Visible-Light-Induced water splitting on a chip

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Cover

The centre image at the cover is a schematic representation of the visible-light-induced water splitting on a chip concept. The cover is build up out of two scanning electron microscopy measurements of Rh:SrTiO₃ (front), and WO₃ (back). The light blue spin of the book represents the platinum divider.

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VISIBLE-LIGHT-INDUCED WATER SPLITTING ON A CHIP

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CHAPTER 1

INTRODUCTION: VISIBLE-LIGHT-INDUCED WATER SPLITTING ON A CHIP

1.1 TOWARDS A HYDROGEN ECONOMY

Climate change and the future energy supply are two of the main challenges facing humanity the coming decades, and they are strongly linked. The economy nowadays is largely based on fossil fuels, which have ending resources, and employing them results in the emission of greenhouse gasses, which effects the climate. Towards a sustainable future, there is a transition necessary from fossil fuels to renewable energy sources. The most promising renewable energy source is the sun, which delivers the earth every hour more energy, than all humans together consume in one year [1]. With solar panels, it is possible to convert the solar energy directly into electricity, however the electricity is only produced when the sun shines. This results in a fluctuating electricity production over time, which is also an issue for wind energy as renewable energy source. Therefore electricity should be stored for the moments the wind and sun do not provide electricity.

A possibility to store the electricity is with batteries, however energy densities and charging times of batteries are not ideal. Hundreds of millions years ago, the energy of the sun was stored in chemical bonds, which we are using now in the form of fossil fuels. An alternative to store the energy in chemical bonds, is by converting water and using hydrogen as energy carrier [2]. Hydrogen does not have the energy density of fossil fuels, however the energy density of H_2 is superior compared to battery technologies. If H_2 will be used as energy carrier, a transition will be required from a fossil fuel-based economy to a hydrogen-based economy. This will require large investments in production of hydrogen, storage and use of hydrogen, but it will lead to a renewable and circular economy.

One of the requirements to an emission-free economy, is having the ability to produce 'renewable' hydrogen in an economic and efficient way. Nowadays, hydrogen is an important reagent in the chemical industry, which is essential in the refining and ammonia industries. However, the H_2 produced for these applications is fossil fuel-based, and is made via gas steam reforming, partial oxidation of oil, or coal gasification. Only a small part of the H_2 is produced by electrolysis [3]. This is logical, because the production costs of H_2 via an electrolysis route are much higher, than the production costs of H_2 produced out of fossil fuels [4]. The higher price depends largely on the electricity price, even when fossil fuels are used for producing the electricity.

The challenge

The H_2 price will be important factor for a possible prosperous future of the H_2 economy, and will determine if it will become reality. As stated before, H_2 produced by renewable sources is much more expensive than H_2 produced out of fossil fuels. The Department of Energy of the USA estimated that the production price per kg H_2 should be between \$2.00 to \$4.00 [5]. When a photovoltaic (PV) cell is coupled to an electrolyser, the price of thus produced hydrogen is much higher. Theoretical calculations show, that with a direct solar-

to-H₂ conversion, prices between \$1.40 - \$10.40 per kg H₂ [5] should be realizable. A direct conversion can be done by integration of a solar cell and electrolyser into one device, based on photocatalytic and photoelectrochemical concepts. Although photocatalytic concepts will work with lower maximum efficiencies compared to photoelectrochemical concepts (5%-10% vs 10%-15%), lower prices should be realizable in the future (\$1.40-\$4.10 vs \$4.05-\$10.40) [5]. The bottleneck for photoelectrochemical water splitting is the expensive PV material, used for the construction of the photocathode. In contrast, photocatalytic water splitting is mostly done with less expensive metal oxides [5]. We think that, although challenging, a possible way to combine the best of two worlds, is to develop a photoelectrochemical water splitting cell, which is made out of metal oxides. The expectation is that a 10% solar-to-hydrogen efficiency will be required. This is similar to a combination of a solar cell and an electrolyser. In the following paragraphs I will discuss the principles relevant for the understanding of the concepts used and evaluated in this thesis.

1.2 PHOTOCATALYTIC WATER SPLITTING

1.2.1 Photocatalysis

Photocatalysis is a process in which a chemical reaction is driven by electron and holes, which are created through absorption of photons in a catalytic particle. This phenomenon was discovered in 1979 by Fujishima and Honda, when applying a TiO₂ photoelectrode [6]. Photocatalysts, are mostly semiconductors. The technology can be used in different application areas, like air and water purification, recycling of CO₂ to useful hydrocarbons, self-cleaning surfaces and, relevant for this thesis, H₂ production via water splitting [7].

In heterogeneous photocatalysis, a semiconductor is illuminated with light. In the particle, an electron-hole pair is created by an absorbed photon, and at the surface of the semiconductor particle the electrons and holes can be used for performing redox-reactions. In a photocatalytic reaction a sequence of several events should occur after a photon absorbs in a semiconductor particle, which is also shown in Fig. 1:

1. Photon incidence on the semiconductor particle
2. An electron is excited from the valence band to the conduction band
3. Electrons and holes move to the surface of the photocatalytic particle
4. A reduction reaction and oxidation reaction happen on the surface of the particle.

Figure 1: Schematic processes occurring in water splitting induced by a photocatalyst.

When electrons are excited to the conduction band, but the follow-up reactions are too slow, the excited electrons recombine with the holes in the valence band. In this case, the photon created a non-effective electron-hole pair and heat is generated. Recombination will limit the efficiency of the photocatalytic reaction and is an unwanted phenomenon. To lower the recombination rate it is important, to minimize defects in the crystal lattice, and by addition of a co-catalyst it is possible to increase the lifetime of the electron-hole pair.

In photocatalytic water splitting, electrons and holes are used in the redox half reactions for water splitting. Holes are used for the water oxidation reaction:

Electrons are used for the proton reduction reaction:

To let both redox reactions take place, at least a potential of 1.23 V should be applied. Further, due to kinetic contributions, an extra overpotential is required over the 1.23 V. This depends on the material used in the (photo)catalytic process.

1.2.2 Photocatalytic Materials

An essential property of a photocatalytic material is the presence of a band gap. Another important aspect, is the matching between the band gap and the redox potentials of the half reactions for water splitting. In Fig. 2, the band gaps of different semiconductors are aligned to the redox potentials of the half reactions for water splitting [8]. Only a few semiconductors are suitable for direct water splitting. The band gaps of these semiconductors, like titanium dioxide (TiO_2) and strontium titanate (SrTiO_3), are large (>

3.0 eV), which means that these semiconductors can only absorb UV-photons. Only 4% of the total solar spectrum exists out of UV-photons, which will limit the maximum efficiency for the large band gap semiconductors, and this makes it impossible to reach solar-to-hydrogen efficiencies up to 5% to 10%. Therefore, a smaller band gap is required, which would make it possible to absorb visible light photons and to use a larger part of the solar spectrum. A semiconductor such as CdS, which has a band gap of 2.4 eV, and overlaps both half reactions, would be ideal. However, when this is suspended in water, this semiconductor will oxidize under illumination. This leads to photocorrosion and the semiconductor will dissolve in the electrolyte. To apply photocatalytic water splitting in practice, it is important to use semiconductor materials, which are stable in solution under illumination.

Figure 2: Overview of several semiconductors, which show overlap of the band gap with the redox reaction potentials for water splitting [8].

1.2.3 Z-scheme water splitting

Via a z-scheme model it is possible to make use of semiconductors, which are alone insufficient for full water splitting. In a z-scheme photocatalytic reaction, two photocatalysts are combined for a full reaction, which are a water oxidation photocatalyst and a proton reduction photocatalyst [9]. In Fig. 3 an example of a Z-scheme is shown, consisting of WO₃ and platinized Rh-doped SrTiO₃. The electron of WO₃ and the hole of Rh:SrTiO₃ are exchanged between the photocatalysts, with the aid of an electron mediator. An electron mediator is a redox couple, which is shuttling between the photocatalysts. For example, Fe-ions are used as sacrificial agents, which will donate their electron or hole to their complementary photocatalyst. A boundary condition for the electron mediator is that the electron of the photoanode and the hole of the

photocathode have sufficient energy to be used in the half reactions. For the example, as shown in Fig. 3, the half reactions at both photocatalysts are:

Reaction at the WO₃ photoanode

Reactions at the Pt/Rh:SrTiO₃ photocathode

Figure 3: Schematic overview of a Z-scheme water splitting process.

Z-scheme concepts

One of the first published Z-schemes was the use of Pt/Rh:SrTiO₃ as photocathode and WO₃, BiVO₄ or BiMoO₆ as photoanodes [10]. A Fe(III)/(II) couple shuttled the electrons between the two photocatalysts. Afterwards a few other systems were published in the literature, over the last decade. Literature on Z-scheme water splitting is summarized in Table 1 [11]. Over the last decade, studies have been done to understand the mechanism of the reaction, as well as the effect of process parameters, like the influence of pH, the role of the electron mediator [12, 13] and addition of co-catalysts [14]. A point of interest, which remains, are the possibilities of back reactions on the surface of the photocatalysts [11]. Therefore, electron-mediator free systems have been studied and developed, where electrons and holes were exchanged through aggregation of the photocatalytic particles [15]. These are developed, because it was reported, that also undesired back-reactions of

the electron mediator can occur over the photocatalysts, which lowers the overall efficiency [11]. Other routes to prevent the need for an electron mediator, are by creating a composite of two photocatalysts [16] or using reduced graphene oxide as electron mediator [17]. Instead of performing the reaction in one compartment, a reactor design, where two compartments are connected by a proton-exchange membrane, showed efficient water splitting [18, 19]. Here WO_3 or BiVO_4 were used with Fe^{3+} as electron acceptor for the oxygen evolution reaction, while Pt/Rh:SrTiO_3 was used together with Fe^{2+} as electron donor for the hydrogen evolution reaction. Fe^{2+} and Fe^{3+} were exchanged via the proton-exchange membrane, to realize the electron transport from WO_3 or BiVO_4 to Rh:SrTiO_3 . The reported efficiencies for z-scheme water splitting are low, and most systems were characterized by UV-filtered light. Sasaki et al. reported an efficiency for a Ru/Rh:SrTiO_3 and BiVO_4 combination of 0.12% under illumination of a 1.5 AM solar simulator [15].

Table 1: Selection of reported Z-scheme concepts with and without an electron mediator.

Systems with electron mediator				Electron mediator free systems		
H_2	O_2	Electron Mediator	Reference	H_2	O_2	Reference
Pt/Rh:SrTiO_3	WO_3	$\text{Fe}^{3+}/\text{Fe}^{2+}$	Konta et al. [10]	Pt/Rh:SrTiO_3	BiVO_4	Sasaki et al. [15]
Pt/Rh:SrTiO_3	BiVO_4	$\text{Fe}^{3+}/\text{Fe}^{2+}$	Konta et al. [10]	Ru/Rh:SrTiO_3	$\text{CoO}_x/\text{Ta}_3\text{N}_5/\text{Ir}$	Ma et al. [20]
Pt/Rh:SrTiO_3	BiMoO_6	$\text{Fe}^{3+}/\text{Fe}^{2+}$	Konta et al. [10]	C_3N_4	BiOI/O_3	Wang et al. [21]
Pt/Ca,Ta:SrTiO_3	Pt/WO_3	I^-/IO_3^-	Sayama et al. [13]	Au/CdS	N:TIO_2	Zhou et al. [22]
Pt/TaON	Pt/WO_3	I^-/IO_3^-	Abe et al. [23]	Rh:SrTiO_3	$g\text{-C}_3\text{N}_4$	Kang et al. [24]
Pt/TaON	RuO_2/TaON	I^-/IO_3^-	Higashi et al. [25]			
CaTaO_2N	Pt/WO_3	I^-/IO_3^-	Higashi et al. [26]			
BaTaO_2N	Pt/WO_3	I^-/IO_3^-	Higashi et al. [26]			
Ru/Rh:SrTiO_3	Ru/Na,V:SrTiO_3	I^-/IO_3^-	Hara et al. [27]			
Ru/Rh:SrTiO_3	BiVO_4	Reduced Graphene oxide	Iwase et al. [17]			

1.2.4 Strategies to improve the efficiency

Doping

A way to increase the light absorption of semiconductors, is by introducing doping levels in the band gap or functionalize the photocatalysts with dyes [28]. Doping of a

semiconductor can be done by introducing non-metallic-ions or metallic-ions into the crystal structure [29]. Doping results in narrowing of the large band gap of UV photocatalysts, like TiO_2 and SrTiO_3 , which makes it possible to absorb visible light photons [30]. A schematic representation is shown in Fig. 4A. Numerous reports have been published with methods to make a visible light active photocatalyst, by modifying TiO_2 [31-34]. However, it is not straight forward to find a suitable dopant, which improves the photocatalyst. There are also publications showing dopants can increase absorption, but the extra imperfections introduced into the material, result into a higher recombination rate, which will decrease the overall activity of the photocatalyst [35].

When the literature for doping of SrTiO_3 is analysed, a few main dopants are used to improve the photocatalytic properties. Theoretical calculations can help to identify dopants which could be interesting [36, 37]. Interesting single dopants to enhance the light absorption and photocatalytic properties of SrTiO_3 are Cr^{3+} and Rh^{3+} [38-41], which are substituting Ti^{4+} in the perovskite crystal structure. Also it is possible to introduce bot an acceptor/donor pair as dopants, for example $\text{Rh}^{3+}/\text{Sb}^{5+}$ or $\text{Cr}^{3+}/\text{Ta}^{5+}$, which will effectuate in a combined n- and p-type doping in the lattice [42-45]. Also for SrTiO_3 the real enhancing effect of doping can be discussed. For example, when the data of Jang et al. is analysed, the photocatalytic activity to UV-illumination of SrTiO_3 decreased drastically after introducing Cr^{3+} [39].

Co-catalysts

Another method to improve a photocatalyst, is addition of a co-catalyst to the photocatalyst. Co-catalysts can have several contributions to enhance the activity of a photocatalyst, like improving the charge separation, discharging of electronic charges at the surface, and an important contribution to photocatalytic water splitting is to lower the overpotential of the redox reactions [46]. The overpotential results in an extra potential required for a water splitting reaction over the theoretical 1.23V based on the half reactions. This is due to the kinetics at the electrode surface, where the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) undergo several intermediate steps. The HER starts with binding of two protons, each to a binding site at the catalyst surface (reaction 7), which is followed by merging of the two H° to H_2 (reaction 8). Here e^- is the negative charge, * is a reaction site at the catalyst surface.

In the OER reactions 9 to 12 occur in sequence. Reaction 9 shows the oxidation of an surface-active site at a metal oxide surface ($*\text{OH}$) with H_2O to a non-stable intermediate species ($[\text{HO}^*\text{OH}]$) at the surface. Reaction 10 shows the chemical conversion of this

unstable species to a stable intermediate species at the surface (HO^*OH). Then the surface is further oxidized following reaction 11. Finally, O_2 evolves due to the combination of two highly oxidized surface sites, see reaction 12.

The intermediate steps of the HER and OER requires an extra potential, which is called the overpotential. In electrolysis for the HER, noble metals such as Pt and Pd are often used as cathode for the HER, due to their low overpotentials for the HER [47]. For the OER, mostly a few metal oxides are used for the anode of the electrolysis cell. The OER mostly requires a higher overpotential, compared to the HER. Metal oxides with a low overpotential for the OER are for example RuO_2 , IrO_2 and PbO [48].

To enhance the efficiency of photocatalysts, a co-catalyst can be loaded at the surface of the photocatalytic material [49]. Two main methods are used to incorporate the co-catalyst at the surface of the photocatalysts, namely via photodeposition or impregnation [14]. A schematic example of a photocatalyst with incorporated HER and OER particles is shown in Fig. 4B. Sasaki et al. showed that the activity of $\text{Rh}:\text{SrTiO}_3$ was improved, after addition of Pt or Ru as co-catalyst [14]. To improve the OER of a water oxidation photocatalyst, Spurgeon et al. showed that loading WO_3 with IrO_2 improved the water

Figure 4: Strategies to Improve efficiencies of photocatalytic materials. A) Addition of doping to enhance the absorption. B) Addition of co-catalysts to improve the catalysis and lower the overpotentials.

oxidation capability of WO_3 [50]. The most used co-catalysts are made up from expensive materials, like Pt, Ru and Ir. To lower costs, it will be helpful to replace these materials by earth-abundant materials. Reece et al. coated a Si-triple junction with Co-Pi as OER catalyst and NiMoZn as HER catalysts, and was able to split water with relative high efficiencies [51]. Co-Pi showed also good OER properties, when F. Abdi et al. added this to a BiVO_4 photoanode [52].

1.2.5 The Photoelectrochemical Cell

If photocatalytic materials are integrated into the electrodes of an electrolysis cell, a photoelectrochemical cell (PEC) is made. In a PEC, one or both of the electrodes is capable to absorb photons and use the created electron-hole pairs for the half reactions at the electrodes. A schematic overview of a PEC with a photoanode for the water oxidation is shown in Fig. 5 [53]. The Fukushima and Honda paper, which can be seen as the discovery of the photocatalytic field, was based on a system where TiO_2 was used as photoanode [6]. When TiO_2 is used as photoanode, it is not necessary to apply an external bias for a reaction. However, in a PEC it is also possible to use materials, which are insufficient for full water splitting, like WO_3 . To let reactions take place, an external bias can be applied under illumination, using a potentiostat.

Figure 5: Schematic overview of a photoelectrochemical water splitting cell with a photoanode [53].

In the model of Fig. 5 the photoactive electrode is a photoanode. When a photon is absorbed by the semiconductor an electron-hole pair is created. The holes are used at the surface of the photoanode for the water oxidation reaction, and the electrons move via the external circuit to the cathode of the PEC. At the electrolyte/photoanode interface, band bending occurs, which will separate the electrons and holes. The upwards bending directs holes towards the semiconductor/liquid interface and electrons towards the back

electrode. Via the back electrode, electrons are transported via the external circuit to the counter electrode. At the counter electrode, electrons are used for the reduction of H^+ to H_2 . In the model different types of energy losses in a photoelectrochemical cell are depicted. Here also the kinetic losses at the interface of the electrode are included, which results in an extra overpotential over the 1.23 V. Instead of using one photoactive electrode, it is possible to change the Pt cathode by a photocathode, which can absorb photons, and which results in extra electron-hole pairs. A schematic illustration of a PEC with a photoanode and photocathode is shown in Fig. 6A.

Figure 6: Two variations on the photoelectrochemical cell concept, where two photoactive electrodes are combined. A) Two separated photoelectrodes are connected via an external circuit, which is a wired configuration [5]. B) Two photoelectrodes are combined via a metal film in between the two photoelectrodes; the unwired configuration [54].

An important factor in a PEC cell is the metal/semiconductor interface. When a semiconductor and metal are combined, charge exchange takes place, which results in levelling of the Fermi level over the interface. This levelling of the Fermi level results in bending of the conduction band (E_c) and the valence band (E_v) of the semiconductor. Three situations are possible. The first possibility is formation of an Ohmic contact, where the E_c and the E_v are slightly bending. Electrons and holes encounter a low resistance moving from metal to semiconductor or from semiconductor to metal. When the bending of the conduction and valence band is stronger, a Schottky barrier is formed. When the E_c and E_v bend down, electrons in the semiconductor feel a low resistance moving into the metal. The electrons in the metal feel a high resistance moving towards the semiconductor. If the bending is up, the opposite situation is created. Electrons moving from metal to semiconductor encounter a low resistance. In this way a diode is formed, which can be applied to control the electron direction. Nozik et al. proposed a concept, using the diode in an unwired PEC, see Fig. 6B. In this concept a metallic interlayer is sandwiched between two different semiconductors. When at the metal/photoanode

interface the band bending of the semiconductor is downwards and at the photocathode/metal interface the band bending is upwards, the two created Schottky barriers can be used to direct electrons from photoanode to photocathode [54].

The semiconductor materials used in photoelectrochemistry are similar to photocatalytic materials [55]. An overview of the most commonly used materials is shown in Fig. 7 [56]. The semiconductors used for the photoanodes are similar to the metal oxides used in photocatalysis. Currents up to 3.5 mA/cm^2 are reported for WO_3 , BiVO_4 and Fe_2O_3 photoanodes. To reach high photocurrent densities in photoanodic materials depends on a balance and optimization of several properties of a semiconductor layer, for example the crystallinity, conduction and catalysis. In literature, different strategies are reported which can be used to maximize the photoactivity of a photoanode or photocathode. An interesting overview of the development of the photocatalytic activity enhancement of a Fe_2O_3 photoanode was made by Sivula et al. [57]. This article describes the following strategies over the last two decades, to improve the photocurrent from almost no current in a Fe_2O_3 photoanode to a record of 3.4 mA/cm^2 at 1.23V vs RHE. F. Abdi showed the promoting effect of a Co-Py OER co-catalyst for BiVO_4 , which increased the photocurrent density from 0.6 mA/cm^2 to 1.5 mA/cm^2 at 1.23V vs RHE [52]. Improving the conductivity of the BiVO_4 by gradient W-doping improved the photocurrent density further up to 3.0 mA/cm^2 at 1.23V vs RHE [58]. Hong et al. reached for a WO_3 photoanode, which was fabricated by a polymer-assisted deposition method, a photocurrent of 2.3 mA/cm^2 [59].

Photocathodes in PEC are mostly similar to materials used in the photovoltaic industry, for example Si and GaAs. These materials are often not stable in solution and result in degradation of the photocathode. When shielded from solution by being placed between the photoanode and a light-inactive cathode, which is often Pt, stability is enhanced [58]. However the cost of the materials are high, when compared to the costs of the metal oxides used for the photoanodes. A way to reduce costs, can be via replacing the expensive PV materials with a dye synthesized solar cell [57], or use of a metal oxide as photocathode. Cuprous oxide (Cu_2O) is a metal oxide, which shows high photocurrents when it is used as photocathode. However, the photocathode is not fully selective to proton reduction, and shows photocorrosion in a water splitting reaction [60]. Protection of Cu_2O was achieved by addition of thin layers of TiO_2 and ZnO via atomic layer deposition. This improved the stability, and the measurements showed still a high photocurrent [61]. However, although the stability was improved, the Cu_2O photocathode showed still photo corrosion during the measurement [61]. In Z-scheme photocatalysis Rh-doped SrTiO_3 is used for H_2 evolution, which also shows stability during photocatalytic reactions. A few studies to make a photocathode of these materials have been reported, however the photoactivity differs hugely. A study by Kawaski et al, where pulsed laser deposition was used to fabricate the Rh: SrTiO_3 photocathode, showed high photocurrents

[62]. However, a study by Iwashina et al., where calcined particles were deposited on a ITO substrate showed low photocurrents [63]. Both studies showed that the highest currents are reached with a doping concentration of about 5%, which is significantly higher than doping concentrations used in photocatalytic particles.

Figure 7: Commonly used materials in photoelectrochemical cells [56].

Photoelectrical water splitting concepts.

Several concepts for photoelectrochemical water splitting devices have been published in the literature, with efficiencies up to 12.7%. A few of the main concepts are shown in Fig. 8. These concepts use a Si- or GaAs-based photocathode. Because, these materials are not stable in solution under illumination, the photocathode is isolated from the electrolyte. In three of the four concepts this is done by using a Pt electrode for the hydrogen evolution reaction. The first concept (Fig. 8A) is a concept based on a GaAs junction, which reached a solar-to-hydrogen efficiency of 12.7%, the highest ever reported [64]. In the other three concepts, the photocathode is based on Si. In the concept of Reece et al. (Fig. 8B), the OER and HER catalysts are not light active, but are coated at a triple Si junction solar cell [51]. In Fig 8B the unwired configuration is shown, which reached an efficiency of 1.7%. When the anode and cathode are faced to each other, in a wired configuration, an efficiency is reached of 4.6%. An interesting aspect of this concept is the use of inexpensive HER and OER catalysts, which are made from earth-abundant materials. The two concepts in Figs. 8C and 8D are similar. A Si photocathode is placed in series with a metal oxide photoanode. F. Abdi et al. used a flat Si junction, which was connected to a BiVO₄ photoanode, see Fig. 8C [58]. The reported solar-to-hydrogen efficiency for this concept is 4.9%. In Fig. 8D a pillared Si junction is covered by WO₃ as photoanode, which showed a solar-to-hydrogen efficiency of 0.0068% [65]. To reduce costs, Grätzel published a concept, where the expensive PV solar cell was replaced with a Dye-synthesised solar cell

[66]. When it was put in series with a WO_3 or Fe_2O_3 photoanode, full water splitting was observed [57].

Figure 8: A) John Turners 12.7% solar-to-hydrogen cell [64]. B) Nocera's wireless cell. A triple junction solar cell, with oxidation and reduction catalysts at the outside [51]. C) A two junction solar cell combined with a BiVO_4 photoanodic layer [58]. D) A single junction n-type Silicon pillar array combined with a WO_3 photoanodic layer [65].

1.2.6 Efficiency definitions

The photovoltaic industry uses a standardized method to compare different types of research cells [67]. The efficiency is determined by measuring the fill factor under a standard illumination of a 1.5 AM solar simulator. This light source has an effective radiation of $1000\text{W}/\text{m}^2$, a light spectrum similar to real solar light. In the photocatalytic community there is not such a standard for the characterization of the efficiency. Experiments are performed with different types of light sources [8]. For example, visible light water splitting experiments are done by UV-filtered light ($>420\text{nm}$), to analyse only

the contribution of the lower energy photons. To test photocatalytic water splitting under realistic conditions, the activity should be analysed under illumination of a 1.5 AM solar simulator. Furthermore, the reactors used in the several experiments differ in size and volume. To compare efficiencies of photocatalytic reactions under different circumstances, the Quantum Yield (equation 13) can be calculated [68]. Here the efficiency is determined by the ratio between the amount of electrons used for the products and the amount of incident photons at the photocatalysts. To correct for different light sources, the Q.Y. can be calculated only for photons in a specific absorption spectra.

$$Q.Y. = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \cdot 100 \quad (13)$$

To determine the efficiency of a photoelectrochemical cell, equation 14 can be used [56]. To be able to use this equation, the measurement should be performed into a two-electrode cell configuration. η_{STH} gives the solar-to-hydrogen efficiency, J_{op} is the measured current density, V_{app} the applied external voltage and P_{in} the intensity of the illumination.

$$\eta_{STH} = \frac{J_{op}(1.23V - V_{app})}{P_{in}} \quad (14)$$

To know the potential of a specific material combination, it is possible to calculate the theoretical maximum efficiency via the Shockley-Queisser limit [69]. L.C. Seitz et al calculated the possible efficiencies for three different configurations, where losses named in Fig. 5 were taken into account [53]. The first configuration, a single absorber, showed a maximum efficiency of 11.2% can be achieved, for a semiconductor with a bandgap of 2.26 eV. However, the efficiency can increase, when two absorbers are combined. The maximum efficiency of 22.8% can be reached, when two semiconductors with band gaps of respectively 1.84 eV and 1.23 eV are stacked. When two semiconductors are placed parallel in a side-by-side configuration, a maximum efficiency of 15.5% should be possible for two semiconductors with band gaps of 1.59 eV. For a combination of WO_3 (2.7 eV) and Rh:SrTiO₃ (2.4 eV), a maximum efficiency of 6% can be achieved in a stacked configuration and a 5% efficiency in a side-by-side configuration.

1.3 AIM AND THESIS OUTLINE

1.3.1 Aim

In this thesis, we introduce a concept for a new type of photoelectrochemical cell, based on materials used in Z-scheme photocatalysis. The concept is shown in Fig. 9. The goal is

to change the electron mediator by integrating the photocatalysts on a conducting Pt divider. This Pt divider is 500 nm thick and is given mechanical stability by a silicon sieve support structure. The idea of the Pt divider, is that electrons can be transported efficiently between the photocatalysts. Furthermore, the divider will directly divide the reactor into two separated compartments, one for H_2 and one for O_2 evolution. To study the effect of the Pt film, a known z-scheme combination, WO_3 and $\text{Rh}:\text{SrTiO}_3$, was chosen to be integrated on the divider. This combination should theoretically be able to reach a 5% efficiency in such configuration. When these materials are applied for water splitting in an acidic electrolyte, they should be stable against photocorrosion. Several goals are formulated towards the concept:

- Study the effect of Rh-doping and Pt co-catalyst on the activity of SrTiO_3 .
- Analyse the efficiency and additional value of an electron mediator in z-scheme water splitting.
- Develop a method, which is applicable to grow a uniform WO_3 layer inside the slits of the silicon support, directly on the Pt divider.
- Develop a photoactive $\text{Rh}:\text{SrTiO}_3$ photocathode, which can be integrated with the Pt divider.
- Integrate WO_3 and $\text{Rh}:\text{SrTiO}_3$ at the Pt divider.
- Test the activity and efficiency of the combination of a WO_3 photoanode and a $\text{Rh}:\text{SrTiO}_3$ photocathode.

Figure 9: Schematic overview of the water splitting on a chip concept. WO_3 and $\text{Rh}:\text{SrTiO}_3$ should be integrated on the opposite sides at a Pt divider.

1.3.2 Thesis outline

In **chapter 2** several procedures are introduced, which are used in the several chapters of this thesis. First the substrate used for the development of the fabrication procedures for the photoelectrodes is shown. Further, the procedures and the methods used to characterize the activity of the photoelectrodes and photocatalysts are explained, which are the used solar simulator, the photoelectrochemical setup and the gas chromatograph.

In the final concept, Rh-doped SrTiO₃ is chosen as photocathode. Almost all literature reports measurements done with UV-filtered light. In **chapter 3** a study is done, to test the water splitting capability of this material under simulated solar light. Undoped SrTiO₃, which is capable to split water with the UV-photons of solar light, is used to compare Rh doped and undoped SrTiO₃. The goal is to see the effect of the Rh-doping on the overall activity of SrTiO₃. Further, the enhancing effect of a Pt co-catalyst on the photoactivity of SrTiO₃ is evaluated.

The role of the electron mediator in Z-scheme photocatalysis is interesting to know, to be able to compare the electron transfer via a Pt film and via an electron mediator. In **chapter 4**, Z-scheme water splitting is studied under illumination of solar light. In the measurements of this chapter no shuttling of electrons between the photocatalysts was observed via the electron mediator. The outcome is, that the second photocatalyst was short circuited by the Fe based half reactions.

In the concept, the objective is to deposit a WO₃ photoanode at the backside of the divider, inside the slits of the silicon support structure. In **chapter 5** a hydrothermal procedure is introduced, which is able to deposit WO₃ selectively at a Pt substrate. Photoelectrochemical activity measurements show a relative high activity for the thus prepared WO₃ photoanodes.

To increase the activity of the WO₃ anode, in **chapter 6** an IrO₂ catalyst was introduced on the surface of the photoanode. Electrodeposition was used to add IrO₂ to the WO₃ layer, however direct electrodeposition resulted in the deposition of IrO₂ at the Pt substrate. To prevent this, after the hydrothermal growth of WO₃ at Pt, a TiO₂ layer was spin coated between the WO₃ crystals. This resulted in deposition of IrO₂ at the WO₃ crystals. Photoelectrochemical characterization showed the enhancement of photocurrent after the addition of TiO₂ and IrO₂.

In **chapter 7** a method is introduced to fabricate a Rh:SrTiO₃ photocathode via a chemical solution deposition procedure, which can be used to deposit the photocathode layer at the frontside of the divider. Initial characterization showed a low photoactivity of the photocathode. A study was done to find the causes of the low activity and try to improve

it. It seems the conductivity of the layer was low, which can be related to the fabrication method and the addition of the doping of Rh^{4+} .

The integration towards visible light water splitting on a chip is discussed in **chapter 8**. Construction of a band diagram showed the possibility to create a photochemical diode consisting of a $\text{WO}_3/\text{Pt}/\text{Rh}:\text{SrTiO}_3$ junction. When a separated photocathode and photoanode were connected in a wired configuration, a small current was measured under illumination. When the WO_3 and $\text{Rh}:\text{SrTiO}_3$ layers were integrated at a platinum divider, a small hydrogen production was observed under illumination.

Finally, practical aspects and feasibility are discussed in **chapter 9**.

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CHAPTER 2

EXPERIMENTAL PROCEDURES

ABSTRACT

In the research of this thesis, standard substrates and characterization methods were used. In this chapter, the fabrication method of the Pt substrates, the solar similar used in the thesis and the photoelectrochemical and gas chromatography setups are introduced.

2.1 THE PT SUBSTRATE

For the development of the fabrication methods for the photocathode and photoanode, homemade 1 cm^2 Pt substrates were used. These Pt substrates were made at a Si wafer in a cleanroom environment, and the structure of the Pt substrates is schematically shown in Fig. 1. The first step of the substrate fabrication, was oxidation of a Si<100> wafer via a dry thermal oxidation procedure. The SiO_2 was aimed to be 50 to 200 nm thick, which should insulate the conducting Pt layer from the Si substrate. The next step, was sputtering of a 13 nm Ti layer as adhesive layer, which was followed by the sputtering of a 100 nm Pt film. The wafer was diced in 10x10 mm pieces. Therefore a photoresist layer was spin coated at the wafer to protect the Pt film during the dicing procedure. To verify the insulation of the Pt film from the Si substrate, the resistance was measured between front- and backside. The resistance measurements at a substrate are shown in Fig. 1. Contact was made with two stainless steel alligator clips, where one of the jaws of each clip was insulated with a non-conductive tape. No conduction was measured between the Pt layer and the backside, see the right measurement in Fig. 1. If both conducting jaws were attached at the Pt layer, a low resistance was measured (left measurement in Fig. 1). This indicates good conductivity of the Pt layer, and that it is insulated from the Si wafer during the experiments.

Figure 1: Schematic overview of the substrates used in this thesis. Included in the figure are resistance measurements between backside and frontside.

2.2 1.5 AM SOLAR SIMULATOR

As light source for the experiments in this thesis, a ABET technologies model 10500 low cost 1.5 AM solar simulator was used [1]. The spectrum of the lamp, which was published in the manual of the solar simulator, is shown in Fig. 2. The light spectrum from the simulator (black line) overlaps with the natural light spectrum of the sun (blue line). The intensity of the simulated solar light is 1000 W/m^2 , i.e. 100 mW/cm^2 . For wavelengths above 800 nm there are a few peaks in the spectrum of the simulator, however these wavelengths should not be absorbed by the semiconductors used in the research of this thesis. The photoelectrochemical experiments were performed in a 25 mL optical glass cuvet (402.013-OG, Hellma). The optical glass will filter partly wavelengths below 350 nm, which will lower the contribution of the UV photons in the simulated solar light.

Figure 2 : Comparison printed in the manual between the ABET Technologies 1.5 AM solar simulator (black line) and the sun (blue line) [1].

2.3 PHOTO ELECTROCHEMISTRY

The photoactivity of the photoelectrodes was characterized via photoelectrochemistry, which was used to determine the contribution of the photoelectrode to the current. Measurements were done in a three-electrode cell configuration, which is schematically shown in Fig. 3, where the photoelectrode was used as working electrode (W.E.). The other two electrodes were the counter electrode (C.E.) and the reference electrode (R.E.). The C.E. consisted out of a Pt mesh ($\sim 2 \text{ cm}^2$), which was connected to a Pt wire. To control the voltage at the W.E., the R.E. is added. As R.E. a 3.0M Ag/AgCl (BESI) R.E. was used. This R.E. has a stable potential of 0.210V vs. NHE (Normal Hydrogen Electrode). The three

electrodes are connected to a potentiostat, which was a Versastat 4 potentiostat, purchased from Princeton Applied Science. During an electrochemical reaction, electrons will flow between the W.E. and C.E. These electrons are measured as current. To let the electrons flow, it is possible to add an external bias over the two electrodes. The voltage will be regulated at the C.E., such that reactions at the C.E. will use the electrons produced at the W.E. or deliver the electrons required for the reaction at the W.E.

Figure 3: Schematics of a three electrode cell measurement.

The Nernst equation can be used to determine the redox potential of a half reaction [2]. Equations 1 and 2 show the two Nernst equations to determine the half-cell redox potentials of the two half reactions applied for water splitting, which are the reduction of H^+ to H_2 and the oxidation of H_2O to H^+ and O_2 . In these equations, there are reaction specific constants and variables, which will determine the actual redox potential. These parameters are the standard redox potential (E_{red}^0/E_{ox}^0), Faraday's constant (F), the gas constant (R), partial pressure of hydrogen (P_{H_2}) or oxygen (P_{O_2}), proton concentration ($[H^+]$), the temperature (T) and the pH of the solution (pH).

$$E_{red} = E_{red}^0 - \frac{RT}{4F} \ln \left(\frac{p_{H_2}^2}{[H^+]^4} \right) = E_{red}^0 - \frac{2.3RT}{F} \left(\log \left(p_{H_2}^{\frac{1}{2}} \right) + pH \right) \quad (1)$$

$$E_{ox} = E_{ox}^0 + \frac{RT}{4F} \ln (p_{O_2} [H^+]^4) = E_{red}^0 + \frac{2.3RT}{F} (\log (p_{O_2}) - pH) \quad (2)$$

Using the Nernst Equation it is possible to compare (photo)electrochemical experiments performed in different electrolytes. The potentials vs a $Ag/AgCl$ R.E. can be converted to a standard potential scale (V_{RHE}) via equation 3. In this equation, the measured potential versus the R.E. ($V_{Ag/AgCl}$), can be corrected with the potential of the R.E. vs NHE ($V_{(Ag/AgCl) \text{ vs NHE}}$) and the pH, to the Reversible Hydrogen Electrode scale (V_{RHE}).

$$V_{RHE} = V_{(Ag/AgCl)} + V_{(Ag/AgCl \text{ vs } NHE)} + 0.059pH \quad (3)$$

We use two main methods to characterize the photoelectrodes:

- Cyclic Voltammetry --> to measure the current, while sweeping the applied potential back and forth.
- Chronoamperometry --> to measure the current, while applying a constant voltage over time.

With cyclic voltammetry (CV), it is possible to determine the onset potentials and analyse the chemical reactions happening at the W.E. In this thesis, every cyclic voltammetry measurement was done for multiple cycles. Mostly 10 cycles were taken and the 10th cycle was taken as final measurement. The 10th loop of a CV of a Pt substrate measured in 0.3 M H₃PO₄ is shown in Fig. 4. When the the voltage at the W.E. gets a little more negative as 0V vs RHE, a negative current is measured. This is characteristic for H₂ evolution at a Pt cathode [3]. When the potential is about 1.7 V vs RHE, O₂ evolution occurs. When Pt is used as anode, this a characteristic value, where the theoretical 1.23 V for water oxidation is enhanced with an additional 0.5 V for the overpotential at a Pt anode. In between the two extremes, a few other peaks are visible, which shows the oxidation and deoxidation of Pt, and the absorption and desorption of hydrogen atoms at Pt. A small difference is measured with and without illumination, which can be explained by a small temperature increase. This is in agreement with a publication by Camargo et al., where small differences are observed for electrolysis over Pt electrodes for different temperatures[4].

Figure 4: 10th loop of a multi cyclic voltammetry measurement for the standard used Pt substrate in light (red) and in dark (black).

In chronoamperometry, the current is measured over time, while a fixed potential is applied during the measurement. The chronoamperometry measurements will show the stability of the photoelectrodes during the reaction over time, and by alternating the illumination between light on and off, it is possible to characterize the response of the photoelectrode to light.

2.4 GAS CHROMATOGRAPHY

A common way to measure water splitting via gas chromatography (GC), is connecting the GC to a reactor in a gas-closed circulation system [5]. These measurements show the total production, measured from the beginning of the measurement. As part of this research, a continuous flow reactor was connected to a highly sensitive GC, see Fig. 5. The continuous flow method makes it possible to monitor the H_2 and O_2 production in the reactor with a minute resolution, and show the transient of the reaction in the reaction. To determine the total production, the measured transient should be integrated. The resolution of the measurement is determined by the measurement time of the GC, the sensitivity of the GC for each compound and the background concentrations of the separate components in the helium purge gas.

Figure 5: Flow chart of the Gas Chromatography setup.

The GC is a CompactGC, purchased from Interscience B.V. and is equipped with a pulsed discharge detector (PDD). This detector uses ionized helium, and the advantage of the detector is the sensitivity compared to common detectors as the thermal conductivity detector (TCD) and the flame ionization detector (FID). The flow chart of the gas chromatograph is shown in Fig. 6. The unique feature of the GC is the capability to measure both H_2 and O_2 accurately with He as carrier gas. The measurements can be done with a part per billion (ppb) sensitivity. The CompactGC is capable to sample every minute. Next to the sampling valve (V0), there are two other valves (V2 and V3), which give the results in three gas inlets. The inlet on V2 is designated for a calibration gas. The reactor is

connected to the inlets of V3. The GC has two separation columns, placed in series. The first column (RT-Q bond 2m) removes water in the gas and the second column (Molsieve plot 5m) is used for separation of the gas compounds, being H₂, O₂ and N₂.

Figure 6: Flow chart of the gas chromatograph purchased from Interscience.

The measurements were done under a constant He purge of 10 mL/min. A 50 µL sample was taken each time. The peaks in the chromatogram were converted automatically by the GC software (EasyChrome) to the compound concentrations in the sample. For a direct conversion, the system was calibrated with a known calibration gas. Calibration showed that every area count under the peak in the chromatograph was in the range of 1 or 2 ppb's. This depended on the compound, where the GC was a bit more sensitive for H₂, than for O₂. Via the ideal gas law and using atmospheric pressure and a temperature of 298K, it was determined that a ppb in a purge flow of 10 mL/min corresponded to an actual amount of $4.464 \cdot 10^{-10}$ mmol/min. To make a clear distinction between H₂ and O₂ production in the reaction, and distinguish this from the background in the reactor, our

experience learned that a peak of around 50 ppb is sufficient, to ascribe the peak to the reaction in the reactor. Therefore, it was possible to monitor production rates of 23.2 pmol/min.

2.5 THE REACTOR DESIGN

The reactor design was based on a commercial 25 mL optical glass cuvette (402.013-OG, Hellma), and it was possible to perform measurement in three configurations:

- characterization of photocatalytic powders in a stirred reactor (Fig. 7A)
- characterization of a photoelectrode by photoelectrochemistry and gas chromatography, by integration of a three-electrode cell into the reactor (Fig. 7B).
- characterization of a free hanging chip, placed in a teflon holder (Fig. 7C). The Teflon holder divided the reactor in two separate compartments.

Figure 7: The configurations of the reactor, which are used for GC measurements. A) stirred reactor for photocatalytic powders. B) a PEC reactor to characterize a half reaction at a photoelectrode and C) the two compartment reactor for testing of an unbiased water splitting chip.

It is essential to isolate the inside atmosphere in the reactor from the outside atmosphere. This to prevent O_2 and N_2 leaking into the reactor. Therefore the glass reactor is clamped tight into the holder, and rubber packings are put between the cuvet and the holder at the bottom and at the top. This removed possible leaks. The electrodes were inserted via Swagelock couplings through the cover of the PEC reactor. To make the electrodes airtight, glass tubes were melted over the Pt wires. Electrical contact to a 1 cm² sample

was made by clamping the frontside of the substrate to the Pt wire in the holder. In all configurations, stirring is applied for realizing a homogenous solution in the reactor. This had directly a positive effect on the evacuation time of the reactor, and the response time during a measurement.

2.6 BACKGROUND REACTOR

Important for the resolution of the measurements, is the O_2 and N_2 background in the reactor before the measurement starts. A comparison was made by measuring the O_2 and N_2 concentrations in the reactor for three different situations:

- just after closing the reactor, which should represent the outside atmosphere.
- a measurement with a calibration gas ($H_2 = 2.30$ ppm; $O_2 = 3.34$ ppm; $N_2 = 6.02$ ppm)
- the background in a fully purged reactor, before the measurement starts.

In Fig. 8A a measurement on the maximum scale is shown of the three measurements. Without zooming in, the signal measured for the calibration gas and the He purge seems to be a flat line. The O_2 and N_2 peaks in the air measurement do not fit on the maximum scale and are very clear. In the zoomed image in Fig. 8B, peaks for H_2 , O_2 and N_2 are visible in the calibration chromatogram. In the chromatogram of the fully purged reactor, small peaks are visible for O_2 and N_2 , but these peaks are in the range of 50 ppb. When the reactor is fully purged, the atmosphere in the reactor has a low O_2 and N_2 background.

Figure 8: Three chromatograms measured by the GC. The green chromatogram represents the outside atmosphere, the red chromatogram shows the measurement of a calibration gas and the blue line is the measurement of a fully purged reactor A) shows the three measurement at the maximum scale. Only the air measurement is visible. B) A zoomed image to make the chromatograms of the calibration gas and the fully purged reactor visible.

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CHAPTER 3

ANALYSIS OF THE DYNAMIC COMPOSITION OF SrTiO_3 -BASED CATALYSTS IN OVERALL WATER SPLITTING

ABSTRACT

We report one of the first studies on the overall photocatalytic water splitting, applying a Continuously Stirred Tank Reactor (CSTR) connected to a micro gas chromatograph equipped with a PDD detector, allowing H_2 and O_2 detection with minute time resolution and in ppb concentration levels. Using this reactor and analysis method, we demonstrate that various catalysts, frequently reported to be active in the overall water splitting reaction, change their chemical composition in the first hours after initiation of illumination with 1.5 AM radiation. SrTiO_3 was found to slightly reduce, evidenced by a higher initial O_2 over H_2 ratio than expected for stoichiometric water decomposition, eventually reaching stoichiometric behaviour. When light was turned off, H_2 production continued for some time in the dark, which we explain by re-oxidation of the surface. When SrTiO_3 is equipped with a Pt co-catalyst prepared by photo-deposition in oxidative conditions, a much stronger O_2 evolution transient was observed, assigned to in situ reduction of PtO_x to metallic Pt. Once Pt had formed, a significantly higher steady state catalytic rate was obtained as compared to SrTiO_3 in the absence of Pt. Unexpectedly, doping of SrTiO_3 with Rh^{3+} resulted in lower activity, while the presence of Rh^{3+} also had a strong negative effect on the catalytic behaviour of the Pt functionalized catalyst. We show that the O_2 transient was of much lower intensity than in the absence of Rh^{3+} , and the obtained steady state product concentrations as well. XPS analysis demonstrates that the Pt surface in the presence of Rh^{3+} is not fully reduced after reaction, contrary to Pt on SrTiO_3 in the absence of Rh^{3+} , which no longer showed traces of PtO_x . Implications of these findings are that structure activity correlations reported in the literature on the basis of ex situ characterization of photocatalysts, should be considered preliminary.

3.1 INTRODUCTION

Technologies based on light induced overall water splitting producing H_2 , achieved with a cheap and effective catalyst system, could alleviate problems associated with the intermittency in solar energy supply. Many catalyst systems have been reported in the literature to be effective for overall water splitting (OWS), mostly TiO_2 -based, and frequently equipped with a platinum co-catalyst [1-3]. Co-catalysts are added mainly to improve the catalysis at the surface, platinum catalyzing the proton reduction reaction [4]. Besides TiO_2 based catalysts, strontium titanate ($SrTiO_3$) is an UV-active photocatalyst, capable of water splitting in a one step process [5, 6]. By adding dopants to $SrTiO_3$, it is possible to shift light absorption by the semiconductor into the visible light range. This is explained by the creation of energy levels in the band gap of $SrTiO_3$, which makes it possible to absorb lower energy photons. The doping can be composed of various atoms, for example Rh-cations, or a combination of multiple compounds [7-12]. Many efforts have focused on finding optimized doping levels, and to create a band gap of around 2.0 eV [13]. Although doped semiconductors are visible light active, this is not always beneficial to the activity, in particular when activity is induced by UV-light [10]. For the well-studied material TiO_2 , reports even claim that addition of doping is a catastrophe for activity [14].

Of particular interest in the application of water splitting, is the addition of Rh cations to strontium titanate ($SrTiO_3$). When combined with tungsten oxide, this visible light sensitive photocatalyst constitutes the H_2 evolution component of a z-scheme for water splitting [15]. The valence state of Rh in Rh: $SrTiO_3$ is subject of debate. Some studies state that Rh is the Rh^{4+} state after catalyst synthesis. This was proposed on the basis of an experiment where H_2 was produced in a photocatalytic methanol oxidation experiment, showing a delay in the production of H_2 [8]. This delay was explained by reduction of Rh^{4+} to Rh^{3+} in the initial stages of the experiment, consuming conduction band electrons. Samples made by pulsed laser deposition support this hypothesis, since higher activity for a photoanode with Rh^{3+} doping has been reported, than obtained with Rh^{4+} containing samples [16]. It should be noted that almost all experiments reported for water splitting with Rh: $SrTiO_3$, either with and without a Z-scheme component, were performed using UV-filtered light ($>420nm$).

Another aspect is the addition of platinum to the photocatalyst. A standard method to add platinum is photodeposition [17]. Here the photocatalyst is suspended in a solution with chloroplatinic acid as precursor, and by illumination with UV light, platinum is deposited onto the photocatalyst. For Rh: $SrTiO_3$ a loading of 1 wt-% has been reported as optimal [8]. Either with or without doping, H_2 production decreased at a higher loading than 1 wt-% [10], whereas the optimal loading was determined at 0.1 wt-%. Interesting is a relatively

old publication, which showed that photodeposition results in a mixture of platinum and platinum oxide [18]. This platinum oxide is the result of incomplete reduction of the platinum chloride anions used in the photodeposition method. When the photocatalyst was used in the water splitting reaction, the PtO was demonstrated to be reduced.

In this chapter, we characterize platinized and Rh-doped SrTiO₃ under realistic solar water splitting conditions. We show by the use of a highly sensitive gas chromatograph, that adding Rh to SrTiO₃ is lowering the obtained rates in the water splitting reaction when illuminated by an 1.5 AM solar simulator. By measuring data with minute time resolution, and by combining these gas chromatography data with X-ray Photo spectroscopy data, we determined that the oxidation state of Pt is determined by the absence or presence of Rh. Implications of these findings for explanations of photocatalysis proposed in the literature, are discussed.

3.2 METHODS

3.2.1 Preparation of the photocatalysts

SrTiO₃ catalysts were made by following the recipe reported in the literature [19]. Briefly, strontium carbonate (SrCO₃), titanium dioxide (TiO₂) and optionally rhodium oxide (Rh₂O₃) were mixed according to the required elemental composition, followed by a high temperature treatment at 1100 °C in air for 18 hours. The platinum co-catalyst was deposited on SrTiO₃ and Rh:SrTiO₃ by suspending 0.8 g powder in 25 mL of a 0.8 mM H₂PtCl₆ solution. Then 3-hours of UV illumination using a 50 W HBO mercury lamp (Zeiss, 46 80 32 – 9902) was applied to create the photo-deposited PtO_x particles. Afterwards the photocatalysts were filtered and washed three times with demineralised water, and dried at 80°C under atmospheric conditions, before use. For thermal reduction of the prepared compounds, these were inserted in a tube oven, and heated to 300 or 700 °C overnight in a 2% H₂/98% Ar atmosphere. Characterization of the photocatalysts was performed by X-ray diffraction (XRD) and scanning tunnelling microscopy (SEM). The XRD measurements were performed on a Bruker D2 phaser (Cu K α source) Diffractometer, and a Nova 600-nanolab HR-SEM (FEI instruments) was used for the SEM experiments.

3.2.2 Photocatalytic activity measurements

The photocatalytic activity of the compounds was measured using a continuously stirred tank reactor connected to a highly sensitive gas chromatograph (CompactGC Interscience). Fig. 1 schematically shows the setup. The GC was equipped with a Pulsed Discharge Detector. By a constant helium (7N) purge (10 mL/min), the gas to be analysed was transferred to the GC. In the GC, A 50 μ L sample loop inserted a sample onto two

columns in the GC. The two columns are a Q-bond, to remove H_2O out of the sample, and a Molsieve 5A, to separate the gaseous components present in the sample, being H_2 , O_2 and N_2 . Every measured ppb/min corresponds to 0.446 pmol/min, assuming ideal gas behaviour at atmospheric pressure and room temperature (298 K). The optical glass reactor (402.013-OG, Hellma) was illuminated by a 1.5 AM solar simulator (ABET technologies model 10500 low cost 1.5 AM solar simulator), which is representative of the intensity profile of solar radiation. The intensity over the whole spectrum is 100 mW/cm^2 . The measurements were performed in an acid electrolyte at pH 1.9, consisting of 0.01 M sulphuric acid. The time of the measurement was chosen such that a stable H_2 (and O_2) production yield was reached.

Figure 1: Scheme of the 25 mL continuously stirred tank reactor coupled directly to a Gas Chromatograph (GC) equipped with a Pulsed Discharge Detector (PDD). A 1.5 AM solar simulator was used to illuminate the optical glass reactor. A 7N helium purge was used to flush air out of the slurry reactor and analyse H_2 and O_2 evolved by the catalytic process.

3.3 RESULTS

3.3.1 Characterization of $\text{Rh}:\text{SrTiO}_3$ and SrTiO_3

In Fig. 2, we show the characterization of the materials synthesized and used in the measurements. In Fig. 2A the X-ray diffractogram clearly shows the peaks of SrTiO_3 for doped and undoped SrTiO_3 . In the diffractograms of doped SrTiO_3 a slight broadening of the line representing the [110]-plane is observed. Further a small peak was observed at 27° 2Theta, which can be likely assigned to traces of SrCO_3 , used in the synthesis procedure. After Pt deposition and reduction of the 1% Rh-doped photocatalyst, the diffractogram of SrTiO_3 did not change. Therefore the assumption is made, that the annealing step did not change the structure of the semiconductor significantly. In Fig. 2B the SEM image shows the rough morphology of 1%Rh: SrTiO_3 . The small particles at the surface are assumed to be the Pt co-catalyst, synthesized by photodeposition.

Figure 2: Characterization of (Rh:)SrTiO₃. A) XRD measurements of SrTiO₃ (Red), 1%Rh:SrTiO₃ as synthesized (Black), and platinized and H₂ annealed 1%Rh:SrTiO₃ (blue). B) SEM image of the platinized 1%Rh:SrTiO₃ catalyst.

3.3.2 Gas chromatography data

Doped vs. undoped SrTiO₃.

The effect of Rh-doping on photocatalytic activity of SrTiO₃ in the production of H₂ and O₂, is shown in Fig. 3. For both samples, SrTiO₃ with and without Rh-cations, an O₂ peak was measured initially, before H₂ production started. Apparently both catalysts are reduced in the initial stages of the reaction, which is light driven. Furthermore, for SrTiO₃, a tailing in the H₂ signal was observed when the light was turned off. The duration of this tailing, and in particular the completely different trend as compared to O₂ fall-off, indicates that H₂ is produced by (reduced) SrTiO₃ in the dark. We suggest that this phenomenon is related to reoxidation of the catalyst.

It seems that Rh-doping in SrTiO₃ has a negative effect on the water splitting efficiency under simulated solar light, given the lower steady state H₂ production (compare Figs. 3A and 3B). Further, the initial O₂ transient is lower in quantity, and Rh seems to introduce a steady decrease in the O₂ signal over prolonged periods of time. Finally, when the light was switched off, the H₂ production stopped immediately, without the delay observed for SrTiO₃ observed in Fig. 3A. Reconstruction/reduction of the surface seems to take place to much less extent in the initial stages of the experiment when Rh is present. What is remarkable, however is the high H₂/O₂ ratio at the end of the measurement, amplified by a slight increase in H₂ production over time. In the literature, H₂ evolution driven by decomposition of a sacrificial agent has been reported [8, 12]. In our study a sacrificial agent was not used. Another phenomenon reported in the literature is the in situ

reduction of Rh^{4+} to Rh^{3+} . However, this cannot explain the high H_2 over O_2 ratio in our experiments, because this reaction will consume electrons, and no holes. The origin of the decreasing O_2 quantity is as of yet not clear, but likely related to reconstruction of the surface or crystal structure of $\text{Rh}:\text{SrTiO}_3$.

Figure 3: Continuous flow measurements of two photocatalytic reactions with A) SrTiO_3 and B) $\text{Rh}:\text{SrTiO}_3$. Both samples were measured a pH 1.9 and illuminated with a 1.5 AM solar simulator.

Effect of the addition of a Pt co-catalysts.

To improve the catalysis, Pt was added to the doped and undoped SrTiO_3 by photodeposition. When Pt/SrTiO_3 was used as synthesized, an extremely high O_2 peak was measured in the beginning of the reaction, see Fig. 4A. Remarkably, this reduction of the photocatalyst upon illumination is irreversible, since no tailing of the H_2 production is observed for this catalytic material when the light is turned off. When steady state is reached, the addition of Pt has a positive effect on the overall water splitting rate of SrTiO_3 , since the O_2 and H_2 production rates are significantly higher than observed in Fig. 3A.

Figure 4: Photocatalytic characterization of 25 mg Pt/SrTiO_3 in 25mL 0.01M H_2SO_4 . A) Pt/SrTiO_3 as synthesized. B) Pt/SrTiO_3 after treatment in 2% H_2 at 300°C (black and grey) and at 700°C (dark and light blue).

By reducing the photocatalyst in a 2% H₂ atmosphere at 300°C or 700°C, the height of the O₂ transient decreased drastically, suggesting most of the PtO_x was reduced to Pt, see Fig. 4B. Further, by reduction at 300°C the steady state activity increased slightly over time. Finally, the H₂ reduction treatment at 700°C significantly decreased the activity.

In Fig. 5, the cumulative amount of excess O₂ (O₂ not produced by stoichiometric water splitting) is shown for the measurement performed with the Pt/SrTiO₃ catalyst, as synthesized. The excess O₂ was calculated by assuming that in the end, where a steady state was realized, O₂ was only produced by overall water splitting. About 0.6 μmol of excess O₂ was produced. In Fig. 5 a table is included, showing that a 1% Pt loading corresponds to 1.28 μmol of Pt. If the O₂ evolution is assumed to be dominated by PtO₂ reduction, a part of the Pt particles was in an oxidized state after the photodeposition, amounting to 46.8% of the Pt present. If PtO is the phase of oxidized Pt, the excess O₂ amounts to close to 100% of the Pt particles present. XPS data will be discussed in the next paragraph, demonstrating that the oxidized state of Pt is most likely PtO.

Figure 5: Excess O₂ produced during the water splitting reaction induced by platinumized SrTiO₃.

For the platinumized 1%Rh-doped samples (Fig. 6A) the O₂ formation transient is also clearly visible and there is still an incubation time before H₂ formation starts. However, the O₂ transient is much lower in quantity as compared to the material without Rh, suggesting that either the quantity of Pt is lower in the Rh containing catalyst, or most of the Pt is not susceptible to reduction. Another difference between the materials with or without Rh is observed after the H₂ treatment, shown in Fig. 6B. It seems that instead of an initial reduction reaction and O₂ formation, pre-reduction in H₂ flow initiates a transient in H₂ formation, accompanied by another oxidation reaction than water oxidation. After a couple of hours both samples showed steady state H₂ and O₂ production in a ratio of 2:1 with comparable reaction rates.

Figure 6: Continuous flow measurements of two photocatalytic reactions with A) Pt/Rh:SrTiO₃ as synthesized and B) Pt/Rh:SrTiO₃ after an overnight H₂ annealing step. Both samples were measured at a pH of 1.9 and illuminated with a 1.5 AM solar simulator.

3.3.3 XPS analysis

Platinized SrTiO₃

To test the origin of the O₂ peak in the beginning of almost all water splitting experiments, the platinized samples were characterized by X-ray photon electron spectroscopy (XPS). The XPS data of platinized SrTiO₃ are shown in Fig. 7. Three measurements were done of this photocatalyst, namely as synthesized, after H₂ reduction, and after a water splitting experiment. No differences were measured in the Sr and Ti peaks for the different samples. The Pt binding energy region showed a clear PtO signal, besides metallic Pt. The PtO signature disappeared after the H₂ treatment, and remarkably also after the photocatalytic reaction. This hints to reduction of the PtO in the beginning of the photocatalytic experiment, explaining the concurrent absence of H₂. Similar trends were observed in the literature with catalysts consisting of Pt photodeposited on TiO₂ [18].

Figure 7: XPS data of the platinum peak of platinized SrTiO₃. A) Pt/SrTiO₃ as synthesized. B) Pt/SrTiO₃ after a H₂ anneal. C) Pt/SrTiO₃ a.s. after a water splitting experiment.

Platinized Rh:SrTiO₃

The XPS data of the same set of samples was taken of the platinized Rh:SrTiO₃, see Fig. 8. So again the XPS spectra of the photocatalyst as synthesized, after H₂ reduction at 300°C, and after the photocatalytic experiment are compared. For the as synthesized and H₂ reduced samples, the same oxidation states of Pt are seen as for undoped SrTiO₃. Clearly oxidic Pt species (PtO) are present after photodeposition, and reduction in a H₂ atmosphere removed this oxide. The most remarkable observation is made when the XPS spectrum of the Rh containing catalyst after water splitting is compared to the spectrum of the sample without Rh: a significant part of the Pt particles is still in oxidic form. Further, no changes in oxidation state of Sr and Ti were observed by either the H₂ treatment or use in overall water splitting. The Ti 2p_{3/2} core level peak at 457.2 eV was taken as reference, to determine the Rh oxidation states via the binding energy values reported by Kawasaki et al. for the Rh⁴⁺, Rh³⁺ and Rh⁰ states [16]. The Rh state in all samples corresponds to Rh⁴⁺, which means that during the two treatments the dopant was not reduced.

A schematic overview of the state of the platinized photocatalysts on the basis of XPS data and the corresponding observations in the water splitting experiments, is given in Table 1.

Figure 8: XPS data of the Pt species (A,B,C) and the Rh species (D,E,F) of platinized Rh:SrTiO₃. A) Pt/Rh:SrTiO₃ as synthesized. B) Pt/Rh:SrTiO₃ after a H₂ anneal. C) Pt/Rh:SrTiO₃ a.s. after a water splitting experiment. The binding energies are referenced to the Ti 2p_{3/2} core level peak at 457.7 eV, and binding energy values for the Rh-valences were compared with Ref. [16].

Table 1: Resume of GC and the XPS measurements of the platinumized undoped and doped SrTiO₃ photocatalysts.

	Pt/SrTiO ₃			Pt/Rh _{0.01} SrTi _{0.99} O ₃		
	Calcined		H ₂ Reduced	Calcined		H ₂ Reduced
Peak in GC	O ₂		O ₂	O ₂		H ₂
	Before	After	Before	Before	After	Before
XPS	Pt & PtO _x	Pt(s)	Pt(s)	Pt & PtO _x	Pt & PtO _x	Pt(s)

3.4 DISCUSSION

In general, all of the catalysts tested in the present study showed activity for the overall splitting of water to H₂ and O₂, including SrTiO₃. The small fraction of UV in the overall solar intensity, was apparently sufficient to induce water splitting. Contrary to what has been reported for measurements performed in visible light, a negative effect of Rh on the water splitting rate achieved with SrTiO₃ was determined. This endorses the statement of Herrmann et al. [14], that doping of a semiconductor usually has an overall negative effect on the activity. Furthermore, when interpreting the results of Jang et al., the highest overall activity was also measured for undoped SrTiO₃ [10]. According to Herrmann et al. [14], doping creates recombination centres and thus decreases the life time of electron-hole pairs in the material. With the addition of Rh⁴⁺, an acceptor level is introduced 1.5 eV below the conduction band of SrTiO₃ [20]. This mid-gap level is presumably the recombination centre for photo-excited electrons, explaining the lower activity for Rh-doped SrTiO₃. The O₂ evolution transient displayed in Fig. 2 for SrTiO₃, accompanied by a slow increase in rate for H₂ production, has to the best of our knowledge not been previously demonstrated or discussed in the literature. Together with the prolonged H₂ production rate in dark conditions, this transient seems to suggest the catalyst changes oxidation state upon illumination, which is reversible once the light is switched off. The mechanism of initial O₂ evolution might be as follows:

The above redox reactions have also been observed after addition of Rh-cations, although the achievable degree of reduction ('X') appears to be lower in the presence of Rh. The creation of the vacancies is likely important to initiate activity because i) these can be beneficial for the life-time of carriers, as was already proposed in the literature [21], and/or ii) the surface vacancies are active sites for H₂ evolution. Although the transients determined in the present study have not been previously observed, a reduction reaction

upon illumination in water has been proposed in the literature for SrTiO₃ doped with Rh, namely the reduction of Rh⁴⁺ to Rh³⁺ [8]. This hypothesis was used to explain a delay in H₂ production, when water splitting was evaluated in a recycle reactor. However, XPS measurements of our systems after solar water splitting experiments did not provide any evidence for a change in the Rh oxidation state, so we prefer the mechanism of creation of oxygen vacancies during the photocatalytic reaction.

The reoxidation of the surface (in the dark) might be expressed by the following reactions:

When Rh was added to SrTiO₃, dark reaction (3) was not observed, which is likely related to the absence of reaction (4). An explanation could be that Rh cations stabilize the O₂ vacancies created by reaction (1) against re-oxidation.

For the Pt catalysts the redox behaviour is likely different. XPS measurements show the co-catalyst is initially a mixture of Pt and PtO_x (or entirely PtO if x=1) and after the experiment mostly metallic Pt. We propose that in the beginning of the photocatalytic reaction, reduction of PtO_x is more favourable than the reduction of protons:

O₂ evolution is likely the result of the water oxidation reaction:

Based on the XPS data, the reduction degree of Pt during water splitting was likely lower for the Rh-doped SrTiO₃, as shown in Table 1. The origin of the higher oxidation state of Pt in the presence of Rh is remarkable, and not easy to explain. One could propose the oxidation and reduction of Pt is reversible:

Reoxidation of Pt might be related to absorption of low energy photons, by the Rh-doping level in the band gap. These associated excited states (holes) can only oxidize Pt, and are insufficient in energy for water oxidation. This is illustrated in Fig. 9 which shows the respective redox potentials involved in the reaction scheme. Furthermore, the equilibrium between Pt and PtO_x can be the reason for the H₂ peak in the transient after H₂ reduction of Pt/Rh:SrTiO₃. The Pt co-catalyst is in a metallic state after reduction, which leads to oxidation of Pt in the beginning of the measurement, and a concurrent peak in H₂

evolution. After the equilibrium of equation 7 is set, the observed steady state H_2 and O_2 reaction rates for reduced Pt/Rh:SrTiO₃ are similar to the reaction rates of as synthesized Pt/Rh:SrTiO₃.

Figure 9: Expected positions of the band gap of (Rh:)SrTiO₃ in comparison to the redox reactions playing a role in the present study.

3.5 CONCLUSION

By using a highly sensitive gas chromatograph, it was possible to observe transients in O_2 and H_2 production rates in solar water splitting induced by SrTiO₃ based photocatalysts. The main conclusions are that i) SrTiO₃ changes oxidation state upon illumination in acidic electrolyte, ii) reoxidation of the surface occurs in the dark, with concomitant H_2 formation, iii) Rh doping decreases overall performance, and eliminates the reversibility of the redox behaviour of SrTiO₃, iv) photodeposition of Pt increases activity of SrTiO₃ and Rh: SrTiO₃, v) the oxidation state of Pt is close to zero during steady state water splitting activity for SrTiO₃ and partly oxidized for Rh: SrTiO₃. The reversibility of SrTiO₃ and the high reduction degree of the Pt particles are likely important features for inducing a relatively high photocatalytic water decomposition rate.

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CHAPTER 4

ANALYSIS OF Z-SCHEME PHOTOCATALYSIS OF WO_3 AND PT MODIFIED Rh:SR TiO_3 IN A CONTINUOUS FLOW REACTOR

ABSTRACT

We analysed the Z-scheme behaviour in solar water splitting of WO_3 and platinized Rh-doped $SrTiO_3$ (Pt/Rh: $SrTiO_3$). In the absence of a sacrificial agent, WO_3 is completely ineffective for production of H_2 and O_2 , whereas Pt/Rh: $SrTiO_3$ is capable to perform overall water splitting upon illumination by a solar simulator (1.5 AM, 100 mW/cm²). Contrary to what has been demonstrated for visible light activation in the literature, the presence of WO_3 deteriorates the catalytic rates obtained with Pt/Rh: $SrTiO_3$ upon solar light illumination. We tentatively explain this by enhanced formation of a film of deposited photocatalyst particles on the walls of the photoreactor. High water oxidation activity of WO_3 was demonstrated by using Fe(III) as sacrificial agent, while Fe(II) addition strongly enhanced the H_2 evolution efficiency of Pt/Rh: $SrTiO_3$, both decreasing over time by stoichiometric consumption of the sacrificial agent. When the electron mediator (either Fe(III) or Fe(II)) was added to a mixture of Pt/Rh: $SrTiO_3$ and WO_3 , similar stoichiometric consumption was observed, since quantities of either H_2 or O_2 formed were decreasing over time. It seems that oxidation or reduction of the sacrificial compound is in strong competition for the water splitting half reactions, while cyclic electron transfer could not be definitively demonstrated.

4.1 INTRODUCTION

Technologies based on light induced overall water splitting producing hydrogen, achieved with cheap, abundant and effective materials, could alleviate the intermittency in solar energy supply [1]. Many catalyst systems have been reported in the literature to achieve overall water splitting, including mixtures of catalysts composing a Z-scheme system. In a Z-scheme, visible light active photocatalysts, which are only capable to induce one of the two half reactions of water decomposition, are combined [2-5]. Typical water oxidation photocatalysts are WO_3 and BiVO_4 , which have been analysed extensively. For proton reduction, Strontium Titanate (SrTiO_3) is an effective UV-active photocatalyst, and overall water splitting using this material has been achieved. By adding dopants to SrTiO_3 , it is possible to shift light absorption by the semiconductor to the visible range [6-8]. In particular, addition of rhodium cations creates a visible light active photocatalyst, which can be used as photocathode for Z-scheme water splitting.

Overall water splitting under UV-filtered illumination was feasible by combining two photocatalysts constituting a so-called Z-scheme. To allow rapid transfer of electrons from one semiconductor to the other, typically electron mediators have been added to the reaction mixture, including $\text{Fe}^{2+}/\text{Fe}^{3+}$ or I^-/IO_3^- [9]. The redox couple should shuttle electrons between the two photocatalysts, i.e. the composites used for H_2 evolution or O_2 evolution. However, it is not straightforward to reach a 2:1 ratio in H_2 and O_2 production [10].

Additional literature shows that this electron mediator might not be required. Direct contact between the two photocatalysts can be achieved autonomously under process conditions [11]. Limitations in effectiveness of the electron mediators have also been addressed by alternatives, e.g. creation of a composite containing graphene oxide as conducting layer [12], or by synthesis of composites of two photocatalysts [5]. Another interesting finding is that Z-scheme water splitting can be achieved in a two compartment reactor, where the half reactions are divided by an exchange membrane. Relatively high efficiencies have been achieved, as compared to Z-scheme water splitting in one reactor [13, 14].

Most research in the literature reports the behaviour of Z-scheme systems when exposed to UV-filtered light. In the present study we characterized Z-scheme photocatalysis under realistic conditions, i.e. when exposed to artificial sun-light, using illumination by a 1.5AM solar simulator ($100 \text{ mW}/\text{cm}^2$). Further, we used a highly sensitive gas chromatograph directly connected to the reactor in a continuous flow configuration, to characterize the H_2 and O_2 production effectively.

4.2 METHODS

4.2.1 Preparation of the photocatalysts

In this study we focus on the Z-scheme catalysts discussed in detail by Kudo and co-workers (Fig. 1) [9]. The Z-scheme is composed of commercially available WO₃ nanopowder (Sigma Aldrich) as photoanode, and a homemade platinized 1%Rh:SrTiO₃ powder as photocathode. The photocathode was made by a solid state reaction, following a recipe from the literature [14], where strontium carbonate, titanium dioxide and rhodium oxide were used as reactants. These were mixed with a little amount of methanol according to the stoichiometric amounts to obtain a SrTi_{0.99}Rh_{0.01}O₃ composition. After methanol evaporation, the mixture was calcined at 1100°C for 12 hours in static air. Platinum co-catalyst nanoparticles were loaded onto SrTi_{0.99}Rh_{0.01}O₃ by a photodeposition method. 1.6 mg of the photocathode composite was suspended in 0.8 mM H₂PtCl₆ solution. The suspension was illuminated for 3 hours by a 50 W HBO mercury lamp (Zeiss, 46 80 32 – 9902). Afterwards the powder was washed with demi water and centrifuged three times, followed by drying at 80°C in ambient conditions.

Figure 1: Overview of the redox potentials of the photocatalysts constituting the Z-scheme in the present study. The redox potentials of the Fe²⁺/Fe³⁺ redox couple are also shown (after Kudo and coworkers [9])

4.2.2 Photocatalytic measurements

The photocatalysts and electrolyte were mixed in a 25 mL optical glass reactor (402.013-OG, Hellma). The measurements of the half reactions were done using 25 mg of photocatalyst, and the Z-scheme measurements with 25 mg of each photocatalyst, i.e. 50 mg combined. As electrolyte, a 0.01M H₂SO₄ solution of pH 1.9 was used. As electron donor Fe(II)SO₄ (2 mM), or as electron acceptor Fe(III)₂SO₄ hexahydrate (4 mM) were added to the electrolyte, when applicable. The reactor was illuminated by a 1.5 AM solar simulator (ABET technologies model 10500 low cost 1.5 AM solar simulator), which

duplicated the intensity profile of solar radiation. A L-42 filter (Hoya) was used for filtering the UV-photons, when applicable. The reactor was coupled to a CompactGC gas chromatograph (Interscience), equipped with a pulsed discharge detector. Measurements were done in a continuous flow configuration, in which a helium purge (7N) of 10 mL/min transferred products from the reactor to the gas chromatograph continuously. A 50 μ L sample loop inserted a sample onto the two columns incorporated in the GC. The first column is a Q-bond to remove H_2O out the sample, and the second column is a molsieve to separate the gas components in the sample. The software (Easychrome) directly converted the measured peak areas to values of concentration, after calibration by a standard gas. Every ppb measured by the GC corresponds to 0.446 pmol, when considering the flow rate, temperature (298 K), pressure (1 Atmosphere), and the ideal gas law. Measurements could be done with minute time resolution.

4.3 RESULTS

4.3.1 Half reactions without electron mediator

First, the individual photocatalytic properties of the two composites of the targeted Z-scheme were measured, without the addition of any sacrificial agent. The results are shown in Fig. 2. As we have shown in Chapter 3, platinumized Rh-doped SrTiO_3 is capable to perform overall water splitting under illumination by a solar simulator. The O_2 peak in the beginning is ascribed to the reduction of platinum oxide, as also discussed in chapter 3. When WO_3 was analysed in a 0.01M H_2SO_4 electrolyte, nor H_2 , nor O_2 could be detected. This is in agreement with the literature, and the knowledge that the conduction band minimum of WO_3 lies below the redox potential required for the H_2 reduction reaction [1]. Photo-excited electrons of WO_3 cannot be transferred to protons, and their faith is recombination with holes.

Figure 2: Comparison of the activity of the two composites of the Z-scheme in the present study, in a 0.01M H_2SO_4 electrolyte. A) Pt/Rh:SrTiO₃ and B) WO₃. The measurements were done under 1.5AM illumination.

4.3.2 Z-scheme water splitting without electron mediator

It was reported that at low pH, Rh:SrTiO₃ and WO_3 can aggregate, allowing Z-scheme based activity without an electron mediator [11]. The result of such experiment with solar radiation is shown in Fig. 3. Integrated values are also displayed to facilitate comparison with the data reported by Kudo and co-workers [11]. The measured trends in the O_2 and H_2 evolution curves correspond well to the data shown for Pt/Rh:SrTiO₃ in Fig. 2. When the light is turned on, in the first two hours of the reaction the O_2 production dominates the reactions. During that time the H_2 production is steadily increasing. At a certain moment a maximum in O_2 concentration is reached. From that moment on the transients in H_2 production and O_2 production eventually lead to the expected ration of 2:1 for H_2 and O_2 , which confirms to overall water splitting. The long term decreasing trend in production, can be related to adhesion of particles to the wall of the glass reactor, which is apparently more effective for the WO_3 containing suspension than for Pt/Rh:SrTiO₃ (Fig. 3). The main conclusion is that WO_3 did not promote the reaction rate of full water splitting of Pt/Rh:SrTiO₃, while the slurry stability of Pt/Rh:SrTiO₃ was decreased by the presence of WO_3 (compare Fig. 2A).

Figure 3: Z-scheme water splitting with WO_3 and Pt/Rh:SrTiO₃ in a 0.01M H_2SO_4 electrolyte without an electron mediator. The left Y-axis shows the values belonging to the H_2 and O_2 transient data, and the right Y-axis displays the cumulative values obtained by integration of the H_2 and O_2 curves.

4.3.3 Addition of $\text{Fe}^{2+}/\text{Fe}^{3+}$

For efficient Z-scheme photocatalysis an electron mediator was claimed in the literature to transport electrons from the O_2 evolution photocatalyst to the H_2 evolution photocatalyst [10]. We have used the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple to evaluate water splitting using a Z-scheme under our experimental conditions. To be able to explain transients in concentration with Fe-mediated Z-scheme catalysis, we first evaluated the effect of the respective Fe-ions on the activity of the individual constituents, as shown in Fig. 4. Fig. 4A shows the

measurement of WO_3 in a electrolyte with 4mM Fe^{3+} ions. Fig. 4B shows Pt/Rh:SrTiO₃ in an electrolyte containing 2mM Fe^{2+} ions. In both measurements high activity is measured towards the by the sacrificial agent determined product. In the case of WO_3 there is a high O_2 production, and with Pt/Rh:SrTiO₃ there is a high H_2 production. The Fe-ions are thus very effective as electron acceptor c.q. donor for the half reactions. So, where WO_3 is not suitable as water splitting photocatalyst, with Fe^{3+} as electron acceptor it can oxidize water efficiently. For Pt/Rh:SrTiO₃ a high H_2 production rate has been measured, and only over an extended period of reaction time, O_2 production is coming up slowly. In the transient, the peak in O_2 in the beginning of the measurement due to reduction of platinum oxide is not so obvious. It is still possible that in the beginning reduction of platinum oxide occurs, as shown in equation 1, but because Fe-ions can be oxidized instead of water, O_2 production is initially absent.

The growth in O_2 concentration over an extended period of time is due to consumption of Fe(II), gradually allowing water oxidation.

Figure 4: GC measurement of the half reaction with the addition of a sacrificial agent in a 0.01M H_2SO_4 electrolyte. A) WO_3 measured with the addition of $4\text{mM Fe(III)}_2\text{SO}_4$ hydrate. B) Pt/Rh:SrTiO₃ with the addition of 2mM Fe(II)SO_4 . Illumination was done by a 1.5AM solar simulator.

4.3.4 Electron mediators in the presence of both photocatalysts.

Fig. 5 shows the effect of the electron mediators when added to the Z-scheme composition of WO_3 and Pt/Rh:SrTiO₃. The measurements were done with the addition of 4mM Fe(III)SO_4 (Fig. 5A) or 2mM Fe(II)SO_4 (Fig. 5B). As seen in the measurements of the half reactions, the Fe-ions had a strong effect on the production rate of H_2 and O_2 . When Fe(III) was added, a strong transient in O_2 production was observed, slightly higher than observed for WO_3 alone. Furthermore, over time an increase in H_2 concentration is

Figure 6: Z-scheme water splitting with WO_3 and Pt/Rh: SrTiO_3 in a 0.01M H_2SO_4 electrolyte and adding A) 4mM $\text{Fe(III)}_2\text{SO}_4$ hydrate or B) 2mM Fe(II)SO_4 . Illumination was done a 1.5AM solar simulator.

apparent (see inset in Fig. 5A), which was not obvious in the case of WO_3 alone. The H_2 concentration is comparable to that observed by exposing the H_2 evolution catalyst to sunlight in the absence of Fe-mediator (Fig. 2), and we conclude that the Fe^{2+} formed in the Fe^{3+} reduction process, barely contributes to H_2 production (over Pt/Rh: SrTiO_3).

When Fe(II) is used as electron mediator (Fig. 5B), a H_2 peak was observed in the beginning of the reaction, although this was significantly lower than in the measurement without WO_3 (Fig. 4B). This might be related to an unwanted oxidation of Fe(II) on WO_3 . This is schematically illustrated in the following Fig. 6. The WO_3 -adsorbed Fe^{2+} will be oxidized by the holes of WO_3 to Fe^{3+} (rather than the holes of Pt/Rh: SrTiO_3), followed by

Figure 5: Schematic representation of the reactions observed in presence of Fe^{2+} ions to both photocatalysts. The goal is to effectuate a shuttling of charge via the Fe-couple between the photocatalysts. However only reactions represented by the dark blue arrows are assumed to happen.

reduction to Fe^{2+} with the photoexcited electrons in WO_3 . In other words, externally induced recombination of electrons and holes of WO_3 is stimulated by the presence of the Fe^{2+} mediator. To verify if Fe^{3+} is made by Pt/Rh:SrTiO_3 and will be available for reduction over WO_3 , sorption experiments could be used to identify if Pt/Rh:SrTiO_3 will release Fe^{3+} from its surface. In the end of the measurement a steady state was reached for the reaction rates of H_2 and O_2 . The steady state rate of O_2 production was similar to that obtained in the measurement of Pt/Rh:SrTiO_3 with Fe(II)SO_4 (Fig.4B).

To get a better understanding and to be able to compare the results with the literature, the measurement of z-scheme water splitting with the addition of Fe^{2+} was repeated with UV-filtered solar light. A L-42 UV filter (Hoya optics) was used, which only transmits photons with wavelengths $>420\text{nm}$. The result is shown in Fig. 7. The H_2 reaction rate was a bit lower as compared to solar illumination, and no O_2 was formed during the reaction. The measurement demonstrates that Pt/Rh:SrTiO_3 is sensitized by visible light, and the excited state has sufficient energy to convert protons in H_2 , and Fe^{2+} in Fe^{3+} . Since O_2 is not produced, apparently the water oxidation reaction is not achieved by visible light excitation of Pt/Rh:SrTiO_3 . Although we have not performed the visible light experiment in the absence of WO_3 , we assume WO_3 reduces the effectivity of Fe^{2+} -mediated Pt/Rh:SrTiO_3 , as a result of competitive adsorption, in agreement with the graph shown in Fig. 5B.

In Fig. 8 the integration is shown of evolved O_2 and H_2 in the z-scheme experiment with solar irradiation and Fe^{3+} of Fig. 5A, which shows that in total $15\text{ }\mu\text{mol}$ of O_2 is made during the 18 hours of reaction. As calculated, a total of 60% of the Fe^{3+} should be consumed. In the end of the measurement the amount of Fe^{2+} and Fe^{3+} are then almost equal. Nevertheless the H_2 production rate of Pt/Rh:SrTiO_3 is similar as in pure water, without

Figure 7: Z-scheme water splitting with WO_3 and Pt/Rh:SrTiO_3 in a $0.01\text{M H}_2\text{SO}_4$ electrolyte and addition of 2mM Fe(II)SO_4 . Illumination with a 1.5AM solar simulator, and a $>420\text{nm}$ band-pass filter.

the additional effect of an extra electron donor. The inability of the in situ produced Fe^{2+} to induce effective H_2 production over Pt/Rh:SrTiO₃ might be related to the high concentration of Fe^{3+} in the solution and on the surface of this catalyst. Similar to Fe-reactions over WO_3 in presence of a high Fe^{2+} concentration, over Pt/Rh:SrTiO₃ the by WO_3 -produced Fe^{2+} can be oxidized, while Fe^{3+} will be reduced. Over time the Fe^{3+} concentration decreased, and resulted in a slight increase of the H_2 production rate over Pt/Rh:SrTiO₃, as is shown in the inset in Fig. 5A.

Figure 8: Integrated O_2 production of the Z-scheme measurement with 4mM Fe^{3+} added to the electrolyte. The calculation shows that 52 % of the Fe^{3+} was used to produce O_2 .

4.4 DISCUSSION

4.4.1 Z-scheme water splitting without electron mediator

The low effectivity of Z-scheme water splitting demonstrated in the present study is in agreement with data reported by Sasaki et al. [11]. In their research, a Z-scheme with Pt/Rh:SrTiO₃ and BiVO₄ did not show any water splitting, while effectivity was only observed using an alternative catalyst, Ru/Rh:SrTiO₃. Part of the data of Sasaki were obtained in a reactor without stirring, where both photocatalysts were mixed and located at the bottom of the reactor. They reported that mixing of the photocatalysts was essential, because a measurement in which the photocatalysts were added separately at the bottom showed almost no reaction, even for the Ru/Rh:SrTiO₃. Further, Sasaki et al. reported that acidic conditions are required, because this leads to aggregation of Ru/Rh:SrTiO₃ and BiVO₄. An important parameter for aggregation is the zeta potential, which determines the charge at the surface. Sasaki et al. determined the zeta potential of

Ru/Rh:SrTiO₃ as a decisive parameter for the aggregation at different pH, because the BiVO₄ had a negative zeta potential in acidic and pH neutral electrolytes. Anik et al. reports that the zeta potential of WO₃ is negative at a pH of 1.9 [15], which suggests the aggregation properties of WO₃ are similar to BiVO₄.

The poor performance of the Pt/Rh:SrTiO₃ catalyst was assigned to back reactions of evolved H₂ and O₂ to H₂O over the Pt co-catalyst. The reaction was analysed by Sasaki et al. in a semi-batch reactor configuration. In our research, the back reaction of H₂ and O₂ is likely suppressed due to constant flushing of the reactor and operation in a CSTR configuration. Furthermore in Fig. 3, after the initiation period, full water splitting over Pt/Rh:SrTiO₃ was demonstrated. The measurements without electron mediator shown in this chapter do not show exchange of charge between WO₃ and Pt/Rh:SrTiO₃ due to aggregation. In realistic conditions, under illumination of a 1.5 AM solar light, Pt/Rh:SrTiO₃ is sufficient to split water by itself, whereas in our study aggregation with WO₃ likely leads to fouling of the reactor wall, slowly deteriorating performance of the slurry. In conclusion, although Z-scheme phenomena have been reported in the literature, these have not been confirmed in this work, because charge transfer between particles is ineffective, and agglomeration phenomena detrimental, rather than beneficial for the water splitting effectivity of Pt/Rh:SrTiO₃.

4.4.2 Z-scheme water splitting with an electron mediator.

When Fe³⁺ was added as electron acceptor to WO₃, a high O₂ production rate was observed, with or without the presence of Pt/Rh:SrTiO₃. The addition of Pt/Rh:SrTiO₃ results in an additional, but low H₂ production, similar to H₂ the rate observed with Pt/Rh:SrTiO₃ without any electron mediator. Our results with the addition of only Fe²⁺ indicate that reduction of in situ produced Fe³⁺ by Pt/Rh:SrTiO₃ over WO₃ does not occur, while a high O₂ evolution rate was measured over WO₃ by the addition of only Fe³⁺.

The results of the addition of an electron mediator correspond to the results published by H. Kato et al. [10]. They measured a negligible amount of H₂, when Fe³⁺ was added to the electrolyte. When Fe²⁺ was added, H₂ was measured in larger quantities. Interestingly, the H₂ production measured was higher when a mixture of Fe²⁺/Fe³⁺ was used, which the authors claimed was due to shuttling of the Fe redox couple. We hypothesize that when a high concentration of one of the Fe-species is present, it will give competition to one of the redox reactions for water splitting. A complete overview of the occurring reactions in the presence of one is illustrated in Fig. 9. For example in presence of a high Fe²⁺ concentration, it is more favourable to oxidize Fe²⁺ rather than H₂O over WO₃, while it reduces the in situ produced Fe³⁺ made by Pt/Rh:SrTiO₃. With a high Fe³⁺ concentration, the reduction of Fe²⁺ is favoured over H⁺ reduction by Pt/Rh:SrTiO₃. The possibility for the reversibility of the redox mediator over the material was proposed in the literature

previously [4]. The half reactions to oxidize Fe^{2+} and reduce Fe^{3+} have lower redox potentials, than the half reactions of water splitting. Moreover, the incubation period of platinized Pt/Rh:SrTiO₃ (Fig. 2A) shows, that when a more energy favourable reduction reaction is possible, as shown for reduction of PtO_x in chapter 3, this reaction is experimentally preferred.

Figure 9: Schematic illustration of the reactions happening with the addition of one of the Fe-ions to both photocatalysts. Green arrows show the reactions in presence of Fe^{3+} , where O_2 will be made at WO_3 and 'short circuiting' of the Fe half reactions over Pt/Rh:SrTiO_3 . Blue arrows show the reactions in presence of Fe^{2+} , which result in H_2 evolution and 'short circuiting' of Fe reactions over WO_3 .

To be sure if backward reactions of Fe-species are indeed a bottleneck for Z-scheme water splitting, it needs to be verified if Fe-species after oxidation or reduction desorb into the electrolyte and become available for the second photocatalyst. When they stay adsorbed on the photocatalyst surface, this explains the lack of electron transfer between the two catalytic materials. Anyway, if 60% of Fe^{3+} was converted by WO_3 , it can be assumed that Fe^{2+} -ions should become available for Pt/Rh:SrTiO_3 to be oxidized, which in this case should have led to H_2 formation. This makes it likely that the absence of enhanced H_2 formation can be explained by the competition between the reduction of Fe^{2+} and H^+ .

The results imply that data reported by C.C. Lo et al [14], where the two half reactions were separated with their complementary Fe-ion, over two compartments and connected via a membrane, are quite remarkable. These authors report efficient exchange of Fe^{2+}

and Fe^{3+} via a membrane to shuttle electrons between the photocatalysts. We are not exactly sure how effective the membrane is for the electron shuttle in such configuration, however it is likely that 'short circuiting' of the Fe-mediator using a membrane is less dominant. Further, favourable Fe-ion sorption and transport properties of the membrane could benefit the electron exchange, in particular when some catalyst particles will adhere to either side of this membrane. To be able to establish Z-scheme water splitting with the electron mediator, it will be interesting to deposit WO_3 and $\text{Rh}:\text{SrTiO}_3$ on either side of an electron conducting divider, similar to the concept of Nozik et al. [16], and discussed in the introduction of this thesis.

4.5 CONCLUSIONS AND RECOMMENDATIONS

We characterized Z-scheme water splitting effectiveness with a highly sensitive gas chromatograph. Due to the continuous flow reactor configuration applied, it was possible to determine the effects of manipulating charge transfer phenomena by addition of Fe(II) or Fe(III) to the electrolyte on H_2 and O_2 evolution rates very accurately. The results imply that upon solar light illumination, shuttling of electrons between the two photocatalytic compositions via oxidation of Fe(II) and reduction of Fe(III) is not feasible. We assume that due to a high concentration of one of the Fe-species, 'short-circuiting' of the Fe-half reactions over the second photocatalyst, is more favourable than to perform the second half reaction for water splitting. This lead to only O_2 evolved in the presence of Fe^{3+} and only H_2 evolved in the presence of Fe^{2+} . This study has shown that under realistic solar illumination conditions, inducing 'communication' between the two photocatalysts by $\text{Fe(II)}/\text{Fe(III)}$ under solar illumination is not straight forward. Connecting the two semiconductors on a metallic divider is likely required to establish the existence and persistence of Z-scheme water splitting.

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CHAPTER 5

SELECTIVE HYDROTHERMAL METHOD TO CREATE PATTERNED AND PHOTOELECTROCHEMICALLY EFFECTIVE Pt/WO₃ INTERFACES

ABSTRACT

A hydrothermal method based on the use of H₂O₂ is described to grow a homogeneous layer of WO₃ on a platinum film supported on a silicon wafer. WO₃ growth is highly selective for Pt when present on Si in a patterned arrangement, demonstrating Pt catalyzes the decomposition of the WO₃ precursor in solution. The obtained Pt/WO₃ interface yields high photocurrents of 1.1 mA/cm² in photoelectrochemical water splitting when illuminated by a solar simulator. The photocurrents are significantly higher than most previously reported values for hydrothermally grown layers on indium-tin-oxide glass and fluorine-tin-oxide glass. The selective growth method thus provides new options to effectively implement tungsten oxide in photoelectrochemical devices. `

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5.1 INTRODUCTION

Tungsten oxide (WO_3) is one of the most frequently studied binary oxides in photoelectrochemical cells, functioning as photoanode [1]. Furthermore, photocatalytic application of WO_3 ranges from water purification (dye degradation) to visible-light induced splitting of water into hydrogen and oxygen. In the latter application, WO_3 shows high water oxidation efficiency when in the presence of other specific semiconducting oxides, such as modified SrTiO_3 , thus creating a so-called Z-scheme configuration [2]. Particles and supported layers of WO_3 can be grown in various morphologies and crystal composition by several synthesis methods [3-7]. In particular, hydrothermal growth has led to compositions effective in the abovementioned applications [8, 9]. A method employing hydrogen peroxide has recently been demonstrated to yield WO_3 -particles with well-defined morphologies, without the need for structure directing additives [10, 11]. When a seed layer was used, homogeneous WO_3 -layers were successfully grown on indium-tin-oxide (ITO)-coated glass substrates [12, 13].

Growth of WO_3 on metal surfaces has not been extensively studied, while having control over growth of well-defined WO_3 layers on (patterned) metal surfaces is highly relevant for creation of new device concepts in photo-electrochemistry. We hypothesize a favorable electron transfer from photoexcited WO_3 to a metal, and in particular Pt, based on the frequently reported positive effect of Pt nanoparticles on the photocatalytic performance of WO_3 . This is typically assigned to electron scavenging by the Pt nanoparticles, enhancing lifetime of excited states [14, 15]. Furthermore, Nozik et al. propose to use the inequality of work functions to create an electron flow from semiconductor to metal [16], on which basis a photoelectrochemical diode was constructed and shown to be effective in water splitting [17].

The objective of this study is to demonstrate the controlled growth of WO_3 on a Si supported thin Pt film. We modified the hydrothermal process described by others [12, 13], to obtain well-defined WO_3 layers without the need of a seeding layer. We confirm a catalytic effect of Pt in the formation of the WO_3 layers by demonstrating the growth to be selective on Pt when present on Si in a patterned arrangement. Finally, we demonstrate excellent efficiency of the Pt/ WO_3 composition in photoelectrochemical applications.

5.2 EXPERIMENTAL

A 100 nm thick platinum film was sputtered on an oxidized <100>-silicon wafer. To allow strong adhesion, a 13 nm Ti layer was used between substrate and film. Sputtering was performed using in-house-developed sputtering equipment, applying a 6.6 mbar argon atmosphere. For Pt and Ti, 2 inch targets were used and a 200 W DC sputter current was

applied. A dot pattern was defined in the Ti/Pt film using photolithography and passive ion beam etching with Ar⁺ ions in an Oxford Ionfab 300 reactive ion beam etching system.

WO₃ layers were grown hydrothermally on the Pt surface, without the need of a seeding layer. H₂WO₄ (Sigma Aldrich) was dissolved in 35% H₂O₂ (Sigma Aldrich) to a concentration of 0.5 M at 80 °C under vigorous stirring. After cooling to room temperature, this solution was diluted to 0.01 M H₂WO₄ by addition of distilled water. Two slightly different procedures for growth were followed. In the first procedure, 20 mL of the 0.01 M solution was transferred directly after into a Teflon beaker, and inserted in a stainless steel autoclave (a 4748 acid digestion vessel (Parr Instruments)). This was followed by immersion of the Si/SiO₂/Ti/Pt substrate, closure of the autoclave, and hydrothermal treatment at 170 °C for 18 hours, applying a heating rate of 10 °C/min. In the second procedure the 0.01 M solution was pre-treated overnight at room temperature by two small pieces of Si/SiO₂/Ti/Pt substrate with a total area of approximately 1 cm². Oxygen evolution due to decomposition of the excess of H₂O₂ was initially clearly visible. The gas evolution had stopped after overnight treatment. The pieces were removed and synthesis continued in hydrothermal conditions as described for the first procedure by adding the solution and Si/SiO₂/Ti/Pt substrate into the Teflon beaker. For both procedures, after cooling the digestion vessel to room temperature by a natural cool down, the substrates were removed from solution, carefully rinsed with distilled water, and dried under mild nitrogen flow. Finally the samples were annealed at 600 °C for 12 hours in static air, applying a heating rate of 10 °C.

Characterization of the grown layers was performed by high-resolution scanning electron microscopy (HR-SEM) and X-ray diffraction (XRD) analysis. For imaging a Nova 600-nanolab HR-SEM (FEI instruments) was used, and for combined imaging/elemental mapping a MERLIN HR-SEM (Metrology Zeiss) system, equipped with energy-dispersive X-ray spectroscopy (EDX). A Bruker D2 powder diffractometer (equipped with a Cu K_α source) was used for analysis of the WO₃ crystal structure.

Electrochemical measurements were performed in a three-electrode cell setup equipped with a Versastat 4 potentiostat (Princeton). A 1.5AM solar simulator (Model 10500, ABET Technologies) was applied as light source. The reactor consisted of a 25 mL optical glass cuvette, which filtered most of the emitted UV-light. The counter electrode (EC) consisted of a platinum mesh connected to a platinum wire. As reference electrode a 3.0 M Ag/AgCl reference electrode (BASi) was used, with a potential of +0.210 V vs. NHE. This value can be converted to the V_{RHE} by the Nernst equation:

$$V_{\text{RHE}} = V_{(\text{Ag}/\text{AgCl})} + V_{(\text{Ag}/\text{AgCl vs RHE})} + 0.059\text{pH} \quad (1)$$

Contact to the Si supported Pt/WO₃ working electrode was accomplished by a stainless steel clamp, protected from the electrolyte by encapsulation in epoxy resin. The WO₃ layer was faced to the light source. The electrolyte consisted of a 0.3M H₃PO₄ solution.

5.3 RESULTS AND DISCUSSION

5.3.1 Material characterization

The morphology of the WO₃ layers hydrothermally grown on Pt in the presence of H₂O₂, can be composed of two different morphologies, see Fig. 1. WO₃ grown in the presence of an excess of H₂O₂ shows a flower-like morphology (Figs. 1A, B), and a high porosity. Cross-sectional views indicate a thickness of this porous layer of around 25 μ m. When the excess of H₂O₂ in the precursor solution was allowed to decompose prior to hydrothermal WO₃ growth, a dense layer with crystals in a rod-like morphology is obtained (Fig. 1D, E). Side-view measurements show a thickness of 560 nm. This thickness is rather independent of the time of hydrothermal treatment, since a large fraction of WO₃ crystallizes in solution. After annealing at 600 °C (Fig. 1C,F), the layers hardly change their morphology, only some facets appear to become more rounded.

Figure 1. Scanning electron microscopy images of hydrothermally grown WO₃ layers: (A,B) side and top view of flower type layer formed in the presence of excess H₂O₂, (C) top view of the layer after subsequent annealing at 600 °C; (D,E) side and top view of an as prepared rod type layer in lower concentrations of H₂O₂, induced by decomposition of excess H₂O₂ prior to hydrothermal treatment (F) top view of layer after subsequent annealing at 600 °C.

Besides the large differences in thickness and morphology, a large difference in adhesion of the WO₃ layer to the Pt film was observed for the two different hydrothermal procedures. The rod-shaped crystals showed strong adhesion upon rinsing and drying procedures, while the thick and porous flower-like layers were substantially washed off when exposed to the same procedure. These characterization results demonstrate the large effect of the absence or presence of an excess of H₂O₂ on surface morphology. Although we did not investigate this aspect, Z. Jiao *et al.* [12], attributed morphology differences to the absence or presence of a WO₃ seeding layer on their applied fluorine doped tin oxide (FTO)-coated glass. With a (spin coated) WO₃ seeding layer, a rod-like morphology was obtained, whereas without the seeding layer WO₃ crystals with a high porosity and flower-like shape were formed.

XRD was applied to characterize the crystal phase of the grown layers, see Fig. 2. The diffraction lines of Pt and Si of the substrates are visible at 40.0 and 47.4 degrees. The WO₃ crystals of both layer morphologies consist of WO₃·0.33H₂O (JCPDS No. 87-1203), with main diffraction lines at 14.3 and 18.2 degrees, as well as two additional characteristic lines around 23.4 and 24.2 degrees. After annealing at 600 °C, the monoclinic WO₃ phase is formed (JCDPS 72-0766) with three main characteristic diffraction lines at 23.2, 23.7 and 24.4 degrees, which are representative of the [200], [020] and [002] crystal planes, respectively. In case of the rod-like morphology there seems to be a preferential orientation in the [002] direction of the crystal, while in the case of the flower-like morphology the distribution for the [200], [020] and [002] planes is approximately equal.

Figure 2. X-ray diffraction patterns of the WO₃ layers with rod and flower type morphologies before and after annealing at 600 °C. As synthesized, both morphologies exhibit a tungsten oxide hydrate phase. By annealing this hydrate phase is converted to the monoclinic tungsten oxide phase.

The following two reactions are proposed to describe the process of WO_3 formation [12]:

Following Eq.(2) the tungstic acid and hydrogen peroxide are converted to a WO_3 precursor containing peroxide and water (peroxo-polytungstic acid). The peroxide containing complex is subsequently converted to (supported) WO_3 crystals and oxygen (Eq.(3)), presumably catalyzed by the Pt surface. The differences in adhesion, crystal orientation and morphology of WO_3 on Pt, relate to the applied H_2O_2 concentration in the precursor solution. In high concentrations of H_2O_2 , Pt catalyzes the decomposition of hydrogen peroxide, which is in competition with the decomposition of the peroxo-polytungstic acid intermediate. H_2O_2 decomposition leads to extensive formation of O_2 bubbles inhibiting the decomposition of the peroxo-polytungstic acid at the Pt substrate.. Presumably WO_3 crystals grow extensively in solution and subsequently deposit on the substrate, which affects the WO_3 adhesion and yields the obtained highly porous morphology. A schematic overview of the two proposed mechanisms for growth is provided in Fig. 3.

Figure 3. Schematic overview of the two proposed growth mechanisms for WO_3 at Pt surfaces in the presence of low and high concentrations of H_2O_2 , respectively. In the presence of high concentrations of H_2O_2 , oxygen bubbles are formed, resulting in a porous (flower type) WO_3 layer loosely attached to the Pt layer. For low concentrations of H_2O_2 , the peroxo-polytungstic acid decomposes on the Pt surface, and a strongly adhering WO_3 layer is formed.

5.3.2 Selective growth of WO_3 at Pt

To evaluate the proposed catalytic effect of Pt in peroxo-polytungstic acid decomposition, preferential growth of WO_3 on Pt was attempted, as previously reported for ZnO nanostructures on Au nanoparticles [18-20]. To this end, a Pt pattern of 10 μm and 50 μm

sized dots was prepared on a Si/SiO₂/Ti substrate by micro-lithography. After application of the hydrothermal growth procedure with relatively low concentration of H₂O₂, the formation of WO₃ was analyzed by SEM in combination with EDX. Results are shown in Fig. 4. The SEM images with the representative EDX map are shown for the 50 μ m dots (Figs. 4A,B) and the 10 μ m dots (Fig. 4C,D), respectively. The SEM images confirm the preferential growth of WO₃ crystals on the platinum dots. Mapping of the specific elements, i.e. Si (red), Pt (magenta), W (green) and O (blue) was performed using EDX. Between the dots a dominant red color is visible, which represents the Si substrate. On the dots the main colors are green and blue, confirming the presence of W and O. Traces of the Pt substrate are visible in the 50 μ m dots, while the EDX result suggests the formation of a less dense WO₃ layer on the 10 μ m sized dots. Only a small part of the Pt appears not to be covered by WO₃.

Figure 4. Images of WO₃ layers grown at patterned platinum surfaces on Si, obtained by Scanning electron microscopy combined with elemental mapping by energy-dispersive X-ray spectroscopy. (A) SEM images of 50 μ m diameter Pt/WO₃ dots and (B) the corresponding EDX map of Si, Pt, W and O. (C) SEM images of 10 μ m diameter Pt/WO₃ dots and (D) the corresponding EDX map of Si, Pt, W and O.

5.3.3 Photoelectrochemical characterization

To analyze the properties of the interface of the Pt film and the deposited WO₃ crystals, photoelectrochemical characterization was performed, of which the results are shown in Fig. 5. During the final annealing step, the thick layers with the flower-like morphology detached from the Pt surface, due to low adhesion. Therefore it was not possible to use

these samples in the photoelectrochemical setup and measure the photocurrent. The cyclic voltammetry (CV) curves of the dense WO_3 layer are compared to the curves of the bare Pt layer (on the Si/SiO₂ substrate) in Fig. 5A. In both cases, at an applied potential of 1.7 V vs. a reversible hydrogen electrode (RHE), current is measured, assigned to electrolysis of H_2O . Oxygen is formed at the working electrode (the bare Pt substrate, or the WO_3 layer (black curve in Fig. 5a), respectively), while hydrogen is formed at the counter electrode (a Pt mesh). This is conform the electrochemical water splitting potential of 1.73 V typically obtained with two Pt electrodes, being the result of the theoretical value of 1.23 V, and a 0.5 V over-potential for water oxidation. When a 1.5 AM solar simulator is used to illuminate the substrates, the bare Pt film does not show a photo-response, as expected. On the other hand, for the WO_3 layer a clear photoresponse is measured. The onset potential where oxygen evolution is initiated, has decreased from 1.7 V to 0.75 V vs. RHE, which indicates a shift of 0.95 V by illumination of WO_3 . The photocurrent obtained at a bias potential of 1.23 V is about 1.1 mA/cm^2 .

To further characterize the response of the system, a chrono-amperometry measurement was performed, see Fig. 5B. The sample was intermittently exposed to light in periods of 30 seconds at a bias potential of 1.23 V vs. RHE. When the sample was illuminated, a photocurrent of about 1.1 mA/cm^2 was measured, in agreement with the curve of Fig. 5A. The photoresponse was relatively independent on the number of light exposure cycles, demonstrating the reproducibility of the photo-response and a high stability of the WO_3 layer.

Figure 5. Photocurrent measurements of the WO_3 layer (grown in relatively low concentrations of H_2O_2) in a 0.3M H_3PO_4 electrolyte. A scan rate of 50 mV/s was applied. (A) I-V-curves of the Si/Pt substrate (dark is blue line, light on is green line) and a Si/Pt/ WO_3 sample (dark is black line, light on is red line). Clearly, photocurrent is measured for the WO_3 layer, when exposed to light. The inset shows the measurement configuration used for the measurements. (B) Chrono-amperometry measurement of the WO_3 layer. The applied bias was 1.23 V vs. RHE. A clear change in photocurrent between light on and off is measured.

According to the Shockley-Queisser limit, the maximum achievable photocurrent at 1.5 AM solar irradiation for WO₃ (2.6 eV band gap) is 6.0 mA/cm² [21, 22]. The 1.1 mA/cm² is thus 18.3% of the maximum achievable photocurrent. In the literature a range of photocurrents are reported for supported WO₃ layers, typically obtained with different light sources. For example a high photocurrent of 2.6 mA/cm² was reported for N-doped WO₃, but this was achieved with a 500 W xenon-lamp emitting light of high intensity [23]. Photocurrents measured with a 1.5 AM Solar Simulator are included in Table 1 for comparison. The photocurrents in the Table are the values at 1.23 V vs. RHE. With the Nernst equation, the potentials were corrected for differences in pH and the used reference electrode. Compared to other hydrothermally grown layers, our WO₃ layers at platinum substrates show a significantly higher photocurrent. This confirms the favorable electron transfer of photoexcited WO₃ to the Pt film and is in agreement with a high electron conductivity. The photocurrent of 1.1 mA/cm² is lower than the photocurrent reported by Hong *et al.* This might be related to the thickness of the WO₃ layer (3.3 µm, prepared by polymer-assisted deposition in the study of Hong *et al.*, vs. 0.5 µm in the present study), as well as to the high crystallinity of the layers prepared by Hong *et al.* [26]. The onset potentials obtained with our layers, showed comparable values as reported for conductive glass substrates, so the Schottky barrier between WO₃ and Pt, if unfavourable, does not appear to significantly inhibit electron transfer.

Table 1. Selected literature overview of photocurrents obtained for WO₃ layers using a 1.5 AM Solar Simulator.

Material system	Growth method	Electrolyte	Photocurrent [mA/cm ²]	Onset [V vs RHE]	Reference
WO ₃ at Pt	Hydrothermal growth	0.3 M H ₃ PO ₄	1.1	0.75	This work
WO ₃ at SnO ₂ :F-coated glass	Hydrothermal growth	0.5 M H ₂ SO ₄	0.6	0.45	S.J. Hong <i>et al.</i> [24]
WO ₃ at SnO ₂ :F-coated glass	Hydrothermal growth	1 M H ₂ SO ₄	0.4	0.55	Z. Jiao <i>et al.</i> [13]
WO ₃ at SnO ₂ :F-coated glass	Reacting RF Magnetron Sputtering	0.33 M H ₃ PO ₄	1.1	0.95	B. Marsen <i>et al.</i> [25]
WO ₃ at SnO ₂ :F-coated glass	Polymer-assisted deposition	0.5 M H ₂ SO ₄	2.3	0.60	S.J. Hong <i>et al.</i> [26]
WO ₃ at SnO ₂ :F-coated glass	Chemical solution deposition	1 M HClO ₄	2.3	0.45	C. Santato <i>et al.</i> [27]

5.4 CONCLUSION

We demonstrate that by the use of a hydrothermal method, growth of WO_3 in intimate contact with a Pt film can be achieved. The growth is likely controlled by the Pt catalyzed decomposition of a peroxo-polytungstic acid intermediate, as confirmed by the spatial distribution achieved using Si surfaces equipped with Pt dots. A tungsten oxide hydrate phase is thus formed, which is converted upon annealing to a monoclinic WO_3 phase. The Pt supported layers show a significant photoresponse of 1.1 mA/cm^2 at a bias potential of 1.23 V vs. RHE. This response is significantly higher than most previously reported values for hydrothermally grown layers on ITO- and FTO glass. This is highly relevant for creation of new devices for photoelectrochemical production of hydrogen. Future studies will involve the use of other metal films, and studying the effect of the composition of such film on the formation of the WO_3 layer, as well as on the achievable photocurrents. Further, the patterned surfaces might find application in advanced sensing and photoelectrochemical devices, requiring efficient metal-semiconductor interfaces.

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CHAPTER 6

ENHANCEMENT OF THE PHOTO CURRENT OF WO_3 BY INSULATING THE SUBSTRATE FROM THE ELECTROLYTE AND ADDING A CO-CATALYST.

ABSTRACT

In this chapter we show that we can improve the photocurrent density and the onset potential of a Pt/ WO_3 photoanode by deposition of an IrO_2 co-catalyst. To deposit IrO_2 directly on WO_3 crystals attached to a Pt substrate, it was necessary to insulate the Pt substrate from the electrolyte. This was achieved via spin coating of a TiO_2 layer after the hydrothermal growth of the WO_3 layer. This insulation with TiO_2 already resulted in enhancement of the photocurrent, which is explained by a decrease in the potential drop induced by the Pt/electrolyte interface. The measurements indicate that this potential drop introduces an extra resistance for the electrons to move from WO_3 in the substrate. Addition of IrO_2 enhanced the photocurrent further, and by both additions it was possible to increase the photocurrent by 140% as compared to the as-synthesized Pt/ WO_3 samples.

6.1 INTRODUCTION

Tungsten oxide (WO_3) is a versatile semiconductor material, which can be used for a variety of applications [1, 2]. In combination with a photocathode, WO_3 can be applied as photoanode in a photoelectrochemical water splitting cell, of which the concept was introduced in Chapter 1 [3]. As photoanode, WO_3 is used for the water oxidation reaction and evolution of O_2 . By a hydrothermal procedure, it is possible to grow WO_3 selectively on a Pt substrate with good water oxidation activity, as shown in Chapter 5 [4]. One of the issues of the Pt/ WO_3 interface is that it showed a high onset voltage under illumination, i.e. the voltage where water oxidation starts, compared to WO_3 photoanodes made on fluorine-doped tin oxide (FTO) [5, 6]. An interesting application for a Pt/ WO_3 photoanode, is using it in a photochemical diode configuration for water splitting, based on a concept introduced by Nozik [7].

WO_3 is not an ideal metal oxide, because it has a relatively high overpotential for water oxidation. This overpotential is determined by the kinetics of the water oxidation reaction at the surface of the photocatalyst, as explained in Chapter 1. It results in an extra voltage which has to be overcome, before water is oxidised. A first basic study by Valdes *et al.* showed that an overpotential of at least 1.04 eV can be expected for water oxidation over WO_3 [8]. In electrochemistry, non-photoactive IrO_2 and RuO_2 are oxygen evolution catalysts which induce low overpotentials [9, 10]. A way to improve photoanodes is by introducing those oxygen evolution catalysts on the semiconductor surface [11, 12]. Literature shows that the efficiency of WO_3 photoanodes can be enhanced by introduction of several co-catalysts [13, 14]. The addition of IrO_2 on WO_3 was beneficial, with stable performance in acidic conditions [15].

In this chapter, we first demonstrate that a direct interface between the Pt substrate and electrolyte limits the efficiency of a photoanode. We show that insulation (coverage) of the exposed Pt substrate with TiO_2 enhances the performance of the photoelectrode. In addition, electrodeposition of IrO_2 will be demonstrated to promote the water oxidation activity. Together with the insulating TiO_2 layer, the photocurrent was enhanced by 140 % compared to the value of an as synthesized Pt/ WO_3 photoanode.

6.2 MATERIALS AND METHODS

6.2.1 Sample growth

The WO_3 samples were grown by a hydrothermal procedure, which is described in detail in Chapter 5, and which has been published [4]. The substrate consists of a Si<100>-wafer with a 200 nm SiO_2 layer, a 13 nm Ti-adhesive layer, and a 100 nm Pt layer (see chapters 1

and 5). The precursor solution for WO_3 was prepared by solving 250 mg H_2WO_4 (Sigma Aldrich) in 2 mL 30% H_2O_2 (Sigma Aldrich). This was diluted by demineralized water to 25 mL to the end concentration of 0.04M. Overnight the excess H_2O_2 in the precursor solution was removed by inserting small Pt pieces ($\sim 1\text{cm}^2$). Si/SiO₂/Pt substrates were immersed in the precursor solution in a hydrothermal vessel (Parr Instruments). The vessel was closed and put in an oven for 18 hours at 170 °C. After a natural cool down, the WO_3 samples were calcined at 700 °C in air, to change the WO_3 from a tungsten hydrate to the monoclinic phase.

6.2.2 Addition of TiO_2 .

To deposit TiO_2 on the substrate by spin coating, TiCl_4 was solved in methanol to a concentration of 0.025 M. This was spin coated with a speed of 6000 rpm for 30 seconds. A 400 °C calcination for 1 hour was performed to convert TiCl_4 into TiO_2 .

6.2.3 Electrodeposition of IrO_2

For the electrodeposition of IrO_2 , first IrO_x nanoparticles were synthesized from K_3IrCl_6 following a method reported by Zhao *et al.* [16]. A 0.2 mmol solution was hydrolysed by increasing the pH to 13 with a 3.0 M NaOH solution. This was kept overnight in the refrigerator. The formed $\text{Ir}(\text{OH})_6^{2-}$ was dehydrated using an acid condensation at 0 °C until pH 1 by addition of a 70% HNO_3 solution. The electrodeposition of IrO_x nanoparticles was performed by chrono-voltammetry, in a three electrode configuration, coupled to a Versastat 3 (Princeton). A scheme of the three-electrode configuration is shown in Fig. 1A, where the photoanode was applied as working electrode (W.E.). The W.E. consisted of the sample, which was connected to the potentiostat by a stainless steel alligator clamp attached to the Pt substrate. The counter electrode (C.E.) was a 1.5 cm² Pt mesh and the R.E. was a 3.0 M Ag/AgCl reference electrode (R.E.) with a potential of +0.210 V vs. NHE

Figure 1: Scheme of the three-electrode cell configuration used for electrochemical experiments. A) Configuration used for electrodeposition of IrO_x nanoparticles. B) Three-electrode cell configuration for photoelectrochemical characterization of the obtained

(BASi). The three electrodes were placed in a beaker glass together containing the IrO_x particles. For the deposition, a current of 100 μA was applied, and the deposition was considered complete when a charge of 200 mC was reached. To obtain fully oxidized IrO_2 , a 400 °C calcination step was performed for 1 hour after completion of the electrochemical deposition.

6.2.4 Photoelectrochemical characterization

Photo electrochemical characterization was done by using a three-electrode cell configuration, which was similar to the configuration for the electrodeposition (Fig. 1B). The C.E. and R.E. were the same as used for the deposition, and the photoanode was applied as W.E.. For the photoelectrochemical experiments, the three electrodes were placed in a 25 mL glass reactor. In this way, the W.E. could be illuminated. Illumination was performed using a 1.5 AM solar simulator (model 10500, ABET Technologies). The used electrolyte in the reactor was 25 mL of a 0.3M H_3PO_4 solution (pH 1.5). Two methods were used for the photoelectrochemistry measurements, namely cyclic voltammetry and chronoamperometry. In cyclic voltammetry the voltage was swept with 50 mVs^{-1} and 10 cycles were taken. The 10th cycle was used as actual measurement, the first 9 were disregarded for stability reasons. In the chronoamperometry measurements, the current was measured over time, while applying a constant voltage. It was possible to use the three-electrode cell configuration in combination with a gas chromatograph (GC), a Compact GC (Interscience) equipped with a pulsed discharge detector (PDD). (The GC had two columns in series: a Q-bond to remove H_2O out the sample and a molsieve to separate H_2 , O_2 and N_2 . These measurements were done using a continuous flow method, where a 7N helium purge (10 mL/min) was used to transfer the products to the GC. Measurements could be done with a minute time resolution and it was possible to measure concentrations up to a few ppb. Every ppb measured by the GC corresponds to 0.446 pmol, when considering the flow rate, temperature (298 K), pressure (1 Atmosphere), and the ideal gas law. In this way, it was possible to correlate the current to the produced amounts of hydrogen and oxygen.

6.3 RESULTS

In this chapter, the effect of TiO_2 (via spin coating) and IrO_2 (via electrodeposition) on the photocurrent achieved with Pt/WO_3 photoanodes is discussed. First, the photoresponse of these components was evaluated by deposition on a $\text{Si}/\text{SiO}_2/\text{Pt}$ substrate individually. IrO_2 showed superior oxidation characteristics compared to TiO_2 at Pt and to Pt itself. The cyclic voltammetry measurements are shown in Fig. 2. The enhancement of the current under illumination for Pt/TiO_2 is comparable to the enhancement observed under illumination for a bare substrate. This is due to the increase in temperature under

illumination, instead of a photoresponse. As expected, the onset potentials did not change by the deposition of a TiO_2 layer on the Pt substrate.

The inset in Fig. 2 shows a blow-out of current range insufficient for water oxidation. In this potential range a double layer, the so-called Helmholtz layer, is formed at the metal/liquid interface [17]. This double layer is due to ionic species in the electrolyte, which mirror the charge of the Pt electrode, and adsorb on the Pt surface [18]. H_2O molecules surround these ions due to their strong dipole. The double layer results in a potential drop over the metal/electrolyte interface. The presence of this Helmholtz layer can be measured in a cyclic voltammetry measurement at lower potentials. The current at 1.1 V vs RHE decreased after addition of TiO_2 or IrO_2 , compared to the current measured for a bare Pt substrate. This is likely due to a decrease in the amount of ionic species adsorbed on the TiO_2 covered Pt surface, as compared to the bare surface, and indicates that the insulation of exposed Pt from the electrolyte will contribute to improved photocurrent values of the eventual WO_3 photoanode.

Figure 2: Photoelectrochemical characterization of spin coated TiO_2 and electrodeposited IrO_2 , used to enhance the enhancement of the photocurrent of WO_3 . This measurement is to analyse possible (photo)electrochemical properties of the different layers in a 0.3 M H_3PO_4 electrolyte. The inset shows the regime where the current is due to the presence of the double layer.

An attempt to deposit IrO_2 nanoparticles directly onto the WO_3 crystals in the absence of a TiO_2 protecting film, is shown in Fig. 3A. The IrO_2 nanoparticles did not end up on the WO_3 layer, but they mainly deposit on the Pt substrate in between the WO_3 crystals. Here the favourable electrochemical properties of Pt played a dominant role. To realize a direct WO_3/IrO_2 interface, a TiO_2 layer was spin-coated on the Pt/ WO_3 samples to insulate the Pt substrate from the solution, following the electrodeposition of IrO_2 nanoparticles. To confirm the deposition taking place, energy dispersive X-ray spectroscopy (EDX) was

performed to measure the atomic composition for a few areas (Fig. 3B) and a few points (Fig. 3C) of the sample after sequential deposition. Results of the measurements are shown in Table 1. The EDX measurements did not show a conclusive image of the exact place of the layers, but it gave a suggestion. Ti was only measured close to the substrate (spectra 22, 27). Further a trace of Ir was measured in point spectrum 25. A close examination of that point shows a brighter spot compared to the surroundings, indicative of a different material composition.

Figure 3: SEM images of A) Direct IrO₂ electrodeposition on Pt/WO₃ sample and B,C) electrodeposition on Pt/WO₃/TiO₂ samples. In B and C EDX surface and point analyses were done at the places indicated in the SEM images. Results are given in Table 1.

Table 1: EDX analyses for the spectra indicated in the SEM images of Fig. 3. The table shows the observed percentage for the specific elements measured in the EDX spectra

Element	Spectrum 22 (%)	Spectrum 23 (%)	Spectrum 25 (%)	Spectrum 26 (%)	Spectrum 27 (%)
Pt	69.9	-	15.9	-	20
Ti	0.2	-	5.1	-	-
Ir	-	-	0.0	-	-
W	18.8	70.0	65.6	79.1	66.1
C	5.4	3.9	0	0	0
O	3.8	22.1	13.4	20.9	13.9
Si	1.9	-	-	-	-
Al	-	3.9	-	-	-

Photoelectrochemical characterization of the Pt/WO₃ samples was done via cyclic voltammetry (CV), measuring the photocurrents before and after addition of the TiO₂ and or IrO₂ nanoparticles. The Pt/WO₃ sample used was the same for all samples. The results are plotted in Fig 4A. For every process step, a CV was measured in light and in dark, to study the effect of illumination. The measurements showed that the addition of TiO₂ to the Pt/WO₃ sample had an enhancing effect on the photocurrent, which increased by almost 0.25 mA/cm². This can be explained by the favourable electrochemical properties

of the TiO_2 -water interface, as discussed previously (Fig. 2). For verification, a sample was made by insulating the Pt from the electrolyte with a polymer instead of TiO_2 . This polymer was made by spin coating of a precursor solution of ethylene glycol and citric acid. For stability, this sample was characterized in a 0.3M $\text{H}_3\text{PO}_4/\text{K}_2\text{PO}_4$ electrolyte with pH 4 and the measurement is shown in Fig. 4B. Here a comparable enhancement of 0.25 mA/cm^2 of the photocurrent was measured as observed for TiO_2 .

After addition of IrO_2 the onset potential for water oxidation of the WO_3 was not changed, contrary to what was measured for Pt/IrO_2 , shown in Fig. 2. The dark current suggests that IrO_2 is not in direct contact with Pt, but that addition of TiO_2 results in the electrodeposition of IrO_2 nanoparticles directly on the WO_3 crystals. This is in agreement with the SEM characterization in Fig. 3 and the EDX analysis. Under illumination the photocurrent was enhanced significantly, by almost 0.75 mA/cm^2 .

Figure 4: 10th cycle of the cyclic voltammetry measurement under dark and light condition of a Pt/WO_3 photoanode before and after addition of A) TiO_2 layer and IrO_2 nanoparticles and B) a polymer layer.

Efficiency and stability of the composite electrode is demonstrated by chronoamperometry measurements shown in Fig. 5. These measurements were taken at the water oxidation potential 1.23 vs. RHE. During the measurements the light was alternated between on and off. The same trend as during the CVs was observed, namely the enhancement of the photocurrent after addition of a TiO_2 layer and the IrO_2 nanoparticles. The insulation of Pt shows an increase of the photocurrent of 45%. The IrO_2 gives an additional improvement of 63%, which means a total improvement compared to the original sample of 140%. Additionally, the current was stable during all three measurements. Even with the processing steps in between the measurements, the photoanode showed a good stability.

Figure 5. Chronoamperometry measurements at 1.23V vs. RHE in a 0.3M H_3PO_4 electrolyte. Measurements were taken before and after each addition of a layer. In total, an increase of 140% of the photocurrent was measured.

To test the origin of the enhancement of the photocurrent by the TiO_2 layer, a chronoamperometry measurement before and after addition of TiO_2 was combined with a direct measurement of the produced H_2 and O_2 , using gas chromatography. The measurement is shown in Fig. 6. The photocurrent and H_2 production both increased in the presence of TiO_2 . The photocurrent increased from 80 to 113 μA , an increase of 41%. The hydrogen production increased from 19.3 nmol/min to 25.7 nmol/min, which is an increase of 33%. These percentages reasonably agree. This indicates the TiO_2 layer improves the photocurrent, and does not contribute photocatalytically. Furthermore, the observed enhancement is similar to the enhancement observed for the sample used in Fig. 5, namely 41% vs 45%.

Figure 6: Chronoamperometry (CA) at 1.23 V vs RHE with corresponding gas chromatography analysis of a Pt/WO_3 photoanode before and after addition of a TiO_2 layer. On the left axis the CA current is plotted, and on the right axis the gas production measured by the GC is shown.

6.4 DISCUSSION

Two different effects enhanced the photocurrent after introducing TiO_2 and IrO_2 to the Pt/WO_3 photoanode. Both additions to Pt/WO_3 are schematically represented in Fig. 7. On the one hand, spin coating of a thin insulating layer of TiO_2 at the Pt substrate between the WO_3 crystals increased the photocurrent (Fig. 7B). This effect took place both with a TiO_2 and a polymer layer. On the other hand, electrodeposition of IrO_2 at WO_3 increased the photocurrent further (Fig. 7C), by improving the catalysis. In Fig. 2, it is clear that IrO_2 leads to a lower onset potential for water oxidation and showed superior oxygen evolution properties. The insulating TiO_2 layer also had an important contribution to the addition of IrO_2 , namely the electrodeposition happened on the WO_3 crystals instead of on the Pt substrate.

An explanation for the enhancement by the insulation of the Pt surface using deposition of a TiO_2 or a polymer layer, should be found at the interface between the Pt substrate and the electrolyte. Because the WO_3 layer is very porous, there is still a lot of Pt surface in contact with the electrolyte. SEM and EDX analyses showed that the TiO_2 layer was deposited mainly at the Pt substrate, in between the WO_3 crystals. Furthermore, the CV measurements in Figs. 4A and 4B of a Pt/WO_3 junction, before and after addition of an insulating layer, showed that the dark current decreased significantly after addition of the TiO_2 and the polymer layer. This means that covering of Pt with TiO_2 or a polymer will positively influence the Pt/electrolyte interface. Without the insulating layer, charge and ions accumulate at the Pt/liquid interface, see Fig. 7A. This results in a Helmholtz layer, and literature shows that this can result in a potential drop of 0.1–0.5 V [17]. An indication of the presence of a Helmholtz layer can be found in the cyclic voltammograms in Fig. 2,

Figure 7: Schematic overview of the several steps with the corresponding increase of the photocurrent in the samples.

where a small current was measured at potentials insufficient for Pt oxidation and O₂ evolution. This current represents the double layer, and the current decreased after covering the Pt substrate with TiO₂ or IrO₂. So, when charge builds up at the interface, a potential drop is created at the Pt/liquid interface. Electrons excited by illumination of WO₃ have to move into the metal substrate towards the C.E., where they will be used for H⁺ reduction. If negative charges accumulate on the substrate, the electrons excited in the WO₃ crystals encounter an extra resistance from the electric field at the interface. This will lower the electron transport from the semiconductor to the substrate, and thus the observed photocurrent.

The IrO₂ could be electrodeposited directly onto the WO₃ crystals, but only after the addition of the TiO₂ layer. The CV measurement in dark of the Pt/WO₃/TiO₂/IrO₂ showed a similar onset voltage compared to the CV measurement in dark of the Pt/WO₃/TiO₂ sample. When IrO₂ was in direct contact with the Pt, the onset voltage was significantly lower. One of the goals of the addition of IrO₂ was to lower the onset potential for water splitting, which unfortunately did not happen significantly. But the second goal, which was to increase the photocurrent, succeeded. The photocurrent measured at 1.23 V vs. RHE was more than double after addition of TiO₂ and IrO₂. The efficiency has increased significantly; about 140% in comparison to the as-synthesized Pt/WO₃ junctions.

The maximum photocurrent density measured after the addition of TiO₂ and IrO₂ was 1.8 mA/cm² at 1.23 V vs RHE. Based on the Shockley-Queisser limit, the maximum achievable photocurrent density possible for a WO₃ photoanode under 1.5 AM solar illumination is 6.0 mA/cm² [19, 20]. This means that the 1.8 mA/cm² achieved is 30% of the maximum current density. Compared to other studies of WO₃ photoanodes, the results obtained after improving the Pt/WO₃ with TiO₂ and IrO₂, are close to some of the highest photocurrent densities (~2.3 mA/cm²) reported for WO₃ photoanodes [21, 22].

6.5 CONCLUSION

We showed that contact between the Pt substrate and the electrolyte limits the photocurrent of the hydrothermal fabricated Pt/WO₃ photoanode. This effect can be explained by the metal/electrolyte interface, where a potential drop is created due to a double-layer. Electrons, which have to move from the WO₃ into substrate, feel a negative charge, which creates an extra resistance at the interface. Covering the Pt by an insulating thin TiO₂ or polymer layer decreased the potential drop at the metal/liquid interface, and lowered the resistance for electrons going from WO₃ into the Pt substrate. That a similar effect was measured by the addition of different (polymer) layers, indicates that, generally insulating Pt from the electrolyte will be effective. By co-addition of IrO₂ the efficiency was

enhanced with 140% compared to the original samples. The measured photocurrent density of $1.8\text{mA}/\text{cm}^2$ is close to the highest values reported for WO_3 photoanodes.

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CHAPTER 7

A CHEMICAL SOLUTION DEPOSITION METHOD TO FABRICATE A VISIBLE LIGHT ACTIVE RHODIUM DOPED STRONTIUM TITANATE PHOTOCATHODE

ABSTRACT

A chemical solution deposition method, based on a chelation route, was used to fabricate a Rh:SrTiO₃ layer on a Pt substrate. By spin coating multiple layers, it was possible to grow a dense, columnar structured Rh:SrTiO₃ layer of around 100 nm thickness. To increase the initially low photoresponse, when the Rh:SrTiO₃ layer on Pt was used as photocathode, the limitations were determined, and ways to increase the photocurrent explored. First, the effect of the Rh oxidation state on the resistance of the semiconductor layer was analysed, and second, the effect of the addition of a Pt co-catalyst to improve the proton reduction kinetics. Our experimental results indicate that the internal resistance of the Rh:SrTiO₃ layer is high ($\sim G\Omega$), and this was identified as the most important limitation of Rh:SrTiO₃ deposits in achieving high photocurrents. Slight improvements in photocurrent were observed when the oxidation state (Rh³⁺) and loading of Rh (5 wt-%) were optimized, as well as when Pt particles were added to the surface layer in contact with the electrolyte, but the values remained in the μA regime.

7.1 INTRODUCTION

A common strategy to develop efficient solar-to-hydrogen devices is to combine a silicon-based photovoltaic (PV) cell with a metal oxide photoanode [1, 2]. To reduce costs, it is beneficial to exchange the silicon solar cell for a less expensive photocathode, for example based on a metal oxide. A currently intensively explored oxide is Cu_2O . However, the stability of this oxide is low, and photocorrosion occurs in hours, when applied as photocathode for H_2 evolution. Unfortunately, numerous options for improvement as reported in the literature, appear not yet sufficient [3].

Another metal oxide often used in Z-scheme water splitting, is Rh-doped strontium titanate ($\text{Rh}:\text{SrTiO}_3$). This material can be used as photocathode for the half reaction of proton reduction [4, 5]. The synthesis and behaviour of this material in a slurry reactor was extensively discussed in Chapters 3 and 4. However, for incorporation in a photoelectrochemical cell, effective deposition of $\text{Rh}:\text{SrTiO}_3$ on a conductive substrate needs to be developed. Two methods have been published in the literature to fabricate a thin film of $\text{Rh}:\text{SrTiO}_3$: via pulsed laser deposition (PLD) [6], and via liquid-phase immobilization of photocatalytic $\text{Rh}:\text{SrTiO}_3$ particles, fabricated by a solid-state reaction [7]. The most active Rh-doped SrTiO_3 photocathode was made by PLD on a (0.05 wt-%) $\text{Nb}:\text{SrTiO}_3$ substrate [6, 8]. A doping concentration of 5% gives the highest current density of these films of around 1.1 mA/cm^2 , while the presence of Rh^{3+} instead of Rh^{4+} , induced a lower onset potential. Another study showed that immobilization of particles, synthesized by a solid-state reaction and deposited on an ITO substrate, resulted in small photocurrents [7]. For these substrates, maximum photocurrents were determined in the range of $50 \text{ }\mu\text{A/cm}^2$, with an optimized Rh-doping concentration of around 7%.

To grow a thin film of a perovskite material, there are several chemical solution deposition methods available, for example via a sol-gel route, a chelation route or a metalorganic decomposition route. [9]. Via a chelation route, literature shows it is a suitable method to grow dense SrTiO_3 layers [10-13]. An advantage of this route is the relatively simple solution preparation, which reduces also the hydrolysis of the compounds. Hoffman *et al.* show that with a one-step calcination, a highly dense columnar layer of SrTiO_3 can be grown, which was fabricated using multiple spins [13]. These processes are performed at relative mild temperatures, compared to a solid-state reaction.

In this chapter, we present a method to grow a Rh-doped SrTiO_3 layer at a Pt substrate via a chemical solution deposition procedure. There are different reasons to choose for this materials combination. First, literature shows it is possible to grow by a chelation route dense SrTiO_3 layers at a Pt substrate. Second, the lattice constant of SrTiO_3 is close to the lattice constant of Pt, which are $3.905 \text{ }\text{\AA}$ and $3.940 \text{ }\text{\AA}$, respectively. Furthermore, as introduced in Chapter 1, the idea is to use the photocathode in a photoelectrochemical

device for water splitting, following the concept for a photochemical diode proposed by Nozik [14]. The idea is to combine the photocathode with a WO_3 photoanode, which showed promising photocurrents when fabricated on a platinum substrate [15], see also Chapter 5. As method to grow the photocathode, we have chosen for a chelation process, because of the simplicity of the method, the relative mild temperature required for the deposition, and the results in literature showing it is possible to grow dense SrTiO_3 on a Pt substrate.

7.2 METHODS

7.2.1 Chelate Chemistry

1.028 g strontium acetate, dissolved in 10 mL acetic acid (0.5M), and 0.740 mL titanium(IV)isopropoxide, solved in 0.256 mL acetylacetone (ratio 1:1), were used as precursor solutions for the SrTiO_3 film. Rh doping was achieved by addition of Rh(III) acetylacetonate to the precursor solution of titanium(IV)isopropoxide. Chemicals were combined following the sequence shown in Fig. 1. After a clear solution was formed in the Rh: SrTiO_3 step, the precursor solution was diluted by methanol to a final concentration of 0.1M. A separate seed solution (0.03M) was made by further dilution of the precursor solution with methanol. As substrate a 1 cm^2 Si/ SiO_2 /Pt sample was used, which was made by sputtering a 13 nm Ti adhesive layer, followed by a 100 nm Pt film, on a Si wafer, passivated by a 200 nm SiO_2 layer. Such substrate was mounted on the spin coater, and kept in place by a vacuum connection. A 100 μL drop of precursor solution was pipetted

Figure 1: Process flow of the used chemical solution deposition method to grow the Rh:SrTiO₃ photocathode on a Si/Pt substrate.

onto the substrate, followed by spinning at 3000 rpm for 40 s. The main method consisted of putting the substrate directly in a preheated oven (700 °C) for 30 min. The spin and calcination process was repeated 5 times, to reach the required layer thickness. The first layer functioned as a seeding layer, which was not included in the final number of layers on the substrate. The seeding layer was added to enhance the crystallinity of the layer [16].

7.2.2 Materials characterization

The Rh:SrTiO₃ photocathodes were characterized by several techniques, being high-resolution scanning electron microscopy (HR-SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). HR-SEM imaging was done with a Nova 600-nanolab HR-SEM (FEI instruments), and for the XRD characterization a Bruker D2 powder diffractometer (equipped with a Cu K_α source) was used. The XPS and UPS measurements were performed in the same ultra-high vacuum chamber, sharing the same detector. The excited electrons were collected by a PHOBIOS 100/150 hemispherical energy analyser (Specs GmbH). A XR 50 X-ray source (Specs GmbH) was used for the XPS measurements, based on an Al K_α source with a main excitation at 1486.6 eV. For UPS, an UVS 10/35 He lamp (Specs GmbH) was used, emitting a photon energy corresponding to 21.218 eV. The UV source contained a mixture of He I and He II lines.

7.2.3 Photo-electrochemical Characterization

Electrochemical characterization of the layers was done in a three-electrode configuration, consisting of a working electrode (W.E.), counter electrode (C.E.) and reference electrode (R.E.). As W.E. the sample was used, and the C.E. consisted of a Pt mesh (~2 cm²). As R.E. a commercial 3.0 M Ag/AgCl reference electrode (BESI) with a potential of 0.210 M vs. NHE was used. The electrodes were connected to a Versastat 4 potentiostat (Princeton Applied Research), using stainless steel crocodile clamps. The electrodes were subsequently inserted in a 25 mL optical glass cuvet (Hellma), containing the electrolytes. Two electrolytes were used for the experiments. To compare the photocurrents with literature, a neutral 0.01 M K₂SO₄ solution (pH 7) was used. Further, an acidic 0.3M H₃PO₄ solution (pH 1.5) was used for characterization in a suitable electrolyte for practical application of WO₃.

7.2.4 Conductivity characterization

The resistance of the semiconductor layers was analysed using a sourcemeter (Keithley 2400). Electrical contacting of the Rh:SrTiO₃ layer was done in a low temperature probe station (500-ST, Jaris Technology). The W probes were landed softly on the semiconductor layer. Direct contact with Pt could be made, by puncturing the W needle through the semiconductor layer.

7.3 RESULTS AND DISCUSSION

7.3.1 Morphology

Scanning electron microscopy (SEM) was used to characterize the morphology of the spin-coated layers, and to characterize the influence of the precursor concentration and doping on the final morphology. In Fig. 2, three samples are shown, obtained after five spinning cycles. Figure 2A and D show a sample without doping and made with a 0.01 M precursor solution. A 5%Rh-doped sample made with the 0.01 M precursor solution is shown in Figs. 2B and E. The sample in Figs. 2C and F is a 5%Rh-doped sample, made with a 0.02 M precursor solution.

Addition of Rh to the precursor solution obviously did not influence the obtained morphology of the layer. A 0.1 M precursor concentration resulted in dense layers. The layer is about 100 nm thick, since every spinning step added about 20 nm to the stack. By using a higher concentration, it was possible to grow layers faster, and each spinning step resulted in the addition of about 40 nm instead of 20 nm. However, the layers obtained with the higher precursor solution look more porous, and do not have the columnar structure. A further important drawback of the higher concentration is the larger amount

Figure 2: SEM images of the morphology of varying concentration of solution and Rh concentraion for 5 sequent layers. A,D) undoped SrTiO₃ with 0.1 M. B,E) 5%Rh-doped SrTiO₃ with 0.1M. C,F) 5%Rh-doped SrTiO₃ with 0.2M solution.

Figure 3: Electrodeposition of Pt on a 5% Rh:SrTiO₃ photocathode in a 0.8 mM H₂PtCl₆ solution for two applied potentials. The black curve shows a deposition run at -0.2 V vs. Ag/AgCl and the red curve a deposition at -0.7 V vs. Ag/AgCl. The insets in the graph show the SEM characterization of the Pt particles belonging to the applied potentials over 10 minutes of deposition.

of imperfections enclosed over the total layer, which are visible as pyramid-type shapes in Figs. 2E and 2F. Creation of thicker Rh:SrTiO₃ layers by additional spinning-calcination cycles resulted in less homogeneous films, with rough surfaces (not shown). Therefore, it can be concluded that the optimized film thickness for high photocurrent efficiency likely amounts to approximately 100 nm.

The current vs. time curves during electrodeposition of Pt on as prepared Rh:SrTiO₃ in a three-electrode cell configuration are shown in Fig. 3. The electrolyte consisted of a 0.8 mM H₂PtCl₆ solution. In Fig. 3 the insets show two SEM measurements of the thus deposited Pt particles. Please note that the scale of the images is different. What is apparent is that the applied voltage and resulting current, largely determines the size and density of the Pt particles. A more negative current results in smaller particles, deposited more densely and homogeneously over the surface of the photocathode.

7.3.2 XRD

By X-ray diffraction (XRD), the crystal phase of the Rh-doped SrTiO₃ layers was characterized. To allow analysis by powder diffraction, the 5% 0.01 M precursor solution was calcined at 700 °C in the absence of the Pt substrate, a 1% Rh-doped SrTiO₃ powder was obtained. The crystallinity of this powder was compared to the crystallinity of 1%Rh-doped SrTiO₃ powder, made by solid-state reaction, according to the recipe reported in chapter 3 [17]. The X-ray diffraction patterns of the powders are shown in Fig. 4A, and

show peaks at similar angles, in agreement with the literature [17]. The measurements show that by calcination at 700 °C, the precursor solution was converted to Rh:SrTiO₃. The small intensity at approximately 27 degrees 2theta can likely be assigned to SrCO₃, used as precursor for SrTiO₃ when prepared by solid state reaction.

The XRD characterization of the 5%Rh:SrTiO₃ photocathode is shown in Fig. 4B (red line). Since the thickness of the film is low, the XRD pattern is dominated by the Si/SiO₂/Pt substrate (black line). However, at 46.3° a peak is visible, which corresponds to the [200] plane of SrTiO₃. For a more in-depth study, a Rh:SrTiO₃ layer was deposited with a different, more porous morphology [13]. To this end, every spin coated layer was annealed at 300 °C, and only after the fifth cycle a calcination temperature of 700 °C was applied. In addition, SrTiO₃ was deposited on an Au substrate according to the method with the high-temperature annealing cycles. In contrast to the standard procedure, which resulted in texturing of the layer in the [200] direction, the alternative method (blue line) and the Rh:SrTiO₃-layer grown on the Au substrate (green line) did not show this preferred orientation. However, a diffraction line corresponding to the [110]-plane can now be observed. Further, a peak corresponding to the [221]-plane is visible in the blue diffractogram also.

Figure 4: X-ray diffraction patterns of Rh:SrTiO₃ prepared by various procedures. A) Comparison between a powder made from the precursor solution (black), and by solid state reaction (red). B) Comparison of 5%Rh:SrTiO₃ films, either prepared by the standard procedure on Pt (red) or Au (green), or via consecutive steps at lower annealing temperature (300 °C). The pattern of a Si/SiO₂/Ti/Pt sample is included (black), for comparison.

7.3.3 Photoelectrochemical characterization of the as-synthesized samples

The photoelectrochemical characterization of the samples was performed in conditions similar to the literature, i.e. in a 0.01 M K₂SO₄ electrolyte, with a pH of 7. The result is shown in Fig. 5. The cyclic voltammogram was recorded from -1.0 to 1.5 vs Ag/AgCl [7]. In

the inset of Fig. 5, a chronoamperometry measurement is shown, taken at the potential of -0.4 V vs. Ag/AgCl, which is a potential which is insufficient for H_2 evolution over the Pt substrate. The difference in current between dark and light conditions is very small ($\sim 10 \mu A/cm^2$), and Rh:SrTiO₃ did not result in a shift of the onset potential for H_2 evolution (< 0.1 V). Moreover, the shape of the CV is similar to a CV characteristic for electrochemical water splitting with two Pt electrodes [18]. This suggests there is still a strong contribution of exposed Pt to the obtained (photo)current. The small response in the cyclic voltammogram could be the result of heating of the solution by illumination. However, the chronoamperometry measurement confirms the light responsive nature of the (photo)current, since the light on-off transient is much faster than the anticipated temperature swing of a 25 mL electrolyte solution. The cyclic voltammogram can be interpreted as follows. Hydrogen adsorption (or desorption) occurs over the Pt substrate at -0.7 V vs Ag/AgCl. The high current below this value can be assigned to hydrogen evolution. The peak around -0.3 V vs. Ag/AgCl is due to reduction of a Pt-oxide film, formed on the Pt substrate at 0.6 V vs. Ag/AgCl.

The small effect of light on the current intensity at variable potential, and in the chronoamperometry measurement at fixed potential, might be related to the doping level of Rh, which is lower than the 7%-doping level reported as optimal for a photocathode made by powder immobilization [7]. However, a high photocurrent density was reported for a 5% Rh-doping level when the photocathode was made by PLD [6]

Figure 5: Cyclic Voltammetry of a 5%Rh-doped SrTiO₃ photocathode in a 0.01M K₂SO₄ solution. In the inset a chronoamperometry experiment is shown, obtained at -0.4 V vs Ag/AgCl, where the light was switched on or off during the measurement.

To further investigate the origin of the very low photocurrent of our photocathode, several parameters were optimized, inspired by a study reported for hematite (Fe_2O_3) in the literature [19], namely:

- The oxidation state of Rh
- The resistance of the metal-semiconductor interface
- The intrinsic conductivity of the semiconductor
- The catalysis at the surface of the photocathode

We will address these variables in the following sections.

7.3.4 Determination of the effect of loading and oxidation state of Rh

In the literature first-principle calculations suggest that efficient $\text{Rh}:\text{SrTiO}_3$ photocathodes should be composed of Rh^{3+} [20]. An advantage from Rh^{3+} doping over Rh^{4+} is the absence of an unwanted donor level in the middle of the bandgap, which will lead to increased recombination of excited electron hole pairs [8]. The XPS spectrum of our $\text{Rh}:\text{SrTiO}_3$ film is shown in Fig. 6. Clearly the oxidation state of Rh is 4+ in the films as prepared by annealing at 700 degrees C. Only after reduction of the film at 700 °C for 12 hours in a 2% H_2 in Ar flow, the presence of Rh^{3+} becomes evident.

Figure 6: XPS results of the 5%Rh:SrTiO₃ layer. Binding energies were determined on the basis of fixing the Ti 2p_{3/2} intensity at 459.1 eV. Rh^{4+} is present in the films after calcination at 700 °C. For comparison, the XPS spectrum of a film treated in 2 vol-% at 700 degrees C is shown.

Photoelectrochemistry with reduced samples and variable Rh concentration

Cyclic voltammograms of the samples after H_2 treatment and variable Rh content are shown in Figs. 7A and 7B. In Fig. 7B, the dark current was subtracted from the current obtained in illuminated conditions, for clarity. Fig. 6A shows the cyclic voltammetry measurement of the hydrogen treated 1% Rh-doped SrTiO_3 photocathode. Comparing Figs. 7A and 5, it is clear that the lower Rh-cation loading and/or hydrogen treatment lead to a stronger light response.

Figure 7: Cyclic voltammetry characterization of H_2 -reduced Rh:SrTiO₃ for a variety of doping concentrations. A) Cyclic voltammetry of a 1% Rh:SrTiO₃ photocathode in a 0.3 M H_3PO_4 electrolyte (pH 1.5). B) Difference between light and dark conditions for several doping concentrations.

This is further corroborated by the data shown in Fig. 8. The photoresponse is much larger for a 2%-doped sample as compared to a 5%-doped sample. At low potentials the photoresponse disappears, which can be explained by the presence of the Pt substrate, which is very effective in hydrogen evolution in dark conditions at potentials close to 0 V vs RHE. In conclusion, H_2 treatment and lowering of the Rh concentration to about 1 wt-% positively affect the photo-responsiveness of the films prepared by chemical solution deposition.

Figure 8: Cyclic Voltammetry of a 2% and 5% H_2 reduced Rh:SrTiO₃ sample, where the current was responsive to light or dark conditions.

7.3.5 The Rh:SrTiO₃/Pt interface

To obtain high photocurrents, the contact between the semiconductor and the conducting substrate is critical, as well as the alignment of the work functions of the semiconductor and the metal. Formation of a Schottky barrier at the interface should be prevented, since this can lead to a high resistance, preventing flow of electrons from the Pt substrate to the Rh:SrTiO₃ semiconductor film. Ultraviolet photon spectroscopy (UPS) spectra of Si/SiO₂/Pt and Si/SiO₂/Pt/2%Rh:SrTiO₃ are shown in Fig. 9A. Based on these UPS spectra (see insert in Fig. 9A), the work function of Pt was determined at 4.5 eV and of Rh:SrTiO₃ at 3.5 eV. Since the bandgap of Rh:SrTiO₃ is 2.4 eV [17], the energy-level diagram of the composite can be drawn as shown in Fig. 9b. The electrons formed by illumination of the Rh:SrTiO₃ layer will be directed to the surface of the photocathode, where they can react with protons to form hydrogen. The holes have the tendency of moving to the Pt substrate, where they can recombine with electrons generated by the water oxidation reaction on the (photo)anode. Jin *et al.* reported for an undoped SrTiO₃/Pt junction a similar, favourable, Schottky barrier [21], and principally the metal-semiconductor interface should not be the main factor in limiting the photocurrent of Rh:SrTiO₃.

Figure 9: A) Ultraviolet photoelectron spectroscopy measurement of the Si/SiO₂/Pt substrate in the absence and presence of a 2%Rh-SrTiO₃ layer. The inset shows a zoom of the crossing of the band edge, from which the work function is determined. B) Schematic representation of the Pt/Rh:SrTiO₃ interface, where a (favourable) Schottky barrier was formed.

7.3.6 Conductivity

I-V curves of two Rh:SrTiO₃ substrates are compared with a curve of 1% -Nb-doped SrTiO₃ sample, made by a similar CSD procedure, in Figs. 10A and 10B respectively. The applied voltage was swept between negative and positive values and the corresponding current was measured. The schematic illustrations added to the graphs, show the contacting of samples by the probes during the measurements. To obtain the *I-V* curves of Rh:SrTiO₃, a

soft approach with the W probes at the semiconductor layer was essential. When both probes punctured through the semiconductor layer, it resulted in a linear I - V curve, which is characteristic for a metal. The measurements of Rh:SrTiO₃ showed a characteristic non-linear I - V curve. Further, the current measured when a positive potential was applied is 1000x smaller as compared to the current measured for Nb-doped SrTiO₃ (Fig. 10B). The asymmetric I - V curve of the Pt/Nb:SrTiO₃ junction corresponds to I - V curves reported in the literature for similar Pt/Nb:SrTiO₃ junctions [22]. The current measured under a negative applied potential was ~10nA, see inset of Fig. 9B, where a current of 1.5 μ A was measured under a positive applied potential. The asymmetry shows there is a Schottky barrier at the interface, which results in the diode like behaviour of the Pt/Nb:SrTiO₃ interface. The I - V curve shows electrons can flow easily from Pt substrate into the Nb:SrTiO₃ layer, and via the 2nd W Probe to the ground. This asymmetry was not measured for the Rh:SrTiO₃ samples. The curve shapes of the 2% and 5% doped samples are similar, although the current measured for the 5% Rh doping was about 3x higher. This can be explained by the extra charge carriers introduced by the doping inside the SrTiO₃. This relation between the doping concentration and conductivity has been observed previously in other n- and p-type doped SrTiO₃ systems [23].

The large difference between p- and n-type doped SrTiO₃, indicates that the high resistance is possibly depending more on the type of doping (creating p, or n-type semiconductor behaviour), than on the applied method (CSD) used to fabricate the modified SrTiO₃ layers. However, literature shows that the conductivity should not directly differ between n- and p-type doping [23, 24]. Where Nb⁵⁺ is used frequently to introduce donor levels in SrTiO₃, mobility studies in literature on p-type SrTiO₃ use mostly other dopants, like In³⁺, to replace Ti⁴⁺ [24]. An important difference between Rh⁴⁺ and In³⁺ as p-type doping, is that Rh⁴⁺ has the same number of electrons in the outer shell as Ti⁴⁺. This will not result in extra free charge carriers in the SrTiO₃ lattice, which could contribute to an enhancement of the conductivity. The XPS study in Fig. 5 showed, that with a H₂ treatment, it was possible to reduce Rh⁴⁺ partly into Rh³⁺, which creates the extra free charge carriers inside SrTiO₃.

Another cause of the low conductivity could be the low degree of crystallinity of the photocathode, and therefore the presence of a lot of defects in the material. The absence of such defects was already identified by Kawasaki et al. to be one of the main reasons for the superior photocurrent of the Rh:SrTiO₃ photocathode made by PLD [6], in comparison to the immobilized powder photocathode reported by Iwashina et al [7]. A high crystallinity of SrTiO₃ could be obtained by calcination at around 1100°C. However in our study, the temperature range which could be used was limited up to 800°C by the Pt substrate.

Figure 10: A) IV-curves measured by contacting W needles with respectively 2%Rh:SrTiO₃ (red) or 5% Rh:SrTiO₃ (blue) and the Pt substrate. B) A similar measurement for a 1%Nb:SrTiO₃ film (prepared by chemical solution deposition using Nb AcAc). The inset is a zoomed image to make the current visible, when a negative potential is applied.

7.3.7 Addition of a Pt co-catalysts

Another factor limiting the photocurrent could be insufficient catalytic activity of the surface for electron transfer to protons. To test this hypothesis, the effect of the addition of Pt nanoparticles, highly effective for proton reduction, on the achievable photocurrents was evaluated. The photocurrent obtained with a platinized 2%Rh:SrTiO₃ photocathode containing the small nanoparticles in high density (Fig. 3), is compared to the photocurrent of the same sample without the Pt nanoparticles in Fig. 11A. The addition of the Pt particles enhances the photocurrent of 2% Rh:SrTiO₃, which is particularly evident from the curves in the inset of Fig. 11A. In the potential range, which is insufficient for proton reduction at the Pt substrate (0.6 V to 0.1 V vs. RHE), before the addition of a Pt co-catalyst, illumination increased the current with about 20 μA/cm². The addition of Pt resulted in a doubling of this difference to about 40 μA/cm². This indicates to more efficient catalysis at the photocatalyst surface and this will decrease the recombination.

In Fig. 11B the effect of Pt nanoparticles at the photocurrent is indicated by subtracting the dark current from the light current. In contrast to the results in Fig. 7B, without the Pt co-catalysts, the highest doping concentration showed the largest difference (~70 μA/cm²) between light and dark. This is in line with the conductivity measurements, where the highest conductivity was measured for the highest doping concentration. It seems that the improved reaction rates at the surface of the Rh:SrTiO₃, decreased the recombination chance of the electron-hole pairs inside the Rh:SrTiO₃ photocathode. Logically, the lower chance of recombination will benefit the photocathode with the highest number of scattering centres the most, which is the 5%Rh:SrTiO₃ sample.

Figure 11: Cyclic voltammetry characterization after addition of Pt co-catalysts on H₂-reduced Rh:SrTiO₃ for a variety of doping concentrations. All Pt depositions were done at -0.7V vs. Ag/AgCl to deposit homogenously small nanoparticles at the photocathode. A) Cyclic Voltammetry of a 2%Rh:SrTiO₃ photocathode in a 0.3M H₃PO₄ electrolyte (pH 1.5). B) Difference between light and dark after addition of a Pt co-catalyst for several doping concentrations

7.4 CONCLUSION

We showed a CSD method for the fabrication of a Rh:SrTiO₃ photocathode at a Pt substrate results in homogeneous dense layers. The photocathode showed a very small photoresponse and we did not observe a clear shift in the onset potential for H₂ evolution. We evaluated several properties of the Rh:SrTiO₃ to find the limitations and possibly improve the photoactivity. Optimizing the Rh:SrTiO₃ via a H₂ treatment and the addition of a Pt co-catalyst resulted in a photocurrent of $\sim 70 \mu\text{A}/\text{cm}^2$, however the onset potential for H₂ evolution still did not improve significantly. Furthermore, it is difficult to distinguish the exact contribution of a photoeffect by Rh:SrTiO₃ to current enhancement from a contribution due to a temperature increase. The low conductivity of the Rh:SrTiO₃ layer was identified as an important limitation towards high photocurrents, which seemed to be caused by a combination of the low crystallinity of the semiconductor and the Rh dopant inside the SrTiO₃. The difference in conductivity between Nb and Rh doping, indicates that finding an alternative for the Rh doping will be required to obtain an effective photocathode. Further, the activity of the Pt substrate towards the H₂ evolution reaction, indicates the importance of the substrate, and an alternative back electrode for Rh:SrTiO₃ will allow to better analyse the effectiveness of the layer. Work done over the last decades on optimizing hematite photoanodes, shows that by changing the fabrication methods and the properties of the photoelectrode, substantial improvements can be realised.

7.5 REFERENCES

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CHAPTER 8

TOWARDS VISIBLE-LIGHT-INDUCED WATER SPLITTING ON A CHIP

ABSTRACT

In this chapter we describe the results of the integration of WO_3 and $\text{Rh}:\text{SrTiO}_3$ thin films into a photoelectrochemical water splitting cell. First the thin films were each deposited on conductive Pt substrates, and electrically connected via a potentiostat. A photocurrent of $10\text{ }\mu\text{A}$ was achieved upon illumination of both films simultaneously. Unfortunately it was not possible to assign this (low) current to full water splitting. Only hydrogen was formed upon simultaneous illumination of both semiconductors when deposited onto opposite sides of one Pt film, via the deposition methods for WO_3 and $\text{Rh}:\text{SrTiO}_3$ developed in Chapters 5 and 7. These results are discussed on the basis of the morphology of the films, and (photo)electrochemical characterization.

8.1 INTRODUCTION

To sustain the transition to renewable energy utilization, development of efficient energy storage systems is required. Storage of solar energy can be achieved by photocatalytic or photoelectrochemical water splitting technologies, yielding hydrogen. A solar-to-hydrogen efficiency up to 22.8% should theoretically be possible for a photoelectrochemical cell, in which two semiconductors are combined [1]. In practice, a water splitting efficiency up to 4.7% has been achieved by solar illumination of a silicon-based photovoltaic (PV) cell in combination with a metal oxide photoanode [2, 3]. However, a feasibility study by Pinaud *et al.* shows that the costs of hydrogen produced via such photoelectrochemical cell will be too high, caused by the high costs of PV materials [4]. When it would be possible to change the silicon-based PV for a photocathode containing a cheap, abundant and stable metal oxide material, this would lead to significantly lower costs. Various attempts for effective hydrogen formation based on this concept have been reported in literature. Kato *et al.* [5] have combined WO_3 and $\text{Rh}:\text{SrTiO}_3$ for Z-scheme based oxygen evolution and hydrogen evolution, using electron mediators to transfer electrons between these materials. As demonstrated in Chapters 3 and 4, Z-scheme water splitting with mediators such as $\text{Fe}^{2+}/\text{Fe}^{3+}$ is not as effective as previously proposed [6]. On the other hand, composites of two photocatalysts have been demonstrated to be capable of full water splitting without an electron mediator [7-9] by establishing physical contact, although overall efficiency was low. In this chapter, we discuss an approach to integrate the photocathode and photoanode materials, inspired by the photochemical diode principle proposed by Nozik [10], in a wired and unwired configurations, like reported in literature [11]. The wired and unwired configurations are schematically shown in Fig. 1. In the wired configuration, two separate photoelectrodes are connected via an external circuit, and both are facing forward to the source of illumination. We have used a combination of WO_3

Figure 1: Simplified schematics of the two configurations studied in this chapter. A) The unwired geometry, where the WO_3 photoanode and $\text{Rh}:\text{SrTiO}_3$ photocathode are deposited at the opposite sites of a 500 nm thick Pt divider. B) The wired configuration, where the photoanode and photocathode are deposited separately on two different $\text{Si}/\text{SiO}_2/\text{Pt}$ substrates, and connected via a potentiostat.

and Rh:SrTiO₃, which are deposited on Pt substrates, as base case for evaluation full water splitting, since many data of this Z-scheme system in other configurations is available in the literature. Besides the photocurrents and hydrogen quantities achieved with such devices, the work functions of the individual components were measured by ultraviolet photoelectron spectroscopy (UPS), and on the basis of these experiments the electronic band structure of the device is discussed. Finally directions for improvements are proposed.

8.2 MATERIALS AND METHODS

8.2.1 Fabrication

For the wired configuration, the substrates for the photoelectrodes were made by sputtering a 13 nm adhesive Ti layer and 100 nm Pt on a 500 μm thick Si<100>-wafer, on which a 200 nm SiO₂ layer was present. The schematics of the micro-fabricated Pt divider used for the unwired configuration is shown in Fig. 2A. The divider was fabricated in collaboration with LNT – VNUHCM (Ho Chi Min City, Vietnam). The used process was based on a process developed for a Pd membrane [12]. Contrary to the Pd membrane, the Pt film was sputtered on the front side and not at the back side of the Si₃N₄ sieve. The Pt divider was fabricated using an oxidized Si wafer, which was back etched through with 400 $\times$ 3500 μm slits. A 1 μm thick Si₃N₄ layer covered the wafer on the front side, which was transformed into a microsieve by dry etching of Si₃N₄. The Si₃N₄ layer contains pores with diameters of 5 μm to 50 μm . A closed 500 nm thick Pt layer covered the sieve structure. In Fig. 2B a scanning electron image (SEM) shows the front side of the Pt divider. The deeper-lying circular-shapes in the structure are due to the pores of the Si₃N₄, of which the front side is covered by the Pt film. At these areas, the Pt layer is free hanging, and accessible at both sides for the electrolyte.

Figure 2: The Pt divider used for integration of both photocatalysts into one unwired device. A) The schematics of the Pt divider shows the dimensions and materials. B) A SEM image of the Pt divider.

The goal was to immobilize a layer of Rh:SrTiO₃ and WO₃ at each side of the Pt divider. Procedures to deposit these catalysts were discussed in Chapters 5 and 7 of this thesis. In Fig. 3 the order of deposition and the individual steps are briefly summarized. Rh:SrTiO₃ was deposited at the front side of the Pt divider via the chemical solution deposition method discussed in Chapter 7. A precursor solution was made by solving Ti(IV) isopropoxide and Rh acetylacetonate in acetyl acetone, and Sr acetate in acetic acid, and mixing the solutions in stoichiometric ratio. The mixture was diluted with methanol to a final concentration of 0.1 M. The precursor solution was deposited on the Pt substrate via multiple rounds of spin coating, to achieve layers of sufficient thickness. Every round of spin coating was followed by a calcination step at 700 °C. Subsequently, a hydrothermal method was used for selective deposition of WO₃ at the Pt in the slits of the Si support. The detailed procedure and results are explained in Chapter 5 [13]. The process started by making a precursor solution by solving 125 mg tungstic acid in 4 mL 30% H₂O₂. This was diluted to 25 mL with demineralized H₂O to a final concentration of 0.02M. The substrate was placed vertically in a hydrothermal vessel containing the solution, and treated for 18 hours in an oven at 170 °C. Afterwards the sample was removed from the vessel and rinsed with H₂O. A 675 °C annealing step under atmospheric conditions for 12 hours was performed to convert WO₃-hydrates into monoclinic WO₃.

Figure 3: Schematic process flow for the deposition sequence of the Rh:SrTiO₃ and WO₃ films on the Pt divider, to create the unwired configuration. In Step 1, Rh:SrTiO₃ (orange) is spin coated on the front side of the Pt divider, which should fully cover Pt. In Step 2, WO₃ (red) is grown by a hydrothermal method at the backside.

8.2.2 Characterization

SEM

Electron microscopy images of the divider were obtained using a Nova 600-nanolab HR-SEM (FEI instruments).

UPS

UPS spectra were recorded to characterize the work functions of the different materials in the system. As UV source, a UVS 10/35 He lamp (Specs GmbH) was used, emitting a photon energy of 21.218 eV. The UV source contained a mixture of He I and He II lines. The excited electrons were collected by a PHOBIOS 100/150 hemispherical energy analyser (Specs GmbH). The kinetic energy measured of the excited electrons was subtracted from the photon energy to determine their binding energy. The difference between the photon energy and the electrons with the highest binding energy was calculated to determine the work function of the material. The substrates were externally biased with a voltage of 4.63 V during the measurements. The UPS system was calibrated with an ozone-cleaned Au sample.

Diffuse Reflectance UV-VIS

The band gaps of WO_3 and Rh:SrTiO_3 were determined out of the adsorption spectra following procedures used in the literature [14, 15]. The reflectivity of the photocatalytic powders was measured via diffuse reflectance ultraviolet-visible (UV-VIS) spectroscopy. The reflectivity was measured using an Evolution 600 UV-VIS spectrophotometer (Thermo Scientific) in combination with a DRS-cell (Harrick, Praying Mantis). The absorption spectrum was determined, using the Kubelka-Munk function (equation 1). R is the absolute reflectance of the photocatalytic powder, with respect to BaSO_4 , which was used as reference.

$$f(R) = \frac{(1-R)^2}{2R} \quad (1)$$

The band gap was determined by the Tauc plot, following equation 2, with h being Planck's constant, ν the photon frequency, $f(R)$ the Kubelka-Munk intensity, A a constant (the slope of the Tauc plot), and E_g the band gap energy.

$$(h\nu f(R))^{1/2} = A(h\nu - E_g) \quad (2)$$

Photoelectrochemistry

The photocurrent of the wired configuration was measured in a two-electrode cell configuration, where the Rh:SrTiO_3 was the working electrode (W.E.) and WO_3 the counter electrode and reference electrode (C.E./R.E.). Here the reference electrode input of the potentiostat was shorted with the C.E. input. The W.E. and C.E./R.E. were aligned parallel

and both were illuminated with an ABET technologies model 10500 low cost 1.5 AMU solar simulator. A Versastat 4 (Princeton Applied Research) was used as potentiostat. The experiments were performed in a 25 mL optical cuvette, filled with a 0.3M H_3PO_4 electrolyte.

Gas Chromatography

A continuous-flow reactor consisting of a 25 mL glass cuvette, and a Teflon holder containing the substrate, was used to determine the hydrogen evolution rate achievable with the wireless configuration. The gas chromatograph (GC) connected to the flow reactor was equipped with a pulsed discharge detector (PDD), and able to measure with high accuracy H_2 and O_2 in the ppb level. Illumination of each side of the divider was achieved using two light sources. The first light source was the ABET technologies model 10500 low cost 1.5 AMU solar simulator used throughout this thesis. The second light source was a UV point source HP-120 lamp (UV-Groebel), with a lamp intensity up to 10 W/cm^2 in the UV-Vis range.

8.3 RESULTS AND DISCUSSION

8.3.1 Energy-level diagram of a $\text{WO}_3/\text{Pt}/\text{Rh}:\text{SrTiO}_3$ junction

UPS spectra of both photoelectrodes, both deposited on separate Pt substrates, are compared to the UPS spectrum of Pt in Fig. 4. In the inset of Fig. 4, the procedure to determine the work functions is illustrated. The work functions derived from the UPS measurements are $4.5 \pm 0.1 \text{ eV}$ for Pt, $4.8 \pm 0.1 \text{ eV}$ for WO_3 and $3.5 \pm 0.1 \text{ eV}$ for $\text{Rh}:\text{SrTiO}_3$.

Figure 4: Work function determination of the separate parts of the water splitting devices. From the UPS measurements the work functions were determined, see inset.

Kubelka-Munk (K-M) corrected diffuse reflectance UV-Vis spectra of WO_3 and $\text{Rh}:\text{SrTiO}_3$ powders are shown in Fig. 5A. For WO_3 light absorption starts below 450 nm, whereas for $\text{Rh}:\text{SrTiO}_3$ absorption is dominant below 375 nm. Small K-M intensity is present above 375 nm, which is assigned to the Rh-cationic doping in SrTiO_3 . The intensity above 375 nm in our measurement is not as strong as reported by Lo et al. [16]. To determine the band gap from the Kubelka-Munk data, the Tauc plots were constructed, as illustrated in Fig. 5B. WO_3 has a band gap of 2.6 ± 0.1 eV. Two band gaps can be extracted from the Tauc plot of $\text{Rh}:\text{SrTiO}_3$. The obtained band gap of 3.2 ± 0.1 eV is assigned to the intrinsic band gap of SrTiO_3 . The 2.4 ± 0.1 eV band gap can be assigned to Rh-doping. The determined values for the band gaps of WO_3 and $\text{Rh}:\text{SrTiO}_3$ are similar to the reported values in the literature, being 2.6 eV for WO_3 and 2.4 eV for $\text{Rh}:\text{SrTiO}_3$ [16].

Figure 5: Absorption data of WO_3 and $\text{Rh}:\text{SrTiO}_3$ powders and determination of their band gaps. A) absorption data plotted in a Kubelka-Munk format. B) The Kubelka-Munk spectra converted to a Tauc plot, which has been used to determine the band gaps of WO_3 and $\text{Rh}:\text{SrTiO}_3$ (see dashed lines).

The values determined for the work function and band gap of WO_3 and $\text{Rh}:\text{SrTiO}_3$ are used to construct the band diagram, which is shown in Fig. 6. At both semiconductor/metal interfaces Schottky barriers are formed. Band bending at the WO_3/Pt interface results in a favourable movement of electrons from the semiconductor into the metal substrate. At the $\text{Pt}/\text{Rh}:\text{SrTiO}_3$ interface the electrons prefer to move in the direction of the semiconductor. Contrary, holes generated in $\text{Rh}:\text{SrTiO}_3$ or WO_3 will prefer to move in opposite directions. The result is that electrons will preferably flow from the photoanode to the photocathode, the direction needed for overall water splitting.

Figure 6: Schematic band diagrams constructed from the data obtained via UPS and diffuse reflectance spectroscopy. The data suggest that a photochemical diode containing a $\text{WO}_3/\text{Pt}/\text{Rh:SrTiO}_3$ junction, is feasible for overall water splitting.

8.3.2 The wired configuration

To determine the maximum achievable photocurrent in a wired configuration, the cyclic voltammetry measurements of $\text{Pt}/\text{Rh:SrTiO}_3$ (Chapter 7) and WO_3 (Chapter 5) are compiled in Fig. 7A [17]. The current densities in dark (grey) and under illumination (black) of the photocathode are plotted inversed, with values corresponding to the scale of the left y-axis. The right y-axis represents the current density of the WO_3 photoanode in dark (light blue), and under illumination (dark blue). The overlap of the two curves under illumination, marked by a red dot, suggests a photocurrent of approximately 0.2 mA is achievable with two 1 cm^2 photoelectrodes under 1 Sun illumination. Here the photoanode will apply the voltage required for the reaction at the photocathode, and vice versa [17]. However, where WO_3 shows a shift in the onset potential of almost $\sim 1 \text{ V}$ upon illumination, the shift in onset by Rh:SrTiO_3 for H_2 evolution is minimal ($< 0.1 \text{ V}$). The small shift, and the dark electrochemical curve, corresponding to voltammetry of a Pt cathode (see chapter 1), makes it impossible to assign the overlap of the curves to full water splitting. The current measured at 0.7 V vs RHE in a CV of a Pt cathode is assigned to the formation of the Helmholtz layer [18, 19].

The actual photocurrent measured in the wired configuration (Fig. 3), where light was alternated every 30 seconds between 'on' and 'off', is shown in Fig. 7B. Each of the photoelectrodes had an effective surface of approximately 0.5 cm^2 . When the light was off, a negligible current of at most 250 nA was measured between the photoanode and photocathode. When the light was switched on, a small current of $-10 \text{ }\mu\text{A}$ was measured.

The negative value indicates that electrons flow from the C.E. to the W.E., which is in the direction anticipated, based on the band diagram of Figure 6. However, since no information on gas evolution at the photoelectrodes is available, other reactions than overall water splitting might be responsible for this small current. The value of the photocurrent is e.g. in the range of the formation (and degradation in the dark) of a double layer at the electrolyte-photocathode interface.

Figure 7: PEC characterization of the combination of a WO_3 photoanode and a Pt/Rh:SrTiO_3 photocathode in a $0.3\text{M H}_3\text{PO}_4$ electrolyte. A) Cyclic voltammetry measurements recorded individually in dark (grey and light blue) and illuminated (black and dark blue) conditions. B) Chronoamperometry in a two-electrode configuration where Pt/Rh:SrTiO_3 is used as W.E. and WO_3 as C.E./R.E. without the application of an external bias (0 V vs C.E./R.E.).

To determine the solar-to-hydrogen efficiency, η_{STH} , equation 3 is applied. The measured current J_{Op} , the minimum required potential for water splitting, 1.23 V , and the power of the light source, P_{in} , are used in this equation. The solar simulator has an intensity of 100 mW/cm^2 . The efficiency obtained in the wired configuration is about 0.01% . The low efficiency can be explained by the poor performance of the Rh:SrTiO_3 film, as discussed extensively in Chapter 7, while it is not possible to assign the measured current to full water splitting.

$$\eta_{\text{STH}} = \frac{J_{\text{Op}}(1.23\text{V})}{P_{\text{in}}} \quad (3)$$

Alternative concepts, which are based on PV materials as photocathode, show efficiencies up to 4.7% . The result we obtained with the wired configuration is at least two orders smaller than this value, and alternative materials for the Rh:SrTiO_3 photocathode need to be applied, to enhance the efficiency.

8.3.3 The unwired configuration

Deposition of photocatalysts at the Pt divider

SEM images of the deposited films of WO_3 and 1%Rh:SrTiO₃, when prepared on a Si/Si₃N₄ supported Pt membrane, are shown in Figs. 8. In the overview image of the front side (8A) the deposited layer of 1%Rh:SrTiO₃ looks rougher and darker inside the deeper-lying circular areas, than the layer outside these circles. Fig. 8B shows that this is due to only deposition of Rh:SrTiO₃ in the deeper-lying circular areas, as a consequence of the spin coating procedure. The images show that spin coating of a 1%Rh:SrTiO₃ layer does not lead to a fully covering layer.

When WO_3 was deposited by the hydrothermal method at the backside of the Pt divider, a uniform layer is grown, as shown in Figs. 8C and 8D. Although deposition of WO_3 was largely selective for the Pt substrate, some WO_3 was also deposited on the Si₃N₄ film of the sieve, which is likely not detrimental to the performance of the wireless configuration.

Figure 8: SEM characterization of the Pt divider with Rh:SrTiO₃ deposited at the front side (A and B) and WO₃ grown hydrothermally at the backside of the divider (C and D).

The SEM images in Figure 9 show the morphology of hydrothermally grown WO_3 layers on the front sides of two dividers, which already contained the Rh:SrTiO₃ film. The first divider has 5 μm pores (Fig. 9A), and the second has 10 μm pores (Fig. 9B). Clearly, WO_3 was not only deposited on the back side of the Pt divider, but also on the front side. This could be explained by the Pt still exposed at the front side after spin coating of Rh:SrTiO₃, see Figs. 8A and 8B. Fortunately, the Rh:SrTiO₃ covered circles appear to be relatively void of WO_3 deposits. The deposition of WO_3 particles in the circular areas is likely the result of incomplete coverage of the Pt film with Rh:SrTiO₃ crystallites.

Figure 9: SEM characterization of the front side of the Pt divider after deposition of Rh:SrTiO₃ via spin coating and WO_3 via a hydrothermal procedure.

Gas Chromatography

The water splitting capability of the divider with both photocatalysts when illuminated from both sides in a 0.3M H_3PO_4 solution, was analysed by gas chromatography (Fig. 10). An initially present air leak was repaired during the measurement, which resulted instantly in a low and constant O_2 background of 250 ppb. H_2 evolution was observed when both light sources were turned on after 30 minutes, in a steady state concentration of 500-600 ppb. H_2 formation is the result of (UV) excitation of the Rh:SrTiO₃ film. When the light was turned off after 20 hours, the H_2 signal instantly decreased to the baseline, whereas the O_2 concentration remained constant, indicative for the background value and showing that O_2 was not a product of overall water splitting. The origin of the absence of O_2 evolution is not known. It could be that residual hydrocarbon contaminants in the film are oxidized to CO_2 , which is not detected by the gas chromatography configuration that was applied. Further, other reactions cannot be excluded as well, for example oxidation of the Pt film or oxidation/corrosion reactions of the Si/Si₃N₄ support structure. Unfortunately, the measurement does not allow to conclude that electron transfer occurs between WO_3 and Rh:SrTiO₃.

Figure 10: Gas chromatography measurement of a Pt divider with WO_3 and Rh:SrTiO_3 deposited on each side (Fig. 3, placed in a Teflon holder in a $0.3\text{M H}_3\text{PO}_4$ solution). The chip was illuminated from both sides. H_2 was produced when the light was switched on.

A rough comparison can be made between the measured photocurrent in the wired configuration, and the measured H_2 quantity in the wireless configuration. The 600 ppb/min H_2 requires 0.54 nmol electrons to be converted. In the wired measurement, a current of $10\text{ }\mu\text{A}$ was determined. This corresponds to 6.0 nmol of electrons. This higher number of electrons as compared to H_2 molecules formed, confirms the observation of Fig. 7A that other reactions than H_2 (and O_2) formation are likely responsible for the photocurrent. Further optimization of the crystal deposition of the two materials comprising the Z-scheme is necessary to further elucidate this discrepancy, in particular preventing deposition of WO_3 on the 'Rh:SrTiO₃-side' of the divider.

8.4 CONCLUSIONS

Selective deposition of both materials comprising the Z-scheme, and evaluated in this thesis, on each side of a Pt divider has been achieved to a large extent, following the procedure illustrated in Fig. 3. Improvement is however still required, to prevent WO_3 deposition at the front-side of the Pt divider. Probably this could be done by covering the exposed Pt after the spin coating of Rh:SrTiO₃ with a protective organic layer. The measured photocurrent is low, and the associated H_2 production even lower. For both, the wired and unwired configuration, it was thus not possible to ascribe the measured photoactivity to full water splitting. As was already discussed in Chapter 7, improving Rh:SrTiO₃ or finding another suitable photocathode material is required to enhance the efficiency of the proposed Z-scheme configuration.

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CHAPTER 9

VALORISATION: THE HYDROSOLIX BUSINESS IDEA

ABSTRACT:

Under the company name HydroSolix, the market feasibility of the visible-light-induced water splitting on a chip concept has been investigated. In this chapter we describe the applications of hydrogen. Commercial application of the visible light induced water splitting on a chip is considered to require an efficiency of at least 10%. Two potential business models for the HydroSolix concept are discussed.

This study has been used as Business Idea proposal, which was included in a granted application for a STW valorisation grant phase 1.

9.1 THE PROBLEM

The world is facing a tremendous energy challenge, and increasing harvesting of solar energy is widely considered as one of the key sustainable energy solutions (if not *the* key renewable energy solution). Over the last decade, a substantial increase in the application of solar cells has taken place, largely stimulated by government subsidies (e.g. in Germany). With an increasing amount of electricity produced by solar cells, a very serious and fundamental problem arises: Solar cells produce energy when the sun shines, so electricity production occurs only during the day. Nowadays, excess electricity generated by solar cells is fed back into the electricity grid. However, this feedback into the grid naturally also has its limitations. In Germany renewable energy sources already cause problems to the electricity grid (see *Der Spiegel*, 16 August 2012 [1]), in particular at a windy sunny day. It is practically impossible to shut down other power plants at such days to balance electricity production. Hence it is crucial that energy production and demand are balanced both in time and geographically, which requires economic and scalable storage of the energy produced by sunlight.

To store energy for other moments when it is needed, electricity should be stored in a carrier. In principle, batteries can be used for this purpose, but calculations show that there are simply not enough resources [lithium (Li), lead (Pb)] to meet the required energy storage demand by batteries. A possible alternative scalable route to store solar energy is the conversion into a fuel, a solution referred to as *solar to fuel* (S2F). The simplest solar fuel one can think of is hydrogen gas produced out of water splitting. Hydrogen is seen by many experts as the fuel of the near future. A solution to produce hydrogen with solar energy is already technically feasible. Photovoltaic solar panels can be used to convert solar energy into electricity, while the generated electricity can be used in a second step to convert water electrochemically (in an electrolyser) into the thermodynamically uphill product hydrogen, oxygen being generated as a co-product. Although efficient storage of hydrogen is not trivial, it is technologically feasible and still being improved. Hydrogen is easily and efficiently (re-)converted into electricity using existing fuel cell technology, presently reaching efficiencies as high as 60% [2]. When more energy dense fuels are needed, hydrogen can be used as input for generating hydrocarbons such as methane (CH_4) or alcohols such as methanol (CH_3OH) by reaction with CO_2 . It is thus expected that hydrogen will rapidly become more and more important as an energy carrier and that a future hydrogen based economy is still realistic, see e.g. Ref. [3].

As mentioned above, it is already technically possible to combine photovoltaics with electrolysis to produce “green” hydrogen, but it is not used much in practice. The reason is the high capital investment that is needed, mainly because of the complexity of the

system and the need of precious metals. The price of sustainable hydrogen is about three times the price of hydrogen produced out of fossil fuels [4], see box 1. So the ultimate problem is how to convert solar energy into hydrogen in an economic way to obtain a sustainable, storable energy source.

Box 1 Hydrogen Consumption and Production

Figure 1: A) Consumption of hydrogen in the process industry. B) Overview of routes used to produce hydrogen (Source: US department of energy)

Besides as an energy carrier, hydrogen is also a heavily used chemical in different industries. Examples of industrial applications of hydrogen are (see Fig. 1A)

- Production of ammonia and methanol
- Hydrotreating: converting heavy crude to lighter products in the refining industry
- Hydrogenation: reduction or saturation of organic compounds, particularly in the food industry to hydrogenate liquid oils
- Pacifying gas in the semiconductor industry

At this moment, 96% of the hydrogen is produced out of fossil fuels (Fig. 1B). Next to the production of H_2 , CO_2 is also produced, one of the most important greenhouse gasses. CO_2 neutral production of hydrogen by means of solar to fuel technologies might be of interest to the chemical industry, as it decouples H_2 production from fossil fuels. Only a small part of the hydrogen is produced by electrolysis, being at least twice as expensive as hydrogen made from natural gas [4]. This is mainly due to the high price of the electrolyser (capital investment).

9.2 THE PROPOSED SOLUTION

HydroSolix will be developing a converter that produces hydrogen (and oxygen) by *photocatalysis*. Solar energy is used **directly** to achieve the water splitting reaction.

The idea of our solar-to-hydrogen converter is based on vertically placed metallic dividers with the oxygen and hydrogen photocatalysts at each side, see Fig. 2. In the translation to the final converter, the idea is to place these dividers parallel to increase the effective surface for hydrogen production. We believe a solar-to-hydrogen efficiency of 10% is feasible, which is the same order of magnitude currently achievable with solar panels connected to electrolyzers. This efficiency implies a production of 1 liter H_2 per 4.5 dm^2 per hour. This translates to the following: with an area of 25 m^2 one can produce 375 kg H_2 per year in the Netherlands, which is the energy equivalent of 1500 liter gasoline per year. From several conversations with experts we have learned that proving the feasibility of this 10% solar-to-hydrogen efficiency is the main driver to obtain follow-up investments and a marketable product. Hence, this is one of the main goals of HydroSoliX, as well as looking for a scalable application. The proposed solution is presented in Fig. 2.

Figure 2: The HydroSoliX concept: photocatalytic water splitting modules.

The main difference with the conventional scheme of a solar cell coupled to an electrolyser is that in photocatalysis the solar cell and the electrodes are as it were combined in one photocatalytic particle. Solar activation of a photocatalytic particle creates electron-hole pairs, which are used in the redox reactions needed to achieve the overall water splitting reaction. This integration provides an opportunity to reduce the complexity and the costs of the overall water splitting device!

Instead of using a single photocatalyst, such as TiO_2 , we will apply a so-called *Z-Scheme*, using two photocatalysts and thereby dividing the water splitting reaction in two half reactions, see Box 2. We will immobilize each of the two photocatalysts on one side of a conducting metallic divider.

At one side of the divider, the O_2 -photocatalyst (e.g. WO_3) will convert H_2O to O_2 and protons (H^+) and electrons:

The electrons are transferred to the other photocatalyst (e.g. $\text{SrTiO}_3\text{:Rh}$) via the metallic divider. The protons can freely move to the other side through the water underneath the

divider, so no (expensive) proton membrane is needed. The H^+ is converted by the $\text{SrTiO}_3\text{:Rh}$ -photocatalyst at the other side of the metallic divider to H_2 :

Box 2 Artificial Photosynthesis: The Z-Scheme of Water Splitting

Figure 3: Schematic representation of the Z-scheme for water splitting by photocatalysis. The photocatalytic particles are suspended in water. From Ref. [5].

In the original Z-scheme the electron transfer between the O_2 -photocatalyst and H_2 -photocatalyst is taken care of by a redox couple (e.g. $\text{Fe}^{2+}/\text{Fe}^{3+}$). In the patented HydroSoliX concept this role is taken over by a metallic divider, with each of the two photocatalysts attached to one side.

For water splitting by photocatalysis it is possible, for example, to use UV-light active TiO_2 . The electron and hole produced by the UV photon can be used for the reduction and oxidation of water, respectively. The big disadvantage of single-photocatalyst water splitting is that UV-light needs to be used, which constitutes less than 5% of the solar spectrum. An alternative approach, somewhat mimicking natural photosynthesis, is a 2-step water splitting process referred to as the Z-scheme, see Fig. 2.

Here the hydrogen and oxygen half reactions are divided over two separate photocatalysts. An important advantage is that visible-light active photocatalysts can be used in the process, which results in a larger amount of usable photons (close to 50% of the solar spectrum) and hence an efficiency increase. The efficiency of Z-scheme water splitting with suspended photocatalytic powders is low. An important limiting factor is the needed electron transfer between the freely suspended catalysts. Therefore, in the HydroSoliX concept the two photocatalysts are directly electronically connected by a metallic film, which is expected to increase the efficiency tremendously. Both for the O_2 -photocatalyst and the H_2 -photocatalyst a number of material options are available.

The metallic divider provides direct separation of hydrogen and oxygen, which saves an extra separation step afterwards. This makes the solution more scalable. The WO_3 photocatalyst was already successfully immobilized at the metallic divider and showed very high photoactivity. In the coming months the immobilization of $\text{SrTiO}_3\text{:Rh}$ should be finalized, and then the proof-of-principle can be demonstrated. In the future other photocatalysts can be developed, where the use of even smaller band gap materials will provide for an increase in efficiency.

9.3 INNOVATIVE ASPECTS

Innovative aspects of our concept compared to current hydrogen production by fossil fuels are:

- Low cost sustainable technology for hydrogen production
- No CO_2 emission
- Hydrogen-price is independent of the oil-price
- Stable supply for the future
- On-site production of hydrogen
- High-purity hydrogen directly in own storage compartment

In addition to the above benefits, the HydroSoliX concept also offers innovations to overcome the hurdles of other photoactive water splitting techniques:

- Use of cheap materials, as compared to e.g. triple junction silicon
- Integration of the solar cell into the electrodes
- Use of visible-light photons
- High electron conductivity between the photocatalysts → higher efficiency
- Direct separation between hydrogen and oxygen
- Scalable technology
- Photocatalysts are metal oxides, so long term stability of the device appears feasible (no issues with oxidation of e.g. Si based functionalities)

9.4 COMMERCIAL ASPECTS

The total hydrogen market in 2010 was worth a total of 10 billion dollar and with the increase of the energy market, the hydrogen market is expected to grow in the coming years to a size of 16 billion dollar (see Fig. 4). Due to the large market size, it is important to aim at a market segment in which our concept can be applied. The production of hydrogen gas is mainly dominated by large gas companies, such as *Praxair* and *Linde Gas*. These companies use installations to produce hydrogen gas from fossil fuels.

Figure 4: Hydrogen market (Source: Praxair, Global Hydrogen Growth Investor Day 2011)

To see where our converter can be used, it is important to look at the typical volumes of hydrogen used in the different sectors (Fig. 5). It is unlikely that small users, like laboratories, who need bottles of hydrogen, buy a separate converter to produce their hydrogen. The large hydrogen consumers in the chemical industry, for refining and other chemical processes, demand large volumes of hydrogen. We think it will be too big a challenge to fabricate converters that can produce these amounts of hydrogen. We are therefore going to aim at markets where users nowadays use small on-site converters. Our converters can be a sustainable alternative for the small on-site production facilities that are currently used. Therefore markets as the domestic power generation industry, car fuel production, electronic industry and glass industry seem to be markets we should aim at.

Industry	Key Applications	Supply Systems	Volume
General Industrial	<ul style="list-style-type: none"> Power generation Heat treating Laboratories 	<ul style="list-style-type: none"> Small on-site Cylinders Tube trailers Liquid H₂ 	Low <5 mmscfd
Electronics	<ul style="list-style-type: none"> Thin-film solar Semi-conductors 	<ul style="list-style-type: none"> Tube trailer Liquid H₂ Small on-site 	
Glass	<ul style="list-style-type: none"> Float glass mfg 	<ul style="list-style-type: none"> Liquid H₂ Small on-site 	Medium 5-15 mmscfd
Other	<ul style="list-style-type: none"> Chemicals Biofuels 	<ul style="list-style-type: none"> Pipeline Large on-site 	
Refining	<ul style="list-style-type: none"> Hydro-processing 	<ul style="list-style-type: none"> Pipeline Large on-site 	High 30-200+ mmscfd

Figure 5: Hydrogen application in different industries. (Source: Praxair, Global Hydrogen Growth Investor Day 2011)

There are several existing competitors in the field of sun-to-hydrogen production. As mentioned before, the combination of a solar cell and an electrolyser is an option to convert the sun's energy to hydrogen. This is however an expensive technique. To decrease costs, several ideas are exploited worldwide by integrating the solar cell into the electrodes. Companies active in this field are *Hydrogen Solar*, *Stored Solar* and *Sun Catalytix*. *Hydrogen Solar* and *Stored Solar* are integrating the solar cell in one of the two electrodes. Here the contribution to the potential which has to be applied by an expensive solar cell is decreased. *Sun Catalytix* uses a solar cell, with light-inactive catalysts deposited at the surface. This technique requires a relatively complicated and hence expensive solar cell, which is placed in water. All these ideas are still in the development stage. A rule of thumb in the solar-to-hydrogen world states that every step of integration decreases the production costs of the device. This trend, including our position in the market, is shown in the graph below.

Figure 6: the HydroSoliX converter compared to competitors in the market in terms of integration and production costs.

In Table 1 a comparison is made between different potentially feasible technologies. We want to demonstrate the 10% target efficiency with the help of the Valorization Grant during the coming year. We believe the main strenght of HydroSoliX will be the relatively low production cost of the converter.

Table 1: Comparison of HydroSoliX with other technologies.

Company	HydroSoliX	Sun Catalytic	Stored Solar Hydrogen Solar	Stored Solar
Method of operation	Z-scheme photocatalysis on a membrane	Triple PN junction + oxygen and hydrogen catalysts	Tandem Cell	Electrolyser driven by Photovoltaics
Efficiency	Unknown yet	4.7%	8%	Electrolyser ~80/90% Solar cell ~15/20% Combined about 12%
Complexity	+ Flexible platform for different catalysts + Integrated Design	+ Integrated Design	- Need to Bias (for Ex. By PV) or UV-light photocatalyst	+ Technique already on the market - Separation of the solar cells from electrolyzers - Voltage regulator
Production Costs	+ Common catalysts - Microfabricated platinum membrane - Rhodium Doping	- Triple junction solar cell - Materials as ITO are expensive	- Platinum counter Electrode - Solar cell to bias	- Platinum Electrodes - Voltage regulator
Durability	+ Oxides as catalysts - Thin Membrane	- Silicon solar cell in the electrolyte	+ Solar Cell separated from electrolyte + Metal oxide as catalyst + Inert Counter Electrodes	+ Solar Cell separated from electrolyte + Inert Counter Electrodes
H ₂ /O ₂ separation	+ Separable H ₂ /O ₂ production	- Separable H ₂ /O ₂ production	+ Separable H ₂ /O ₂ production	+ Separable H ₂ /O ₂ production

9.5 BUSINESS MODEL

HydroSoliX will manufacture and sell the solar-to-hydrogen converters. The converter is constructed of dividers stacked in parallel. R&D activities are aimed at increasing the efficiency of the solar-to-hydrogen converter. In the current hydrogen market, HydroSoliX is preceding the gas supplier in the chain, see Fig. 7. Gas suppliers, as *Praxair* and *Linde Gas*, can use the converters to produce hydrogen. The small on-site converters can be applied for domestic power generation and storage, and in the electronic, fuel, and glass industries. By selling the converters via the gas suppliers, HydroSoliX will use existing logistics and client databases for the end consumers. Therefore, we aim to approach a gas supplier as key partner and as launching customer. This partner will become essential to develop the converter towards the standards of the gas industry. The feasibility of this business model will be evaluated in phase 1 of the Valorisation Grant.

Figure 7: Business model for using the HydroSoliX concept for industrial H₂ production.

If our solar-to-hydrogen converter is coupled to a proton exchange membrane fuel cell (PEMFC), it creates an energy supply and storage system decoupled from the grid, see Fig. 8. When the sun shines, energy will be stored in the form of hydrogen. When energy is

needed, the fuel cell converts hydrogen back to electricity. Next to electricity, warm water is made in the fuel cell and this can be used to heat the home. Our concept provides a practical and *sustainable* solution to prevent overcharging of the electricity grid. Another application that will be looked at is whether it is feasible to produce small fueling stations together with a partner for fuelling cars that have a similar fuel cell. For the Valorisation Grant I, the goal is to determine the most suitable market for the converter.

Figure 8: Business model for an off-grid energy supply with storage.

9.6 THE IP POSITION

A patent with title “Photocatalytic water splitting” was filed on 16 July 2010 (priority date) and internationally filed on 15 July 2011 (WO2012008838) [6].

In January 2013 continuation of the patent is applied for in the following countries: Europe, United States of America, Japan, China, India, Brazil, and South-Korea. The international examiner of the PCT application deemed all 15 claims of the patent novel, inventive and industrially applicable. With this very positive outcome, we expect that the filing of our patent in the abovementioned countries is a formality. We note that the costs related to the patent applications in these countries (~40 kEUR) is covered for 50% by the Patent Fund of the University of Twente (*Octrooifonds UT*), demonstrating the commitment and enthusiasm of the University of Twente and its business development team

9.7 CONCLUSIONS

In the industry at this moment, there is already a high demand for hydrogen. This hydrogen is mainly produced out of fossil fuels via chemical routes. Only a small part of the hydrogen is made via electrolysis. In the future the demand for hydrogen will increase,

because it can be used as energy carrier for a sustainable energy supply. The solar-to-hydrogen converter, following the HydroSoliX concept, could play a role in this. Compared to other alternative solar-to-hydrogen converters, if a 10% efficiency could be reached with this solution, the HydroSoliX concept will have certain concerning stability and the hydrogen price. For final applications, we see there are two business models possible for the HydroSoliX concept. In the first business the HydroSoliX converter can be used to produce hydrogen for existing markets. The second business model will be aiming at a niche market, where in combination with a fuel cell, the solar-to-hydrogen converter will be part of a decentralized energy supply. Here households can produce, store and use their own produced energy, and homes can be decoupled from the electricity grid.

9.8 REFERENCES

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Summary

In this thesis, a photoelectrochemical water splitting cell concept is discussed, based on a combination of semiconductors comprising a Z-scheme. The motivation for the development of the cell is that in the future a transition will take place from a fossil fuel-based economy, to an economy based on renewable energy sources. These renewable energy sources, like solar and wind, fluctuate in yield over time, and require temporary storage of energy till the moment it is needed. An option to store the energy is by decomposition of water, by which H_2 is formed, which can be used as an energy carrier. Alternatively to a single photoelectrochemical cell, electricity generated by solar cells can be fed into an electrolysis cell, in which water splitting into H_2 and O_2 can be achieved. However, H_2 produced in this way is much more expensive than H_2 made out of fossil fuels. If the goal of a single cell solar-to- H_2 efficiency of 10% could be reached, the price per kg H_2 could be between the \$2.00 - \$4.00. The photoelectrochemical water splitting concept we propose and discuss in this thesis, consists out of a Pt divider, on the opposite sides of which WO_3 is deposited as photoanode, and Rh:SrTiO₃ as photocathode. The Pt divider is a thin Pt film, mechanically strengthened by a microfabricated silicon sieve support. In the thesis we studied the performance of the basic elements, i.e. SrTiO₃ in modified forms, and WO_3 , in a slurry reactor operated in continuous mode. In addition, methods for immobilization of the photocatalysts on a Pt film were developed, and the obtained electrodes (photo)electrochemically characterized.

In **chapter 3** Pt/Rh:SrTiO₃ powder was analysed with a sensitive GC under illumination of a 1.5 AM solar simulator. The effect of Rh-doping on photocatalytic performance under realistic solar illumination conditions is discussed, including a discussion on the preferred oxidation state of Rh, being Rh^{4+} to Rh^{3+} . Our measurements showed that under illumination with solar light, Rh-doping decreases the overall activity of SrTiO₃. The extra absorption of visible light photons by the introduced doping levels, does not compensate for the decrease in activity, due to introduction of defects in the structure of the photocatalyst. Another interesting observation in the GC measurements, was a delay in H_2 production. It was assessed that this was not due to reduction of Rh^{4+} to Rh^{3+} , but originated from reduction of the PtO_x co-catalyst. The first indication for this reaction, was that the delay in H_2 was also observed in a measurement with undoped Pt/SrTiO₃. Analysis via XPS before and after the photocatalysis measurement showed that for the undoped photocatalyst a complete reduction of PtO_x was achieved. However, when Rh-doping was present, an equilibrium composition between Pt and PtO_x was obtained.

In **chapter 4** we evaluated z-scheme water splitting, under illumination of a 1.5 AM solar simulator, for the combination of WO_3 and Pt/Rh:SrTiO_3 photocatalysts. The role of an $\text{Fe}^{2+}/\text{Fe}^{3+}$ electron mediator was characterized by GC experiments. Without the addition of Fe-species, no electron exchange was observed between WO_3 and Rh:SrTiO_3 . The measured transients were similar to the water splitting transients, measured for Pt/Rh:SrTiO_3 in chapter 3. When each photocatalyst was analysed in the presence of the complementary Fe-ion, WO_3 showed good O_2 evolution properties and Pt/Rh:SrTiO_3 showed good H_2 evolution properties. However, when both photocatalyst were combined with one of the Fe-ions, exchange of electrons due to shuttling of Fe^{2+} and Fe^{3+} could not be demonstrated. The measurements indicate that the Fe half reactions are ‘shorted’ via back reactions on the photocatalyst particles on which the initial reduction (or oxidation) took place.

The first step towards visible light water splitting on a chip was the development of a deposition method for the WO_3 photoanode. In **chapter 5** we introduced a hydrothermal procedure, which allowed to deposit WO_3 selectively on a Pt substrate. A precursor solution was made by solving H_2WO_4 in H_2O_2 . The H_2O_2 concentration in the final solution determined the morphology and adhesion of the WO_3 on Pt. By application of a structured Pt substrate, the capability of the procedure to deposit WO_3 selectively at Pt was demonstrated. Photoelectrochemical characterization showed a photocurrent density of 1.1 mA/cm^2 at 1.23 V vs RHE of the obtained photoanode.

To improve the water oxidation properties of the Pt/WO_3 photoanode, the effect of an IrO_2 co-catalyst was evaluated in **chapter 6**. The plan was to use electrodeposition, to adhere IrO_2 directly on the WO_3 crystals. However, the porous morphology of WO_3 resulted in deposition of IrO_2 directly on the Pt substrate. To prevent this, a TiO_2 layer was spin coated, resulting in TiO_2 particle growth in between the WO_3 crystals. In this way deposition of IrO_2 on the Pt substrate was prevented, and intimate contact between WO_3 and IrO_2 contact could be realized. The addition of TiO_2 was demonstrated to already enhance the photocurrent, likely due to insulation of the Pt substrate from the electrolyte. This lowered the amount of charges trapped at the Pt surface, and decreased the resistance induced by the Helmholtz layer. Our explanation for the current enhancement is that electrons excited in the WO_3 , encounter less resistance going into the substrate. By the addition of the insulating TiO_2 layer, in combination with the catalytic effect of the IrO_2 co-catalyst, an enhancement in the photocurrent of 140% was realized.

In **chapter 7** a fabrication method for a Rh:SrTiO_3 photocathode on a Pt substrate was introduced. A chemical solution deposition procedure, based on chelate chemistry, was used to deposit dense Rh:SrTiO_3 layers on a Pt substrate via spin coating. Initially measured photocurrents were low, and this required improvements in the structure and

composition of the photocathode. Several aspects of the Rh:SrTiO₃ photocathode were evaluated. Reducing Rh⁴⁺ to Rh³⁺, and addition of a Pt co-catalyst resulted in a small enhancement of the photocurrent, however the final photocurrent was orders of magnitude lower than the photocurrents measured for the WO₃ photoanode. Furthermore the effect of the SrTiO₃ film on the onset potential for H₂ evolution was minimal. *I-V* measurements showed that the resistance in the Rh:SrTiO₃ layer is much larger, than the resistance measured in Nb-doped SrTiO₃, made via a similar procedure.

In **chapter 8** the deposition procedures developed in chapter 5 for WO₃ and chapter 7 for Rh:SrTiO₃ were combined, and the practical realization of the visible light water splitting on a chip concept evaluated. The first characterization of the concept was done by connecting a separated photoanode and photocathode via an external circuit. When the illumination was altered between light and dark, a small current of 10 μA was measured under illumination. The next step was integrating WO₃ and Rh:SrTiO₃ on a 500 nm thick Pt divider via the developed deposition methods. The Pt divider was a 500 nm thick film, mechanically supported by a Si₃N₄ sieve structure. It was obtained via a collaboration with the LNT – VNUHCM institute in Ho Chi Min City, Vietnam. The Rh:SrTiO₃ deposition did not fully cover the frontside of the Pt divider, resulting in a-selective deposition of WO₃ at both sides of the membrane. A gas chromatograph measurement showed H₂ evolution under illumination, however no O₂ evolution was measured. Clearly further improvement in the conductivity of the Rh:SrTiO₃ is required for successful implementation of the Z-scheme based photoelectrochemical device.

When all the gained results and knowledge presented in this thesis are combined, a straight forward conclusion is that in the end, the goal of a 10% solar-to-H₂ was not accomplished. The main limitation based on all experiments, is the Rh:SrTiO₃ photocathode. When Rh:SrTiO₃ is deposited via a chemical solution deposition route on a Pt substrate, the photoactivity is low compared the photoactivity of a WO₃ photoanode. This can be due to the deposition route, used for the photocathode, although when the results of Chapter 3 are taken into account, Rh:SrTiO₃ will anyway not be the ideal photocathode for the final concept. We have chosen for this photocathode, to start with a photocathode/photoanode combination already extensively investigated in the photocatalysis community. Our photocatalytic experiments on a Pt/Rh:SrTiO₃ system, showed that Rh-doping introduces defects in SrTiO₃, which lower the photoactivity. Towards the future, the first step should be the improvement of the photocathode, or the development of alternative photocathode material. This will be required to evaluate the feasibility of the concept. The measurements of the powdered z-scheme system show, that using an electron mediator to exchange electrons between two photocatalysts has limitations. The half reactions of the electron mediator are ‘short circuiting’, and the

second photocatalyst is not reached efficiently. Therefore the concept, where a chemical inert Pt film, connecting two photocatalysts and directly dividing the reactor in compartments for separated H₂ and O₂ evolution, can still be interesting. The selective deposition of WO₃ on the Pt substrate results in good photocurrents, although for a final application and to reach a 10% efficiency, another photoanode with a smaller bandgap will be required. However, the most important step to continue towards a working concept, is improving the photocathode.

Outlook

In this final chapter, I will try to give my view on the future of the work presented in this thesis, and discuss follow up experiments and the possible future of photocatalytic water splitting via our concept. As concluded in the Summary chapter, the solar-to-hydrogen efficiencies obtained in the experiments reported in this thesis are low, and far off the 10%, where we aimed for at the start of the project. Furthermore, it is also far off other reported solar-to-hydrogen efficiencies realized with alternative concepts. There are still a lot of challenges, which should be solved, before the realization of a final commercial application.

The material challenge

Towards a commercial application, it is required to find semiconductor materials, for the photocathode and photoanode, which can be used to reach at least a solar-to-hydrogen efficiency of 10%. In my view, important will be aiming at the development of new photocatalytic materials, which are suitable for reaching this 10%, and which can be combined following a Z-scheme.

The two semiconductors researched in this thesis, are both not sufficient for reaching a 10% efficiency, based on their band gaps. However, Rh:SrTiO₃ requires improvement or replacement by another photocathode, to measure the potential of the visible-light-induced water splitting on a chip concept. Although a small photoresponse was observed in the experiments, further analysis is required to relate the photoresponse to hydrogen evolution. This should be done via a combined GC/PEC measurement.

Also further experiments should be done to try to improve the semiconductor material, and conclude if there is eventually potential for this photocathode. In literature, several methods can be found, which should be possible to overcome limitations due to a high resistance in the photocathode. The first thing which should be changed, is the fabrication method for Rh:SrTiO₃, for example via a spray pyrolysis procedure. Possibly another deposition method, can improve the crystallinity of the semiconductor, and lower the resistance. For a final application, it is important to base the deposition method on economical competitive techniques.

Research is required to find alternative semiconductors. However, there are billions of combinations possible by combining different elements, which makes it practically impossible to research all combinations. Therefore, an option will be to make a first

selection by using the expertise of theoretical scientists, who can propose semiconductor materials by Density Functional Theory modulation studies. If the interesting materials are synthesized in the laboratory, and then characterized with a Gas Chromatograph used in this thesis, it should be possible to follow the reactions taking place at different semiconductors under illumination, and identify the potential of the materials. To analyse the capability for one of the half reactions, a sacrificial agent can be added to test the oxygen and hydrogen evolution properties separately. The results of the first experiments could be used to optimize the theoretical identification models. Further, with a successful outcome, it can be a start for further development and improvement of the semiconductor materials. The advantage of all knowledge reported by the community at the small selection photocatalysts used presently, is that different fabrication techniques and deposition methods are available, to solve limitations of the new materials, and analyse the full potential.

Although I proposed that it is possible to do follow-up experiments with Rh-doped SrTiO_3 , I think, based on the results in this thesis, that it is important to prevent the addition of dopants. Further, the different photocatalytic materials should be analysed under illumination of a 1.5 AM solar simulator, because this mimics realistic conditions. In the first chapters of this thesis, it has been shown, that if doping is added to enhance the adsorption of visible light photons, the overall water splitting efficiency of SrTiO_3 under realistic conditions decreased. For a final application, the pursuance should be to use doping-free semiconductor materials. Furthermore, stability under reaction conditions should be a main property of the semiconductor.

The efficiency definition

An in the community defined goal is to reach a solar-to-hydrogen efficiency of 10%. In literature, several concepts have been reported, reaching solar-to-hydrogen efficiencies up to 12.7%. However, the efficiencies of these concepts are extracted from the current measured under illumination, and are not supported by gas chromatography characterization of evolved gases. Due to relative short life-times of most reported concepts, the decrease of the photocurrent indicates other reactions, next to the water splitting reaction, occur and contribute to photocurrents. The combined GC and PEC measurements in chapter 6 of this thesis showed the importance of supporting the photocurrent with analysis of the produced H_2 and O_2 . If GC characterization is done parallel to the PEC measurement, it is possible to determine the Faraday efficiency of the full water splitting reaction. With the definition for the solar-to-hydrogen efficiency used by the PEC community, the Faraday efficiency is assumed to be 100%, which should exclude photocorrosion of the PEC cell. However, without supporting GC analysis, the reported efficiencies do not represent the solar-to-hydrogen efficiency, but the solar-to-electrons efficiency. If PEC cells will be used in practice, the cell should be stable over a

long period. I think, it is better to calculate the efficiency by measurement of the evolved H_2 and O_2 .

The future for the concept

In the future, a transition to sustainable energy sources will be required, to secure an energy supply, and to minimize climate change. To overcome the fluctuations of these energy sources, it will be necessary to be able to store the renewable energy in an economically viable way. Ideally, this energy should be stored in hydrocarbons, which have high energy densities. However realizing a direct solar-to-hydrocarbon conversion via a photo(electrochemical) method, is challenging. Storage in batteries also can be an option, however the low energy densities of batteries makes it a bulky, and expensive solution. Therefore, in my opinion, hydrogen as energy carrier, can be an ideal option.

During the PhD study, we have made a business examination for the visible-light-induced water splitting on a chip concept. This was used to apply for a valorisation grant, and the examination has been added as chapter 9 of this thesis. Two different main concepts were proposed as possible applications for the concept. The first concept is to produce hydrogen for the existing hydrogen markets, and the second concept is to use the concept for an off-grid energy supply, when the solar-to-hydrogen converter is combined with a fuel cell. The second option will be the most interesting for commercialization of a direct solar-to-hydrogen converter. Here, the issue of a fluctuating renewable energy supply causing problems of the electricity grid, will be overcome, and households can be made self-sufficient. Furthermore, it is a market, where the hydrogen production should not be directly competitive to hydrogen produced out of fossil fuels. However, before any commercialization is possible, the development of the concept will require a couple of years.

Samenvatting

In dit proefschrift is een fotoelektrochemisch water splitsing concept onderzocht, gebaseerd op een combinatie van twee halfgeleiders. Deze twee halfgeleiders, die gebruikt kunnen worden als fotokatalysatoren, kunnen samen gecombineerd worden volgens een zogenaamd Z-schema. De motivatie voor de ontwikkeling van een cel op basis van fotoelektrochemische water splitsing, is dat in de toekomst een transitie gaat plaatsvinden van een op fossiele brandstoffen gebaseerde economie, naar een economie gebruik makend van duurzame energie bronnen. De energie opbrengst uit duurzame energie bronnen, zoals zon en wind energie, fluctueert echter over tijd. Dit maakt een tijdelijke opslag van energie nodig, tot het moment dat de energie gebruikt wordt. Een mogelijkheid voor het opslaan van duurzame energie, is door deze duurzame energie te gebruiken voor het splitsen van water, naar waterstof en zuurstof. De waterstof kan dan gebruikt kan worden als energie drager. Als alternatief voor een directe productie van waterstof via een fotoelektrochemische cel, kan ook eerst elektriciteit gemaakt worden met een zonnecel. Deze elektriciteit kan dan gebruikt worden in een elektrochemische cel, waarmee water gesplitst kan worden in waterstof en zuurstof. Echter, de waterstof die geproduceerd wordt op deze manier, is duurder dan waterstof geproduceerd uit fossiele brandstoffen. Wanneer het mogelijk zou zijn, om een directe omzetting te realiseren met een zon-naar-waterstof efficiëntie van 10%, zou het mogelijk moeten zijn om waterstof voor \$2,00 tot \$4,00 per kg H_2 (waterstof) te maken. Het concept van de fotoelektrochemische cel, dat wij voorstellen en behandelen in dit proefschrift, bestaat uit een platina afscheider, waar op aan weerskanten een wolfram oxide film als fotoanode en een rhodium gedoopte strontium titanaat film als fotokathode worden gezet. De platinum afscheider, die direct de reactor in twee compartimenten verdeeld, bestaat uit een dunne platina film, die mechanisch is versterkt via een micro gefabriceerde silicium zeef. In dit proefschrift zijn we begonnen met het bestuderen van de afzonderlijke componenten waaruit dit concept bestaat, dat wil zeggen met strontium titanaat en wolframoxide poeders in een slurry reactor. De water splitsing reactie werd continue geanalyseerd. Verder zijn de poeders geïmmobiliseerd op een platina substraat, en gekarakteriseerd door middel van het meten van de verkregen fotostromen.

In hoofdstuk 3 is Pt/Rh:SrTiO₃ poeder geanalyseerd met een gevoelige gas chromatograaf onder belichting van gesimuleerd 1.5 AM zonlicht. Het effect van Rh-doping op de fotokatalytische activiteit onder gesimuleerd zonlicht wordt behandeld, alsmede de oxidatie toestand van rhodium, die Rh⁴⁺ bleek te zijn in plaats van Rh³⁺. Onze metingen laten zien dat onder belichting met gesimuleerd zonlicht, de toevoeging van Rh-doping de

totale activiteit van strontium titanaat verlaagt. De extra geabsorbeerde zichtbaar licht fotonen, door het introduceren van een doping niveau, compenseert niet de verlaging van activiteit, door het introduceren van defecten in de structuur van deze fotokatalysator. Een andere interessante observatie in de gas chromatografie metingen is het achterblijven van de waterstof productie. Dit kan niet gerelateerd worden aan een reductie van Rh^{4+} naar Rh^{3+} , maar wordt veroorzaakt door het reduceren van de platinum oxide co-katalysator. De eerste indicatie voor deze reductie reactie, was de observatie van een achterblijvende waterstof productie in ongedoopt Pt/SrTiO_3 . Een XPS analyse, voor en na de fotokatalytische metingen, lieten zien, dat voor ongedoopt strontium titanaat een volledige reductie van platinum oxide inderdaad werd behaald. Echter, wanneer Rh-doping aanwezig was, werd een evenwicht gerealiseerd tussen Pt en PtO_x , en de oxidatie toestand van Pt lijkt dus afhankelijk van de halfgeleider waarop Pt nanodeeltjes zijn aangebracht.

In hoofdstuk 4 is het fotokatalytisch water splitsen via een z-schema behandeld. De experimenten werden gedaan voor een combinatie van WO_3 en $\text{Pt}/\text{Rh}:\text{SrTiO}_3$ als fotokatalystoren en onder belichting van gesimuleerd 1.5 AM zonlicht. De rol van een $\text{Fe}^{2+}/\text{Fe}^{3+}$ koppel voor elektronen transport werd gekarakteriseerd via de GC metingen. Zonder de toevoeging van de ijzer-ionen, werd er tussen WO_3 en $\text{Pt}/\text{Rh}:\text{SrTiO}_3$ geen uitwisseling van elektronen geobserveerd. De gemeten transiënten waren vergelijkbaar met de water splitsing transiënten, die werden gemeten in hoofdstuk 3 voor de aanwezigheid van alleen $\text{Pt}/\text{Rh}:\text{SrTiO}_3$. Wanneer beide fotokatalystoren werden geanalyseerd met het bijbehorende ijzer-ion, liet WO_3 goede zuurstof evolutie eigenschappen zien en $\text{Pt}/\text{Rh}:\text{SrTiO}_3$ goede waterstof evolutie eigenschappen. Echter, wanneer beide fotokatalysatoren werden gecombineerd met één van de ijzer-ionen, werd er geen uitwisseling van elektronen geobserveerd via een ijzer koppel. De metingen wijzen erop dat de ijzer half reacties worden kortgesloten door terug reacties over de fotokatalysator, waar de eigenlijke tweede half reactie zou moeten plaats vinden.

De eerste stap tot het realiseren van het met zichtbaar licht water splitsen op een chip was het ontwikkelen van een depositie methode voor de WO_3 photoanode. In hoofdstuk 5, is een hydrothermale procedure gedemonstreerd, die gebruikt kan worden om WO_3 selectief af te zetten op een platina substraat. Een oplossing werd gemaakt van wolframzuur in waterstofperoxide. De concentratie van de waterstofperoxide in de uiteindelijke oplossing had een bepalende rol op de morfologie en adhesie van WO_3 op Pt. Door middel van een gestructureerd Pt substraat was het mogelijk om de selectiviteit van de depositie methode voor Pt aan te tonen. Fotoelektrochemische karakterisatie liet een fotostroom dichtheid zien van $1,1 \text{ mA}/\text{cm}^2$, wanneer er een spanning van 1,23 V versus RHE werd aangelegd.

Om de water oxidatie eigenschappen van de Pt/WO₃ fotoanode te verbeteren, is in hoofdstuk 6 het aanbrengen van een IrO₂ co-katalysator onderzocht. Het doel was om door middel van elektrodepositie, IrO₂ rechtstreeks te deponeren op de WO₃ kristallen. Echter, door de poreuze morfologie van WO₃, resulteerde de elektrodepositie van IrO₂ in het afzetten van de co-katalysator direct op het Pt substraat. Om dit te voorkomen, werd er een TiO₂ laag gespincoat, die resulteerde in de vorming van een TiO₂ laag tussen de WO₃ kristallen. Op deze manier kon voorkomen worden, dat IrO₂ afgezet werd op Pt en kon er een direct contact tussen WO₃ and IrO₂ gerealiseerd worden. De toevoeging van TiO₂ tot de Pt/WO₃ photoanode verhoogde de fotostroom, waarschijnlijk door isolatie van het Pt substraat van de elektrolyt. Dit verlaagde het aantal van de gevangen ladingsdragers aan het oppervlakte van het Pt substraat, wat in het verkleinen van de door de Helmholtz laag geïnduceerde weerstand resulteerde. Onze uitleg voor de verhoging van de fotostroom is, dat de elektronen, die gevormd worden in de wolframoxide kristallen, minder weerstand ondervinden, wanneer ze in het substraat gaan. Door toevoeging van een isolerende TiO₂ laag, in combinatie met de katalytische eigenschappen van de IrO₂ co-katalysator, heeft een verhoging van de fotostroom van 140% gerealiseerd.

In hoofdstuk 7 is een fabricatie methode voor een Rh:SrTiO₃ fotokathode geïntroduceerd, om de halfgeleider te deponeren op een Pt substraat. Een chemische oplossing methode, gebaseerd op chelatie chemie, is gebruikt, om dichte Rh:SrTiO₃ lagen te deponeren op Pt substraten door middel van spincoating. De eerste gemeten fotostromen waren klein en daardoor was er een noodzaak voor het verbeteren van de structuur en samenstelling van de fotokathode. Verschillende eigenschappen van Rh:SrTiO₃ zijn onderzocht. Het reduceren van Rh⁴⁺ naar Rh³⁺ en het toevoegen van een Pt co-katalysator resulteerde in een kleine verbetering van de fotostromen. Echter de uiteindelijke fotostroom was enkele ordes kleiner dan de fotostromen gemeten voor WO₃ fotoanodes. Verder was de geobserveerde verandering voor de potentiaal waarbij waterstof evolutie aanvangt minimaal. *I*-*V* metingen laten zien, dat de weerstand in de Rh:SrTiO₃ laag veel groter is, dan de weerstand in een Nb-gedoopte SrTiO₃ laag, die gemaakt werd via een vergelijkbare depositie methode, wat mogelijk een verklaring is voor de kleine fotostromen.

In hoofdstuk 8 zijn de ontwikkelde depositie methoden uit hoofdstuk 5 voor WO₃ en uit hoofdstuk 7 voor Rh:SrTiO₃ gecombineerd, en is de praktische realisatie van zichtbaar licht geïnduceerd water splitsen op een chip geëvalueerd. De eerste karakterisatie van het concept werd gedaan, door het verbinden van een aparte fotoanode en fotokathode via een extern elektrisch circuit. Wanneer de belichting werd afgewisseld tussen licht en donker, werd er een kleine fotostroom van 10 µA gemeten onder belichting. De volgende stap was het integreren van WO₃ en Rh:SrTiO₃ op een Pt verdeler door middel van de ontwikkelde deposities methodes. The Pt verdeler bestond uit een 500 nm dikke film, die mechanisch ondersteund werd via een Si₃N₄ zeef structuur. De Pt verdeler werd verkregen

via een samenwerking met het LTN – VNUHCM instituut in Ho Chi Min City, Vietnam. De depositie van Rh:SrTiO₃ bedekte niet volledig de voorkant van de Pt verdeler, wat een aselectieve depositie van WO₃ aan beide kanten van het membraan tot gevolg had. Een gas chromatograaf meting liet H₂ ontwikkeling zien onder belichting. Echter werd er tegelijkertijd geen O₂ gemeten. Het is duidelijk, dat een verbetering van de geleiding in Rh:SrTiO₃ essentieel is voor een succesvolle implementatie van een op een Z-schema gebaseerde fotoelectrochemische concept.

Wanneer alle verkregen resultaten en kennis, die gepresenteerd zijn in dit proefschrift, gecombineerd worden, is een kort-door-de-bocht-conclusie, dat de uiteindelijke doelstelling van een 10% zon-naar-waterstof efficiëntie niet is gerealiseerd. De belangrijkste beperking, gebaseerd op alle metingen, is de Rh:SrTiO₃ fotokathode. Wanneer de Rh:SrTiO₃ fotokathode is aangebracht via een chemische oplossing depositie methode op een Pt substraat, is de gemeten fotoactiviteit laag ten opzichte van een WO₃ fotoanode. Dit kan veroorzaakt worden door de gebruikte depositie methode voor de fotokathode. Echter wanneer er rekening wordt gehouden met de resultaten uit hoofdstuk 3, zal Rh:SrTiO₃ niet een ideale fotokathode zijn voor het uiteindelijke concept. We hadden de keuze voor deze fotokathode gemaakt, omdat we op deze manier begonnen met een uit de literatuur bekende fotokathode/fotoanode combinatie. Deze combinatie is al uitvoerig geanalyseerd in de fotokatalyse gemeenschap. Onze fotokatalyse experimenten aan een Pt/Rh:SrTiO₃ systeem lieten zien dat het toevoegen van Rh als doping, defecten introduceert in SrTiO₃ en de fotoactiviteit verlaagt. Met de blik op de toekomst, is het noodzakelijk om te beginnen met het verbeteren van de Rh:SrTiO₃ fotokathode, of het ontwikkelen van een alternatieve fotokathode. Dit is nodig om de haalbaarheid van het concept aan te tonen. De metingen op het z-schema in het poeder systeem lieten ons zien, dat het gebruik van een elektronen bemiddelaar, om elektronen uit te wisselen tussen twee fotokatalystoren, zijn beperkingen heeft. De half reacties van de elektronen bemiddelaar zorgen voor het kortsluiten van de half reacties. Dit heeft tot gevolg dat de tweede fotokatalysator niet efficiënt wordt gebruikt. Daarom is het interessant om het voorgestelde concept in dit proefschrift verder te onderzoeken. De selectieve depositie van wolframoxide op een Pt substraat heeft geleid tot goede fotostromen. Echter voor een uiteindelijke toepassing, en het bereiken van een efficiëntie van 10%, zal het ook nodig zijn om een andere photoanode te ontwikkelen met een kleinere band gap. De belangrijkste stap om het concept aan te tonen, is echter het verbeteren van de fotokathode.

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LIST OF PUBLICATIONS

Published

1. Zoontjes, M.G.C., M. Huijben, J. Baltrusaitis, W.G. van der Wiel, and G. Mul, *Selective Hydrothermal Method To Create Patterned and Photoelectrochemically Effective Pt/WO₃ Interfaces*, *ACS Applied Materials & Interfaces*, 2013, 5(24): p. 13050-13054.
2. A.W. Maijenburg, J. Veerbeek, R. de Putter, S.A. Veldhuis, M.G.C. Zoontjes, G. Mul, J.M. Montero-Moreno, K. Nielsch, H. Schäfer, M. Steinhart and J.E. ten Elshof, *Electrochemical synthesis of coaxial TiO₂-Ag nanowires and their application in photocatalytic water splitting*, *Journal of Materials Chemistry*, 2014, 2: p. 2648-2656

In Preparation

3. M.G.C. Zoontjes, M. Huijben, W.G. van der Wiel, and G. Mul; *Analysis of the Dynamic Composition of SrTiO₃-based catalysts in Overall Water Splitting; to be submitted*
4. M.G.C. Zoontjes, M. Huijben, W.G. van der Wiel, and G. Mul; *Analysis of Z-scheme photocatalysis of WO₃ and Pt modified Rh:SrTiO₃ in a continuous flow reactor; to be submitted*
5. M.G.C. Zoontjes, R. Jong, M. Huijben, W.G. van der Wiel, and G. Mul; *Enhancement of the photo current of WO₃ by insulating the substrate from the electrolyte and adding a co-catalyst; to be submitted*
6. M.G.C. Zoontjes, R. van Aalst, M. Huijben, W.G. van der Wiel, G. Mul; *A chemical solution deposition method to fabricate a visible light active Rhodium doped Strontium Titanate photocathode; to be submitted*

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