University of Twente

Photocatalytic watersplitting with WO_3 and $SrTiO_3$:Rh on a chip

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Abstract

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Photocatalasis can be used as method to split water in hydrogen and oxygen. The goal of this project was to successfully integrate the photocatalysts WO_3 and $SrTiO_3$:Rh in a Z-scheme configuration to split water. First WO_3 and $SrTiO_3$:Rh are integrated on Si/Pt substrates, there cyclic voltametry and chronoamerometry measurements have been made with a solar simulator to measure their photocatalytic activity. UPS measurements have been made to see if there would be a hindering Schottky-barrier at the interfaces of the photocatalysts and the Pt. The cyclic voltametry measurements showed that WO_3 has good photocatalytic activity while $SrTiO_3$:Rh has little photocatalytic activity. The chronoamperometry measurements showed that a small current of a few μA was created when the photocatalysts where illuminated by a solar simulator, indicating that there are electron-hole pairs created in the photocatalysts. The UPS showed shottkey-barriers favorable for separating electron-hole pairs. Secondly both photocatalists are integrated on Pt membranes with Si support. One on each side. By the membranes it couldn't be averted that WO_3 also grew on the $SrTiO_3$:Rh side of the membrane. GC measurements of the membrane showed hydrogen production but no oxygen production.

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Chapter 1

Introduction

The topic of renewable energy gets a lot of attention in the world. Fossil fuels are limited resources and the public prefers clean energy. But existing methods of renewable energy harvesting are not yet sufficient to provide the whole world of energy. A lot of research is going on to search for new methods of energy harvesting.

One of these methods is photocatalytic water splitting. With photocatalytic water splitting water is split through photocatalysis into oxygen and hydrogen. The advantages of splitting water through photocatalysis are that only water is needed and no greenhouse emissions take place. Single photocatalyst can only split water in UV light, but configuring two photocatalyst with overlapping band gaps makes it possible to split water in visible light. Jong[10] and Aalst[9] have researched the photocatalytic behavior of the two photocatalysts WO_3 and $SrTiO_3$:Rh. This report will use the photocatalysts they improved and try to integrate them in a Z-scheme configuration to split water in visible light.

Chapter 2

Theory

Splitting water has been of interest because the hydrogen can be used as fuel. To split water free electrons and holes are needed that can react with the water. These electrons and holes can be generated by applying a potential of 1.48 V over two metal electrodes like by electrolyse or like in this project the electrons and holes are created through photocatalysis. This has as advantage that it doesn't need external current applied.

2.1 Photocatalytic water splitting

The global process photocatalytic water splitting is schematically represented in figure 2.1.

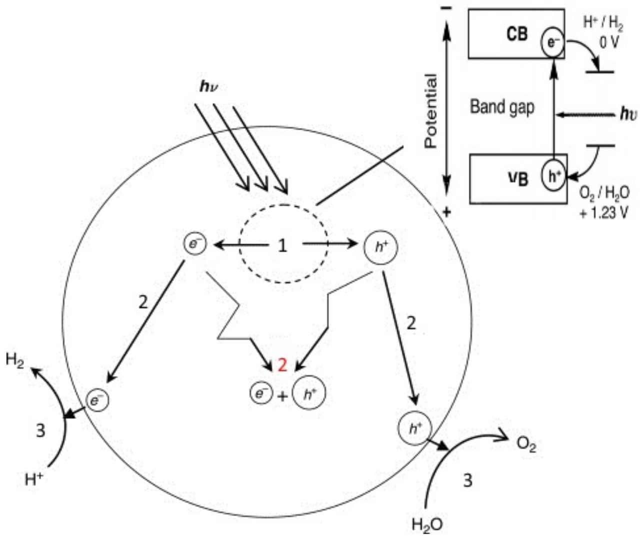


Figure 2.1: Three steps of water splitting. 1: photon absorption and creation of an electron-hole pair. 2: separation of the electron-hole pair and migration to the surface. 3: half reaction with water.[1], [2]

Step 1 is to create an electron and hole. Semiconductors and insulators have a conduction band and a valance band where electrons can occupy energy levels. In the valence band all unexcited electrons reside while in the conduction band all excited electrons reside. When a photon with more energy than the band gap hits an electron in the valence band the electron will get excited and jump to the conduction band. Leaving a positive hole behind in the valence band(1). Semiconductors are good photo-catalysts because they have a small band gap. Making it for photons with in the visible and UV spectrum able to excite electrons. After the hole and electron are created it is important to separate them so they wont recombine. At surface interface between the water and the semiconductor band bending occurs. This depends on the pH of the solution, protons and/or OH^- groups will absorb on the interface creating a charged layer(Helmholtz layer). The conduction band and valence band of the semiconductor at the interface will increase a bit. This creates a depletion region at the interface where electrons are moving away from and holes are gathering. Thus creating an electric field inside the depletion region[3], [12]. This electric field can separate the electron and hole. Next to separation, easy migration is also important. A high pure crystal semiconductor prevents the electrons and holes to get trapped in vacancies or interstitial molecules. Also a closed packed structure makes the distances the electron and holes need to travel between the atoms smaller and thus easier.[2] Step 3 are the half reactions at the surface of the photocatalyst with water:

Half reaction of oxygen: $2\,H_2O + 4\,h^+ \longrightarrow 4H^+ + O_2$ O_2/H_2O: +1.23 vs RHE
Half reaction of hydrogen: $2\,H^+ + 2\,e^- \longrightarrow H_2$ H^+/H_2: 0V vs RHE
Overall water splitting reaction: $2\,H_2O + 4\,h^+ + 4\,e^- \longrightarrow O_2 + 2\,H_2$

For the half reactions to work the electrons and holes need to be at a energy level of 0 V vs RHE and 1.23 V vs RHE respectively where RHE(Reversible hydrogen electrode) is a reference where the potentials needed for half reactions are compared to the half reaction of H^+/H_2. To get this potential the bottom level of the conduction band of the semiconductor needs to be more negative than 0 volt vs RHE and the highest level of the valence band needs to be more positive than the O_2/H_2 1.23 volt Vs RHE.[2] This results into a theoretical minimal band gap of 1.23 eV, which responds to photons of about 1000 nm which is in the infrared spectrum. In reality however an over potential is needed for the half reactions due to the band banding at the surface of the semiconductor resulting in a practical potential needed of 1.46 eV. Semiconductors close to this band gap do not exist or are not found yet. A list of semiconductors and their band gaps are listed below in figure 2.2. ZrO_2, $KTaO_3$, $SrTiO_3$ and TiO_2 are suitable semiconductors for water splitting but all contain band gaps of 3 eV or more, which responds to 400 nm and lower which lies in the ultraviolet spectrum and thus the materials are too large for water splitting in visible light spectrum.

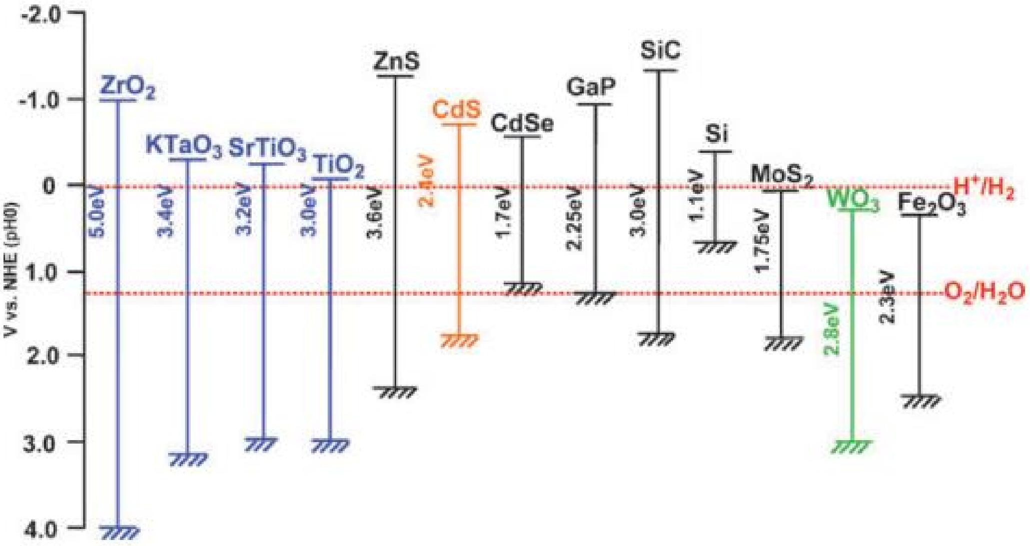


FIGURE 2.2: List of semiconductors[2]

2.2 Z-scheme

To be able to split water in the visible light spectrum a Z-scheme configuration can be used. Instead of one, two photocatalysts are used that together have an overlapping band gap at 0 and 1.23 eV. See figure 2.3.

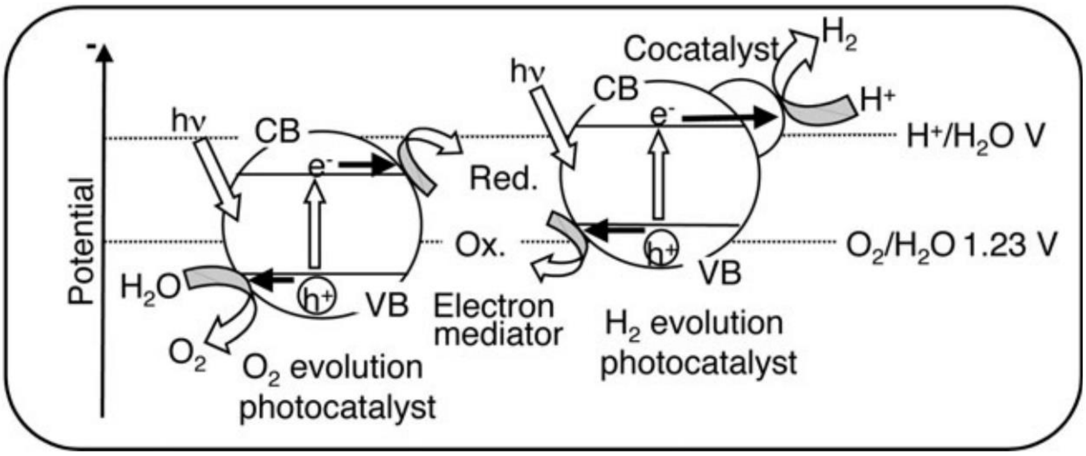
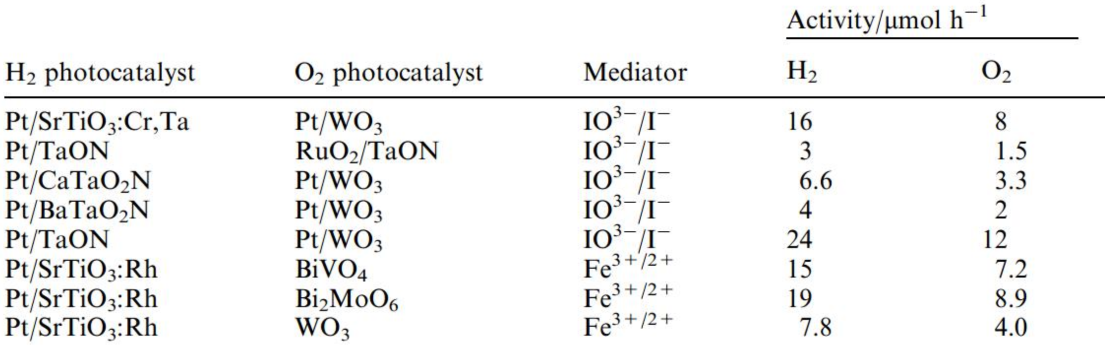


FIGURE 2.3: Z-scheme[2]

Each photocatalyst will contribute just to one of the half reactions. Thus one photocatalyst only needs electrons while the other only needs holes. An electron mediator is used to recombine electrons and holes left by the photocatalysts. An electron mediator is an ion that has two different charges, such as Fe^{2+} and Fe^{3+}. If one of the photocatalysts donates an electron to the Fe^{3+} it will become Fe^{2+}. The other photocatalyst can then donate a hole by taking an electron of Fe^{2+} and it will become Fe^{3+} again. This way Fe^{2+}/Fe^{3+} is not spent. But because the electron mediator needs to have the right charge when the photocatalyst wants to donate an electron or hole the electron mediator may be a limited factor. A list of possible photo catalysts and their electron mediator is given in figure 2.4. The activity is measured when radiated with a 300W Xe lamp with cutoff filter.[2] In this project WO_3 and $SrTiO_3$:Rh are used as photocatalysts. WO_3 has a band gap of 2.8 eV[2] which corresponds to a wavelength of 443 nm. $SrTiO_3$ has a band gap of 3.2 eV which responds to a wavelength of 387.5 nm. The latter one has a wavelength in the UV spectrum but by doping it with Rhodium levels are created in the band gap for electrons to occupy, thus shortening the band gap to 2.3 eV[4] which corresponds to 530 nm. Because the efficiency of using an electron mediator is low it will be replaced by the metal platinum. The metal will conduct the electrons from one semiconductor to the holes of the other semiconductor.



			Activity/μmol h^{-1}	
H_2 photocatalyst	O_2 photocatalyst	Mediator	H_2	O_2
Pt/$SrTiO_3$:Cr,Ta	Pt/WO_3	IO^{3-}/I^-	16	8
Pt/TaON	RuO_2/TaON	IO^{3-}/I^-	3	1.5
Pt/$CaTaO_2N$	Pt/WO_3	IO^{3-}/I^-	6.6	3.3
Pt/$BaTaO_2N$	Pt/WO_3	IO^{3-}/I^-	4	2
Pt/TaON	Pt/WO_3	IO^{3-}/I^-	24	12
Pt/$SrTiO_3$:Rh	$BiVO_4$	$Fe^{3+/2+}$	15	7.2
Pt/$SrTiO_3$:Rh	Bi_2MoO_6	$Fe^{3+/2+}$	19	8.9
Pt/$SrTiO_3$:Rh	WO_3	$Fe^{3+/2+}$	7.8	4.0

FIGURE 2.4: Different types of photocatalyst pairs and their electron mediator[2]

2.3 Metal-semiconductor interface and Schottky barrier

In the water splitting cell there are two metal-semiconductor interfaces. The WO_3/Pt interface and the $SrTiO_3$:Rh/Pt interface. At these interfaces band bending can occur which can give rectifying properties to the system. This phenomenon occurs because the highest electron states occupied differ in the two materials, so that at the interface the electrons in the material with the highest electron states can jump to the other material with lower electron states, causing the Fermi-levels of the materials to align so that the conduction band and valance band bend as can be seen in figure 2.5B. This is called a Schottky barrier.

When the bands have bend like in figure 2.5B it will become difficult for electrons to jump from the metal to the semiconductor, because it will need to be excited to a higher level. Thus the material will act as a diode because only an electron flow from the right to left is possible. To determine how the band bends the work function is measured with UPS(Ultraviolet Photo-electron Spectroscopy). The work-function is the minimum

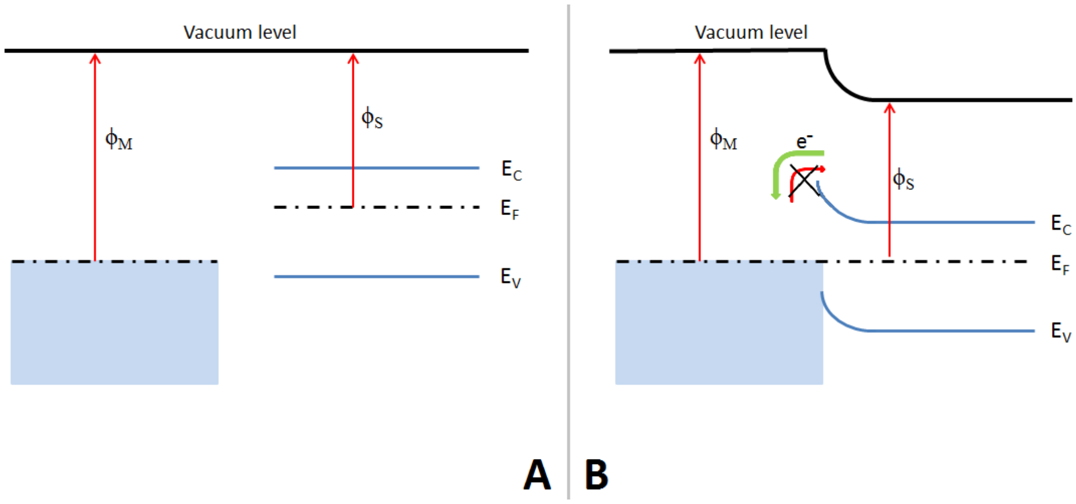


FIGURE 2.5: Band diagram of a metal-semiconductor interface. A: Metal and semiconductor are not touching so the bands don't bend. B: Metal and semiconductor touch and the bands of the semiconductor bend.

energy required to excite an electron to vacuum level and are denoted in figure 2.5 with φ_M and φS. Because the work function is related to the Fermi-level through the relation $\varphi = E_{vacuum} - E_F$ the Fermi-levels of the materials can be determined and the way the band bends can be constructed.

2.4 The photo catalytic cell

The goal of this project is to achieve full water splitting with WO_3 and $SrTiO_3$:Rh. To achieve this a water splitting cell is constructed such as figure 2.6. WO_3 and $SrTiO_3$:Rh

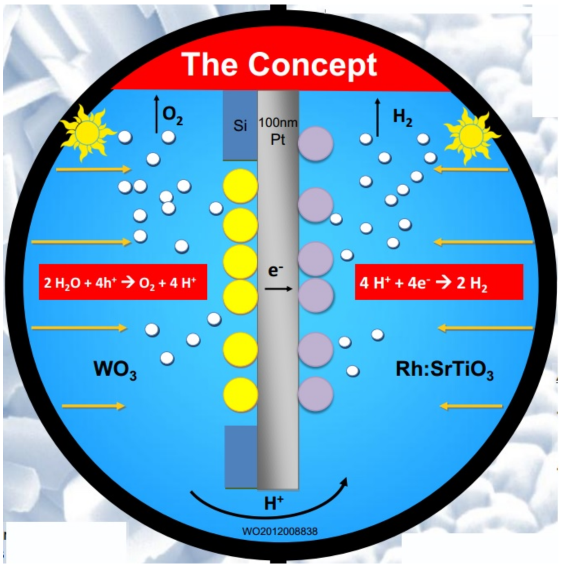


FIGURE 2.6: Water splitting cell lay-out[14]

are each integrated on a Pt membrane side. WO_3 is the hydrogen evolving catalyst and $SrTiO_3$:Rh is the oxygen evolving catalyst. Both are manufactured on a side of a Pt film. The cell will be closed at the sides but not at the bottom so that liquid can be diffused to both sides of the chip but not gass, so that the oxygen and hydrogen gas created are separated. Because liquid diffusion is possible protons created at the $SrTiO_3$:Rh can diffuse to the other side to react with the WO_3. The Pt film will be put in low pH aquatic solution for faster proton exchange between WO_3 and $SrTiO_3$:Rh. On this cell GC(Gass Chromatography) measurements can be made from both compartments to see if hydrogen and oxygen are created.

Chapter 3

Material synthesis and Characterization methods

The goal of this project is to make a sample with on one side WO_3 and on the other side $SrTiO_3$:Rh. Si/Pt substrates are used to grow either WO_3 or $SrTiO_3$:Rh on for cyclic voltametry, chronoamperametry, XRD and UPS measurements. Pt foils and on nanoscale crafted membranes are used to grow on one side WO_3 and on the other side $SrTiO_3$:Rh. $SrTiO_3$:Rh is integrated through chemical solution deposition. With this synthesis method it is fairly easy to keep one side of the sample clean. WO_3 is integrated with hydrothermal synthesis where WO_3 selectively grows on Pt. Thus the best way to integrate both catalysts is by first integrating $SrTiO_3$:Rh on one side of the sample, covering the Pt on one side so that the WO_3 grows only on the other side during the hydrothermal synthesis.

3.1 structure of membranes

Membranes where manufactured in a nanolab to use as substrates. The membranes consist of Silicon frame with a thin Pt layer in between. A picture of the cross section of the membrane can be seen in figure 3.1. There were three batches of membranes crafted. One of the batches had holes with a diameter of 5 µm, but the Si layer on the underside was not etched completely away so that the platinum holes where not free. The other two batches had holes with a diameter of 10 µm and a diameter of 50µm. First on the top of the membrane $SrTiO_3$:Rh will be synthesized and after that WO_3 will be synthesized on the bottom.

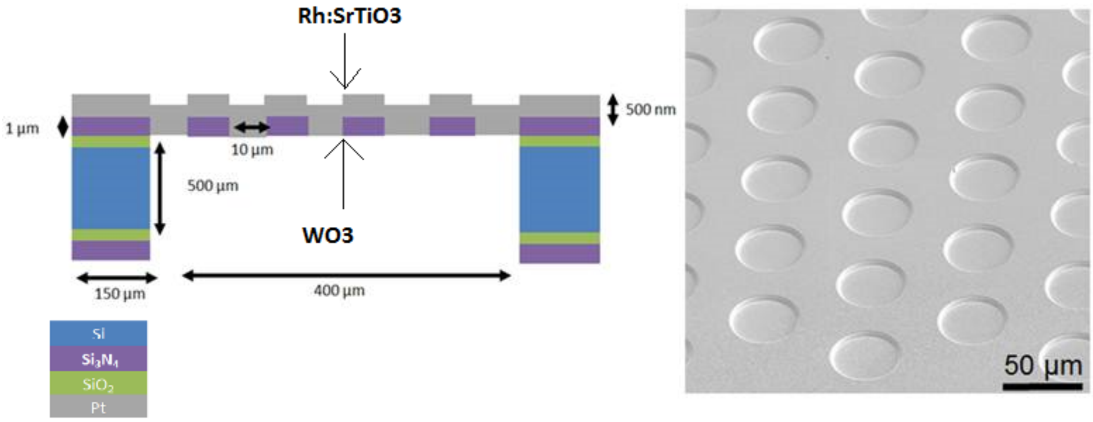


FIGURE 3.1: Membrane crossection

3.2 Synthesis of $SrTiO_3$:Rh

The integration of $SrTiO_3$:Rh is done through chemical solution deposition. The method can be divided into three steps[6]:

- Making of the precursor. The precursor is a solution of the materials wanted on the substrate dissolved in a solution that easy evaporates at high temperatures.
- Depositing the precursor on the substrate. This is done with spin coating, the substrate is held in place on a plate through a vacuum. A droplet of the precursor solution is then deposited on the substrate and the plate starts spinning for a specific time creating a homogeneous layer on the substrate. The thickness of the layer is determined by the amount of precursor deposited on the substrate, the rounds per minute of the plate and the time spun.
- Heat treatment of the chip. After the precursor is deposited on the substrate the substrate is placed in the oven. There the solution is evaporated and the ions crystallize in a layer on the substrate.

The process of chemical solution deposition of $SrTiO_3$:Rh is summarized in figure 3.2. First Strontium Acetate is mixed in acetic acid. Because Strontium Acetate is hard to dissolve in acetic acid this will take approximately 30 minutes. Titaniumisopropoxide is stabilized with acetylacetone to prevent TiO_2 formation. This will take approximately 5 minutes. These two solutions are stoichiometric mixed. Small quantities of Rhodium acetate are added as doping. Methanol is added until Precursor solution of 0.1M is made. The exact quantities of the reactants can be found in table 3.1.

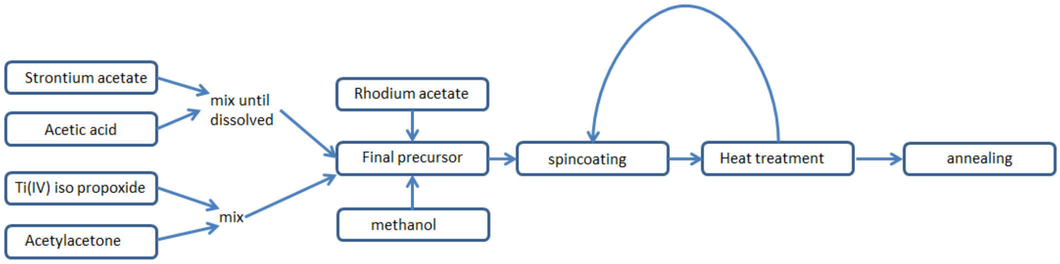


FIGURE 3.2: Diagram of $SrTiO_3$:Rh synthesis

Reactant	quantity
Strontium Acetate	0.733 gr
Acetic acid	0.251 ml
Titanium(IV)isopropoxide	0.514 ml
Acetylacetone	10 ml
Rhodium acetate	10 gr
Methanol	Add until total solution is 25,ml ml

TABLE 3.1: Chemicals needed for $SrTiO_3$:Rh

100 µl of the precursor solution is spin coated at 3000 rpm for 40 seconds on the platinum substrates. While spin coating the vacuum of the spin coater sucks precursor underneath the sample, leaving traces of $SrTiO_3$:Rh on the side of the sample where WO_3 is supposed to be synthesized. To prevent this, a piece of tape is stuck on the backside of the sample. This piece of tape is removed before the heat treatment. After enough layers have been synthesized WO_3 is grown on the other side through hydrothermal synthesis. The substrate is then placed in a calcination oven at 700 °C for 30 minutes. After the heat treatment the spin coating step and heat treatment step are repeated 5 times to get a thicker layer of $SrTiO_3$:Rh. With the Si/Pt samples Pt co-catalyst is deposited by vaporization. A droplet of H_2PtCl_6 is dropped on the chip and put in the calcination oven at 500 °C for a few minutes.

3.3 Synthesis of WO_3

WO_3 is synthesized on the substrates using the hydrothermal synthesis technique. Hydrothermal synthesis is a synthesis technique used to form crystals, powders and different types of shapes of nanoparticles by placing an aquatic solution in an autoclave under high temperatures. Because the autoclave is sealed the pressure in the autoclave will rise when it is heated. Under these conditions reactants in the aquatic solution will form crystals, powders and different types of shapes of nanoparticles. The solution is made by dissolving tungstic acid(H_2WO_4) in 30% H_2O_2 by stirring it at 80 °C for 15 minutes. This will react to $WO_3{\cdot}H_2O_2$ like in the equation:

$$H_2O_2 + H_2WO_4 \longrightarrow WO_3 * xH_2O_2 + O_2$$

After the solution has turned from a yellow turbid liquid to a clear solution it is diluted with demi-water. Three concentrations are made, 0.01M, 0.02M, 0.04M and the corresponding quantities of the reactants can be seen in table 3.2.

Molair	0.01M	0.02M	0.04M
H_2WO_4	0.0625 g	0.125 g	0.25 g
H_2O_2	0.5 ml	1 ml	2 ml
demi water			

TABLE 3.2: Chemicals needed for WO_3

Little bits of Pt pieces are added to the solution for a night to remove the excess H2O2. If this is not done, at the hydrothermal synthesis the excess H_2O_2 will form oxygen bubbles on the Pt film that obstruct the WO_3 growth. (see figure 3.3). The excess H_2O_2 will now instead react with the Pt pieces into water and oxygen[8].

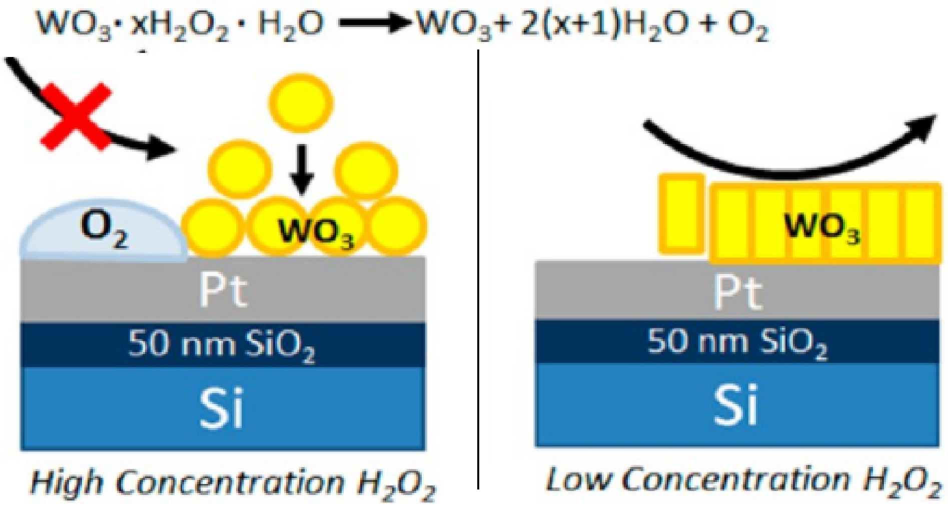


FIGURE 3.3: WO_3 growth with and without excess of H_2O_2[8]

The next day the small pieces Pt are removed and the solution are put with the substrates in the hydrothermal vessels. The membrane and the Pt foil the $SrTiO_3$:Rh was covered because WO_3 would cover the $SrTiO_3$:Rh as explained in section 4.3. The hydrothermal vessels are put in an oven for 18 hours at 170 °C with a heat rate of 10 °C per minute.

Here orthombic $WO_3{\cdot}0.3H_2O$ will grow on the Pt surface of the substrates. After 18 hours the vessels are naturally cooled to room temperature. The substrates are removed and carefully rinsed with distilled water, then dried under a mild nitrogen flow. In the final step the samples are annealed at 675 °C for 10 hours in static air applying a heating rate of 10 °C/minute to transform the orthombic $WO_3{\cdot}0.3H_2O$ to Monoclinic WO_3.

3.4 Characterization techniques

3.4.1 Photo electro chemistry

Photo electro chemistry is a method to measure how much electrons and/or how many holes are generated. This is done by applying a potential on the chip. Two different setup are used in this project. The cyclic voltametry setup(figure 3.4) and the chronoamperometry setup(figure 3.5).

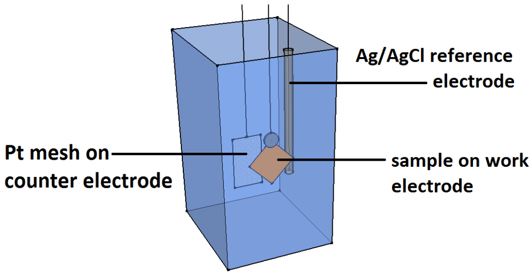


FIGURE 3.4: Set up for a cyclic voltammetry measurement

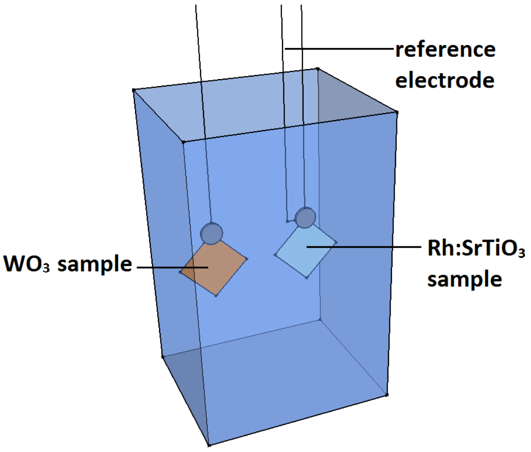


FIGURE 3.5: Set up for a chronoamerometry cell

In cyclic voltametry three electrodes are submerged in liquid. The sample is the work electrode. A platinum mesh is used as counter electrode and a 3 M Ag/AgCl is used as the reference electrode[5]. Because water is not very conducting, all the electrodes are submerged in a H_3PO_4 solution. The H^+ and PO_4^{3-} ions work as charge carriers[5]. The Versastat 3 is used to apply a potential difference to the reference electrode and the work electrode. If the right potential of 0 Vs RHE is used the half reaction of hydrogen evolution takes place and at 1.23 Vs RHE the half reaction of oxygen evolution takes place. The potential versus the reference electrode is in a different scale then RHE that are dependent on the pH of the electrolyte and the zero potential of the reference electrode. The potential can be translated through the Nernst equation:

$$V_{RHE} = V_{Ag/AgCl} + V0_{Ag/AgCl\ Vs\ SHE} + 0.059 * pH \tag{3.1}$$

Where $\mathrm{V_{Ag/AgCl}}$ the potential measured is and $\mathrm{V0_{AG/AGCl}}$ vs SHE the potential of the reference electrode versus SHE is in H_3PO_4.

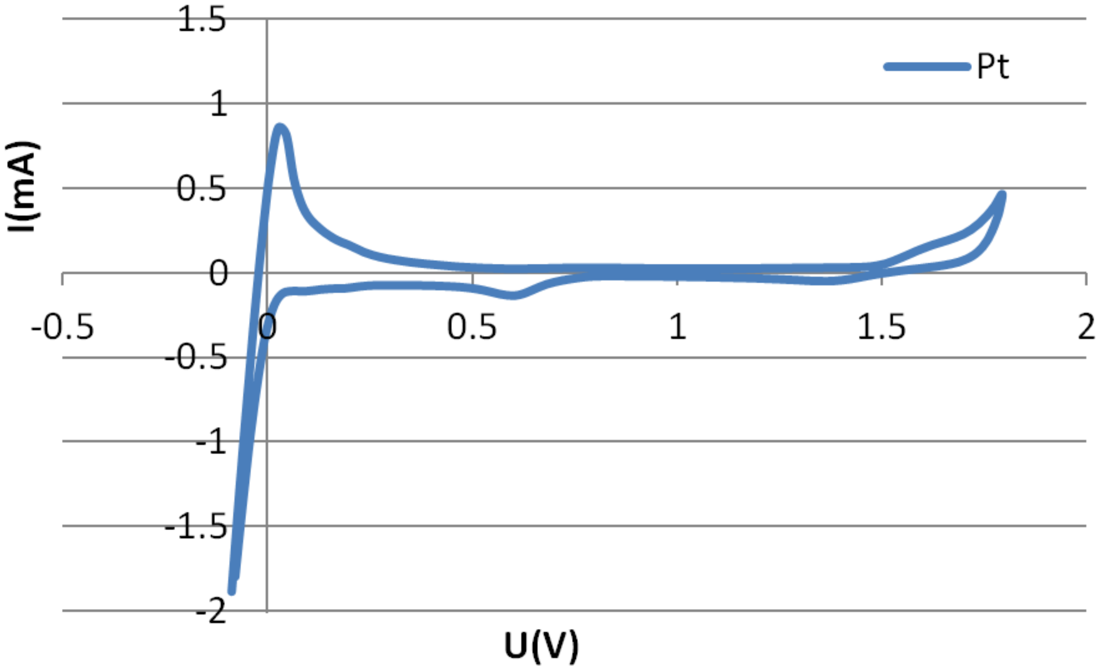


Figure 3.6: Cyclic voltametry measurement of a Pt sample

Figure 3.6 is an example where cyclic photochemistry has been performed on a clean platinum substrate. At 1.8 V Pt oxidation takes place. A positive current is seen because Pt uses holes for the oxidation. At -0.1 V Pt hydrogenation takes place and a negative current is seen because Pt uses electrons for teh hydrogenation. At 0 V dehydrogenation takes place from the Pt surface.

With Chrono Amperometry the efficiency z-scheme is tested. The Chrono Amperometry that can be seen in figure 3.5 is almost identical as the cyclic photo electro chemistry setup, only the counter electrode is replaced with a second sample and the voltage difference used is the voltage between the two samples instead of against the reference. So now the two photocatalysts are connected through a conducting wire. The Voltage is set constant at 0 Volt and the current between the chips is measured against time. A solar lamp is used to illuminate at the two samples in time steps of 60 seconds. If everything is correct when the lamp is out no current flows through the wire, but if the lamp is on there is electron and hole transfer from the half reactions through the wire.

3.4.2 Gas Chromatography(GC)

Gas chromatography can be used to identify the composition of a gaseous sample. The sample is carried by a carrier gas into a tube. The surface of the tube is covered with a small layer of liquid or polymer that makes the surface polar or a-polar. The gas sample reacts with the surface of the tube and individual components are slowed down at a specific rate, thus separating them. If a reference is used, components in the sample can be identified. It is important that the carrier gas is inert otherwise there may be a reaction between the carrier gas and the compound thus altering your compound. For this setup helium is used as carrier gas. For the GC measurement a reactor is made just like in figure 2.6. The reactor is completely sealed of so that there can only the carrier gas can go in and out. Because there is just one working GC channel available, the gas caught in both compartments are led through a T-joint into a single channel.

3.4.3 Ultraviolet Photon Spectroscopy(UPS)

With UPS the work function of the photo catalysts and Pt can be measured. By radiating the sample with ultraviolet light, the photocatalyst will be ionized. The electrons coming from the material will follow Einstein's photoelectric law:

$$Ek = \lambda v - I \tag{3.2}$$

The ionization energy I is equal to the work function when the electron ionized comes from the fermi-level. The photon energy λv used for the measurements is 21.218 eV. A potential is applied to conduct the caught electrons and thus make sure that all ionized electrons are measured. By subtracting the applied potential and the kinetic energy from the photon energy the work function can be acquired.

3.4.4 X-Ray Diffraction (XRD)

X-Ray Diffraction is a characterization technique used to determine the crystal structure and composition of a sample. A beam of x-rays is shot at the sample at different angles, where they diffract against the atoms of the sample and are captured in a detector. In this way, the angle of the x-ray is measured against the intensity of the x-ray's captured. If the atoms are in a crystal structure at some angles the atoms are in one line and a lot more x-rays are reflected then when the atoms are not in line. At these angles the intensity of the x-rays will be a lot higher and you get a peak. With braggs law: $2d*\sin(\theta)=n\lambda$, the distance between the atoms can be calculated. Because every composition has a different distance d the composition can be determined.

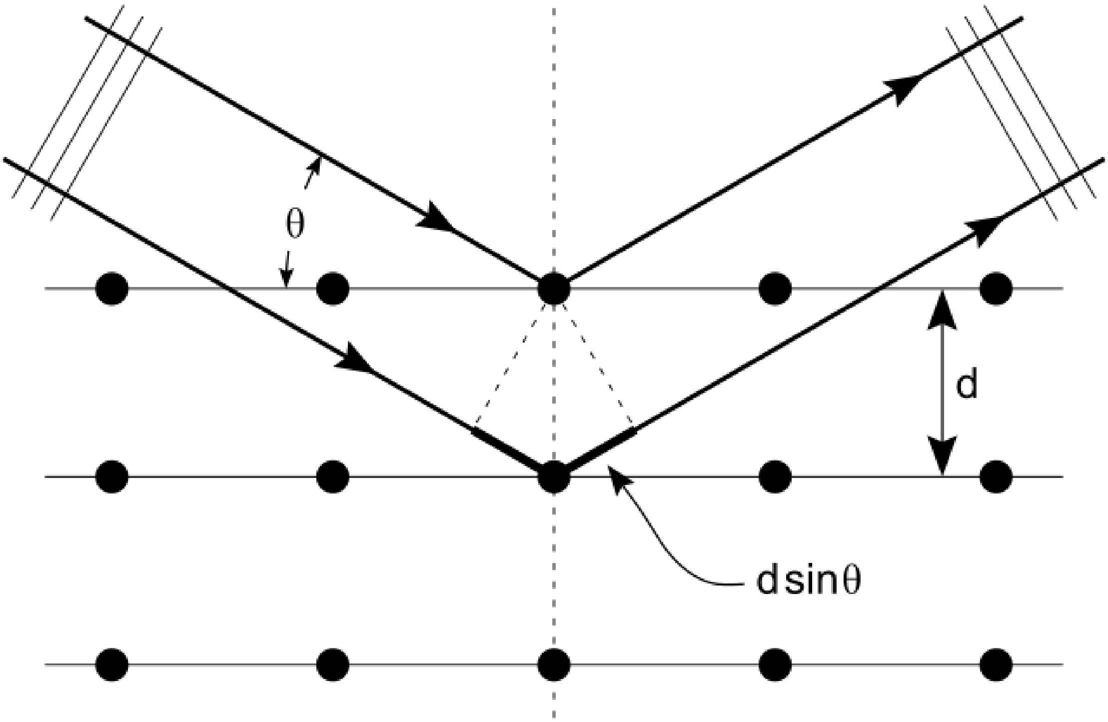


FIGURE 3.7: Braggs difraction

3.4.5 Scanning Electron Microscope (SEM)

To get a look at the crystal structure of the deposited photocatalysts on nanoscale SEM images can be made. A schematic of the SEM can be seen in image 3.8. The

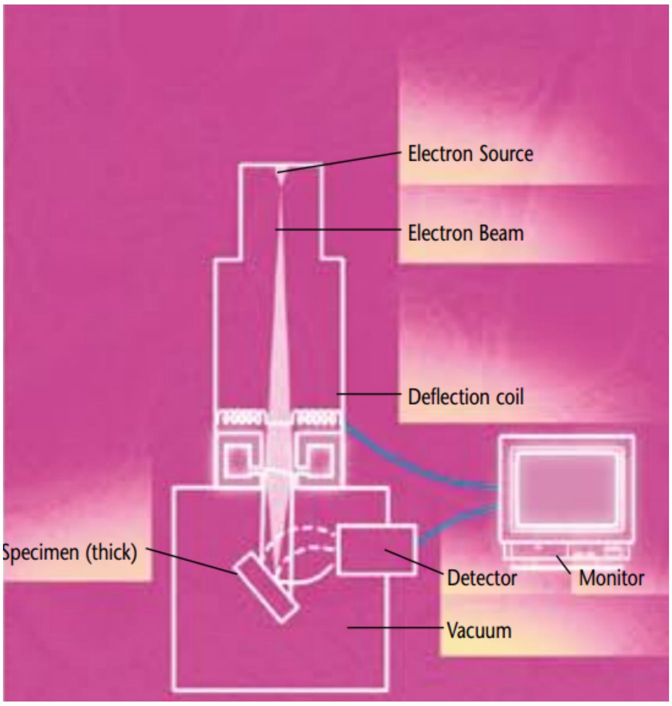


FIGURE 3.8: Schematic diagram of a SEM[11]

sample is put in the SEM under high vacuum so that the electrons don't interact with air molecules. The SEM shoots then a thin beam of electrons with high energy at the surface. When these high energized electrons hit the surface they knock electrons from the surface away from their atoms. These electrons have low energy and are caught in the detector. When the electron beam scans over the surface at high places of the sample structure more electrons will be knocked out of the surface while at deeper parts where the electron beam is reached more difficult, less electrons are knocked away of the surface. These different amounts are measured in the detector and images can be constructed of these intensity differences.

Chapter 4

Results and Discusion

First the photocatalyst where integrated on Si/Pt substrates. This went without problems. Photo electrochemstry characterization techniques have been applied on these samples to test the photocatalytic activity of WO_3 and $SrTiO_3$:Rh. These discussed in section 4.1. After it was confirmed that both photocatalysts have photocatalytic activity both photocatalysts where integrated on membranes. A few attempts where made to integrate the photocatalysts on Pt foil but because Pt foil would easy wrinkle under the pressure of the spincoaters vacuum. Further attempts where dropped. SEM images have been made to see how WO_3 and $SrTiO_3$:Rh would integrate on the surface of the membranes. These results are discussed in section 4.2. UPS measurements have been made to make a band structure of the metal-semiconductor interface and are discussed in 4.3. At the end of the project one GC measurements was made of membrane sample and is discussed in 4.4.

4.1 Synthesis

4.1.1 Synthesis of WO_3 samples

Of the WO_3 samples made the 0.04 M solution showed a thick inhomogeneous layer while the samples of 0.02 M had a homogeneous layer on it. Cyclic voltammetry measurements of the 0.04 M samples also showed bad photocatalytic activity. Thus were the 0.02 M samples used for the rest of the measurements. An XRD graphic can be seen in figure 4.1. The intensity is in logarithmic scale so that the peaks can be better distinguished. The XRD measurements corresponds to the XRD in the literature[8], [13]. The XRD shows monoclinic WO_3 growth. The peaks at 28.5 and 35.5 2θ correspond to $WO_3 \cdot 0.3H_2O$. This means not all $WO_3 \cdot 0.3H_2O$ has been transformed to WO_3 during annealing.

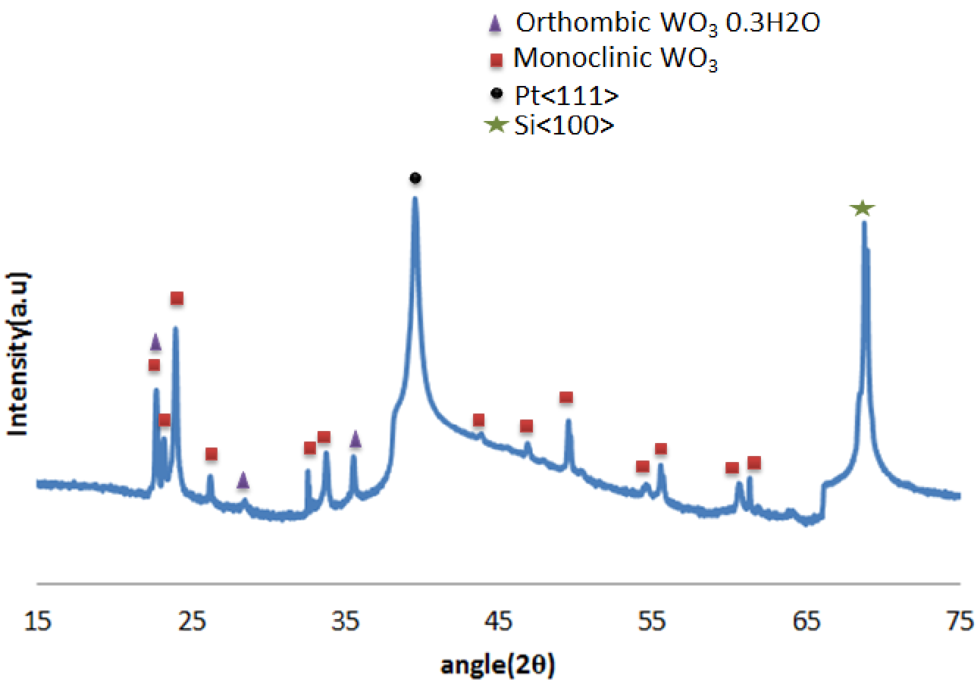


FIGURE 4.1: XRD of WO_3

4.1.2 Synthesis of $SrTiO_3$:Rh

$SrTiO_3$:Rh was successfully integrated on the substrates. The XRD seen in figure 4.2 shows the growth of $SrTiO_3$:Rh in the (110) plane at the 33 2θ peak and in the (211) at the very small 57 2 θ peak. Other undefined peaks are probably rests from the precursor or from the SiO_2 in the substrate.

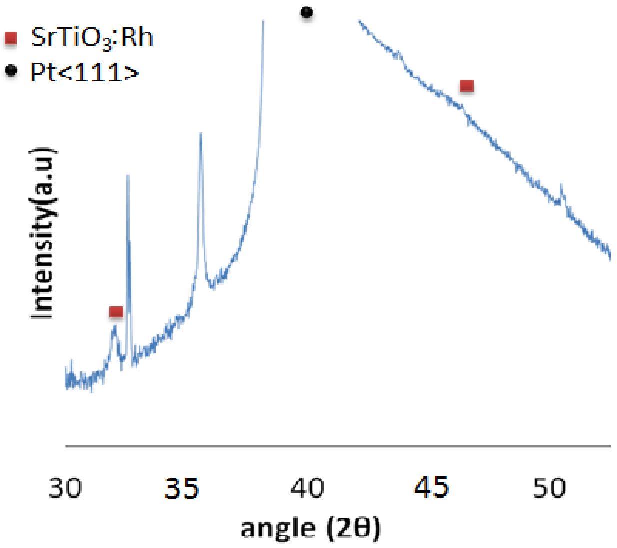


FIGURE 4.2: XRD of $SrTiO_3$:Rh

4.2 Photocatalytic activity of WO_3 samples and $SrTiO_3$:Rh

To test the photocatalytic activity of the photocatalysts, cyclic voltametry and chronoamperometry characterization techniques have been applied on the WO_3 and $SrTiO_3$:Rh samples. In figure 4.3 the cyclic voltametry of WO_3 and $SrTiO_3$:Rh is displayed. The current of the $SrTiO_3$:Rh is displayed in reverse order for easier comparison with WO_3. The potential was not swiped from the -0.1 to 1.8 V Vs RHE for these samples because they would break if reverse bias would be applied. The WO_3 was swiped from 0 Vs O.C.(open circuit) to 1.8 Volt Vs RHE. When the solar simulator is turned on the current increases, because the WO_3 supplies holes to the circuit. At the $SrTiO_3$:Rh sample the voltage is swiped from 0 Vs O.C to -0.1 V Vs NHE. Here electrons are given to the surface when the solar simulator is turned on and thus results in an extra negative current. From the results can be seen that the WO_3 sample has a good photocatatyc activity while the $SrTiO_3$:Rh sample hardly has one. This could be because $SrTiO_3$ has a bad conductivity and doping it with Rh would decrease the conductivity even more.

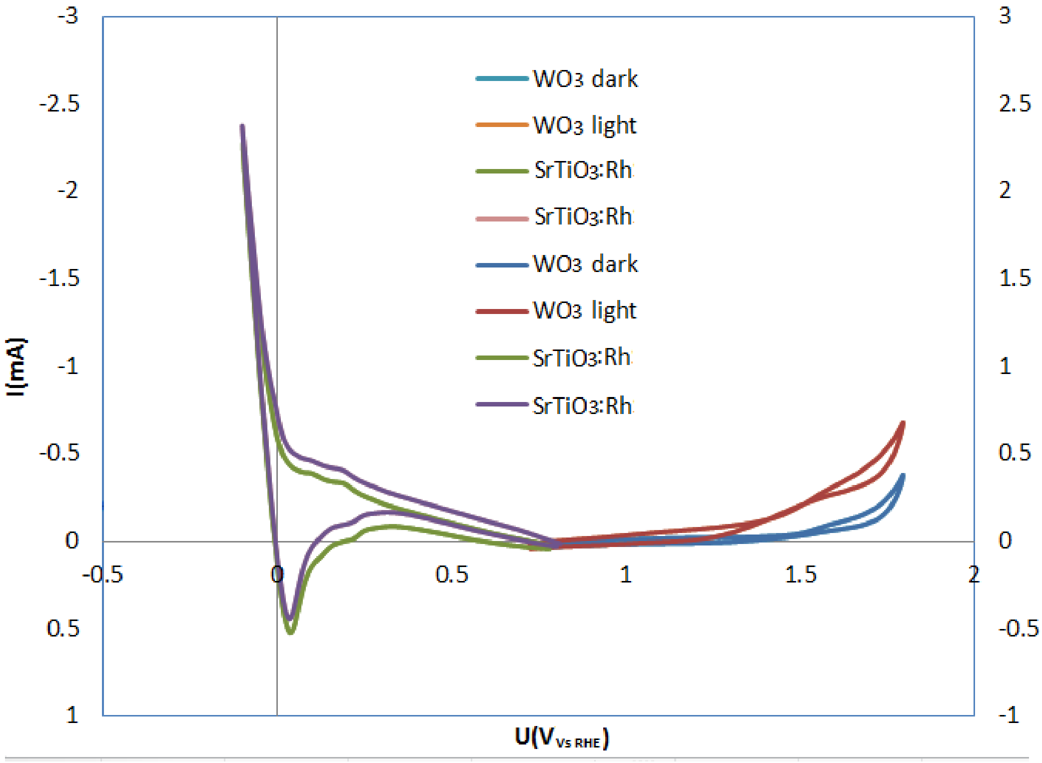


FIGURE 4.3: Cyclic voltametry measurements

Chronoamperometry has been used to see if full water splitting is possible. The theoretical value obtained from these samples would be the current at the cross section of the cyclic voltametry light on measurements. As can be seen this value is very close to 0. But the chronoamperometry gives a result and is displayed in figure 4.4 .

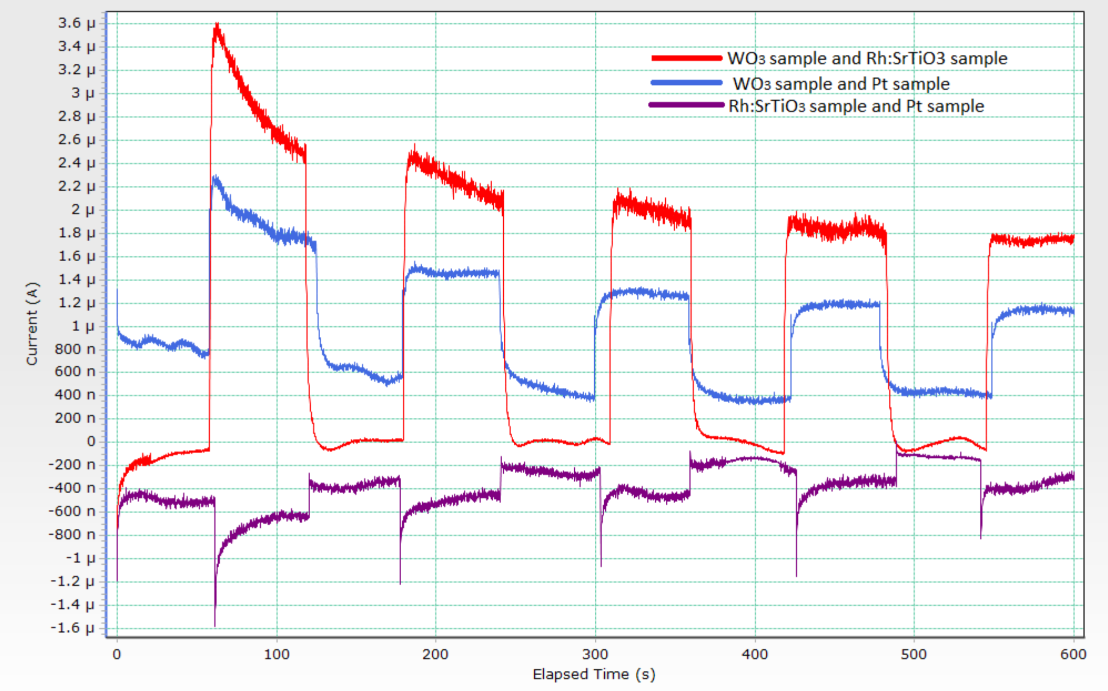


FIGURE 4.4: ChronoAmperometry results.

The WO_3 sample is used as work electrode and the $SrTiO_3$:Rh is used as counter electrode. Three types of measurements have been made. One with both photocatalyst samples. One where the $SrTiO_3$:Rh sample is replaced by a Si/Pt substrate and one where the WO_3 is replaced with a Si/Pt substrate. This is done to see if the photocatalytic activity is actual due to the photocatalysts or due to the Pt. The measurement shows a current flows when the light turns on. The electron and holes from the current are probably result of electrons getting excited in the photocatalysts, although the response is just 2-3.6 µA,. This is not strange because the theoretical value was almost 0. But compared to the measurements with one Si/Pt substrate it shows best results which indicates that the Z-scheme works. The measurements with the Si/Pt substrates probably still get a small current because the helmotzlayer creates a small potential difference in the system.

4.2.1 Integration of WO_3 and $SrTiO_3$:Rh on membranes

The integration of the catalysts on both sides of a membrane proved to be difficult. The integration needed to be done carefully because the width of the Pt layer on top of the membrane is just 500 nm. The samples didn't handle the heat treatment of the $SrTiO_3$:Rh well, which caused in peeling of the Pt layer from the Si support at the corners. So it was decided to only grow three layers of $SrTiO_3$:Rh on the membrane. In figure 4.5 SEM images are displayed of a clean membrane and in figure 4.6 SEM images are displaced of a membrane sample with $SrTiO_3$:Rh grown on it.

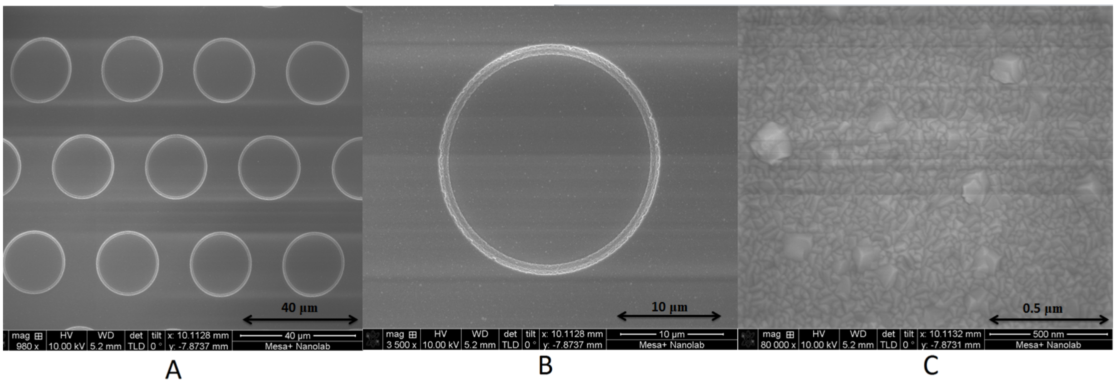


Figure 4.5: SEM images of the top of a clean membrane.

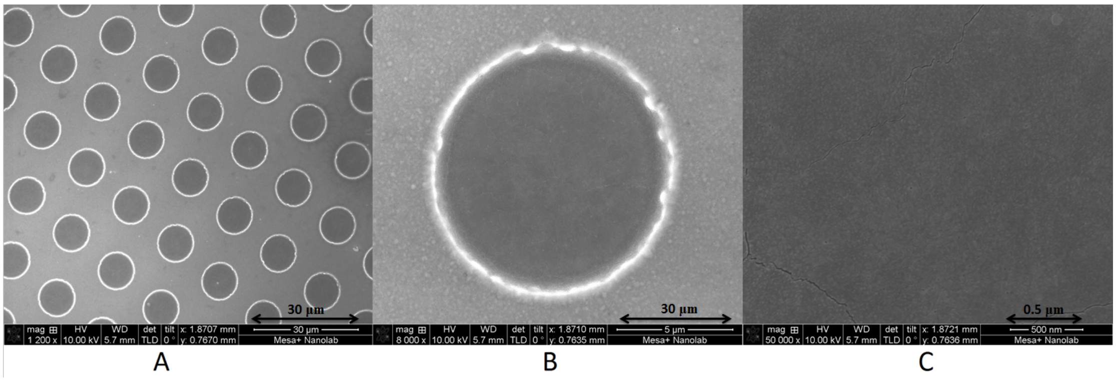


Figure 4.6: SEM images of the top of a membrane with three layers of $SrTiO_3$:Rh layer on it.

In the image can be seen that a homogeneous layer of $SrTiO_3$:Rh has grown on the Pt layer in the holes but not outside the holes. An explanation can be found when looking back at figure 3.1. It can be seen that the holes lay a little deeper in the membrane. This would cause the precursor, after the spin coating step during the $SrTiO_3$:Rh syntheses, to flow into the holes. This would leave thick layers of $SrTiO_3$:Rh in the holes and hardly any $SrTiO_3$:Rh outside the holes. A SEM image of an peeled in piece of membrane can be seen in figure 4.7 which clearly shows that this is the case.

Because there is not so much $SrTiO_3$:Rh outside the holes WO_3 grows on the $SrTiO_3$:Rh side of the sample. This is bad because the WO_3 would still act as photocatalist and oxygen generation would take place on the wrong side of the membrane. SEM images are displayed in figure 4.8 of a membrane where also WO_3 is grown. In the first pictures A, B and C a sample where the $SrTiO_3$:Rh side was is not covered is displayed. As can be seen WO_3 almost covered the entire sample, even in the holes where there is a layer $SrTiO_3$:Rh. Although in picture B and C holes can be seen where there hasn't grown WO_3. The WO_3 in the holes comes in the holes by growing on the sides of the

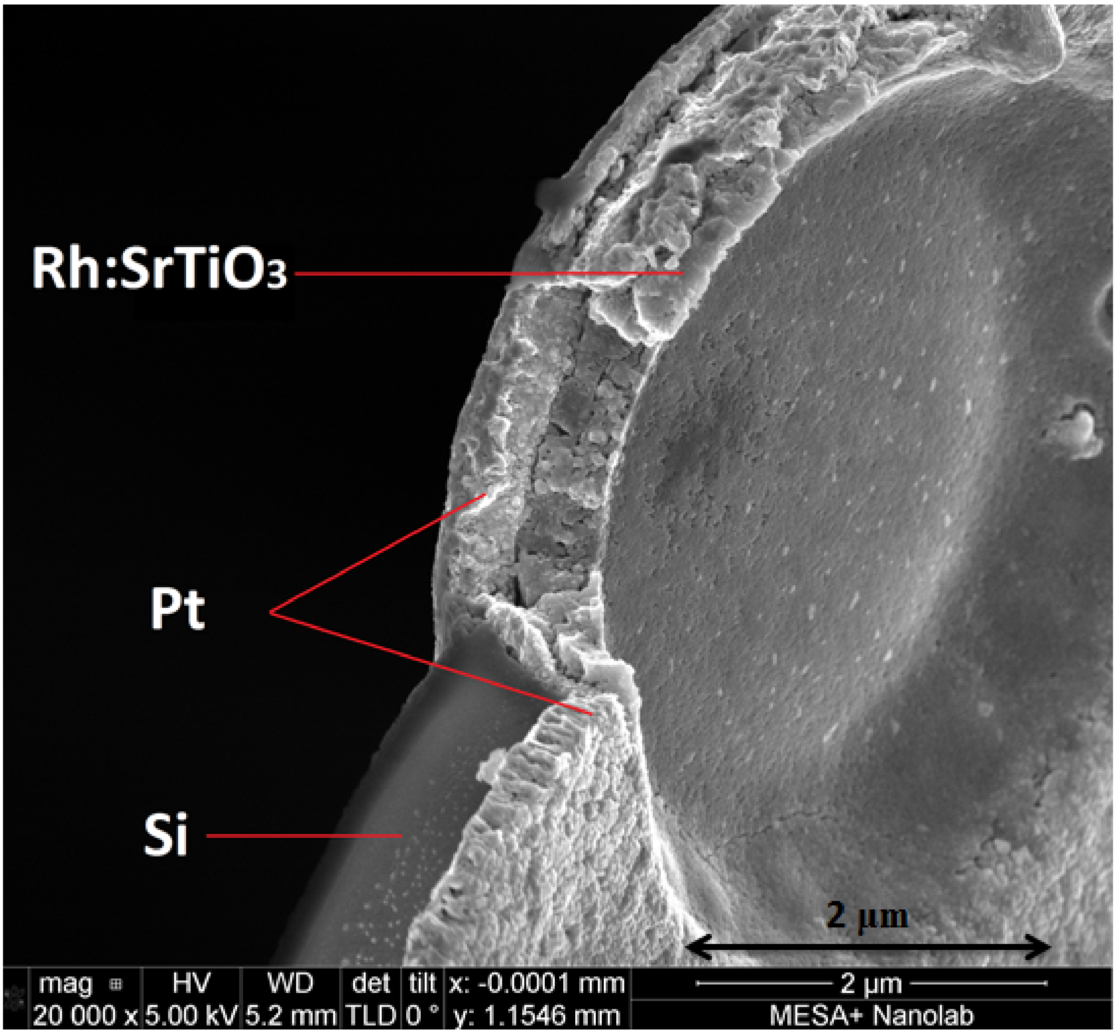


FIGURE 4.7: SEM image of peeled in membrane with $SrTiO_3$:Rh layer on it.

WO_3 outside the holes. The difference in growth of WO_3 in picture A and B is probably because the samples were laid down with the $SrTiO_3$:Rh face down in the hydrothermal vessels at the hydrothermal syntheses to cover the $SrTiO_3$:Rh a little. At high pressure and free liquid flow this kind of covering is not sufficient. But the liquid flow would be different in each vessel and thus would the growth of WO_3 also be different. In the pictures D, E and F the sample has been put in a sample holder and covered at the $SrTiO_3$:Rh side with a Si substrate. This was the best kind of coverage that could be achieved in the time period of this project. The coverage was not complete because WO_3 could still seep in through the sides. But achieved already a great decrease of WO_3 growth on the $SrTiO_3$:Rh. A third attempt was made on membranes where carefully 5 layers of $SrTiO_3$:Rh have been synthesized. With more layers it was hoped to achieve such a thick layer that also outside the holes a layer of $SrTiO_3$:Rh has grown. Pictures G, H and I shows SEM images of these membranes. Here the holes are also covered with WO_3 particles, which is the opposite of what was expected. But for this example

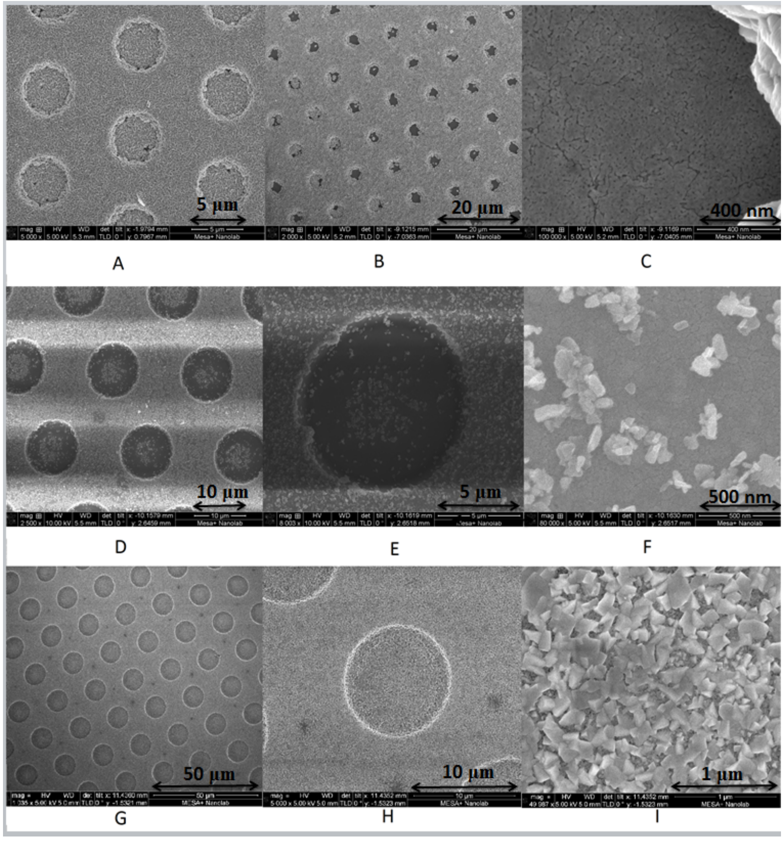


FIGURE 4.8: A, B: SEM images of the top of two different membranes with 5 layers $SrTiO_3$:Rh grown on top of it and with WO_3 grown on it. C:zoomed in SEM image of the same membrane B. D, E, F: SEM images of a membrane with 3 layers of $SrTiO_3$:Rh and covered while WO_3 grown on it. G, H, I: SEM images of a membrane with 5 layers of $SrTiO_3$:Rh and covered while WO_3 grown on it.

a membrane of the 10 µm batch was used while the others where all of the 5 µm batches. This was because it wasn't discovered until SEM images D, E and F where made that the 5 µm membranes where defect on the backside. A double in diameter means a quadruple in cylindrical volume. Thus even with two extra layers the width of the $SrTiO_3$:Rh layer is smaller than before.

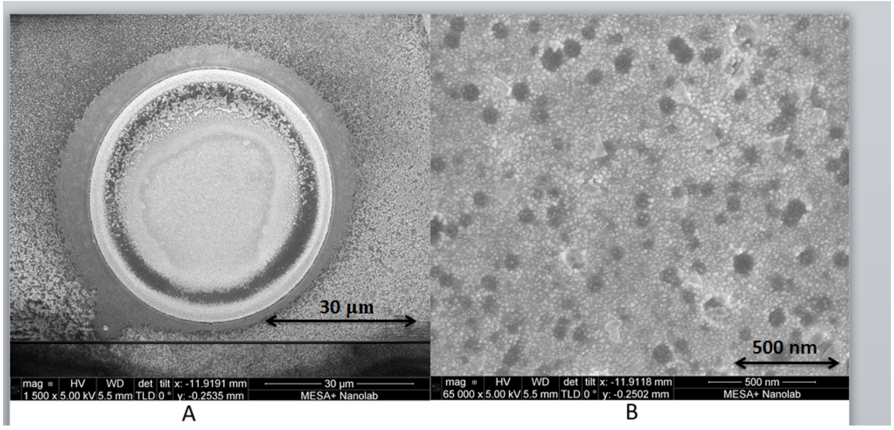


FIGURE 4.9: Back side of the membrane with WO_3 growth.

In figure 4.9 SEM images are displayed of the back side of a membrane covered with WO_3. The morphology of the WO_3 is not of the type useful for photocatalysis and should be like the crystals as can be seen in picture. These SEM images are made of a sample with holes of 50 µm. Microscope images have also been made of this sample and a sample with 10 µm holes. Although the morphology can't be seen in the microscope, through the color still can be distinguished that the WO_3 morphology on the 10 µm sample is better for photocatalyst growth.

4.3 The work functions of WO_3, $SrTiO_3$:Rh and Pt

UPS measurements have been made of WO_3, $SrTiO_3$:Rh and Pt and can be seen in figure 4.10.

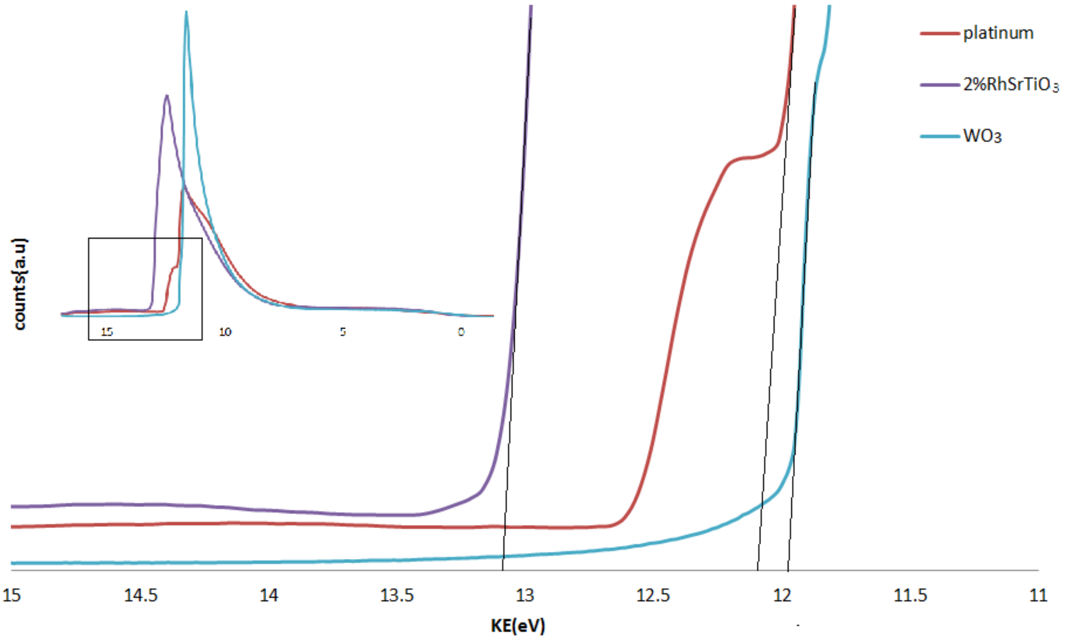


Figure 4.10: UPS measurement, amount of electrons counted Vs the kinetic energy of these electrons

The graph shows the electron counted with a specific kinetic energy. From 0 to 10 eV represent the electrons in lower states of the material. Because they are hard to reach and cost a lot of energy to ionize they are with few and have low kinetic energy. Then a peak occurs, these are the electrons in the highest levels of the valence band that are first met by the UV photons and where most electrons get excited. The peak ends with a steep slope with hardly any electrons counts after. This indicates the fermi-level is reached. The few electrons counted after the peak are the few electrons of the conduction band that is mostly empty. The cross section between 0 counts and the slope of the peak is a good indication of what the kinetic energy electrons would have been if they came from the fermi-level. Now subtracting the kinetic energy and the applied voltage(4.6 eV) of the energy of the photons(21.218 eV) gives us the work function. This results in a work function of 3.5 eV for $SrTiO_3$:Rh, 4.5 eV for Pt and 4.6 for WO_3. A band diagram constructed from these work functions can be seen in figure 4.11.

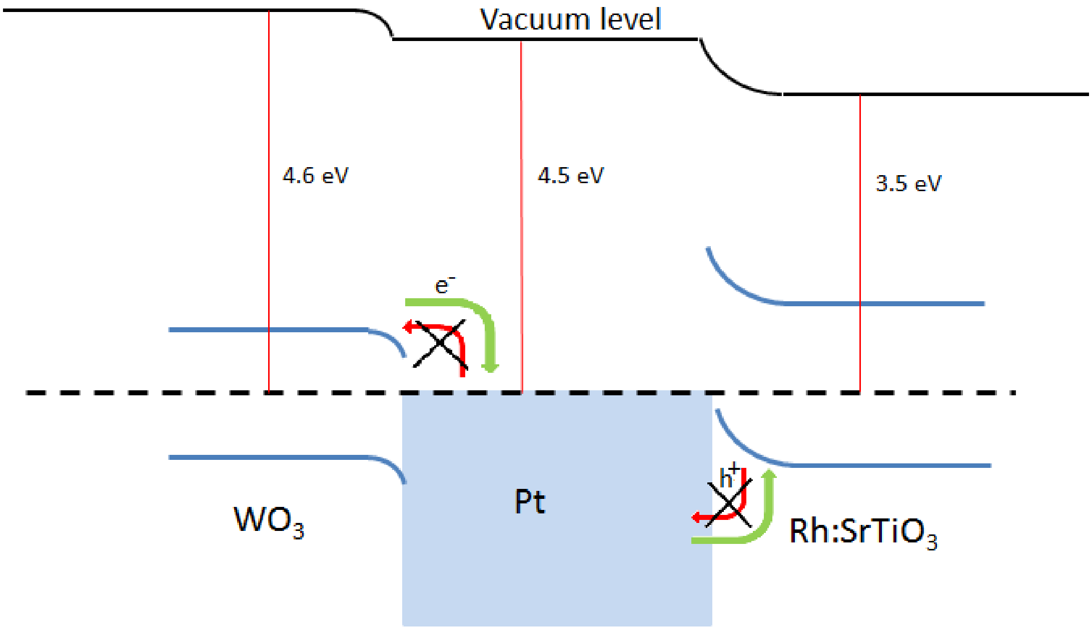


FIGURE 4.11: Band diagram of WO_3, Pt and $SrTiO_3$:Rh and there interfaces

The band structure shows that the bands bend in such way that the interfaces cause rectifying properties, but in the right direction. When an electron-hole pair is created in WO_3 the electron will favor the lower energy state in Pt, and with $SrTiO_3$:Rh the hole will favor the higher energy state in Pt. This makes the separation of electron-hole pairs in the semiconductors easier.

4.4 GC measurement

Of the membrane where SEM images D, E and F have been taken one GC measurement has been made. This was the first and only measurement so the results are not conclusive. The result of the GC measurement can be seen in figure 4.12. The GC shows the presence of nitrogen and oxygen. These are probably dissolved from the air in the electrolyte. When the light is turned on after 30 minutes hydrogen is measured and a large the peak of nitrogen and oxygen is seen at the beginning. This peak is probably the dissolved air in the water that evaporates due to UV light shining on it. The hydrogen peak indicates that the $SrTiO_3$:Rh is active. But the WO_3 should also be active, because the Pt membrane should receive both electrons and holes. Also, cyclic voltametry measurements showed that WO_3 should be more active then $SrTiO_3$:Rh. An explanation could be that the Si of the membranes support oxidizes. The support should have an protective layer of SiO_2 and SiN_3N_4.

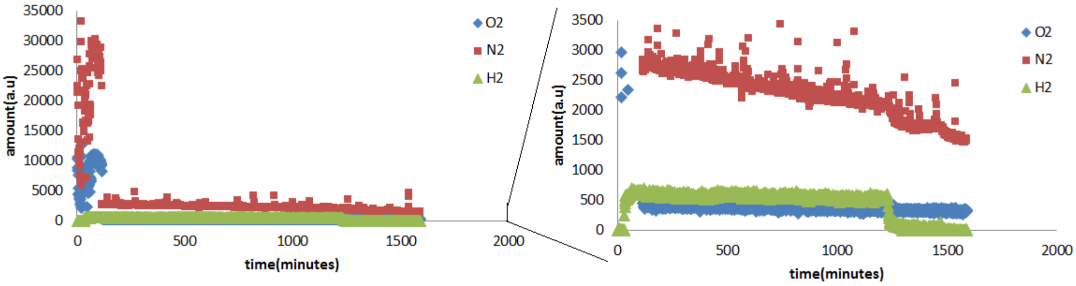


FIGURE 4.12: GC measurement of a membrane with WO_3 and $SrTiO_3$:Rh integrated on it.

Chapter 5

Conclusion and Recommendation

5.1 Conclusion

The goal of this project was to split water with $SrTiO_3$:Rh and WO_3 in a Z-scheme configuration. With photo electrochemistry measurements there is looked at the photoactivity and the electron transfer from WO_3 to $SrTiO_3$:Rh and with UPS the work functions are determined to see if there are any Schottky-barriers and a GC measurement is done to prove if the chip actually splits water.

The voltametry measurements showed good photocatalytic activity for WO_3 but poor photocatalyc activity for $SrTiO_3$:Rh. This is bad for the Z-scheme configuration because $SrTiO_3$:Rh becomes a major limiting factor. The chromoamperometry confirms this because there is hardly any electron transfer from WO_3 to $SrTiO_3$:Rh is seen.

On the integration of WO_3 and $SrTiO_3$:Rh on nanoscale manufactured Pt membranes still some improvement has to be done. The $SrTiO_3$:Rh is successfully integrated on the membranes holes, but not outside the holes. This will cause growth of WO_3 on the top of the membrane which can cause oxygen generation in the compartment of the water splitting cell where only hydrogen is supposed to be created. To prevent WO_3 from growing on the top side also a layer $SrTiO_3$:Rh outside the holes needs to be grown. The integration of a good layer of WO_3 layer on the bottom of the membrane is still not very well consistent. For good layers membranes with holes with smaller diameter shows better results.

The UPS showed Schottky-barriers favorable for this projects configuration. The bands will bend at the metal-semiconductor interfaces in such manner that it gives rectifying property's to the chip that make electron transfer from WO_3 to $SrTiO_3$:Rh possible but not the other way around. This will decrease the effect of recombination.

Only one GC measurement was taken so the conclusions drawn are at this stage only suggestions. The GC showed hydrogen generation, which indicates the splitting of water. But there was no increase in oxygen measured. Oxygen is likely produced because the Z-scheme doesn't work half way so it probably oxidizes somewhere in the water splitting cell.

The final conclusion is that water splitting with $SrTiO_3$:Rh and WO_3 works but not sufficient compared to photocatalysis without a Z-scheme. Maybe a Z-scheme where $SrTiO_3$:Rh is replaced by photocatalyst with a higher photocatalytic activity could give a higher productivity. But splitting water with a Z-scheme remains difficult because it is depended on variables of two photocatalysts instead of one.

5.2 Recommendations

There is still a lot that can be improved or researched to improve the water splitting cell. $SrTiO_3$:Rh proved to be a bad photocatalyst. This is probably due to its bad conductivity. Doping $SrTiO_3$ with Nb instead would increase the conductivity enormous, but the band gap would also increase so research is needed to see if one would gain more photocatalytic activity from the increased conductivity than loss of the increased band gap. Another option is to replace $SrTiO_3$:Rh with another photocatalyst where the band gap overlaps WO_3 . One with better photocatalyic activity such as TaON(see figure 2.4).

Another point of improvement is implementing the photocatalysts on a membranes where the Pt inside and outside the holes are on the same level. This would prevent the flow of precursor solution in the holes so that a homogeneous layer of $SrTiO_3$:Rh can be grown over the hole membrane. Further research can be done about the exact effect of the size of the holes of the membrane have on the quality of the WO_3 growth.

Last, the GC measurement can be repeated to test the consistency of hydrogen production. A GC measurement without a T-junction can give more information on where the hydrogen is produced and if there is oxygen produced on the WO_3 side of the chip.

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