats Linder, Lin Li, Tore Brinck, Anders Hagfeldt, Bo Albinsson, and Licheng Sun

VIII. **Type-II colloidal quantum dot sensitized solar cells with a thiourea based organic redox couple**
    Zhijun Ning, Chunze Yuan, Haining Tian, Ying Fu, Lin Li, Licheng Sun and Hans Ågren
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1. Introduction

It is clear that energy is crucial to modern human society. Today, we obtain energy mainly from energy dense fossil fuel. Unfortunately, due to the extensive use of fossil fuel, some problems are arising. These problems mainly include the insufficient energy supply, due to the fast world growing demand, and the environmental pollution produced by the use of fossil fuel. Therefore, these issues have caused a reorganization of energy policies and drew attention to clean and renewable energy to maintain a sustainable development.

Clean and renewable energy comes from natural resources such as sunlight, wind, rain, tides and geothermal heat. Among them, solar energy shows a strong potential, which is the energy derived from the sun through the form of solar radiation.

The applications of solar technology mainly include conversion of solar energy into thermal, electricity or solar chemical. However, huge investments about how to use solar energy as an efficient and economical way should be required. Moreover, energy storage is another issue to be considered due to continuous consuming energy in the modern society, because solar energy is not available all the time. Thus, inexpensive and direct conversion of solar energy into electrical energy, with efficient means of storage is the best choice.

To store solar energy, a highly desirable strategy is photo-induced water splitting into hydrogen and oxygen to build a clean and sustainable energy cycle. Nowadays, most of hydrogen is produced from natural gas, oil and coal. The major industrial use of hydrogen is to synthesize chemicals such as ammonia, methanol, and hydrogenation of petrochemicals. Actually, hydrogen could be the energy of the future, as quoted from Jules Verne’s novel, The Mysterious Island, 1875: “Yes, my friends, I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable… I believe, then, that when the deposits of coal are exhausted we shall heat and warm ourselves with water. Water will be the coal of the future.”[1]
1.1. Photosynthesis

Splitting water into oxygen and hydrogen is also known as an artificial photosynthesis. The net reaction is

$$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{H}_2$$

(1.1)

Nearly all the oxygen in the atmosphere is from photosynthetic water splitting on our planet. In nature, water oxidation occurs in plants via a series of biological activities, in particular photosystem II (PS II) and photosystem I (PS I). The function of photosystem II is summarized here. P680 absorbs sunlight, gets excited and trapped by the primary electron acceptor (plastoquinone), and gives an oxidized cation radical $\text{P680}^+$. To refill the deficit of electrons in $\text{P680}^+$, electrons are extracted from water oxidation reaction under the effect of an oxygen-evolving complex (OEC, a $\text{Mn}_4\text{CaO}_5$ cluster). In more details, $\text{P680}^+$ repeatedly oxidizes OEC. When this reaction reaches four times, the OEC will convert water into oxygen and protons.

The electron from plastoquinone will travel through cytochrome to plastocyanin, where PS I mediates electron transfer from plastocyanin to ferredoxin under the illumination.

![Figure 1. A schematic diagram of light driven reactions in photosynthesis.](image)

1.2. The dye-sensitized solar cell (DSSC)

1.2.1. Background

The dye-sensitized solar cell (DSSC) had been developed since 1960s by Gerischer. However, the efficiency was extremely low mainly due to the use of smooth semiconductors (single crystal), which could only adsorb a limited amount of mono-lay of dye sensitizers further leading to the poor light harvesting efficiency (LHE). In 1991, the breakthrough was made by Grätzel and co-workers who reported efficiencies of 7-8%. This new generation of DSSC employed a mesoporous semiconductor instead of single crystal. The
mesoporous semiconductor is important because the special feature of high internal surface area which could adsorb much more dye sensitizer without losing charge collection efficiency. The ideal porosity of the mesoporous film is around 50-60%. Further improvement of the porosities will cause poor contacts between nano-particles and lose charge collection efficiency.\[8\] Recently, the conversion efficiency of more than 12% has been obtained.\[9\]

1.2.2. The configuration and principle of the DSSC

Until now, most researches in this field are mainly focused on n-type DSSC, which contains a dye sensitized n-type semiconductor such as titanium dioxide (TiO\(_2\)) or zinc oxide (ZnO),\[10\] electrolyte, and a passive platinum cathode (Pt).\[11\]

Figure 2 (a) provides a schematic illustration of the architecture of n-type DSSC. A transparent conducting glass, in our case, which is fluorine-doped tin oxide (FTO) glass, is used as a support substrate with low resistance and high transparency. On the top of the FTO, a mesoporous layer of TiO\(_2\) has been deposited. Typically, the thickness of this layer is around 10 \(\mu\)m. On the surface of the nano-particles of TiO\(_2\), the dye molecules are bound as the antenna to absorb light energy. This FTO-TiO\(_2\)-Dye electrode is also known as a photo-anode. An electrolyte containing a redox couple (I\(^-\)/I\(_3^+\)) is filled between two electrodes. The redox couple could regenerate dye molecules and mediate electrons between the working electrode and counter electrode. Platinized FTO is usually employed as counter electrode to catalyze the reduction of the redox couple and complete the electric circuit.\[12\] Other materials such as polymers,\[13-15\] carbon black,\[16-18\] cobalt sulfide,\[19\] and carbide-based catalysts\[20\] have also been investigated as counter electrodes. Between the two electrodes, a sealing material is required to prevent the leakage and evaporation of the electrolyte.

A strategy to improve the performance of DSSC is to form a tandem DSSC with two photo-active electrodes,\[21, 22\] which imitates two photo-active centers (PS I and PS II) in the nature. For this purpose, a photo-cathode is developed.\[23, 24\] Obviously, this technology must rely on a good performance of the photo-cathode. To investigate the performance of the photo-cathode, p-type DSSC was developed independently.\[25-27\] For a typical p-type DSSC, the
photo-cathode is based on a dye sensitized p-type semiconductor such as nickel oxide (NiO),\textsuperscript{28} while the anode is Pt (Figure 2(b)). Dye and electrolyte play the same roles as in an n-type DSSC.

![Figure 2. Schematic illustration of the architectures of (a) n-type and (b) p-type DSSCs.](image)

1.2.3. **The principle of the DSSC**

The mechanism of the DSSC is fairly well understood.\textsuperscript{29-31} For a typical n-type DSSC, the light is first captured by dye molecules. When a photon of light is absorbed by a dye molecule, the dye is excited from the ground state to the excited state (Dye*) and injects an electron into the conduction band of TiO\textsubscript{2}, leaving the dye in its oxidized state (Dye\textsuperscript{+}). The injected electron travels through TiO\textsubscript{2} toward the FTO and further reaches to the counter electrode through the external circuit. The oxidized dye is regenerated by the electron transfer from the redox couple in the electrolyte, which leads to the oxidized redox mediator (I\textsubscript{3}\textsuperscript{−}). The oxidized species (I\textsubscript{3}\textsuperscript{−}) in the redox couple will be recovered by the catalytic effect of platinum at the counter electrode. These processes can be represented as follows:

\[
\begin{align*}
\text{Dye} + h\nu &\rightarrow \text{Dye}^* \quad \text{(dye excitation)} \quad (1.2) \\
\text{Dye}^* &\rightarrow \text{Dye}^+ + e^- (\text{TiO}_2) \quad \text{(electron injection)} \quad (1.3) \\
2\text{Dye}^+ + 3\text{I}^- &\rightarrow 2\text{Dye} + \text{I}_3^- \quad \text{(dye regeneration)} \quad (1.4) \\
\text{I}_3^- + 2e^- (\text{Pt}) &\rightarrow 3\text{I}^- \quad \text{(redox couple regeneration)} \quad (1.5)
\end{align*}
\]

For a typical p-type DSSC, the working principle is inversely to the n-type DSSC. When the dye gets excited, instead of injecting an electron into the
conduction band of TiO$_2$, the dye injects a hole into the valence band of NiO, leaving a reduced state (Dye$^-$). The reduced dye is regenerated by electron transfer from an oxidizing agent of the redox couple in the electrolyte. The reduced species in redox couple will be recovered by the catalytic effect of platinum at the counter electrode. These processes can be represented as follows:

$$\text{Dye} + h\nu \rightarrow \text{Dye}^* \quad \text{(dye excitation)}$$  \hspace{1cm} (1.6)

$$\text{Dye}^* \rightarrow \text{Dye}^- + h^+(\text{NiO}) \quad \text{(hole injection)}$$  \hspace{1cm} (1.7)

$$2\text{Dye}^- + I_3^- \rightarrow 2\text{Dye} + 3I^- \quad \text{(dye regeneration)}$$  \hspace{1cm} (1.8)

$$3I^- \rightarrow I_3^- + 2e^-(\text{Pt}) \quad \text{(redox couple regeneration)}$$  \hspace{1cm} (1.9)

During these electron transfer reactions, four energy levels of the components are crucial (Figure 3). They are the Fermi level of the semiconductor, the ground state (approximately highest occupied molecular orbital, HOMO), the excited state (around lowest unoccupied molecular orbital, LUMO) of the photosensitizer, and the energy potential of the redox couple in the electrolyte ($E_{\text{redox}}$). The Fermi level locates near the conduction band (CB) of TiO$_2$ or the valence band (VB) of NiO. In the case of n-type DSSC, the LUMO of dye must be more negative (the gap is approximately 200 mV) than the CB of TiO$_2$ for the electron injection. The HOMO of the dye must be more positive than the $E_{\text{redox}}$ for the dye regeneration. On the contrary, for a p-type DSSC, the HOMO of the dye must be more positive than VB of NiO for the hole injection, while the LUMO must be more negative than the $E_{\text{redox}}$ for the dye regeneration.
It is necessary to ensure a high driving force for electron (or hole) injection into the semiconductor and regeneration of the oxidized (or reduced) dye. A subsequent critical issue is the lower open-circuit voltage ($V_{oc}$) compared to the band gap of the photosensitizer.\cite{32} The band gap is the energy level difference between LUMO and HOMO, around 1.5 eV. The $V_{oc}$ is determined by the energy level difference between the Fermi level of the semiconductor and the energy potential of the redox couple in the electrolyte. The Fermi level locates near the conduction band of n-type semiconductor or the valence band of p-type semiconductor (around 0.54 V vs. NHE at pH 7.0 for NiO).\cite{33} Thus, the theoretical $V_{oc}$ is expected to be nearly 0.9 V for a n-type DSSC with TiO$_2$ as the electrode and $\Gamma^-/I_3^-$ as the redox couple, while it is approximately 0.1 V for p-type DSSC with NiO as the electrode and $\Gamma^-/I_3^-$ as the redox couple. However, in a real working DSSC, the potential of the redox couple is dependent on the ratio of concentrations between the reduced and oxidized species. That is one of the reasons why some p-type DSSCs can achieve $V_{oc}$ up to 218 mV.\cite{34}
1.3. Photo-electrochemical cell for water splitting

1.3.1. Background

A Photo-electrochemical cell (PEC) is a solar cell where energy from photons drives electrochemical reactions. In principle, this type of cell can be applied to obtain electricity directly or used for the generation of chemical fuels through a series of electron-transfer processes. Some of the electron-transfer processes are quite similar to those in the photosynthesis of plants.

Basic processes of a typical PEC are shown in Figure 4 (a). This PEC consists of a photo-anode, an electrolyte containing redox species, and a passive metal counter electrode. When the photo-anode absorbs light, electrons are extracted from redox1 through electron-transfer processes. The electrons move to the counter electrode, where reduction reactions of the oxidized species occur. In this example, the photo-anode is a photo-active center. It should also be mentioned that a photo-cathode can also be the photo-active center, where the passive counter electrode is replaced by a photo-cathode. Needless to say, it is possible to assemble two active centers, photo-anode and photo-cathode, in just one device.

![Figure 4. Schematic illustration of (a) a PEC using a photo-anode electrode and a metal as counter electrode. (b) A PEC for water splitting. Oxygen is formed at the photo-anode, while hydrogen is generated at the counter electrode.](image)

For the water splitting reaction, the water oxidation reaction takes place at the positively charged anode, giving electrons to the cathode. At the cathode, the electrons from the anode meet the protons, and the hydrogen production occurs. (Figure 4 (b)).

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad \text{Water oxidation at the anode. (1.10)}
\]
\[
2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad \text{Hydrogen generation at the cathode. (1.11)}
\]
The total reaction is:

\[ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + \text{H}_2 \]

Water splitting. \( (1.1) \)

The thermodynamic potentials for these half reactions are:

\[ E(\text{H}_2\text{O/H}_2) = 0 \text{ V} - 0.059 \times (\text{pH}) \text{ V vs. } \text{NHE} \]  \( (1.12) \)

\[ E(\text{H}_2\text{O/O}_2) = 1.23 \text{ V} - 0.059 \times (\text{pH}) \text{ V vs. } \text{NHE} \]  \( (1.13) \)

There are several reasons why the PEC for water splitting is promising. The first reason is that oxygen and hydrogen are generated at separate electrodes. These separate electrodes allow easy separation and collection of oxygen and hydrogen, which avoid safety problems. The second reason is that the PEC can be carried out in moderate conditions, i.e. at room temperature and pressure. The third reason is that this PEC can be designed to be cheap and environmentally friendly.

### 1.3.2. The semiconductor as the photo-electrode

The critical aspect for the design of a PEC for water splitting is to choose photo-active electrode materials. Semiconductor can be used as photo-active electrode,\(^{[35]}\) but has to fulfil the following requirements:

1. Visible light absorption/ overlap the spectrum of solar energy.
2. Suitable band positions of CB and VB to promote water oxidation/reduction reactions.
3. High catalytic activity for water oxidation/reduction reactions.
4. High stability
5. Efficient charge transport

One key requirement for a semiconductor photo-electrode is to efficiently absorb solar energy, which means to overlap with the solar spectrum. To overlap with the solar spectrum, the visible light spectrum from 400 nm to 800 nm is highly desired. This spectrum is corresponding to the energy from 3.12 eV to 1.56 eV according to equation 1.14. Thus, to absorb more visible light, small band gap (from 1.56 eV to 3.12 eV) semiconductors are more promising for solar water splitting.

\[ \text{Band gap (eV)} = \frac{1240}{\lambda} \text{ (nm)} \]  \( (1.14) \)

Another crucial requirement is the potential of band positions.\(^{[35, 36]}\) The potential for the photo-excited electron in the CB of the semiconductor has to
be more negative than the potential needed for water reduction $E(\text{H}_2\text{O}/\text{H}_2)$. On the other hand, the potential of VB of the semiconductor has to be more positive than the potential needed for water oxidation $E(\text{H}_2\text{O}/\text{O}_2)$. Figure 5 lists the band positions of several common semiconductor materials in the pH 1 aqueous electrolyte compared with the energy potentials for water splitting reaction. These band levels usually shift in different pH in accordance with ($-0.059 \times \text{pH}$) at room temperature.$^{[37]}$

For a semiconductor like TiO$_2$, the band positions are suitable for the total water splitting reaction. In 1972, Fujishima and Honda first reported a PEC for water splitting with a TiO$_2$ (rutile) electrode as the photo-anode and Pt as the cathode.$^{[38]}$ Under illumination of UV light on TiO$_2$ electrode, electrons and holes are generated and separated from each other due to the presence of an electric field inside TiO$_2$. The photo-generated electrons move toward CB and further to the Pt cathode through external circuit, where hydrogen generation occurs due to the negative potential of CB. Simultaneously, the photo-generated holes oxidize water to O$_2$ on the TiO$_2$ electrode due to the potential of the very positive VB. However, the limitation restricting its use is that this material could only adsorb UV radiation rather than visible light. This
limitation is due to the wide-band gap (3.2 eV) of TiO$_2$. Current research in this field is to enhance the visible light photo-activity of wide band gap semiconductors. Unfortunately, as far as we know, all reported efforts are in limited success for total water splitting.

For a semiconductor such as GaInP$_2$, GaAs, Fe$_2$O$_3$\cite{39} or WO$_3$,\cite{40} the band gap is small enough to obtain more energy from the sun. However, the band positions are not suitable for the water splitting reaction. Although the CB of GaInP$_2$ or GaAs is negative enough to reduce hydrogen, the VB is not positive enough to promote oxygen evolution from water. By contrast, the potentials of WO$_3$ and Fe$_2$O$_3$ are favorable for water oxidation rather than hydrogen evolution. In these cases, a bias voltage is needed for total water splitting. Moreover, to increase catalytic activity for water oxidation, a layer of catalytic material such as cobalt oxide film has been coated on the semiconductor.\cite{41}

As an alternative, a smart design of hybrid-junction configuration is also applied. For instance, Turner and Khaselev reported a PEC with p-GaInP$_2$/n-GaAs/p-GaAs and Pt.\cite{42} However, it is very expensive due to the complicated fabrication and the use of Pt as the catalyst. Although, Pt-free devices are reported based on a silicon solar cell, Fe-Ni-O and Co-Mo under basic condition (pH 13), the corrosion issues have to be considered.\cite{43} Very recently, Daniel G. Nocera and co-workers reported a solar water splitting cell using a triple-junction amorphous silicon solar cell cooperated with cobalt/borate catalyst as water oxidation catalyst and NiMoZn as hydrogen evolution catalyst.\cite{44} This report offers a path to design a PEC for water splitting.

CdS and CdSe seem to meet the requirements of visible light absorption and suitable band positions. However, these materials are unstable under continuous irradiation,\cite{45} since the S$^{2-}$ or Se$^{2-}$ are oxidized to the elemental S or Se at the same potential used to oxidize water.

A solution has been developed to help a wide band gap semiconductor to capture more light energy, which is sensitization of the semiconductor with molecular photosensitizers. This dye sensitized electrode with Pt on the surface has been applied into a so-called tandem PEC as the photo-cathode for hydrogen generation, while the photo-anode is WO$_3$/Pt or Fe$_2$O$_3$/Pt.\cite{46} Pt is
used to catalyse both oxygen evolution and hydrogen generation. WO$_3$ or Fe$_2$O$_3$ is mainly used to capture the solar energy but not to promote oxygen evolution, because the photo-generated holes are inefficient to extract electrons from water.$^{[39, 47]}$

It is extremely challenging to choose one single semiconductor material for total water splitting. Thus, multiple components of photo-electrodes are needed. An obvious promising trend is to combine photosensitizer and catalyst with a wide band-gap semiconductor. In this case, the semiconductor is used as a substrate to hold other components and transport charge. The photosensitizer is responsible to capture solar light. The catalyst is in charge of promoting water oxidation/reduction reactions.

1.4. The aim of this thesis

The aim of this thesis is to develop photo-electrochemical devices to convert solar energy to electricity or split water into oxygen and hydrogen. The devices will operate by mimicking the electron transfer reactions of the photosynthesis. The devices will combine photosensitizer and catalyst with a wide band-gap semiconductor. This combination offers possibility and flexibility to design the device with several molecular components.

The main strategy has been to select the candidates of molecular components such as photosensitizer, water oxidation catalyst and hydrogen production catalyst, apply these components into the devices and evaluate the performance of the devices.
2. Cobalt-based catalyst modified electrode for electrochemical water oxidation

(Paper IV)

2.1. Introduction

Electrolysis of water into O₂ and H₂ was found in 1800s. In principle, an electrical potential is applied to two electrodes (typically made from metal such as platinum) immersing in the water. This potential requires more energy than the thermodynamic potential of water splitting reaction. This extra potential is called over-potential. Over-potential will vary under different operational conditions. In particular, it will be reduced through the use of a suitable catalyst.

Water oxidation is generally viewed as the major kinetic obstacle for total water splitting since this reaction requires multiple proton-coupled electron transfer processes and the O-O band formation. To promote this reaction, suitable catalysts are highly demanded. Widely studied catalysts are platinum and transition metal oxide such as ruthenium oxide. However, their high prices are a major obstacle for a large scale application. For a large scale application, a suitable catalyst should fulfill the criteria such as high activity, long-term stability, low cost and based on earth abundant materials. Among the candidates, cobalt-based catalysts show strong promising possibility due to the nature of cobalt. But how to apply these catalysts into the device is another main issue for the industrial applications. To promote the industrial application, an easy way for attachment of the catalysts into the electrode would be highly desired.

The aim of this chapter is to describe photo-deposition of a cobalt-based catalyst on a nano-structured TiO₂ electrode for electrochemical water oxidation, as shown in Figure 6.
Figure 6. An electrochemical device, consisting of an anode for water oxidation based on photo-deposited cobalt-based catalyst on nanostructured TiO₂ film supported by a FTO conducting glass, a Pt cathode for hydrogen generation, and an aqueous electrolyte (0.1 M potassium phosphate buffer, pH 7.0), for electrochemical water splitting.

2.2. Materials

2.2.1. A cobalt-based catalyst for water oxidation

In 1980s, cobalt ions (Co(II)) were found to catalyze the water oxidation reaction in the presence of chemical oxidants in pH 7 phosphate solutions. The chemical oxidant is Ru(bpy)₃³⁺ (bpy=2,2'-bipyridine) with the potential 1.26 V vs. NHE. Ru(bpy)₃³⁺ will oxidize Co(II) to inactive Co(III) species and active Co(IV) species. However, Co₂O₃ or a related solid is produced during the reaction. Consequently, O₂ yield drops because the catalytically active species (Co(II) and Co(IV)) is removed from the reaction phase.

Recently, Nocera and coworkers reported electro-deposition of a water oxidation cobalt-based catalyst (CoOₓ), which is generated in-situ by applying a potential on an ITO or FTO electrode in phosphate electrolyte and other proton-accepting electrolytes containing Co(II). This catalyst self-assembles through the oxidation of Co(II) to Co(III). Phosphate is responsible for the self-healing and the release of protons from the water oxidation. Lately, they have shown that the performance of the electrode could be
significantly improved by using a conducting substrate Ni foam which has a high surface area.\[60\]

In addition to the electrodeposition method, photochemical deposition was developed to directly photo-deposit Co-based catalyst on the surface of n-type semiconductor such as $\alpha$-Fe$_2$O$_3$\[^{41, 61, 62}\] or ZnO.\[^{63}\] In photochemical deposition, the generation of this Co-based catalyst relies on the photo-generated hole in the valence band of the semiconductor reacting with Co(II) instead of the electro-deposition method with the application of the extra bias voltage. As we discussed above, the irradiation of a semiconductor leads to the formation of conduction band electrons and valence band holes. If the level of the valence band (VB) of the semiconductor lies more positive than approximate 1.1 V vs. normal hydrogen electrode (NHE) which is required to generate Co-based catalyst, the photo-generated holes can be used to oxidize Co(II) to produce the Co-based catalyst. Meanwhile, the photo-generated electrons flow through the external circuit to the cathode for reduction reactions. These processes are shown in Figure 7.

![Figure 7](image.png)

**Figure 7.** A) Schematic diagram of band positions of TiO$_2$ and potential for generation of the Co-based catalyst. B) Photo-deposition process of Co-based catalyst on TiO$_2$ particle.

2.2.2. *Nano-crystalline porous TiO$_2$ film*

TiO$_2$ is an important n-type semiconductor material which shows various interesting properties such as high electron mobility, high photo-catalytic activity, easy to process and high stability in aqueous environment over a wide range of pH values and applied potentials. Nano-structured porous TiO$_2$ is even more interesting due to the high porosity and large surface area. These unique
characteristics are favorable for the adsorption of organic molecules. It already has shown an advantage in dye sensitized solar cells (DSSC). Due to the larger surface area and good collection of charge carriers in the nano-crystalline TiO$_2$ film, more dyes were adsorbed on the electrode and lead to ca. 600 times higher IPCE than the cell with the single-crystal TiO$_2$ film.$^{[7]}$

TiO$_2$ is a good candidate for photo-deposition of Co-based catalyst. The energy potential of photo-generated holes (VB of TiO$_2$) lies at 2.91 V vs. NHE,$^{[64]}$ which is much more positive than the required potential for generation of Co-based catalyst (1.1 V vs. NHE). Thus, photo-deposition of Co-based catalyst is thermodynamically favorable for TiO$_2$, as shown in Figure 7. Moreover, the optical band gap of TiO$_2$ is 3.2 eV, which is corresponding to the light spectrum of 387 nm.$^{[65]}$

Nano-structured TiO$_2$ electrodes were prepared by the following procedure. A cleaned FTO glass (Pilkington TEC8, sheet resistance 8 Ω/square) was used as a substrate. A commercially-available TiO$_2$ paste containing nano-crystalline TiO$_2$ with an average nanoparticle size of 20 nm (anatase, DSL 18 NR-T, DYESOL) was used for the preparation of porous TiO$_2$ film. The paste was coated on the FTO glass by using screen-printing approach. First, a layer of paste was screen-printed in an active area of 5 × 5 mm, and then dried for 10 min at 125 °C. This screen-printing procedure (with coating, and drying) was repeated to grow the thicker TiO$_2$ electrode. Typically, the thickness of one layer was around 3 μm. These TiO$_2$ coated electrodes were gradually sintered at 450 °C for 30 min to remove extra organic compounds and solvents.

2.2.3. The electrode (TiO$_2$-Co-catalyst)

TiO$_2$-Co-based-catalyst electrodes were prepared as following: Two electrodes, which are a TiO$_2$ electrode and a platinum wire, were connected to each other through a wire and placed in a photo-electrochemical cell (PEC). The PEC was filled with an electrolyte of 0.1 M potassium phosphate buffer (pH 7.0) containing 0.5 mM CoSO$_4$. The TiO$_2$ electrode was illuminated under a 500 W xenon light source for 15 min, 30 min, 1 hour, or 2 hours. As a result, the Co-based catalyst was directly photo-deposited on the surface of nano-structured TiO$_2$, which is shown as a dark green-black film. The electrodes were washed
with 0.1 M potassium phosphate buffer (pH 7.0) prior to use. The light intensity of 500 W xenon lamp was about 0.35 W/cm².

2.3. Method

2.3.1. UV-vis. absorption spectroscopy
Ultraviolet-visible (UV-vis.) absorption spectroscopy is used to analyze the absorption of a sample. It measures the intensity of light before (I₀) and after (I) passing through a sample. The ratio between I and I₀ (I/I₀) is the transmittance (T).

\[ T = \frac{I}{I_0} \]  

(2.1)

Based on T, the absorbance (A) is obtained:

\[ A = -\log \left( \frac{T}{100\%} \right) \]  

(2.2)

UV-vis absorption spectrum in this chapter is to identify the absorption of the film, which reflects the existence of the Co-based-catalyst. The absorbance of the film was recorded as a function of wavelength of light. All spectra of the electrodes were recorded using HR-2000 Ocean Optics, fiber optics spectrophotometer. The analysis was carried out on the film with air as the blank.

2.3.2. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX)
Scanning electron microscopy (SEM) is used for high magnification imaging of the surface of the sample. Energy-dispersive X-ray spectroscopy (EDX) is utilized to analyze the element or quantitative chemical characterization of the sample.

SEM and EDX spectra were obtained with a LEO 1530 FEG-SEM equipped with an Oxford INCA EDX system. For SEM images, an acceleration voltage of 5 kV was applied. While for EDX, the acceleration voltage of 12 kV was applied.

2.3.3. Electrochemical measurements
All electrochemical measurements were recorded by an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie). For a three-electrode setup: a prepared TiO₂ electrode was used as a working electrode, a Ag/AgCl
redox couple in 3 M KCl as a reference electrode, and a platinum foil as a counter electrode. The potential was applied between the reference electrode and the working electrode, while the current was measured between the working electrode and the counter electrode. All measured potentials were converted to the NHE using $\text{[Ru(bpy)₃]^{2+}}$ as an internal reference (1.26 V vs. NHE).

Cyclic voltammetry (CV) is one of the commonly used electrochemical measurements, which is used for the measurement of the redox potential or the observation of a catalytic property of a complex.

Bulk electrolysis is a typical method to generate hydrogen and oxygen from water by using the electricity. For bulk electrolysis experiment, a tight cell was used, when a constant potential 1.3 V vs. Ag/AgCl was held at the working electrode.

2.3.4. **Gas chromatography (GC)**

A gas chromatography (GC) is an analysis instrument to analyze compounds that can be vaporized without decomposition, such as oxygen and hydrogen. Helium and nitrogen were selected as the carrier gases to evaluate oxygen and hydrogen, respectively. To evaluate oxygen generation, 0.5 mL of the headspace of the device was transferred into a GC using a Hamilton Sample Lock syringe. All measurements were carried out by using GC-2014, Shimadzu (Molecular sieve 5A, TCD detector).
2.4. Results and discussions

Figure 8. EDX spectra of the electrodes of (a) bare TiO$_2$ and (b) TiO$_2$-Co-Catalyst

Figure 8 shows the EDX spectra of the electrode of bare TiO$_2$ and TiO$_2$-Co-catalyst. The electrode TiO$_2$-Co-catalyst shows extra peaks which belong to Co and P. This extra peaks give a good agreement with previous publication regarding the principal elemental components of the Co-based catalyst.$^{[56]}$ This result indicates that the Co-based catalyst was indeed photo-deposited on the surface of TiO$_2$. 
**Figure 9.** The UV-vis absorption spectra (I) and SEM images (II) of the electrodes TiO$_2$ (a) and TiO$_2$-Co-Catalyst with photo-deposition for 15 min(b), 30 min(c), 1 hour(d), and 2 hours(e).

**Table 1.** All elements analysis (Normalized, obtained from EDX), all results in weight %

<table>
<thead>
<tr>
<th>Photodeposition of Co-based catalyst for</th>
<th>Co</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min (bare TiO$_2$)</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>15 min</td>
<td>13.68</td>
<td>86.32</td>
</tr>
<tr>
<td>30 min</td>
<td>18.60</td>
<td>81.40</td>
</tr>
<tr>
<td>1 hour</td>
<td>20.59</td>
<td>79.41</td>
</tr>
<tr>
<td>2 hours</td>
<td>25.29</td>
<td>74.71</td>
</tr>
</tbody>
</table>
Figure 9 shows the UV-vis absorption spectra and SEM images of the electrode of bare TiO₂ and TiO₂-Co-catalyst with photo-deposition for 15 min, 30 min, 1hour and 2 hours. In these results, the TiO₂-Co-catalyst films can be easily recognized against the bare TiO₂ film. For the TiO₂-Co-catalyst films with longer procedure of the photo-deposition, stronger absorption and a better coverage of the surface (larger particles and denser surface) were observed. Moreover, the elements analyses of Co:Ti ratio in different films were shown in Table 1. Again, a higher Co:Ti ratio was shown for longer procedure of the photo-deposition. Overall, these results indicated that more catalyst was loaded on the surface of the electrode with longer procedure of the photo-deposition.

Figure 10. CVs of bare TiO₂ electrode and TiO₂-Co-catalyst electrodes in 0.1 M potassium phosphate buffer (pH 7.0). Scan rate is 100 mV/s.

Figure 10 shows CVs of bare TiO₂ electrode and TiO₂-Co-catalyst electrodes in 0.1 M potassium phosphate electrolyte (pH 7.0). The TiO₂-Co-catalyst films exhibit anodic waves from ca. 1.13 V vs. NHE and strong catalytic waves up to 1.48 V vs. NHE, which are due to the electrochemically active catalyst species.[57] Moreover, the electrode with more catalyst loading on the electrode surface shows higher activity.
Electrocatalytic water oxidation was investigated at the electrodes in pH 7.0 buffer by applying a potential of 1.48 V vs. NHE for 1 hour. The O₂ generation was confirmed and analyzed by GC. The TiO₂-Co-catalyst films lead to more O₂ evolution than bare TiO₂ electrode. Electrocatalytic hydrogen evolution was also confirmed by GC.

2.5. Conclusion

In conclusion, the TiO₂-Co-catalyst electrode was successfully manufactured by directly photo-deposition method, which shows activity for electrochemical water oxidation in an electrochemical device in pH 7 solution. For a longer photo-deposition, more catalyst was loaded on the electrode, which showed higher activity for water oxidation.

However, an obvious disadvantage regarding this device is the light collection. Even though UV-light can carry enough energy to do the job, the electrode for light driven water splitting is inefficient. It is necessary to develop an electrode which could collect the visible light of sun energy.
3. A molecular ruthenium catalyst modified photo-anode

(Paper II)

3.1. Introduction

Recently, several PECs with photo-active anodes for water oxidation have been developed. [66-69] For these photo-anodes, a molecular catalyst is combined with a photosensitizer on a wide band-gap semiconductor (TiO$_2$). The photosensitizer was used to capture the light energy, while a catalyst was used to accelerate the water oxidation reaction. However, this research is still in the level of the “proof the concept” due to the poor performance of the components such as catalyst or photosensitizer.

The aim of this chapter is to describe a very first attempt to design a photo-active electrode for water oxidation based on an efficient ruthenium catalyst and dye-sensitized nanostructured TiO$_2$ as the anode in PEC (Figure 11). Pt is used as the cathode to catalyze hydrogen evolution and complete external circuit.

Upon the illumination on the photo-anode, photosensitizer absorbs light, gets excited, injects election into the conduction band of TiO$_2$, and gives an oxidized photosensitizer. This oxidized photosensitizer extracts electrons from the water oxidation reaction through the catalytic effect of an oxygen-evolving catalyst. Meanwhile, protons are released as starting materials for H$_2$ production. These protons meet electrons from the external circuit at the cathode, where hydrogen generation occurs. Ultimately, water is split into H$_2$ and O$_2$ driven by visible light in the PEC.

All figures (except figure 12 and 13) in this chapter were reprinted with permission from Chem. Commun. 2010, 46, 7307-7309. Copyright 2010, The Royal Society of Chemistry
Figure 11. A PEC device, consisting of an anode based on RuP sensitized TiO₂ film on a FTO conducting glass coated with a Nafion film penetrated with complex 1⁺, a Pt cathode, and an aqueous electrolyte, for light driven water splitting.

3.2. Materials

3.2.1. Nano-crystalline porous TiO₂ film

The details of nano-crystalline porous TiO₂ film have already been discussed in the chapter 2.2.2.

3.2.2. Nafion

Nafion membrane is used to immobilize the cationic catalyst for water oxidation in this chapter.⁷⁰-⁷⁴

![Molecular structure of Nafion](image)

Figure 12. Molecular structure of Nafion

Nafion is a synthetic copolymer material, which has been widely exploited due to a high chemical and thermal stability and cation conduction properties, especially for protons. The molecular structure is shown in Figure 12. It
contains a considerable number of sulfonic groups. These groups show an electrostatic interaction with cationic complexes, which allows the cationic complexes to penetrate into the Nafion. In another word, the pores in Nafion membrane allow the movement of cations but not anions or neutral compounds. The pores size is around 30-50 nm. Please note that the sulfonate exchange sites in the Nafion are extremely acidic.

A Nafion membrane was prepared by the following procedure. A precursor solution was Nafion® perfluorinated resin solution 5wt. % in mixture of lower aliphatic alcohols and water. This precursor solution was neutralized to pH 7.0 or pH 9.8 by using a NaOH solution. The commercially available or neutralized Nafion solution was coated on prepared dye-sensitized TiO₂ electrode with a Scotch® tape as a mask (0.25 cm² active area), followed by heating on a hot plate at 120 °C for 3 min to form Nafion membrane or modified Nafion membrane.

3.2.3. Photosensitizer

An ideal photosensitizer (also called as dye) in a PEC has to perform as required:

1. Visible light absorption/overlap the spectrum of solar energy.
2. Suitable potential of excited state. (This potential must be more negative than CB to inject electron into CB of TiO₂).
3. Sufficient long lifetime to undergo a chemical reaction.
4. Suitable potential of oxidized forms. (This potential must be more positive than the onset catalytic potential of a catalyst to drive a catalyst toward water oxidation reaction).
5. A strong anchoring group to attach to the electrode.

Ru(bpy)₃²⁺ (bpy=bipyridine) is used as a photosensitizer due to its visible light absorption, suitable energy potential, long lifetime of the excited state, and good stability of oxidized state. Ru(bpy)₃²⁺ adsorbs visible light because of a metal to ligand charge transfer (MLCT) transition, resulting in an excited state dye (Ru(bpy)₃²⁺*).

\[
\text{Ru}^{II}(\text{bpy})_3^{2+}(d^6) \xrightarrow{hv} \text{Ru}^{III}[(\text{bpy})_2(\text{bpy})^-]^{2+*}(d^5\pi^*)
\] (3.1)
This excited state photosensitizer can be long-lived for around 600 ns in solution.\textsuperscript{[76]} This excited state is also well known to undergo a rapid electron-transfer reaction.\textsuperscript{[77]} The electron transfer could occur either through a oxidized quenching to give a oxidation state \([\text{Ru(bpy)}_3]^{3+}\) or by a reductive quenching to give a reduced state \([\text{Ru(bpy)}_3]^{-}\), as shown in Figure 13.

![Schematic diagram of electron transfer processes and the redox potential diagram of \(\text{Ru(bpy)}_3^{2+}\).](image)

Figure 13. Schematic diagram of electron transfer processes and the redox potential diagram of \(\text{Ru(bpy)}_3^{2+}\).

When this photosensitizer attached to the surface of TiO\(_2\), the electron transfer will occur from the excited state dye to the CB of TiO\(_2\). Because the energy of the excited state dye is negative than the CB of TiO\(_2\) (Figure 13), the electron transfer is thermodynamically allowed. This excited state electron transfer reaction gives an oxidation state dye \([\text{Ru(bpy)}_3]^{3+}\). This \([\text{Ru(bpy)}_3]^{3+}\) is a strong oxidant. In our case, \([\text{Ru(bpy)}_3]^{3+}\) will draw electron from an oxygen-evolving complex (OEC), leading to the regeneration of dye. The photochemical processes are

\[
\begin{align*}
\text{Ru(bpy)}_3^{2+} + h\nu &\rightarrow \text{Ru(bpy)}_3^{2+\ast} \quad \text{(dye excitation)} \quad (3.2) \\
\text{Ru(bpy)}_3^{2+\ast} &\rightarrow \text{Ru(bpy)}_3^{3+} + e^- (\text{TiO}_2) \quad \text{(electron injection)} \quad (3.3) \\
\text{Ru(bpy)}_3^{3+} + \text{OEC} &\rightarrow \text{Ru(bpy)}_3^{2+} + \text{OEC}^+ \quad \text{(dye regeneration)} \quad (3.4)
\end{align*}
\]

The photosensitizer must attach to the surface of the semiconductor to inject electron after excitation. Assuming the lifetime of an excited singlet state and triplet state are 10\(^{-9}\) s and 10\(^{-6}\) s, the corresponding diffusion lengths of excited singlet state and triplet state molecules are calculated to be 1 nm and 30 nm.\textsuperscript{[36]} With the help of an anchoring group, the excited dye will be limited only
around the surface of the semiconductor, which will benefit for the excited dye to inject electron into the CB of semiconductor. A strong well-known anchor group is phosphoric acid. Thus, in this chapter, ruthenium bipyridine complex with a phosphoric acid group \((\text{Ru(bpy)\textsubscript{2}(4,4'-(PO\textsubscript{3}H\textsubscript{2}bpy)})^2+\) (\text{RuP}, see Figure 11) was used as the photosensitizer. \text{RuP} was prepared according to the literature.\(^{[78]}\)

3.2.4. A ruthenium water-oxidation catalyst

Oxygen-evolving complexes with high activity, robustness and low over-potential are highly demanded.\(^{[53]}\) We have reported a series of these compounds with the strategy of introducing negatively charge ligands.\(^{[79-82]}\) One of the best performing catalysts is \([\text{Ru}^{(II)}\text{L(pic)}_2]\) (complex 1, see Figure 11) (\(\text{H}_2\text{L} = 2,2'\text{-bipyridine-6,6'-dicarboxylic acid; pic = 4-picoline}\)).\(^{[83]}\) The catalytic water oxidation by complex 1 is highly pH-dependent. The catalytic onset potential for this complex is ca. 1.5 V vs. NHE in a pH 1.0 aqueous solution or ca. 0.98 V vs. NHE in pH 7.0 neutral solution, which is corresponding to the overpotential of 0.16 V vs. NHE. In another word, lower pH condition would shift the catalytic onset potential to a more positive position.

The catalysis of water oxidation was demonstrated in a homogeneous system using Ce\textsuperscript{IV} as an oxidant, which is a sacrificial electron acceptor, in acidic condition (pH 1.0). Complex 1 gives a TON of ca. 2000 and an initial TOF of 18 s\textsuperscript{-1}.\(^{[84]}\) Another oxidant \([\text{Ru(bpy)}_3]^{3+}\) was also investigated in a pH 7.0 buffer solution with the presence of complex 1. But the results shows a very low reaction rate.\(^{[85]}\)

The photochemical water oxidation was demonstrated by employing a three-component homogeneous system including \([\text{Ru(bpy)}_2]\text{Cl}_2\) as a photosensitizer, complex 1 as a catalyst, and \([\text{Co(NH}_3)_2\text{Cl}]\text{Cl}_2\) or \(\text{Na}_2\text{S}_2\text{O}_8\) as a sacrificial electron acceptor.\(^{[85]}\) By irradiation of the system, complex 1 gives a maximum TOF of 550 h\textsuperscript{-1}. Under the illumination, \([\text{Ru(bpy)}_3]^{3+}\) species was generated according the following equations.\(^{[77, 86, 87]}\)

\[
[\text{Ru(bpy)}_3]^{2+} + \text{hv} \rightarrow [\text{Ru(bpy)}_3]^{2+*} \quad (3.5)
\]

\[
[\text{Ru(bpy)}_3]^{2+*} + \text{S}_2\text{O}_8^{2-} \rightarrow [\text{Ru(bpy)}_3]^{3+} + \text{SO}_4^- + \text{SO}_4^{2-} \quad (3.6)
\]
\[
[Ru(bpy)_3]^{2+} + SO_4^{-} \rightarrow [Ru(bpy)_3]^{3+} + SO_4^{2-} \quad (3.7)
\]
\[
[Ru(bpy)_3]^{2+*} + [Co(NH_3)_5Cl]^2+ \rightarrow [Ru(bpy)_3]^{3+} + Co^{2+} + 5NH_3 + Cl^- \quad (3.8)
\]

In these cases, sacrificial electron acceptors are used to accept photo-generated electrons from the photosensitizer. However, these sacrificial electron acceptors are not needed in a PEC because the semiconductor will receive the photo-generated electrons.

To achieve penetration into the Nafion assembled in electrode, the cationic complex \( 1^+ \) was prepared by one-electron oxidation of complex \( 1 \) with a certain amount of \( Ce^{IV} \) in pH 1.0.

3.2.5. The photo-anodes

The photo-anode was prepared as the following procedure. TiO\(_2\) film electrodes (0.25 cm\(^2\) active area, thickness is 6 \( \mu \)m) were prepared as discussed in the chapter 2.2.2. To adsorb the dye molecule, the electrodes were dipped into a 0.2 mM dye solution for overnight. These electrodes were washed with ethanol and dried by air flow to remove unbounded dye and solvent. The dye sensitized TiO\(_2\) electrode was masked with a Scotch\® tape (0.25 cm\(^2\) active area), coated with a Nafion solution, followed by heating at 120 °C for 3 min. A uniform Nafion membrane was recast on the electrode. This electrode was penetrated with a drop of Complex \( 1^+ \) solution, followed by drying with air flow, rinsing with acetonitrile, and drying again.

The photo-anode with only RuP or complex \( 1^+ \) is called TiO\(_2\)-RuP-Nafion or TiO\(_2\) -Nafion-complex \( 1^+ \). With full assemble of photosensitizer and catalyst is called TiO\(_2\)-RuP-Nafion-complex \( 1^+ \).

3.3. Method

3.3.1. UV-vis. absorption spectroscopy

UV-vis absorption spectrum in this chapter is to determine the amount of complex \( 1^+ \) and photosensitizer on the film. An intrinsic property of a chemical species is the molar extinction coefficient (\( E \)), which reflects how strongly this
species absorbs light at a certain wavelength. In another word, $E$ is a constant value. It could be measured via the Beer-Lambert law,

$$E = \frac{A}{cl}$$  \hfill (3.9)

Where $A$ is the absorbance of the sample, $c$ is the concentration of the sample, $l$ is the pathlength of the sample.

Dye loading on the electrode: three prepared identical RuP sensitized TiO$_2$ films were immersed into 0.1 M NaOH solution (water/ethanol = 1:1, V/V) for two hours to make the dye desorbed from the electrodes.$^{[88]}$ The absorption of resultant solution was measured and compared to a known concentration of RuP ($1\times10^{-5}$ M) to calculate the dye loading on the electrode.

Amount of complex $1^+$: Absorption of complex $1^+$ on Nafion film was measured and compared with a known concentration of complex $1^+$ ($5\times10^{-5}$ M) in the solution.

3.3.2. **Cyclic voltammetry (CV)**

Cyclic voltammetry (CV) in this chapter is used for the measurement of redox potential of the photosensitizer and the catalyst. The details of the electrochemical measurements were discussed in the chapter 2.3.3.

3.3.3. **Transient short-circuit photo-current**

Photo-current is used to determine how many electrons travel from the photo-anode through the outer circle to cathode. Assuming 4 or 2 electrons were involved in oxygen or hydrogen generation, the photo-current also reflects how much oxygen or hydrogen generated.

The photocurrent measurements were carried out in a two electrode system using the above prepared photo-anode as the working electrode, a platinum foil as the counter electrode. 0.1 M Na$_2$SO$_4$ was used as the electrolyte. The photo-anode was illuminated using a light emitting diode. The current was recorded by an Autolab potentiostat with a GPES electrochemical interface (Eco Chemie).
3.3.4. Oxygen

A Clark-type oxygen electrode was used to record the oxygen evolution. The Clark electrode is a technique which allows measurement of nano-mole/mL (µM) level of oxygen dissolved in a liquid. It consists of a cathode and an anode. At the cathode, oxygen will be reduced and create an electrical current. This electrical current keeps a linear relationship with the oxygen concentration. Two known concentration of 0% and 100% air saturation of oxygen in water was used to calibrate the system.

A prepared photo-anode, the working electrode, was connected to a Pt counter electrode. These two electrodes were immersed in a vessel of Clark-electrode. The vessel was charged with a pH 7.0 phosphate buffer solution (total 2 mL) or 0.1 M Na₂SO₄ as an electrolyte. Then, the system was enclosed and degassed for 20 min to remove the air. The photo-anode was irradiated by a 500 W xenon light source through a 400 nm cut off filter, while oxygen was recorded in terms of time.

3.3.5. Hydrogen

A Micro-GC (Micro-GC CP 4900 Quad, Varian) was used to detect hydrogen evolution.

3.3.6. TON and TOF

Turnover number (TON) is to describe the productivity of the catalyst, which is a molar ratio of converted substrate (oxygen generation) to the catalyst. Turnover frequency (TOF) is used to reflect the catalytic activity, which is the TON per time unit.

\[
TON = \frac{\text{Oxygen (mol)}}{\text{catalyst (mol)}}
\]  
\[
TOF = \frac{TON}{\text{Time (h or s)}}
\]  

(3.10)  
(3.11)
3.4. Results and discussions

Figure 14. CVs of TiO$_2$-RuP (dash line) in phosphate buffer (pH 7.0, 50 mM) solution and complex 1 with a glassy carbon disk as the working electrode (solid line) in phosphate buffer (pH 7.0, 50 mM) solution containing 10% acetonitrile. Ag/AgCl is used as the reference electrode and [Ru(bpy)$_3$]$^{2+}$ as the internal reference.

CV of TiO$_2$-RuP electrode was compared with complex 1 in phosphate buffer pH 7.0 solution, as shown in Figure 14. It is clear that the oxidation potential $E_{1/2}$(Ru$^{III}$/II) of RuP is more positive than the onset catalytic potential of complex 1 in pH 7.0 condition. This indicates that photo-generated Ru$^{III}$ of RuP could drive complex 1 to oxidize water.

Figure 15. UV-Vis absorption spectra of a). complex 1$^+$ on Nafion film (solid line) and complex 1$^+$ (5×10$^{-5}$ M) in a solution (water/acetone = 1:1, V/V) (dash line) b). RuP desorbed from sensitized TiO$_2$ electrodes (dash line); and pure RuP (1×10$^{-5}$ M) (solid line) in 0.1 M NaOH solution (water/ethanol = 1:1, V/V) (dash line).
The assembly of complex $1^+$ in Nafion was confirmed by UV-Vis spectra (Figure 15). Based on the absorbance of complex $1^+$ comparing to a known concentration of complex $1^+$, the total amounts of complex $1^+$ on the Nafion film were estimated to be $1.7 \times 10^{-8}$ mol. Photosensitizer $\text{RuP}$ desorbed from the electrode and compared with a known concentration of $\text{RuP}$, the total amounts of $\text{RuP}$ on each $\text{TiO}_2$ film were estimated to be $1.8 \times 10^{-8}$ mol.

**Figure 16.** The transient short-circuit current responses to on-off cycles of illumination in a PEC device with two electrodes without applying any bias voltage. The anode was $\text{TiO}_2-\text{RuP}-\text{Nafion}$ (solid line) or $\text{TiO}_2-\text{RuP}-\text{Nafion-complex } 1^+$ (dash line), where Nafion film was prepared by a commercial solution with the pH 2. The cathode was Pt. $0.1\text{M Na}_2\text{SO}_4$ aqueous solution was used as the electrolyte. The illumination was provided by a light emitting diode.

The transient short-circuit photo-current was shown in Figure 16. Unfortunately, there is no significant difference for the transient short-circuit photo-current between $\text{TiO}_2-\text{RuP}-\text{Nafion}$ and $\text{TiO}_2-\text{RuP}-\text{Nafion-complex } 1^+$, when the photo-anode was assembled by a Nafion film prepared by a commercially available Nafion solution. This result indicates that the electron transfer from the complex $1^+$ to $\text{RuP}$ did not occur. We notice that the pH value of the precursor Nafion solution is ca. 2. This acidic condition could shift the catalytic potential of complex 1 to a higher potential. Ultimately, this catalyst could not be driven by the photo-generated oxidized $\text{RuP}^+$. 
Figure 17. The transient short-circuit current responses to on-off cycles of illumination in a PEC device with two electrodes without applying any bias voltage. The anode was TiO$_2$–RuP–Nafion (black line), TiO$_2$–Nafion-complex 1$^+$ (blue line) or TiO$_2$–RuP–Nafion-complex 1$^+$ (red line), where Nafion film was prepared by a neutralized solution with the pH 7.0. The cathode was Pt. 0.1M Na$_2$SO$_4$ aqueous solution was used as the electrolyte. The illumination was provided by a light emitting diode.

We modified the precursor Nafion solution by neutralization to pH 7.0 before preparing the Nafion membrane (Nafion pH 7.0). The transient short-circuit photo-current was carried out again (Figure 17). A clear difference was found for different photo-anodes. The photo-anode TiO$_2$–Nafion pH7.0-complex 1$^+$ generates a negligible current, indicating that almost no electrons flow through the external circuit, which is not surprising due to its inability for electron injection. The electrode only in the presence of RuP (TiO$_2$–RuP–Nafion pH7.0) shows a small initial photo-current with fast decay. By contrast, in the presence of both photosensitizer and catalyst (TiO$_2$–RuP–Nafion pH7.0-complex 1$^+$), a dramatic photocurrent enhancement was recorded, which is very likely due to electron transfer from the catalyst to the photo-generated oxidized RuP. It was observed that the photo-current decay is very quick for the electrode TiO$_2$–RuP–Nafion-complex 1$^+$. 
Figure 18. The photo-current decays of the photo-anode in a PEC device with two electrodes without applying any bias voltage. The anode was TiO\textsubscript{2}-RuP-Nafion pH 7.0 (black line), TiO\textsubscript{2}-RuP-Nafion pH 7.0-complex 1\textsuperscript{+} (red line) or TiO\textsubscript{2}-RuP-Nafion pH9.8-complex 1\textsuperscript{+} (green line). Nafion pH7.0 or pH9.8 representing the related Nafion film prepared by pH 7.0 or pH 9.8 precursor Nafion solutions, respectively. The cathode was Pt. 0.1M Na\textsubscript{2}SO\textsubscript{4} aqueous solution was used as the electrolyte. The illumination was provided by a light emitting diode.

Further to increase the initial pH value of the precursor Nafion solution to pH 9.8 to prepare Nafion membrane, we found that the photo-current decay for the electrode based on Nafion pH 9.8 solution (TiO\textsubscript{2}-RuP-Nafion pH 9.8-complex 1\textsuperscript{+}) is slower than that for Nafion pH 7.0 solution (TiO\textsubscript{2}-RuP-Nafion pH 7.0-complex 1\textsuperscript{+}), as shown in Figure 18. The main reason for this pH dependent photo-current decay is probably due to the rapid proton release during water oxidation thereby affecting the catalytic properties of complex 1\textsuperscript{+}. Meanwhile, other factors such as the decomposition of the photosensitizer and the undesirable charge recombination could probably also be contributed to the current decay. The recombination could be between oxidized species of complex 1\textsuperscript{+} and conduction band electrons in TiO\textsubscript{2}. 
Figure 19. Oxygen evolution in PEC devices without applying any bias, operated in a pH 7.0 phosphate buffer solution, detected by a Clark electrode, and illuminated by 500 W Xenon lamp through a 400 nm cut off filter.

Water oxidation was confirmed by a Clark type electrode, as shown in Figure 19. Under dark, no oxygen was detected for all cases. Under illumination, the electrodes with only catalyst or photosensitizer (TiO$_2$-Nafion pH 9.8-complex 1$^+$ and TiO$_2$-RuP-Nafion pH 9.8) show negligible amount of oxygen. In contrast, with a full assembly of catalyst and photosensitizer (TiO$_2$-RuP-Nafion pH9.8-complex 1$^+$), 140 nmol/ml oxygen was obtained after 60 min irradiation. These results clearly prove the light-driven water oxidation occurring by the complete catalytic assemble through the electron transfer as we expect in Figure 11.

Based on the oxygen generation, assuming all complex 1$^+$ participate in oxygen generation, a turnover number (TON) and a corresponding initial turnover frequency (TOF) were 16 and 27/h, respectively. Related TON and initial TOF based on theRuP were 15 and 25/h, respectively.

When a two-electrode system was investigated in a PEC device without applying any bias, we did not observe the hydrogen generation by GC, probably due to the low concentration of hydrogen which is under the
limitation of detection of GC. A small bias of –0.325 V vs. Ag/AgCl was applied in cathode to promote hydrogen generation. Indeed, the formation of hydrogen has been confirmed by GC.

3.5. Conclusions

In this chapter, we have demonstrated that visible light driven water splitting is successfully achieved in a PEC device with TiO$_2$-RuP-Nafion-complex 1$^+$ as the photo-anode for water oxidation, and a platinum electrode as the cathode for proton reduction.

During the study, we found that strong acidity of commercial Nafion caused the shift of the onset potential of complex 1$^+$ for water oxidation, and lead to the fast decay of photocurrent. To improve the performance of this type of PEC, an alternative polymer support for catalyst replacing Nafion is needed. Another option is to functionalize the catalyst which could be attached to the electrode without the supporting polymer.
4. A molecular cobalt complex assisted photo-anode for water oxidation

(Paper V and VI)

4.1. Introduction

In the chapter 3, we have demonstrated a photo-anode with the assistance of Nafion to hold the catalyst. However, the strong acidity of Nafion limits the performance of the photo-anode. A potential solution is to functionalize the catalyst with an anchoring group and apply this catalyst into the electrode.[89]

Catalysts based on low-cost and earth-abundant materials have to be developed in order to make PEC suitable for a global scale. Cobalt complexes are promising, because they already demonstrated impressive water oxidation catalytic activity.[90] However, until now, as far as we know, none of them have been investigated in a PEC.

The aim of this chapter is to describe a cobalt molecular complex with a methylene phosphate anchoring group. With this anchoring group, we have applied it in a photo-anode for visible light driven water oxidation, as shown in Figure 20. The photo-anode for water oxidation is based on a cobalt complex 2 co-sensitized onto the dye-sensitized nanostructured TiO$_2$. Pt is used as the cathode to catalyze hydrogen evolution and complete external circuit in the PEC.
Figure 20. A PEC device, consisting of a photo-anode based on complex 2 and RuP co-sensitized porous nanocrystalline TiO$_2$ film on a FTO coated conducting glass, a Pt cathode, and an aqueous electrolyte, for light driven water splitting.

4.2. Materials

4.2.1. Nano-crystalline porous TiO$_2$ film
Nano-crystallin porous TiO$_2$ film was used as a supporting material as discussed in the chapter 2.2.2.

4.2.2. Photosensitizer
RuP was used as a photosensitizer as discussed in the chapter 3.2.3.

4.2.3. A cobalt water-oxidation complex
Cobalt complexes with diglyoxime ligands (cobaloximes) have already been investigated as catalyst for hydrogen evolution during the past three decades. In particular, [Co\textsuperscript{III}(dmgH)\textsubscript{2}PyCl] (dmgH = dimethylglyoximate, Py = pyridine, see Figure 21) is a well-known cobaloxime proton reduction electrocatalyst.

In this chapter, [Co\textsuperscript{III}(dmgH)\textsubscript{2}(PMPA)Cl](Et\textsubscript{3}NH) (complex 2, PMPA = (4-pyridinylmethyl) phosphonic acid), was developed based on Co\textsuperscript{III}(dmgH)\textsubscript{2}PyCl with an extra methylene phosphate group. This group is beneficial to the solubility of complex 2 in water, which is an important consideration for the application in homogeneous solution. Moreover, this group can provide a linkage to the metal oxide, which will help further application into a PEC for water splitting. This complex was synthesized according to a similar published method.

The initial purpose of this complex is for electro-catalytic production of hydrogen. However, we found that this complex shows electrocatalytic activities for both hydrogen generation and water oxidation. Since the electrocatalytic activity for hydrogen generation is quite similar to the known complex [Co\textsuperscript{III}(dmgH)\textsubscript{2}PyCl], we will not discuss it. In contrast, we will focus on the discussion of catalytic water oxidation, especially the application in a PEC.
4.2.4. *The photo-anodes*

The TiO$_2$ film electrodes (0.25 cm$^2$ active area, thicknesses were 3, 6, 8 or 11 μm) were prepared as discussed in the chapter 2.2.2. The TiO$_2$ film electrodes were dipped into a 0.2 mM dye bath for 1 hour. After washing with ethanol and drying by air flow, the dye sensitized TiO$_2$ electrodes were dipped into a 0.3 mM complex 2 or 0.3 mM CoCl$_2$ in MeOH overnight. The electrodes were washed with ethanol and dried by air flow.

The photo-anode with only RuP or complex 2 is called TiO$_2$-RuP or TiO$_2$-complex 2. The full assembly of photosensitizer and catalyst is named as TiO$_2$-RuP-complex 2. When complex 2 is replaced by CoCl$_2$, the electrode is named as TiO$_2$-RuP-CoCl$_2$.

The electrode TiO$_2$-RuP-CoO$_x$ film: A general method to form cobalt oxide (CoO$_x$.) film is to apply a potential of 1.1 V vs. Ag/AgCl on the TiO$_2$-RuP electrode in 0.1 M potassium phosphate buffer (pH 7.0) containing 0.5 mM CoCl$_2$ for 300 s. The electrode was washed with deionized water and dried by dry air flow.

4.3. *Method*

4.3.1. *Electrochemical measurements*

Cyclic voltammetry (CV) in this chapter is used for the measurement of redox potential and catalytic activity of cobalt complex 2.

Bulk electrolysis in this chapter is used to confirm the catalytic effect of cobalt complex 2 towards water oxidation.

The details of the electrochemical measurements were already discussed in the chapter 2.3.3.

4.3.2. *Faradaic efficiency*

Faradaic efficiency reflects how efficient the charges convert to oxygen, which is a ratio between the real O$_2$ generation and the theoretical O$_2$ generation. The theoretical O$_2$ generation is calculated from the record current, assuming four moles of electrons were consumed to form one mole of O$_2$. 
4.3.3. *UV-vis absorption spectroscopy*

The details of UV-vis absorption spectra have been discussed in the chapter 2.3.1.

4.3.4. *Transient short-circuit photo-current*

The details of the Transient short-circuit photo-current measurements have been discussed in the chapter 3.3.3.

4.3.5. *The monochromatic incident photon to current conversion efficiency (IPCE)*

The monochromatic incident photo to current conversion efficiency (IPCE), which describes how efficiently the incoming incident photons are converted to electrons, is a fundamental measurement used for DSSC.

The IPCE spectra were obtained by illuminating the photo-anode of the PCE with the light of a specific wavelength (from 360nm to 650 nm) and measuring the resulting short-circuit current. The current was recorded using a computer-controlled setup consisting of a potentiostat (EG&GPAR 273). The illumination was supplied by a xenon light source (Spectral Products ASB-XE-175) and calibrated using a certified reference solar cell (Fraunhofer ISE). The specific wavelength was controlled by a monochromator (Spectral Products CM110).

4.3.6. *Gas chromatography (GC)*

The details of the GC measurements have been discussed in the chapter 2.3.4.
4.4. Results and discussions

Cyclic voltammogram (CV) of the complex 2 was investigated in pH 7.0 aqueous solution, as shown in Figure 22. The CV of complex 2 shows a current increase in the anodic region, very likely due to catalytic water oxidation. Electro-catalytic water oxidation was confirmed by bulk electrolysis experiments performed in a three-electrode electrochemical cell. A controlled-potential of 1.3 V vs. Ag/AgCl was applied on the working electrode for 1800 s in the presence of 0.5 mM complex 2 in 0.1 M potassium phosphate buffer (pH 7.0), while the current was recorded. Based on the current, assuming four moles of the passed electrons contributed to one mole of O₂ generation, the theoretical O₂ generation of $2.3 \times 10^{-6}$ mol was calculated. Meanwhile, the real oxygen generation confirmed by GC was $1.8 \times 10^{-6}$ mol. Thus, faradaic efficiency was 78% for complex 2. In addition, the CoOₓ species were not observed by employing a number of complementary methods, including CV, UV-vis, SEM, and Photo Cross-correlation Spectroscopy (please check the paper V for more details).

Figure 22. Cyclic voltammograms (CV) in the presence of complex 2 (0.5 mM, solid line) and absence of complex 2 (blank, dash line) in 0.1 M potassium phosphate buffer (pH 7.0), with glass carbon as the working electrode, Ag/AgCl as the reference electrode, and Pt as the counter electrode. The scan rate is 100 mV s⁻¹.
The complex 2 has to transfer an electron to the photo-induced oxidized RuP as shown in Figure 20. In order to prove this electron transfer, nanosecond transient absorption measurements were performed in an aqueous solution with three components. These three components were RuP, complex 2 and a sacrificial electron acceptor Na$_2$S$_2$O$_8$. This sacrificial electron acceptor was used to accept photo-induced electrons from RuP. In other words, RuP is excited by adsorbed light and transfers an electron to Na$_2$S$_2$O$_8$, giving an oxidized dye [RuP$^+$]. The results of nanosecond transient absorption measurements are shown in Figure 23. A transient signal is observed and rises to its maximum with a time constant of 4.0 ± 0.5 µs, in the absence of complex 2 in the solution (Figure 23 (a)). This suggests the oxidation of the dye on this time scale. This signal decays, probably because the oxidized form of the dye could slowly be regenerated by water. When the catalyst is added to the solution, no transient signal for the oxidized dye is detected within the time resolution of our setup as shown in Figure 23 (b). This indicates that RuP is regenerated by complex 2 very fast in solution.
We further attached RuP and complex 2 on a photo-anode, where the sacrificial electron acceptor is no longer needed. The transient short-circuit photo-current of the photo-anodes was investigated, as shown in Figure 24. The photo-anode with only catalyst but without photosensitizer (TiO$_2$-complex 2) shows a negligible photo-current. This indicates that almost no electrons flow through the external circuit, which is not surprising due to the non-absorptivity of complex 2 in the visible light region. The electrode only in the presence of photosensitizer (TiO$_2$-RuP) generates a small initial photo-current with fast decay upon the illumination, revealing the injection of electrons from the excited RuP. By contrast, in the presence of both photosensitizer and catalyst (TiO$_2$-RuP-complex 2), a dramatic photocurrent enhancement was observed, which is very likely due to the electron transfer from complex 2 to the photo-generated oxidized RuP, consistent with visible light driven water
splitting in the PEC as described in the chapter 3. Based on the photo-current during initial 20 s irradiation in Figure 24 and assuming all complex 2 participated in oxygen generation with four electrons per \( \text{O}_2 \) molecule, a turnover frequency of 55 \((\text{mol} \ \text{O}_2)(\text{mol complex 2})^{-1}\text{h}^{-1}\) was achieved. Photo-generated oxygen and hydrogen were confirmed by a Clark-electrode and a gas chromatograph (GC). Please check paper VI for more details.

![Graph showing IPCE spectra](image)

**Figure 25.** Comparison of Incident Photon to Current Efficiency (IPCE) spectra of the photo-anode TiO\(_2\)-RuP, TiO\(_2\)-complex 2 and TiO\(_2\)-RuP-complex 2, in 0.1M Na\(_2\)SO\(_4\) aqueous solution in PEC devices with two-electrode system without applying any bias voltage.

The IPCE spectra of the photo-anode TiO\(_2\)-RuP, TiO\(_2\)-complex 2 and TiO\(_2\)-RuP-complex 2 were investigated in 0.1 M Na\(_2\)SO\(_4\), shown in Figure 25. The electrode TiO\(_2\)-RuP and TiO\(_2\)-RuP-complex 2 exhibited photo-current in the range of 400-600 nm, which give a response corresponding to the UV-Vis spectra of RuP (Figure 15, page 30). This result indicates that the photocurrent is indeed induced by the dye RuP. Again, this IPCE enhancement was very likely due to the electron transfer from complex 2 to the photo-generated oxidized dye, consistent with the photo-current results in Figure 24. Moreover, the photo-anode TiO\(_2\)-RuP-complex 2 showed a 3.6 folds higher IPCE at 460 nm than TiO\(_2\)-RuP, which is higher than the reported results, to the best of our knowledge.
Figure 26. The transient short-circuit current responses to on-off cycles of illumination, in PEC devices without applying any bias. The illumination is provided by a light emitting diode. (a). The working electrodes are TiO$_2$-RuP (black line) and TiO$_2$-RuP-CoCl$_2$ (red line) operated in 0.1M Na$_2$SO$_4$ aqueous solution. (b). The working electrodes are TiO$_2$-RuP operated in 0.1 M potassium phosphate buffer (pH 7.0) with 0.5 mM CoCl$_2$ (red line) or without any CoCl$_2$ (black line), and TiO$_2$-RuP-CoO$_x$ film in 0.1 M potassium phosphate buffer (pH 7.0) (blue line).

Heterogeneous CoO$_x$ formed in situ from cobalt(II) are well known as water oxidation catalyst.[56, 57] To exclude the photo-current enhancement is from free cobalt ions or CoO$_x$ species, we did following control experiments: (1)
Comparison of TiO$_2$-RuP and TiO$_2$-RuP-CoCl$_2$, where CoCl$_2$ was used instead of complex 2 in the preparation of the photo-anode (Figure 26.a). (2) Comparison of TiO$_2$-RuP and TiO$_2$-RuP-CoO$_x$, where a CoO$_x$ was prepared on the electrode TiO$_2$-RuP (Figure 26.b). (3) Study of TiO$_2$-RuP in 0.1 M potassium phosphate buffer (pH 7.0) with and without CoCl$_2$ (Figure 26.b). However, all these control experiments showed lower photo-current than the electrode TiO$_2$-RuP. These control experiments suggest that the photo-current in Figure 24 can be attributed from the molecular catalyst complex 2 rather than free cobalt ions or CoO$_x$ species.

4.5. Conclusions

A cobalt complex 2 was synthesized and showed catalytic activity towards water oxidation. Further application of this complex in a PEC device was achieved by co-sensitization with dye-sensitized TiO$_2$ electrode. The device gives a ca. 250 $\mu$A/cm$^2$ photo-current and 7.2 % IPCE without applying any bias voltage, which is much higher than the reported results in the sample type PEC. Meanwhile, we have shown that the catalytic activity is not due to free cobalt ions or CoO$_x$ species formed in situ by using complex 2 in the device.
5. A photo-cathode for p-type DSSC

(Paper I)

5.1. Introduction

Recently, we have reported a photo-cathode for p-type dye-sensitized solar cells (DSSCs) based on p-type nanostructured NiO and a push-pull designed p-type organic dye. This push-pull structure of the organic dye increased the charge separation upon light absorption, reducing the recombination of charge and increasing the current compared to incorporated dyes in earlier devices.\cite{95, 96}

The aim of this chapter is to describe optimization of a photocathode in the p-type DSSC.

5.2. Materials

5.2.1. Nano-crystalline porous NiO film

Nano-crystalline porous NiO film has been used as a supporting material in p-type DSSCs since 1999.\cite{28, 97} Most of the NiO films in the previous studies of p-type DSSC have been prepared by using a paste of Ni(OH)$_2$ solution.\cite{33} By using this paste, it is challenging to make a thicker electrode with good mechanical stability. The thicker film is particular important for adsorption larger amount of dye and further to obtain enough photo-current in a device. Thus, a method to make a thicker electrode with good mechanical stability is extremely critical for the development of p-type DSSC.

A sol-gel method was developed by using a copolymer template to prepare a paste.\cite{25, 98} Using this paste to prepare NiO, the crystal size of NiO was increased about a three-fold compared with non-template paste. Meanwhile, the porous and mechanical stability was improved.

Based on this paste, we have developed the NiO film by using a stepwise procedure. The paste was coated on a cleaned FTO glass by using a doctor-blading procedure, as illustrated in Figure 27. One film (one step film) was prepared in one step using two layers of tape and gradually sintered at 450 °C
for 30 min to remove extra organic compounds and solvents. The other film (two steps film) was prepared in two steps using one layer of tape and sintering in between applications of doctor-blading procedure. The thickness of both films was ca. 1.1-1.2 \( \mu \)m. The crystal sizes of the NiO were 16 nm in both films.

**Figure 27.** Illustration comparing the preparation of the films in one step (a) compared to two steps (b). (a): The NiO precursor is applied using multiple layers of Scotch tape to achieve a film of the same thickness. (b) The NiO precursor is applied using a layer of Scotch tape as a spacer which is removed and the film is sintered at 450 °C for 30 min, cooled and followed an application of second layer of precursor solution. Since the film is porous, some precursor solution may penetrate into the first layer before the film is sintered again, resulting in a more dense film than a film prepared in one step.

5.2.2. Photosensitizer \( P1 \)

**Figure 28.** Molecular structure of \( P1 \).

\( P1 \) is one of the most famous organic dyes applied in NiO-based p-type DSSCs. The molecular structure of \( P1 \) is shown in Figure 28. This dye is carefully designed with a push-pull structure, which helps to increase the charge separation. When this dye is excited, the electron density moves from the part that is close to NiO towards to the part which is pointing away from
the surface. This electron density moving would facilitate the electron transfer from the excited dye to the electron acceptor.

**Figure 29. Schematic diagram of electron transfer processes and redox potential diagram of P1**

Figure 29 shows a schematic diagram of electron transfer processes of P1. The excited state (P1\(^*\)) is both a strong reductant and a strong oxidant. This means hole injection from P1 to NiO (P1\(^*/P1^-\)) and electron transfer from P1 to other electron-acceptor (P1\(^+/P1^-\)) can both happen. However, hole injection from P1 to NiO (P1\(^*/P1^-\)) is a primary reaction because this hole injection is very efficient and rapid on a time scale of 1-10 ps.\(^{[99, 100]}\) In such a rapid time scale, any other electron transfer is not likely to compete. Redox potential diagram is also shown in Figure 29.

Upon light illumination, the ground state dye (P1) is transformed into the excited state dye (P1\(^*\)), which injects hole to the VB of NiO. This photo-induced hole transfer reaction gives a reduced state for the dye (P1\(^-\)). This P1\(^-\) will be regenerated by hole transfer from tri-iodide/iodide redox couple or other electron-acceptor complex. The photochemical processes are shown below:

\[
P1 + h\nu \rightarrow P1^* \quad \text{(dye excitation)} \quad (5.1)
\]

\[
P1^* \rightarrow P1^- + h^+(\text{NiO}) \quad \text{(hole injection)} \quad (5.2)
\]

\[
P1^- + \frac{1}{2} I_3^- \rightarrow P1 + \frac{3}{2} I^- \quad \text{(dye regeneration)} \quad (5.3)
\]
5.2.3. **The fabrication of p-type of DSSCs**

The NiO film electrodes were prepared as discussed in the chapter 5.2.1. These prepared NiO film electrodes were soaked in an acetonitrile solution containing P1 (0.3 mM) for overnight at room temperature for sensitization. The dye-sensitized NiO electrode was assembled face-to-face with a platinized counter electrode using a 50 μm thick thermoplastic frame (Surlyn 1702). An electrolyte, containing LiI (1.0 M) and I₂ (0.1 M) in acetonitrile as the redox couple, was introduced into the cell through the pre-drilled hole in the counter electrode. The hole was sealed afterwards.

5.3. **Method**

A numbers of analysis methods have been developed to inspect the performance of the DSSC.

5.3.1. **Photovoltaic performance of the DSSCs**

Current-voltage characteristic (I-V curve) is used to reveal the power conversion efficiency (η). From the I-V curve, some common parameters can be obtained, which are open-circuit voltage (Voc), short-circuit current (Jsc) (or short-circuit current density, Jsc), fill factor (FF) and the power conversion efficiency (η). Jsc is found where the voltage of the cell is equal to zero (at V = 0 V intercept, short-circuit condition), while, Voc is determined where the current of the cell is equal to zero (at J = 0 V intercept, open-circuit condition).

The η is determined by the input of the illumination intensity (Pin) and the maximum output power of the solar cell (Pmax). Pmax is found where the J×V reaches a maximum. Please note that Jmax and Vmax are not the same as Jsc and Voc.

The power conversion efficiency of the solar cell is given by the equation 5.4.

\[ \eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{J_{\text{max}} \times V_{\text{max}}}{P_{\text{in}}} \]  

(5.4)

Fill factor (FF) is introduced to describe the efficiency in terms of the Jsc and Voc, according to the equation 5.5.

\[ \text{FF} = \frac{J_{\text{max}} \times V_{\text{max}}}{J_{\text{sc}} \times V_{\text{oc}}} \]  

(5.5)

Thus, the efficiency can be further recorded by the equation 5.6.
Most researchers have analysed the performance of the cells in terms of these four classical parameters which are $J_{sc}$, $V_{oc}$, FF, and $\eta$.

5.3.2. **Light harvesting efficiency (LHE)**

Light harvesting efficiency (LHE) was calculated according the equation 5.7 based on the absorbance in the UV-visible absorption spectra of the sensitized electrodes.$^{[101]}$

$$\text{LHE}(\lambda) = 1 - 10^{-A}$$ (5.7)

Where, $A$ is the absorbance of the dye on NiO at $\lambda$ wavelength in the UV-vis. absorption spectrum.

5.3.3. **The monochromatic incident photon to current conversion efficiency (IPCE)**

The details of IPCE have been discussed in the chapter 4.3.6.

5.3.4. **Scanning electron microscopy (SEM)**

SEM is used for high magnification imaging of the surface and cross-section of NiO electrodes. SEM images were taken by a field emission scanning electron microscope (Zeiss, Leo 1550) with an acceleration voltage of 5 kV. For the surface, a working distance of 3 mm and 500 000 × magnification was used. For the cross-section a working distance of 4-5 mm and 100 000 × magnification was used.

5.4. **Results and discussions**

SEM images of the cross-section and the surface of NiO films prepared in one and two steps are shown in Figure 30. Both films were uniformly distributed with mesoporous particles (I (a) and II (a)). The particles at the surfaces were more densely packed than the body of the films. For the cross-section of two steps film (II (a)), a boundary could be observed where two layered had been applied. Two-steps film appeared to be more compact than one-step film.
Figure 30. SEM images of (a) cross-section and (b) surface of NiO films prepared in one (I) and two (II) steps.

The photocathodes based on NiO films prepared in one and two steps with the similar thickness were investigated in p-type DSSCs with P1 as photosensitizer and tri-iodide/iodide redox couple. Performance characteristics of DSSCs employed these photocathodes are listed in Table 2. Both DSSCs suffered from a typically low $V_{oc}$, around 100 mV. That is because the $V_{oc}$ is determined by the energy difference between the Fermi-level of NiO and energy potential of tri-iodide/iodide redox couple. Thus, the $V_{oc}$ cannot be significantly improved only by optimizing the NiO films.\textsuperscript{[28]} However, the photocurrent could be improved. The photocurrent of NiO prepared by two steps produced a $J_{sc}$ of 5.48 mA cm$^{-2}$, which is almost double that produced from the NiO electrode prepared by one step. This improvement of photocurrent matches that detected from the IPCE as shown in Figure 31. The highest IPCE value for the NiO electrode prepared in two steps was 64\% at 475 nm, but only 38\% for the electrode prepared in one step. There are three reasons for this improvement. The first reason is probably mainly due to the NiO film (i.e. with a greater number of NiO particles per unit volume) which allows an increase in the dye loading. The more dye loading leads to better absorption of the film and higher LHE. The second reason is that the two steps NiO film showed better charge collection efficiency (more details can be found
in paper I). The third reason is that this film preparation may also have an effect on charge injection efficiency.

**Table 2.** Performance characteristics of DSSCs assembled using 0.32 cm² NiO films prepared in one step and two steps, sensitized with dye P1. The electrolyte is LiI (1.0 M) and I₂ (0.1 M) in acetonitrile.

<table>
<thead>
<tr>
<th>NiO Film</th>
<th>( V_{OC} ) (mV)</th>
<th>( J_{SC} ) (mA cm(^{-2}))</th>
<th>FF</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>One step</td>
<td>106</td>
<td>3.01</td>
<td>0.37</td>
<td>0.12</td>
</tr>
<tr>
<td>Two steps</td>
<td>84</td>
<td>5.48</td>
<td>0.34</td>
<td>0.15</td>
</tr>
</tbody>
</table>

**Figure 31.** (a) Absorption spectra and (b) LHE of NiO films prepared in one (dashed line) and two (solid line) steps, sensitized with P1. (c) IPCE spectra of DSSCs prepared from the films. The electrolyte is LiI (1.0 m) and I₂ (0.1 m) in acetonitrile.
5.5. Conclusions

We have optimized the NiO films prepared in two steps rather than one step and applied these films in p-type DSSCs. This two steps film shows better charge collection efficiency and could adsorb more dyes, leading to a significant LHE and IPCE in DSSCs. Meanwhile, the mechanical stability of the film is good enough for the application in a PEC with water present.

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6. A molecular cobalt complex assisted photo-cathode for hydrogen generation

(Paper III)

6.1. Introduction

In the chapters 3 and 4, a photo-anode was used to achieve visible light driven water oxidation in a PEC, where a passive cathode namely Pt was used to generate hydrogen. In principle, a photo-active cathode is also possible to generate hydrogen under visible light. This photo-cathode could be in combination with a discussed photo-anode into a PEC, which imitates two photo-active centers in photosynthesis. In such a PEC with two photo-active electrodes, water oxidation occurs on the photo-anode, while hydrogen generation happens on the photo-cathode. If this PEC is realized, then total water splitting employing earth abounded materials could be achieved.

The aim of this chapter is to describe a first attempt to design a photo-active cathode for hydrogen generation based on a hydrogen generation catalyst, organic dye and NiO.

![Figure 32. A PEC device, consisting of a photo-cathode based on P1 sensitized nanostructured NiO film on a FTO conducting glass coated with Complex 3, Pt counter electrode, and an aqueous electrolyte pH 7.0 buffer, under an applied potential of -0.4 V vs. Ag/AgCl, for light-driven hydrogen generation.](image-url)
Figure 32 represents a PEC device employing complex 3 on P1 sensitized nanostructured NiO film as photo-cathode. Upon the illumination on the photo-cathode in such a PEC, P1 harvests visible light, gets to the excited state P1*, injects hole into valence band of NiO (or, in another word, electron transfer from the valence band of NiO to the excited state P1*) and gives a reduced P1−. This reduced P1− will be regenerated to P1 trough hole transfer from the complex 3 (II). This will lead to form complex 3 (I), from which the reduction of protons starts. The mechanism for hydrogen evolution involving complex 3 (I) has been discussed in the reported literature.\textsuperscript{[93, 103]}

6.2. Materials

6.2.1. Nano-crystalline porous NiO film
The details of nano-crystalline porous NiO film have been discussed in the chapter 5.2.1.

6.2.2. Photosensitizer P1
The details of photosensitizer P1 have been discussed in the chapter 5.2.2.

6.2.3. Cobalt catalyst
To design a working photocathode for visible light-driven hydrogen production, a hydrogen evolution catalyst with a suitable energy potential is needed. The energy potential of the catalyst should be matched with the energy potential of the photosensitizer. In particular, the catalytic onset potential of the catalyst has to be more positive than the reduction potential \(E(P1/P1^-)\) of the photosensitizer. This energy match would allow the hole transfer occurring from the catalyst to P1− (in Equation 6.1). Thus, the candidate catalyst has to be carefully selected.

\[
P1^- + \text{cat.} \rightarrow P1 + \text{cat.}^- \quad \text{(dye regeneration)} \quad (6.1)
\]
Cobaloximes as hydrogen evolution catalysts have been successfully investigated as catalyst in several homogeneous systems driven by visible light.\[104-110\] As far as we know, complex 3 (the structure in shown in Figure 33) possesses the lowest catalytic onset potential (−0.43 V vs. NHE),\[103, 111\] which is more positive than \(E(P1/P1^-)\) of \(P1\). Thus, hole transfer from complex 3 to \(P1^-\) is thermodynamically favorable.

6.2.4. The photo-cathodes

The preparation of dye sensitized NiO electrode (called NiO-P1 electrodes) has been discussed in the chapter 5.2.3. The complex 3 was introduced by direct deposition of an acetonitrile solution of the catalyst complex 3 (100 μl, 2mM) onto the surface of NiO-P1, resulting in the photocathode NiO-P1-complex 3. The electrode with only complex 3 and without \(P1\) is shown as NiO-complex 3.

6.3. Method

6.3.1. Photo-current in PEC

The photo-current measurements were carried out in a standard three-electrode system. An above prepared photo-cathode was used as a working electrode, while Ag/AgCl in 3M KCl and a platinum wire were used as reference and counter electrodes, respectively. A potential of −0.4 V vs. Ag/AgCl was applied as approximately equal to the position of the conduction band of TiO\(_2\). This is necessary to facilitate future studies in combination with a TiO\(_2\) based photo-anode to achieve visible light-driven total water splitting. All the measurements were recorded with an Autolab potentiostat and a GPES electrochemical interface (Eco Chemie).
6.3.2. Detection of Hydrogen

![Figure 34. Schematic diagram of modification of Clark-type electrode.](image)

A modified Clark-type oxygen electrode was used to record the hydrogen evolution, which allows to measure nano-mole level of hydrogen dissolved in a liquid. In a typical Clark-type oxygen electrode, there is a platinum electrode set in the central dome as the cathode, while a silver electrode in the floor of the disc as the anode (as seen in Figure 34). For detection of hydrogen evolution, the anode is platinum black while the cathode is silver chloride. Thus, we converted platinum to platinum black and silver to silver chloride. Two known concentrations (0% and 100% saturation of hydrogen in water) were used to calibrate the system.

6.3.3. Gas chromatography (GC)
The details of the GC measurements have been discussed in the chapter 2.3.4.

6.4. Results and discussions

![Figure 35. Visible light-driven hydrogen generation using a three-component homogeneous system, consisting of P1 as photosensitizer, complex 3 as proton reduction catalyst, and triethanolamine (TEOA) as sacrificial electron donor.](image)
We have demonstrated P1 was an appropriate photo-sensitizer for NiO based p-type DSSC in the chapter 5. Then, the following question is whether P1\textsuperscript{—} extracts holes from complex 3 (II), which then further catalyzes hydrogen evolution? To this end, we investigated a three-component system in homogeneous solution for light driven hydrogen evolution (as shown in Figure 35). This three-component system contains P1 as a photosensitizer, complex 3 as a proton reduced catalyst, and triethanolamine (TEOA) as a sacrificial electron donor. This sacrificial electron donor is used to generate P1\textsuperscript{—}. The results of visible light driven hydrogen evolution are shown in Figure 36. For all cases, no hydrogen was formed in the dark. Under illumination, no hydrogen formation was detected in the absence of the complex 3 or P1. However, irradiation of the solution contains complex 3, P1 and TEOA immediately resulted in the evolution of hydrogen. After 6 min, the concentration of hydrogen reached the highest value of ca. 322 nmol, which is corresponding to a turnover number of 2, assuming all complex 3 participated.

![Figure 36. Photoinduced hydrogen evolution from homogeneous solution systems containing a). P1 (5 × 10\textsuperscript{-5} M), black line; b). Complex 3 (2 × 10\textsuperscript{-4} M), blue line; c). P1 (5 × 10\textsuperscript{-5} M) + Complex 3 (2 × 10\textsuperscript{-4} M), red line, in 1 mL solution contains 5% TEOA in 1:1 MeCN/H\textsubscript{2}O pH 7, detected by a modified Clark electrode, and illuminated by 500 W Xenon lamp through a 400 nm cut off filter.](image)
Figure 37. a). The photo-current responses to on-off cycles of illumination on photocathodes under an applied potential of -0.4 V vs. Ag/AgCl in the PEC with Pt as the counter electrode, operated in a 0.1 M CH$_3$COONa (pH 7.0) solution. The illumination was provided by a light emitting diode >400 nm. b). The photo-current decays for photocathodes, which were detected after three on-off cycles of illumination.
We applied complex 3 and P1 into photo-cathodes in PECs where the sacrificial electron donor is no longer needed. The photo-cathodes were then explored as working electrodes in a three-electrode system. The results of photo-current measurements are shown in Figure 37. The photo-cathode assembled only with complex 3 (NiO-complex 3) generated a negligible amount of photocurrent, indicating almost no electrons flow through the external circuit, which is not surprising due to its incapable of catalyzing light-driven hydrogen evolution. The photo-cathode only in the presence of P1 (NiO-P1) yielded a small amount of initial photo-current with fast decay. In contrast, the photo-cathode in the presence of photosensitizer and catalyst (NiO-P1-complex 3), a dramatic photocurrent enhancement was recorded, indicating a functional device for light driven hydrogen generation. It was noticed that photocurrent decay has been observed in this device. However, the photo-current can be revived by the addition of fresh catalyst on the surface of electrode, which indicates that the decay in the photocurrent might be due to the catalyst decomposition or escaping from the electrode surface to the solution, with higher possibility in latter case because of the loose contact of the catalyst with the photocathode.

Light-driven hydrogen formation on the photo-cathode has also been confirmed using a modified Clark-type electrode sensor. Unfortunately, we could not estimate a TON of the device since the real amount of working catalyst in the device is hard to determine. Because there is no link between the catalyst and the surface, the catalyst could escape from the electrode surface to the solution.

6.5. Conclusions

We have successfully demonstrated visible light-driven hydrogen evolving with a photo-active cathode employing organic dye P1 and cobalt-based catalyst complex 3, and p-type semiconductor NiO.
7. Future outlook

We have successfully demonstrated photo-active anode and cathode for respective visible light-driven water oxidation and hydrogen evolving based on wide band gap semiconductors, molecular photosensitizers and catalysts. However, the performances of these electrodes are still poor, and they are far away for large-scale production of water splitting. For the purpose of large-scale application, several aspects should be considered.

**High Efficiency**: 1. Photosensitizer should absorb more light energy with wide absorption spectrum, good charge separation and fast electron/hole injection. Moreover, the energy potential of dye should be matched with catalyst with enough driving force. For a photo-anode, positive $E(D^+/D)$ is desired, which should be more positive than onset catalytic potential of a water oxidation catalyst. For a photo-cathode, negative $E(D/D^-)$ is needed which should be more negative than the catalytic potential of hydrogen generation catalyst. 2. Catalyst should be highly efficient, which means low over-potential, high turnover number, high turnover frequency. 3. A suitable method to immobilize the catalyst on the electrode is urgently needed. This immobilization should support electron transfer between photosensitizer and catalyst. 4. Proton transfer should be quick. Otherwise, pH environment around the electrode will be changed during water oxidation and hydrogen generation reaction. 5. Fundamental studies, such as electron transfer rate, rate limiting step, decomposition pathway of catalyst and photosensitizer and interfacial complexity, should be performed. By understanding these studies, the PEC can be designed in a better way.

**Long stability**: Each component, such as photo-sensitizer, catalyst, semiconductor and subtract supporting materials, should be stable under working conditions. The binding between these components and the electrode should be strong and stable.

**Low cost**: Each component should be cheap, which means based on earth abundant materials and facile reliable fabrication with low cost. Each component should be easily coupled to the semiconductor electrodes into a
device. The device should be operated with high efficiency under naturally friendly conditions.

A PEC with two photo-active electrodes appears to be quite promising. In such a PEC, water oxidation occurs on the photo-anode, while hydrogen generation happens on the photo-cathode. To achieve such a PCE, the current from photo-anode should be matched with that from photo-cathode. Thus, development of both photo-anode and photo-cathode is the first step. As we already pointed out, improvement of these electrodes are possible. There are bound to be many in the near future.
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Appendix A

The following is a description of my contribution to Publications I to IV, as requested by KTH.

Paper I, II, III, IV, V and VI: Major contribution to the initiation of the projects. I am responsible for assembling the devices, carrying out all electrochemical experiments, the investigation of the performance of the devices, and the writing of the main parts of the manuscripts.
Appendix B

References


