High-throughput photoelectrochemical characterization of semiconductor thin film materials libraries
This work was carried out between June 2011 and September 2015 in the Chair of Analytical Chemistry - Elektroanalytik & Sensorik under the supervision of Prof. Dr. W. Schuhmann, Ruhr-Universität Bochum, Germany.

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"We try to solve very complicated problems without letting people know how complicated the problem was. That's the appropriate thing."

Sir Jonathan Ive,
Senior Vice President of Design at Apple
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1 List of abbreviations

A

ABPE
applied bias photon-to-current efficiency · 42
AM1.5G
Air Mass 1.5 Global · 42
APCE
absorbed photon-to-current efficiency · 42
ATR
attenuated total reflectance · 48

C

CB
conductance (conduction) band · 11
CPP
combined potentiodynamic photocurrent · 89
CVD
chemical vapor deposition · 41

D

DOS
density-of-states · 12

E

E_F
Fermi energy, Fermi level · 12
E_F,solution
solution Fermi level · 16
E_F^*
quasi-Fermi energy level · 23
E_g
bandgap energy, bandgap · 12
EQE
external quantum efficiency · 47

F

FOM
figure of merit · 56
FWHM
full width at half maximum · 99
full with half maximum · 72

G

GUI
graphic user interface · 77

H

HTC
high-throughput characterization · 10
HTP
high-throughput preparation · 10
HTS
high-throughput screening · 51

I

IPCE
incident photon-to-current efficiency · 42
IQE
internal quantum efficiency · 47
ISTC
intrinsic solar to chemical · 42

L

L_D
diffusion length · 25
LHE
light harvesting efficiency · 48
M
- MA
  measurement area · 64
- MDI
  multiple document interface · 83

N
- $N_a$
  acceptor impurity concentration · 14
- $N_d$
  donor impurity concentration · 14

O
- OOP
  object-oriented programming · 77
- OSDC
  optical scanning droplet cell · 67
- $\alpha$
  oxidized (species) · 17

P
- PEC
  photoelectrochemical · 9
- PMMA
  polymethylmethacrylat · 69
- PTFE
  polytetrafluoroethylene · 68
- PV
  photovoltaic · 29
- PVD
  physical vapor deposition · 52
- PZC
  potential of zero charge · 19

Q
- QE
  quantum efficiency · 47

R
- red
  reduced (species) · 17
- RF
  radio-frequency · 51

S
- SC
  semiconductor · 9
- SCLJ
  semiconductor-liquid junction · 15
- SCR
  space-charge region · 15
- SDC
  scanning droplet cell · 66
- SECM)
  scanning electrochemical microscopy · 59
- SFI
  single frequency impedance · 105
- SHE
  standard hydrogen electrode · 16
- STH
  solar-to-hydrogen · 31

V
- VB
  valence band · 11
- $V_{oc}$
  photovoltage · 23

A
- $\alpha$
  light absorption coefficient · 22

$\mu$
- $\mu$
  carrier mobility · 2
2 Introduction

Development of a long-term, sustainable energy economy is a very important technical problem facing humanity.\textsuperscript{1} Based on BP’s 2014 “Statistical Review of World Energy” the global primary energy consumption increased by 2.3% in 2013, despite stagnant global economic growth.\textsuperscript{2} 87% of this energy was generated from carbon-based fuels. Renewable energy sources continued to increase in 2013, reaching a record 2.7% of global energy consumption, up from 0.8% a decade ago. Renewable energy used in power generation grew by 16.3% and accounted for a record 5.3% of global power generation. BP’s World Energy Outlook 2035 predicts world’s primary energy production growth at 1.5% p.a. from 2013 to 2035.\textsuperscript{3} By the year 2050 doubling of global energy consumption from 15 TW we consume today to 30 TW that we are projected to demand, will be achieved.\textsuperscript{4} Initially, gas will fulfill this energy demand, but renewable energy resources will play an increased role. Among renewable sources, solar energy with an incident power level on the earth surface of 1000 W/m\textsuperscript{2}, which exceeds all human energy needs, is of great interest.\textsuperscript{4-5}

The Intergovernmental Panel on Climate Change (IPCC) estimates the potential for power generation by photovoltaics at around 600 GW - 800 GW in 2050, but still this represents only 2% of the total primary power required.\textsuperscript{6} The main problem with photovoltaic is the need to develop suitable electrical and chemical storage methods. The development of these methods becomes an important research priority, and countries are establishing large programs of research into solar fuels.\textsuperscript{5} Hydrogen is believed to be the primary media for the storage and distribution of energy in the future.

Among possible renewable hydrogen-production methods, photoelectrochemical (PEC) water splitting is a very intriguing one. A PEC system combines the harvesting of solar energy and the electrolysis of water into a single semiconductor (SC) based device. PEC hydrogen production can potentially provide a clean, cost-effective and efficient production of O\textsubscript{2}/H\textsubscript{2} from water by taking advantage of the 120,000 TW of radiation that strikes the earth surface.\textsuperscript{4,7-11} The concept of PEC water splitting for hydrogen production was first demonstrated in 1972.\textsuperscript{12} Work by other groups to reproduce the discovery established the conditions necessary for sustainable, spontaneous water splitting.\textsuperscript{13-15} The current world record solar-to-hydrogen efficiency of 12.4% was achieved using a multijunction PEC device based on III-V semiconductors but it lacks long-term stability and is very expensive.\textsuperscript{16} A key challenge is to find a semiconductor material with high stability in a given electrolyte solution upon continuous solar irradiation which simultaneously possesses high-energy conversion efficiency and can be cheaply produced.\textsuperscript{17-23} There is no semiconductor system, which achieves all of the above criteria. PEC devices based on thin-film metal oxides semiconductors have stable hydrogen conversion efficiencies in the 3% - 5% range, but there is no substantial progress in the search for new
materials and increasing of the efficiency level of existing ones in recent decades.\textsuperscript{24} The predominantly investigated binary oxides Fe\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2} and WO\textsubscript{3} do not show sufficient stability, suitable bandgaps, efficient light absorption, catalytic activity, or charge carrier lifetimes.\textsuperscript{25}

It is likely that a material for bias-free solar water splitting rather consists of more than two elements, each contributing to the required properties such as stability, light absorption, and catalytic activity.\textsuperscript{26} There are about 20,000 possible 1:1:1 ternary oxide combinations, if 50 metallic elements are chosen as starting materials and very many more, when various structures and relative compositions are considered. Up to now, only a tiny fraction of all possible metal oxides has been investigated and only a few of them show promising properties for solar water splitting.\textsuperscript{27} Despite the fact, that applying of advanced high-throughput theoretical methods for determining of materials optoelectronic and electrocatalytic properties was successful,\textsuperscript{28-30} the properties of complex systems cannot be predicted in a straightforward way. The huge number of possible multicomponent materials compositions demand use of high-throughput combinatorial methods to discover and optimize candidate materials.\textsuperscript{31-33} Automated synthesis and screening using combinatorial methodologies accelerates elucidation of materials composition-structure-performance correlation.\textsuperscript{34} The combinatorial approach combined with high-throughput preparation (HTP) and high throughput characterization (HTC) of a large number of different materials should allow efficient search for materials, which fulfill the required specifications.\textsuperscript{35}
3 State of the art

3.1 Semiconductors physics and electrochemistry

3.1.1 Energy levels in semiconductors

In order to understand the process of PEC water splitting, the properties and electronic structure of semiconducting electrodes have to be examined. In contrast to molecular species, energy levels in semiconductors are so dense, that the electronic structure of these solids is typically discussed in terms of energy bands. As shown by experiments and theoretical works, if atoms are brought to each other so close, that they form a solid, the valence electrons interact with each other. Thereby their sharp atomic energy levels are broadened into wider regions called energy bands. Due to interaction between atoms, a huge number of different energy levels are generated from each atomic level. Two atomic levels which are of considerable importance have to be considered: the highest occupied and the lowest unoccupied by electrons. These two atomic levels are two different bands: the one resulting from the highest occupied level is called the valence band (VB) and that resulting from the lowest unoccupied level is called the conductance (conduction) band (CB). The valence band is fully occupied by electrons; the conduction band will be either free of electrons or partially filled with them. If the valence and conduction bands overlap, or if the valence and conduction bands do not overlap but the conduction band is partially filled with electrons at \( T = 0 \) K a solid has metallic properties (Figure 1a).

![Energy band diagram of a) metal, b) semiconductor and c) dielectric.](image)

If the valence and conduction bands do not overlap and the conduction band is free of electrons at \( T = 0 \) K a solid has either semiconductor or insulator properties. The distinction between semiconductors and insulators is arbitrary. The difference between the top of VB and bottom of CB is called the optical or electronic bandgap.
Typically, semiconductors have $E_g$ in the range of 1 eV – 4 eV (Figure 1b). The bandgap of dielectrics should be larger than 4 eV (Figure 1c).

In contrast to metals, semiconductors have two types of electronic carriers. After thermal electron excitation from the VB into the CB, there is a free electron in the CB and a vacancy hole in the VB left. The hole can be considered as a missing electron in a chemical bond and is mobile, since holes are created by migration of electrons. The energy level in solids at which the probability to find an electron at one-half of the VB and CB difference is called Fermi energy level $E_F$. This energy level can be calculated as:

$$E_F = \frac{1}{2}(E_{VB} + E_{CB}) + \frac{1}{2} \left( kT \ln \frac{N'_{VB}}{N'_{CB}} \right)$$

Equation 1

$E_{CB}$ and $E_{VB}$ are the energy levels of the CB and VB respectively, $k$ is the Boltzmann constant which is equal to $1.38 \times 10^{-23}$ J/K, $T$ is the temperature in Kelvin. $N'_{VB}$ and $N'_{CB}$ are the effective density of states function in the valence and conduction bands, respectively:

$$N'_{VB} = 2 \left( \frac{2\pi m^*_h kT}{\hbar^2} \right)^{3/2}$$

Equation 2

$$N'_{CB} = 2 \left( \frac{2\pi m^*_e kT}{\hbar^2} \right)^{3/2}$$

Equation 3

Here, $\hbar$ is Planck’s constant, $m^*_h$ and $m^*_e$ are the effective masses of holes and electrons, respectively. The effective mass takes into account the ability of charges to move through the atomic lattice. The concentration of electrons and holes at equilibrium in an intrinsic semiconductor can be calculated as:

$$n_0 = N'_{CB} \cdot e^{-\frac{E_{CB}-E_F}{kT}}$$

Equation 4

$$p_0 = N'_{VB} \cdot e^{-\frac{E_F-E_{VB}}{kT}}$$

Equation 5

$n_0$ and $p_0$ represent the electron and hole densities respectively. $N'_{CB}$ is the density-of-states (DOS) at the lower edge of the conduction band and $N'_{VB}$ is the DOS at the
upper edge of the valence band. By multiplying these equations an equilibrium concentration can be expressed as:

\[ n_0p_0 = N_{CB}^* N_{VB}^* \cdot e^{\frac{E_{CB} - E_{VB}}{kT}} = N_0 \cdot e^{\frac{E_G}{kT}} = n_i^2 \]

Equation 6

\( n_i^2 \) is the intrinsic carrier concentration. It exponentially decreases with increasing bandgap.\(^{21}\)

In an intrinsic semiconductor, which does not contain any impurity, the concentrations of both types of carriers are ideally equal, hence \( N_{CB}^* = N_{VB}^* \) and the second term in the Equation 1 cancels out. The Fermi level lies in the middle of the bandgap, which means, the probability, that the VB is occupied is very high and the probability, that the CB is occupied is very low, but this does not mean, that an electron can be found at the energy level equal \( E_F \). For instance, undoped Si in its intrinsic state has a very low carrier concentration under ambient conditions: both \( N_{CB}^* \) and \( N_{VB}^* \) are approximately \( 10^{19} \) cm\(^{-3}\), correspondingly \( N_0 \) is equal to \( 10^{38} \) cm\(^{-3}\). Si has a bandgap energy of 1.11 eV with \( n_i \) of \( 10^{10} \) cm\(^{-3}\) at 300 K. The intrinsic carrier concentration is so low, that addition of impurities on the parts-per-billion scale has big effects on electric properties of the semiconductor. This is called doping. If an intrinsic semiconductor is doped with a donor impurity, then electrons get more abundant; if the semiconductor is doped with an acceptor impurity, then holes are more abundant charge carriers in the semiconductor and are called majority carriers. They are primarily responsible for the current transport. The less abundant charge carriers are called minority carriers. In the bulk of the semiconductor, the position of the Fermi level depends on the doping. For a \( n \)-type semiconductor the Fermi level shifts towards the conduction band, while for a \( p \)-type semiconductor it shifts towards the valence band.

Figure 2. A schematic representation of semiconductor energy band levels.

Figure 2 shows, that for intrinsic (undoped) semiconductors the number of holes and electrons is equal, correspondingly the Fermi energy level \( E_F \) lies in the middle
of the bandgap. Introducing impurities in the semiconductors making electrons majority charge carriers, results in an $n$-type semiconductor. A semiconductor with holes as majority charge carriers is a $p$-type semiconductor. For $n$-type semiconductors the Fermi level lies just below the conduction band, for $p$-type semiconductors it lies just above the valence band. Electron and hole concentrations can be obtained as a function of donor and acceptor impurity concentrations ($N_d$) and ($N_a$) respectively:

$$n_0 = \frac{N_d}{2} + \sqrt{\left(\frac{N_d}{2}\right)^2 + n_i^2}$$

Equation 7

$$p_0 = \frac{N_a}{2} + \sqrt{\left(\frac{N_a}{2}\right)^2 + n_i^2}$$

Equation 8

From equation 4 and equation 5 the energy difference between the energy band edges and the Fermi level can be calculated as:

$$E_{CB} - E_{F,n} = kT \ln \frac{N_{CB}^*}{n}$$

Equation 9

$$E_{F,p} - E_{VB} = kT \ln \frac{N_{VB}^*}{p}$$

Equation 10

For example in an $n$-type semiconductor having the donor impurity concentration much greater than the intrinsic carrier concentration, $N_d \gg n_i$, then $n_0 \approx N_d$. Equation 9 can be transformed to:

$$E_F = E_{CB} - kT \ln \frac{N_{CB}^*}{N_d}$$

Equation 11

The distance between the Fermi energy level and conduction band is a logarithmic function of the donor concentration. As higher is the donor concentration as closer is the $E_F$ to the CB edge. For a $p$-type semiconductor the distance between $E_F$ and the VB edge is also a logarithmic function of acceptor impurity concentration. With increasing acceptor impurity concentration, the hole concentration in the VB increases too, thus the Fermi level moves closer to the valence band.
3.1.2 Semiconductor-semiconductor junction

When a semiconductor contacts another material having a different Fermi level a junction is formed. This junction formation can occur between n- and p-type semiconductors, between a metal and a semiconductor or between a semiconductor and a redox electrolyte. It is important to distinguish between a semiconductor-electrolyte and a metal-electrolyte junction. In the former case, the potential drop occurs on the side of the semiconductor, as well as the side of the electrolyte. In the latter case, the potential drop only occurs on the solution side. The process of the semiconductor-liquid junction (SCLJ) formation can be compared with a solid-state np*-junction, as shown in figure 3. The n-region is doped with donor atoms, which provide electron excess, while the p*-region is doped with acceptor atoms, thus having a high concentration of holes. The plus sign means, that the region is doped more heavily. Figure 3a shows the classic band-diagram representing the separated semiconductors in thermal equilibrium and corresponding positions of Fermi levels. For the n region the Fermi level is close to the conduction band, while in the p*-region, very close to the valence band. Figure 3b shows the np*-junction, formed after the materials are brought in contact to each other.

![Figure 3. Energy band diagram of a) separated semiconductors in thermal equilibrium, b) np*-junction.](image)

Leaving fixed positive charges of ionized donor atoms free electrons diffuse from the n-doped semiconductor into the p*-side. On the contrary, holes exposing fixed negative charges in the p*-side diffuse to the n-semiconductor. The Fermi levels align thereby across the device. This results in a band bending as shown in figure 3. The mutual free carriers diffusion is counter-balanced by the electric field generated by the fixed positive and negative charges in the n- and p*-sides, respectively, which is called depletion region or space-charge region (SCR). The typical width of the space-charge in the n-region with an initial carrier density of $10^{15} \text{cm}^{-3}$ is around 1 µm, while the SCR width in the p*-region with an initial carrier density of $10^{16} \text{cm}^{-3}$ is only 0.1 µm. The built-in electric field established by the fixed charges is the critical mechanism for separating the electron-hole pairs (excitons) under illumination.

3.1.3 Semiconductor-electrolyte junction

To describe the formation of the junction at semiconductor/electrolyte interfaces the model developed by Heinz Gerischer is applied. This model makes important
connections between the electrochemical potentials in solution and the solid-state Fermi levels. The semiconductor-electrolyte junction description follows the above-presented np⁺-junction. Using semiconducting materials as electrodes for (photo)electrochemical applications requires combination of solid-state physics and electrochemistry. While in solid-state physics the Fermi level and the positions of the band edges are measured in high vacuum and all potentials are referred to the vacuum level of an electron, the standard hydrogen electrode (SHE) is the reference potential for electrochemistry in liquids. Prior to further discussion of the semiconductor-liquid junction formation and other photoelectrochemical processes the referencing of electrode potentials to the vacuum scale is described.

### 3.1.3.1 Referencing of the electrode potential to the vacuum scale

Since photoelectrochemistry deals with semiconductor-electrolyte interfaces it is important to locate electronic energy levels in the (photo)electrode and solution at the same scale. This might be achieved by using the vacuum scale of electrode potentials, where these potentials are referenced to the energy of electrons in vacuum. The electrode potential on an electrochemical reference scale cannot be directly referenced to the electronic energy levels in the electrode. In order to enable such referencing, a scale, which is not based on a reference electrode, but on a reference electronic energy level is needed. The local vacuum level of the solution, which is the energy of an electron just outside the solution phase, allows comparison of different electrodes placed in the same electrolyte solution. The absolute electrode potential of an electrode/electrolyte half-cell can be described as the work required to remove an electron from the electrode to the local vacuum. The electrolyte in an electrochemical cell does not contain free electrons, but does contain a redox couple, which can equilibrate with the free electrons in the electrode brought into contact with the electrolyte. This allows using the „Fermi level“ term for non-fermionic solution species. Similar to the classic Fermi level \( E_F \) the solution Fermi level \( E_{F,\text{redox}} \) is defined as the energy level, at which the probability to find an occupied electronic state equals one-half. The Fermi level is related to the electrochemical potential of electrons and holes given with respect to a reference electrode, such as SHE, and is described by the following relation:

\[
E_{F,\text{redox}} = -eV_{\text{redox}} + \text{const}_{\text{ref}}
\]

**Equation 12**

\( V_{\text{redox}} \) is the redox potential vs. a reference electrode and \( \text{const}_{\text{ref}} \) is the free energy of the electrons in the reference electrode with respect to vacuum level. As mentioned, the electrochemical scale arbitrarily based on a reference electrode can be connected to the vacuum level by a work function for the removal of an electron from the Fermi level of the reference electrode to the vacuum level. For SHE, the
constant has a value of $-4.44 \text{ eV}$. Thus, equation 12 with respect to vacuum level can be written as:

$$E_{F,\text{redox}} = -4.44 \text{ eV} - eV_{\text{redox}}$$

**Equation 13**

The rather convenient widely used Ag/AgCl/3 M KCl reference electrode has a potential of $U_{\text{Ag/AgCl/3 M KCl}} = 0.2100 - 0.0073(T - 298)$ V vs. standard hydrogen electrode (SHE).

---

![Figure 4. A schematic representation of semiconductor energy band levels and the energy distribution of the redox system in the electrolyte.](image)

Relationships between the energy levels of solids and liquids are depicted in Figure 4. In an electrolyte containing one redox pair three energy levels exist, $E_{F,\text{redox}}, E_{\text{ox}}$ and $E_{\text{red}}$. The occupied level corresponds to the reduced (red) species and the unoccupied level to the oxidized (ox) species. The Gaussian distribution in the density-of-states of $E_{\text{ox}}$ and $E_{\text{red}}$ is a consequence of energy level fluctuations of redox species in solution. As the energy levels of a redox couple in an electrolyte is controlled by the ionization energy of the reduced species $E_{\text{red}}$ and the electron affinity of the oxidized species $E_{\text{ox}}$ and their interaction with the surrounding electrolyte, a considerable fluctuation in these energy levels occurs. This probability distribution of energy states can be described for each single redox species:

$$W_{\text{ox}}(E) = e^{-\frac{(E_{\text{ox}}-E)^2}{4kT\lambda}}$$

**Equation 14**

$$W_{\text{red}}(E) = e^{-\frac{(E_{\text{red}}-E)^2}{4kT\lambda}}$$

**Equation 15**
The width of the distribution functions in these equations is defined by the reorganization energy $\lambda$, which is the energy needed to bring the solvation shell of one redox species from its most probable state into the most probable solvation structure of its redox counter part.\textsuperscript{[48]} The standard redox potential is an average of the ionization energy and the electron affinity. The following symmetrical relations give the distances between maxima of these distributions or the standard redox potentials and standard redox Fermi level:

$$E_{\text{red}} = E_{F,\text{redox}} - \lambda$$  \text{Equation 16}

$$E_{\text{ox}} = E_{F,\text{redox}} + \lambda$$  \text{Equation 17}

3.1.3.2 Energy diagram of the semiconductor-electrolyte junction

3.1.3.2.1 Band bending at the interface

The electrochemical potential of the solution is determined by the standard redox potential of the electrolyte solution and the electrochemical potential of the semiconductor by the Fermi energy level of the semiconductor. The Fermi level of an $n$-type semiconductor is usually higher than the redox potential of the electrolyte. For a $p$-type semiconductor the Fermi level lies below the redox potential. If a semiconducting material is brought into contact with a redox electrolyte and the two levels do not lie at the same energy, the majority carriers will be forced to flow from the semiconductor to the electrolyte across the semiconductor-solution interface. For $n$-type semiconductor these will be electrons, while for $p$-type, holes. Equilibrium between the two phases at a semiconductor-electrolyte interface, solid and liquid, will be achieved when their electrochemical potential is the same. Hence, this charge transfer continues until the semiconductor’s Fermi level equilibrates with that of the electrolyte, $E_F = E_{F,\text{redox}}$. Charge transfer from the semiconductor to the electrolyte leads to the formation of a surface excess charge, which is compensated by opposite charges induced in the electrolyte within the Helmholtz layer formed by oriented water molecule dipoles and adsorbed electrolyte ions at the electrode/electrolyte interface. These majority carriers do not react with the redox species in the electrolyte, but just accumulate at the semiconductor/electrolyte interface in order to maintain overall neutrality. The conduction band is bent with an exponential change of majority carriers concentration between bulk and interface. The difference between Fermi level and conduction band is maintained after band bending, as it is related to the magnitude of dopant concentration, which is constant. Since the bandgap is also constant, the valence band has to bend. Finally, since the position of the conduction band on the
vacuum scale is not changed, the vacuum level follows the band bending. Actually, three different situations can appear after equilibration (Figure 5). For an *n*-type semiconductor immersed in an electrolyte a *depletion layer* is formed, when a positive excess charge is left in SCR and it is compensated by negative counter ions from the electrolyte (Figure 5a). Another situation is the excess of negative charges within the SCR compensated by positive ions of the electrolyte. This forms an *accumulation layer* (Figure 5b). Finally, if no net excess of charge on the semiconductor is observed, the bands are not bending and the photoelectrode exhibits its potential of zero charge (PZC), which is also called the *flat band* potential, $E_{FB}$. At the flat band potential the electrostatic potential remains constant throughout the semiconductor (from bulk to surface) as shown in figure 5c.\(^49\)

![Figure 5. Band bending at SCLJ, a) depletion layer, b) accumulation layer and c) flat band.](image)

For a *p*-semiconductor an *accumulation layer* forms when holes accumulate at the interface which are compensated by negative ions of the electrolyte, while a *depletion layer* forms when the space-charge region is depleted of holes and correspondingly contains fixed negative charges compensated by positive counter ions from the electrolyte. *Flat band* conditions occur when no net excess charge is observed at an interface.

### 3.1.3.2.2 Determination of the flat band potential and the SCR capacitance

If a SCLJ is in equilibrium ($E_F = E_{F,redox}$) with established band bending a potential $V_E$ can be measured between the immersed photoelectrode and a reference electrode. This potential is the potential of the bulk of the semiconducting electrode matched to the potential of the redox couple in solution. It depends on the charge concentration in the space-charge region. A potential difference $\varphi$ across the SCLJ is established as a consequence of the formation of an electrical double layer. This double layer is formed by a diffuse SCR on the SC side and a thin counter ionic charge on the electrolyte side. The potential difference comprises of an interfacial difference potential between the solid and the liquid phases $\varphi_H$, also called Helmholtz potential, and of the potential difference developed across the space charge layer, $\varphi_{SCR}$. The potential difference across the diffuse double layer (Gouy region) can be neglected if
sufficiently concentrated electrolytes are used. A potential distribution across the interface is shown in figure 6 for an n-type SC. The potential of the bulk solution is taken as zero.

Figure 6. Potential distribution at a semiconductor-electrolyte interface at equilibrium.

The applied potential affects the band edges of bulk n-type and p-type semiconductors. Applying a potential more positive than the flat band potential \( V_E > E_{FB} \) induces a depletion layer formation in an n-type semiconductor and the bending of the bands at the surface to higher energies. For a p-type semiconductor the surface concentration of electrons decreases creating an accumulation layer of holes also causing bending of the bands to higher energies. When the applied potential is more negative than the flat band potential \( V_E < E_{FB} \) an accumulation layer forms in the n-type semiconductor, as there is an excess of electrons in the SCR. For a p-type semiconductor the additional electrons produce a depletion layer, bending the energy bands at the surface downward to lower energies. \( \phi_H \) remains constant even if the applied potential between the semiconductor electrode and the reference electrode is varied, so that the measured potential difference is the sum of the \( E_{FB} \) and \( \phi_{SCR} \). As the applied electrode potential \( V_E \) is varied, the electronic charge distribution in a semiconductor varies as well. This determines the resulting differential capacitance at the interface.\(^{17,50}\) The capacitance of the SCR \( C_{SCR} \) can be quantitatively derived by relating the charge density and the electric field.\(^{48}\)

\[
C_{SCR} = \frac{\varepsilon\varepsilon_0 A}{w}; \quad \frac{1}{C_{SCR}^2} = \left( \frac{2}{e\varepsilon\varepsilon_0 N_D} \right) \left( \phi_{SC} - \frac{kT}{e} \right)
\]

Equation 18
$\varepsilon$ is the dielectric constant of the semiconductor, $\varepsilon_0$ is the permittivity of the free space, $w$ is the width of the depletion layer and $e$ is the electronic charge.

From the first equation it can be derived, that the space charge layer capacitance is inversely proportional to the width of the depletion layer $w$, which is a regular equation of a capacitor. Change in band bending varies the width of the depletion layer. At the flat band potential the width of the depletion layer approaches zero, hence, the capacitance of the SCR approaches infinity. At the flat band potential $\frac{1}{C_{SCR}}$ is zero. The flat band potential is the difference between the Fermi level of the semiconductor and the Fermi level of the reference electrode. Hence the measured potential difference between the SC and RE is the sum of the $E_{FB}$ and $\phi_{SC}$ and the Mott-Schottky relation can be described as:

$$\frac{1}{C_{SCR}^2} = \left( \frac{2}{\varepsilon \varepsilon_0 N_D} \right) \left( V_E - E_{FB} \right) - \frac{kT}{e}$$

Equation 19

$C$ is the capacitance of the space charge layer, $\varepsilon_0$ is the permittivity of vacuum, $\varepsilon$ is the dielectric constant of the semiconductor, $e$ is the electronic charge, $N_D$ is the doping density and $V_E$ is the applied electrode potential.

Observing the capacitance dependence on the applied potential is an important method of characterizing a semiconductor-electrolyte interface.\textsuperscript{51-52} Using Mott-Schottky type plots the donor density can be calculated from the slope of $\frac{1}{C_{SCR}^2}$ vs. applied potential $V_E$, and the flat band potential $E_{FB}$ can be determined by extrapolation to $\frac{1}{C_{SCR}^2} = 0$. Once the flat band potential and the donor density are known, the position of the conduction band edge can be determined using equation 11. Determining the bandgap value using photocurrent spectroscopy allows calculation of the valence band edge position with reference to the vacuum energy level.

3.1.3.2.3 pH dependence of band edge positions

In many cases, the flat band potential and hence the semiconductor band edge positions are affected by the pH variation in the aqueous electrolyte solution, namely by varying the potential drop in the Helmholtz layer, $\varphi_H$. The conduction band energy position can be expressed as:

$$E_{CB} = E_{CB}^0 - \varphi_H$$

Equation 20

$E_{CB}^0$ is the energy of the conduction band edge at the surface at $\varphi_H = 0$. The reason is that the acidic or basic character of a metal oxide semiconductor surface induces
interaction with H\(^+\) or OH\(^-\) ions of an aqueous electrolyte: oxygen in metal oxides act as Lewis-base attracting protons, metal atoms act as Lewis-acid, thus adsorbing hydroxyl ions:

\[
\begin{align*}
M - O + H_2O & \leftrightarrow HO - M^+ + OH^- \\
M - O + H_2O & \leftrightarrow M - (OH)_2 \leftrightarrow HO - M - O^- + H^+
\end{align*}
\]

Equation 21

M stands for metal ions. Since the charge balance across the solid-liquid interface is potential dependent, the Helmholtz double layer varies with the change in the H\(^+\) or OH\(^-\) concentrations, that is to say the pH value of the electrolyte. Hence, depending on the pH value, the surface of the semiconductor is positively or negatively charged. This behavior can be expressed as:

\[
\varphi_H = \text{const} + 0.059pH
\]

Equation 22

Considering Equation 20 it can be seen, that increasing the pH value of the solution shifts the band edge positions to more negative potentials by 59 mV per pH unit at normal conditions.

### 3.1.3.3 Semiconductor-electrolyte junctions under illumination

When a photon with energy larger than the bandgap hits a photoelectrode it can be absorbed either in the space-charge region, in the diffusion layer or even deeper in the bulk of the SC depending on the photon penetration depth. Light absorption induces creation of electron-hole pairs. Depending on the SC crystal structure either direct or indirect momentum transitions take place. In direct transitions (Equation 23) the momentum is conserved, while for indirect transitions (Equation 24) a change in the momentum is required. The light absorption coefficients (\(\alpha\)) of such transitions are described by:\(^{53}\)

\[
\alpha = A \sqrt{h\nu - E_g}
\]

Equation 23

\[
\alpha = A(h\nu - E_g)^2
\]

Equation 24

\(A\) is a constant of proportionality. The absorption depths given by \(1/\alpha\) are very different for direct and indirect transitions. While for a direct transition the depth spans the 100-1000 nm range, it can be 10000 nm for an indirect transition.\(^{54}\) If a
photon is absorbed in the space-charge region of the SC it excites an electron into the conduction band. This photoexcited electron bearing a corresponding hole counterpart experiences an electrostatic potential in the space-charge region. This electrostatic field is very strong and could be for instance $10^5$ V/cm, if a contact potential of 1 V is spanned along a space-charge region of 1 µm. This field prevents the recombination of the excitons in the space-charge regions and forces them to separate, whereby the majority carriers migrate towards the diffusion region and the minority carriers towards the interface. If the photon absorption occurs in the diffusion layer of the SC, this also may cause excitons formation. There is no electrostatic field existing in this region, however, a drift current is established due to the flow of minority carriers towards the bulk of the SC. This drift current is the only driving force for preventing recombination of the excitons. The lower the drift current is, the more carriers undergo recombination. Photons absorbed in the bulk of the SC undergo 100% recombination, since there is no force preventing the recombination process.

Light absorption induces a shift of the free energy of the minority and majority charge carriers and leads to a non-equilibrium condition. Energies of photogenerated charges can be quantified by quasi-Fermi energy levels $E_F^*$. $^{17,40,55-56}$ The quasi-Fermi level is a description of the electrochemical potential of one carrier type at a time under non-equilibrium conditions. The free energy produced by a SCLJ does not reach the energy of the SC bandgap. The useful free energy depends on the kinetics of the charge carriers under illumination and is given by the difference between the hole and electron quasi-Fermi levels under illumination. The degree of splitting between the electron and hole quasi-Fermi levels under no net current flow conditions is the open-circuit voltage. $^{57-59}$ An expression for the photovoltage $V_{OC}$ generated at a SCLJ is given by the ideal diode equation:

$$V_{OC} = \left( nk_B T / q \right) \ln \left( J_{photo} / \gamma J_{sat} \right)$$

Equation 25

$n$ is the diode quality factor, $k_B$ is Boltzmann constant, $T$ is the temperature, $q$ is the charge of an electron, $J_{photo}$ is the photocurrent density (3.1.3.3.1), $\gamma$ is the ratio of the actual junction area to the geometric surface of the electrode (3.1.3.3.2)$^{60}$ and $J_{sat}$ is the saturation current density, which is related to the sum of the recombination pathways (3.1.3.3.3). This equation shows a logarithmic dependence of the photogenerated free energy on the illumination intensity under equilibrium conditions. At a higher photon flux more minority carriers are generated, which results in a larger splitting of the quasi-Fermi levels. While the photovoltage is determined by the quasi-Fermi energy levels, $E_F^*$, the photocurrent and its spectral distribution can be described by applying the Gärtner model.
3.1.3.3.1 Photocurrent density

A theory of photoconduction through the reverse-biased p-n-junction in SCs excludes the assumption that carrier generation in the junction depletion layer is negligible. A more general treatment presented by Gärtner explained the voltage dependence of the photocurrent and its spectral distribution.\(^6^1\) Since the semiconductor-metal interface behaves very similar to the SCLJ, this model was applied to a photoelectrochemical cell.\(^6^2\) The photocurrent \(J_{SCR}\) caused by carriers generated in the space-charge region is given as:

\[
J_{SCR} = q I^0 (1 - e^{-\alpha w})
\]

Equation 26

\(q\) is the charge of the electron, \(I^0\) is the incident photon flux, \(\alpha\) is the energy dependent absorption coefficient of photons, \(w\) is the space-charge region width. The photocurrent \(J_{diff}\) originating from the diffusion layer is given as:

\[
J_{diff} = -q I^0 \left\{ \frac{\alpha L_{min}}{1 + \alpha L_{min}} \right\} e^{-\alpha w} - q I_{min} \left( \frac{D_{min}}{L_{min}} \right)
\]

Equation 27

\(L_{min}\) is the width of the diffusion layer, \(I_{min}\) is the equilibrium concentration of the minority carriers, \(D_{min}\) is the diffusion coefficient of the minority carriers. The total photocurrent generated by the illuminated photoelectrode is the sum of both components and can be written as:

\[
J_{total} = q I^0 (1 - e^{-\alpha w}) + \left[ -q I^0 \left\{ \frac{\alpha L_{min}}{1 + \alpha L_{min}} \right\} e^{-\alpha w} - q I_{min} \left( \frac{D_{min}}{L_{min}} \right) \right]
\]

Equation 28

\(I_{min}, L_{min}\) and \(D_{min}\) are very small for large bandgap SCs and can be neglected, which leads to the following expression for the total photocurrent:

\[
J_{total} = -q I^0 \left\{ \frac{1 - e^{-\alpha w}}{1 + \alpha L_{min}} \right\}
\]

Equation 29

3.1.3.3.2 Roughness factor

In planar PEC cells the direction of light absorption and charge-carrier collection is the same. This means, that the absorber must be thick enough to absorb all the light, but not too thick, so that the minority carriers photogenerated deep within the SC
are able to diffuse to the surface. The distance that a minority carrier can diffuse before recombining (diffusion length $L_D$) is defined as:

\[ L_D = \sqrt{D\tau} \]

Equation 30

$\tau$ is the minority-carrier lifetime and $D$ is the minority carrier diffusion coefficient, which is related to the minority-carrier mobility $\mu$:

\[ D = \frac{\mu k_B T}{q} \]

Equation 31

Using non-planar geometries, such as a rod arrays allows decoupling of the diffusion length requirement from the absorption length. The distance that minority carriers must travel is reduced in high surface area SC structures; hence near-unity collection efficiencies, despite a short minority carrier diffusion lengths, can be achieved.\(^{60, 63-64}\) While in a planar device, photogenerated charge carriers must traverse the entire thickness of the cell before collection, in a rod-array cell, the carriers must only reach the rod surface. Since there is lower current flux per real area of the structured SC electrodes electrocatalytic losses in the form of overpotentials should also be reduced. This might allow photocatalysts with low activities to replace highly active precious metal catalysts.

The drawback of increasing the junction area via nanostructuring is the concomitant reduction of the photovoltage, $V_{OC}$.\(^{60, 65}\) This phenomenon results from the reduced splitting of the quasi-Fermi levels as the photogenerated charge carriers are diluted over a large junction area.\(^{57-59, 66}\) The photovoltage decreases by 60 mV per order of magnitude increase in SCLJ area. Thus, highly nanostructured SC electrodes suffer from a loss in $V_{OC}$ if light absorption is not enhanced significantly by optimizing their geometry: enhancement of absorption compensates increased charge-carrier concentration as discussed above. To achieve the highest performance from a nanostructured electrode, the SCLJ area should be enhanced just enough to collect all the carriers.

3.1.3.3.3 Recombination pathways

The photogenerated charge carriers can recombine in the bulk of the solid ($J_{br}$), in the depletion region ($J_{dr}$), tunnel through the electric potential barrier near the surface ($J_s$), thermally surmount the interfacial potential barrier ($J_{et}$), or recombine at defects at the SCLJ (surface states) ($J_{ss}$) (Figure 7).\(^{67}\) Surface recombination ($J_{ss}$) or charge transfer across the interface ($J_{et}$) dominate recombination processes.\(^{68}\)
Figure 7. Recombination pathways for photoexcited charge carriers in a SC photoelectrochemical cell.

If any of these recombination currents contribute to $J_{\text{sat}}$ (Equation 25), this limits the photovoltage of the device, and thus the ability to drive photoelectrochemical reactions. This very important point has to be considered when it is said that a SC meets the thermodynamic requirements regarding the position of the valence and conduction bands with respect to the redox potentials for HER and OER.
3.2 Photoelectrochemical water splitting

3.2.1 Photoelectrochemical cells

In general a photoelectrochemical cell (PEC) converts incident light into a different useful energy through a light-induced electrochemical process. While one or more electrodes absorb light, current and voltage are simultaneously generated in a PEC cell. The output is either electrical or chemical energy. The construction of a simplistic photoelectrochemical cell (see 3.2.3) for water splitting is depicted in figure 8a.\(^{19}\) It consists of three electrodes placed in an electrolyte solution: the working electrode (WE), counter electrode (CE) and reference electrode (RE). The working electrode, also called photoelectrode, is usually made of a semiconducting material which absorbs the incident light, inducing a chemical reaction at its surface. Depending on the initiated reaction, the WE can be the anode or the cathode. The CE is correspondingly cathode or anode and is typically a corrosion resistant metal, mostly platinum. The electrolyte is referred to as the internal circuit, while the electrical connection between the anode and the cathode is referred to as the external circuit.

![Diagram of a photoelectrochemical cell](image)

Figure 8. a) Schematic representation of a conventional three-electrode photoelectrochemical cell, b) PEC water splitting reaction: (i) light absorption; (ii) charge transfer; (iii) charge transport; and (iv) surface chemical reactions.

In a simplistic PEC cell design, oxygen is evolved at an \(n\)-type semiconducting photoanode, while hydrogen is evolved at the metallic CE (cathode). Another possible PEC cell configuration is a \(p\)-type semiconducting photocathode, which reduces protons into hydrogen upon light irradiation. Oxygen is evolved at the anode. Alternatively both electrodes can be photoactive: the \(n\)-type electrode acting as the photo-anode; the \(p\)-type electrode as the photo-cathode. If an external bias potential is needed to invoke the water-splitting process, a RE is used.

3.2.2 Photoelectrochemical water splitting reaction

There are many actual processes involved in photoelectrochemical water splitting.\(^{69-71}\) The fundamental steps of PEC water splitting can be summarized as shown in
Figure 8b. Once the SCEJ is illuminated with light having an energy higher than the bandgap of the SC \((h\nu \geq E_g)\), which is also called bandgap light, photogenerated excitons are formed. Excitons are bound states of an electron and an electron hole, which are attracted to each other by electrostatic Coulomb forces. The electron-hole pairs are then separated in the SCR by the built-in electrostatic field.

\[ h\nu + SC \rightarrow h^+ + e^- \]  

Equation 32

The next step is the transport of the separated electrons and/or holes to preferable catalytically active sites: photogenerated majority carriers (electrons in \(n\)-type SCs and holes in \(p\)-type SCs) diffuse towards the backside of the photoelectrode and accumulate there. Since the backside of the photoelectrode is wired, these charges are transported to the CE via a load. Oxidation of the redox electrolyte occurs with \(n\)-type semiconductor photoelectrodes while reduction is invoked with \(p\)-type photoelectrodes. In a PEC cell with an \(n\)-type photoelectrode the photogenerated holes \(h^+\) react with water to form oxygen and protons at the interface between the photoelectrode and electrolyte.

\[ 2h^+ + H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2H^+ \]  

Equation 33

Oxidation and reduction reactions at the photoelectrode and CE are inverse or complementary to each other. The protons are travelling through the aqueous electrolyte to the cathode. The photogenerated electrons, transferred through the external circuit, react with protons at the cathode, reducing them to gaseous hydrogen.

\[ 2e^- + 2H^+ \rightarrow H_2 \]  

Equation 34

The overall water-splitting reaction in the PEC cell can be expressed in the following form:

\[ H_2O + 2h\nu \rightarrow H_2 + \frac{1}{2}O_2 \]  

Equation 35

The half-reactions described in Equation 33 and Equation 34 are simplifications of more complex multistep electrochemical reaction pathways. The minimum electric potential required to sustain reversible water electrolysis under standard conditions (25°C and 1 bar) is 1.229 V, which is derived from the relationship:
\[
\Delta G^0 = -nF\Delta E^0 = 237.18 \frac{kJ}{mol}
\]

Equation 36

\(\Delta G^0\) is standard Gibbs free energy change, representing the thermodynamic minimum for water splitting into oxygen and hydrogen at standard conditions, \(n\) is the number of exchanged electrons, \(F\) is the Faraday constant, \(\Delta E^0\) is the standard potential of the reaction. These values do not include unavoidable process losses, such as kinetic overpotential losses at the anode \(\eta_a\) and cathode \(\eta_c\), ionic conductivity losses in solution \(\eta_\Omega\) and other system losses \(\eta_{sys}\). The operating voltage for water splitting must exceed the minimal reversible potential \(V_{rev}^0\) and all above-mentioned losses:

\[
V_{op} = V_{rev}^0 + \eta_a + \eta_c + \eta_\Omega + \eta_{sys}
\]

Equation 37

In practice, water electrolysis requires operating voltages of 1.6 V to 1.9 V and more, depending on the gas-production rates.\textsuperscript{73-74}

3.2.3 Classification of PEC devices

Solar energy converting devices can be divided into two classes: (electrochemical) photovoltaic cells and photoelectrochemical synthetic cells (Figure 9).\textsuperscript{18,75-76} Solid-state photovoltaic (PV) cells are based on a buried junction formed exclusively on the interface between two solid-state electronic conductors. Under illumination, charge separation is mediated by the difference in the electrochemical potential of these two solids and a photovoltage and a photocurrent are produced.\textsuperscript{77}

Despite solid-state solar cells have good solar-to-electricity performance, they remain expensive and new concepts of energy conversion involving junctions between a semiconductor and an electrolyte were introduced. A device utilizing a SCLJ generates photovoltage and photocurrent under illumination, while charge separation occurs because of differences in the electrochemical potentials of the solid and the electrolyte, as well as from asymmetries in the charge-transfer kinetics for electrons and holes across the junction.\textsuperscript{22} In electrochemical PV cells the electrochemical reaction at the photoelectrode is the opposite to that occurring at the CE. The optical energy (light) is thereby converted into electricity with no net change in the redox electrolyte or electrodes. Such photovoltaic cells are also called regenerative photoelectrochemical cells. Gerischer first demonstrated a cell comprised of a CdS single crystal n-type photoanode, the \([\text{Fe(CN)}_6]^{4-}/[\text{Fe(CN)}_6]^{3-}\) redox couple and a doped SnO\(_2\) cathode.\textsuperscript{78} In the Gerischer cell, photo-excitation of n-CdS single crystal causes the transfer of holes to the reduced form of the redox couple. At the transparent doped SnO\(_2\) cathode the circuit is completed by reducing
[Fe(CN)₆]³⁻: Improved electrochemical photovoltaic cells used CdSe as a photoanode with lower bandgap, allowing utilization of the whole sunlight irradiation spectrum, as well as a modified electrochemically active electrolyte preventing photoanode degradation.⁷⁹

Regenerative electrochemical photovoltaic solar cells, demonstrated in 1976 by Hodes, Cahen, Manassen, Wrighton, Heller and Miller, generated electricity with a substantial and sustained efficiency of 7%.⁷⁹-⁸¹ Licht discovered the importance of the cation used in the electrolyte, as well as the positive effect of copper ions in the solution and demonstrated a sustained solar to electrical conversion efficiency of 12.7% in 1985.⁸² By adding of cyanide to n-CdSe/Fe(CN)₆³⁻/⁴⁻ PEC cells he achieved an efficiency of 16.4%.⁸³ Another type of electrochemical photovoltaic device is a dye-sensitized PEC cell. The photoanode in these cells consists of an n-type SC covered with molecular dyes. Upon light absorption, electrons from dyes in their excited state are injected into the conduction band of the SC. The oxidized dye oxidizes the reduced form of a redox couple and the complementary redox process takes place at the counter electrode.⁸⁴-⁸⁵ As electrochemical- or solid-state PV cells generate sufficient voltage for water splitting, coupling thereof to an electrolyzer device seems to be the simplest, efficient and sustainable solution for water splitting using solar energy as only energy input.⁸⁶-⁸⁸ An important advantage of the arrangement is absence of the SCLJ, which means there is no need to match the positions of CB and VB edges to redox potentials of the electrolyte. A recently designed solid-state four-junction PV with solar-to-electricity efficiency of 44.7%⁸⁹ coupled to a modern PEM electrolyzer device having up to 90% conversion efficiency⁹⁰ would result in 40% solar-to-hydrogen (STH) conversion efficiency, which is far beyond the ultimate goal of 25% STH efficiency, which is driven by the cost of H₂ at $2.10/kg.⁹¹ The main drawback of PV/electrolyzer systems are the high costs of photovoltaic devices, that such implementation is not yet economically
viable. Using a relatively cheap 10% amorphous silicon PV system and 60% PEM electrolyzer results in only 6% STH, which is not economically viable. The above described regenerative electrochemical photovoltaic cells cannot be directly used as photoelectrosynthetic cells for water photoelectrolysis (in other words cannot use water as quasi-regenerative electrolyte), since for the photoelectrolytic hydrogen production from water the $O_2/O_2^-$ redox couple has to be used. The main difficulty thereby is the corrosion of the photoactive electrode at high anodic potentials required for water decomposition. Only when electricity generation is the purpose, other redox couples with much lower redox potential can be used, thus maintaining semiconducting electrodes’ integrity. Then, such regenerative PEC cells can be coupled to metallic electrodes resulting in a PEC-biased electrolysic cell.\(^{92}\)

Visible light has sufficient energy to split water into hydrogen and oxygen, therefore a combination of cheap light harvesting and water-splitting systems is required. Excluding the PV-electrolyzer implementation, two general approaches to achieve semiconductor-based PEC water splitting are possible: the semiconductor-liquid junction (SCLJ) approach and a photo-assisted electrolysis cell. For industrial scale application PEC devices must have at least the same internal photon-to-electron conversion efficiency as commercial PV devices. Since the electrode overpotential increases logarithmically with current density as given by the Tafel relation,\(^{93}\) lower operational current density, when using direct solar light, leads to higher relative efficiency from PEC devices as compared to PV/electrolysis.\(^{94}\) Bubble formation by the product gases is also a source of activation and ohmic overpotentials,\(^{95-97}\) correspondingly, at lower reaction rates these are reduced.

PEC cells that produce fuels directly at the SCLJ are referred to as photoelectrosynthetic cells.\(^{77}\) A photoelectrosynthetic cell utilizes optical energy to induce chemical reactions. A net chemical change of the redox electrolyte occurs under illumination. This cell type can be further divided into photocatalytic and photoelectrolytic cells.\(^{98}\) Photocatalytic cells use light as activation energy for exergonic ($\Delta G < 0$) reactions, e.g. ammonium formation from elemental hydrogen and nitrogen. Photoelectrolytic cells allow storing of the optical energy as chemical energy in endergonic reactions ($\Delta G > 0$), for instance water splitting into hydrogen and oxygen.

In the SCLJ approach the water splitting potential is generated at the semiconductor-liquid interface. The efficiency of such a system is defined by the ability of the semiconducting material to absorb irradiation in a broad spectral range, as well as efficiently separate the generated charges. The Shockley-Queisser limit, which is the calculated maximum theoretical efficiency of a solar cell made from a single $pn$-junction\(^{99}\) is also applicable for the estimation of the maximum theoretical efficiency
of PEC water splitting systems. Here, both maximum photocurrent density and minimal required photopotential have to be considered. Figure 10 shows the maximum photocurrent densities obtainable from a single junction PEC device as a function of semiconductors bandgap calculated for AM1.5G solar irradiation. This plot assumes, that all incident photons with energy exceeding the bandgap energy are absorbed and converted into excitons, while every electron-hole pair is separated and converted to photocurrent.

![Figure 10. Maximum attainable AM1.5G photocurrent densities for single junction PEC devices as a function of semiconductor bandgap. Adapted from ref.103](image)

If the semiconductor bandgap is too low, the photoelectrode system cannot sustain photoelectrolysis, as the generated potential is too small. Thus, there is no photocurrent density, and the conversion efficiency is 0% STH. In order to achieve efficient direct water splitting by a single junction PEC device, considering kinetic overpotentials and other loss mechanisms, the minimum required photopotential is about 1.6 V - 2.0 V. In an idealized single-junction PEC cell, the required bandgap of 2.0 eV causes significant diminishment of the theoretical maximum of conversion efficiency. Analysis of various schemes for PEC water splitting showed that single-gap schemes have efficiencies limit of up to 10% ($E_g = 2.0$ eV). Assuming real systems and utilization of 50% of the bandgap (quasi-Fermi-level separation in the SC), the absolute minimum bandgap value is 3.2 eV. Accordingly, this limits the photocurrent density to maximum 1 mA/cm². From equation 39 the maximum STH amounts to 1.23%.

Besides semiconductors bandgap and absorption efficiency irradiation, positions of the conduction and valence bands relative to the redox potentials of the electrolyte determine the ability of the system to drive the water splitting reaction. The energy levels of many oxides are not favorable for water decomposition since the $H^+/H_2$ energy level is located above the SC electrons quasi-Fermi level. Under illumination, both, the photoelectrodes surface potential and the water reduction potential are
lowered, but still the $H^+/H_2$ reduction potential remains above the SC electrons quasi-Fermi level and correspondingly the counter electrode’s Fermi level. Anodic bias is thus needed to raise the Fermi level of the counter electrode above the water reduction potential. The applied bias increases the semiconductor band bending to maintain the required electric field driven charge separation in the semiconductor and provides overvoltage at the counter electrode needed to reduce protons. Several oxides have their $E_{FB}$ lying above the $H^+/H_2$ level, thus no external bias is needed to produce $H_2$ and $O_2$. The drawback of these oxides are large bandgap energies that result in low optical absorption, and hence low visible spectrum photoconversion efficiencies. Using of external bias in PEC system results in the process called photo-assisted water splitting. Photo-assisted electrolytic cells can operate under illumination in combination with thermal, chemical or electrical bias. The bias serves either to facilitate electrolytic reaction, or to accelerate chemical reaction by reducing electron-hole recombination in the bulk of the SC through widening the built in SCR. A chemically biased photo-assisted electrolysis cell has two half-cells placed in two different electrolytes in a two-compartment cell. The electrolytes are chosen in the way to reduce the potential required to drive the corresponding half reactions. An example is an $n$-SC anode placed in alkaline electrolyte, which facilitates OER, while the metallic cathode is kept in acidic solution, which facilitates HER. The bias can be recalculated into electric potential equivalent based on Nernst equation and equals to $0.059 \times \Delta pH$. Electrical bias can be achieved by combination of a photovoltaic and a SCLJ (PV/SCLJ) approach. Such photo-assisted electrolysis cells can be made as a SCLJ serially connected to an external single- or multijunction PV system.

The desire to eliminate the need for bias in a photoelectrolysis cell leads to another so-called tandem configuration, where both the anode and cathode are photoactive. In a two-semiconductor electrode device a semiconductor of relatively smaller bandgaps, able to capture a larger amount of solar spectrum energy, can be used. The Fermi level of the majority carriers in the illuminated semiconductor does not have to be of an energy suitable for driving the counter electrode reaction. This helps to overcome the trade-off between insufficient voltage for water decomposition generated by a single gap device and poor absorption of the solar spectrum. In contrast to a single semiconductor electrode cell, a $p$-$n$ photoelectrolysis cell does not require external bias when the flat band potential is below the $H^+/H_2$ level. Tandem PEC devices contain two or more absorber materials with different mid-bandgaps ($<2.2$ eV) in one of two possible configurations: as two separated photoelectrodes or combined into a monolithic structure. When both electrodes ($p$- and $n$-type SC) are simultaneously illuminated, a hole in the $n$-type semiconductor and an electron in the $p$-type semiconductor are generated. The majority carriers recombine at the ohmic contacts, but a greater part of the potential
energy is available to drive the chemical reactions. The available electron-hole potential for driving chemical reactions is enhanced if the electron affinity of the \( n \)-type electrode is greater than that of the \( p \)-type electrode. The energy diagram of such a system is shown in figure 11.

![Energy Diagram of Chemical Reactions](image)

**Figure 11.** Schematic of an idealized tandem-junction photoanode and photocathode device. Left: two electrode system, right: monolithic “photodiode” device.

Nozik published the first monolithic photoelectrosynthetic cell designated "photochemical diode" able to decompose water.\(^{115}\) It consists of a small multiple junction semiconductor structure, directly immersed in an electrolyte. Illumination with light causes the redox reaction to occur. In order to reach the needed potential for driving the desired redox reaction, the semiconductor layers were connected in series one behind the other, thus forming one monolithic device generating sufficient potential to split water. Operation of photochemical diodes was verified for \( n \)-GaP/Pt and \( n \)-CdS/Pt Schottky-type diodes\(^ {15} \) and an \( n \)-TiO\(_2\)/\( p \)-GaP heterotype \( p-n \) diode,\(^ {112} \) which correspondingly represent a single gap device and a tandem device. The conversion efficiency can be significantly increased if the light transmitted through a solar cell with larger bandgap is absorbed by a subsequent cell with a lower bandgap. Modern monolithic four-junction devices manufactured by epitaxial deposition reached solar-to-electricity efficiency of above 44%.\(^ {89} \) Photovoltaic tandem cells consisting of a gallium indium phosphide (GaInP\(_2\)) on top of a gallium arsenide (GaAs) homojunction were utilized for photoelectrochemical water decomposition.\(^ {16, 94, 116-117} \) In these systems direct water splitting was achieved by the PEC cell, which was biased with an integrated photovoltaic device. The tandem cell device consisted of a GaAs bottom cell connected to a GaInP\(_2\) top cell. A tunnel diode was used for interconnection. The top \( p/n \) GaInP\(_2\) junction with a bandgap of 1.81 eV absorbs the visible portion of the solar spectrum. The bottom \( p/n \) GaAs junction with a bandgap of 1.42 eV absorbs the near-infrared portion of the spectrum transmitted through the top junction. The hydrogen production efficiency of this system was 12.4%. Licht published experimental results obtained from a cell
containing AlGaAs/Si with solar to electrical conversion efficiency of up to 20%. In the same work he utilized an AlGaAs/Si cell decorated with RuO₂/Ptblack, which evolved hydrogen and oxygen at a record efficiency of 18.3% and predicted systems with efficiencies of up to 30%. The common drawback of these devices are stability problems caused by serious photocorrosion, since both semiconductors have to be stable in the same aqueous electrolyte solution, in the dark and under illumination.

Both for PV and PEC multi-junction cells the maximal theoretical efficiency and optimum bandgap energies were calculated. Importance of water-absorption losses of solar irradiation were considered.

![Figure 12. Maps of theoretical tandem PEC efficiency limits over the bandgap energies of bottom and top junctions, for a) idealized case without water coverage and b) under 2 cm of water.](image)

Figure 12 shows two maps of theoretical tandem PEC efficiency limits as function of bandgap energies of bottom and top junctions. In the first case (Figure 12a) no losses associated with overvoltages or electrolyte are considered. These calculations agree very well with results published by Hanna and Nozik: for single gap photovoltaic devices 33.7% conversion efficiency can be reached. An ideal two-gap tandem photovoltaic system yields up to 45.7% conversion efficiency. For an ideal 1.40 eV and 0.52 eV bandgap combination PV/electrolyzer device a maximum efficiency of 40% was predicted. Figure 12b shows the effect of sunlight absorption in a 2 cm thick electrolyte film. Since the water-based electrolyte absorbs nearly the complete irradiation with wavelengths beyond 1100 nm, low bandgap SC cannot be utilized. Of course the subcell generating the smallest photocurrent limits the maximal efficiency of the whole device. According to this, the top-junction bandgap has to be increased from 1.39 eV to 1.78 eV in order to leave enough light for a current match of the bottom junction.
3.3 Materials for photoelectrodes

3.3.1 Requirements

Considering the needs described in the above chapters new thin-film semiconductor materials with good absorption and carrier-transport properties have to be developed. The interface of the photoelectrodes needs to be designed with energetic and kinetic properties sustaining the water-splitting reactions and being chemically stable both under illumination and dark. Integrated devices need to be constructed and manufactured using low-cost, commercial-scale processes.\textsuperscript{25, 108, 121} Figure 13 summarizes the requirements for new semiconducting materials. Bandgaps of new materials for multi-junction tandem devices have to lie in the range from 0.4 eV - 1.1 eV and 1.7 eV - 1.9 eV to absorb maximum solar radiation. The material has to generate sufficient photopotential to split water. The sum of the effective quasi-Fermi level splits in thin films of a multi-junction device has to be large enough to overcome the reversible potential plus the overpotentials for water splitting, typically over 1.6 V in practical systems. Simultaneously, the materials have to generate sufficient photocurrent for efficient hydrogen production, which means the materials has to support the efficient generation, separation, transport and collection of photogenerated charges to drive the water-splitting reactions.

The surface bandedge potentials have to match to the $H^+ / H_2$ reduction potential and $O_2/O^{2-}$ oxidation potentials: bandedge positions of the resulting PEC device have to bracket the water redox potentials. The material has to possess moderate conductivity; as too high conductivity causes electrical short circuit between electrolyte and the photoelectrochemical cell, too high resistance reduces the efficiency. The electron-hole mobility and lifetimes has to be long enough to allow the electron-hole pair to reach the active sites. Absence of charge recombination centers is crucial to prevent recombination of the photogenerated charge carriers. The rate for water-splitting should be faster than any recombination reaction.

![Figure 13. Requirements for suitable semiconducting materials for PEC water splitting.](image-url)
Photocurrents exceeding 10 mA/cm² are needed for STH conversion efficiencies above 12.3%. The material also needs to be stable in aqueous environment under illumination. Most reported PEC devices lose their activity after 24 hours or less. Only some SCLJ devices remained stable for more than one day. In order to be economically viable, the minimal operational lifetimes of solar water splitting devices with an efficiency of 10% have to be at least several years. Finally, the potential material for water oxidation has to be inexpensive and cost less than US$ 160/m², which means the semiconductor has to be composed of cheap abundant materials. Moreover, the production technique needs to be largely scalable and PEC devices have to be fabricated by a large-scale technique such as spray deposition.

3.3.2 Materials classes
Initially semiconductor materials for water splitting devices were the solid-state photovoltaic materials adapted for use in PEC cells. First devices with more than 10% STH conversion efficiency were based on crystalline Si and compound III–V and II–VI materials. Amorphous silicon compounds including silicon carbides and nitrides also show interesting performances in PEC applications. New materials, such as (copper indium gallium selenides) CIGS and halide perovskite-based cells were also adapted for PEC applications, with performances exceeding 10% STH efficiency. System optimization is still needed in order to overcome problems with stability and interface properties. Tandem photocathodes based on high-quality crystalline III–V semiconductor compounds composed of gallium, indium, phosphorous and arsenic demonstrated STH efficiencies between 12% - 16%. Although such STH efficiencies are the current world-record, these devices are subject to degradation. InP-based PEC half-cells show significant hydrogen evolution efficiency, but require an external bias to complement the insufficient voltage, as the half-cell was not implemented in a tandem device. Limited durability is the barrier for practical PEC hydrogen production using III–V semiconductor compounds. Furthermore, the III-V materials are not compatible with the cost targets mentioned above.

Chalcopyrite alloys formed with copper and gallium, indium, sulfur and selenium have been widely characterized in the PV world as chalcopyrite thin films are the best absorbers of solar energy. This class of materials allows bandgap tailoring in a wide range, from 1 eV (CuInSe₂) to 2.43 eV (CuGaS₂) by varying composition. Photocurrent densities of up to 13 mA/cm² were demonstrated for a CuGaSe₂ photocathode in biased PEC cell. Several problems concerning stability, surface kinetics and energetics have to be addressed in order to achieve low-cost thin-film copper chalcopyrite solar water splitting systems.
In contrast to chalcopyrites, which are unable to sustain hydrogen evolution, tungsten and molybdenum sulfide nanostructures are excellent hydrogen evolution catalysts. A disadvantage of these materials is their small bandgap (below 1.2 eV), which is too low for PEC water splitting. Novel studies on MoS$_2$ are focused on establishing synthesis routes of nanostructures in order to increase the bandgap by quantum confinement.\textsuperscript{137}

As the problems of the stability of photoelectrodes are solved only for metal oxides this class of materials has received substantial research interest, progressing in recent decades. Among their stability, metal oxide semiconductors are prime candidates for solar water splitting application, since they are low cost materials. However, oxide materials possessing large bandgap lack visible spectrum light absorption and lower bandgap oxides on the other hand are less stable and prone to corrosion. Metal oxides usually have low carrier mobility, compared to III-V semiconductors or silicon. Further limitations of known semiconducting oxides are limited charge carrier diffusion lengths and modest catalytic activity for water oxidation. The challenge is to overcome these limitations, but keeping the advantage of stability and low-cost of metal oxides.

Fujishima and Honda demonstrated for the first time, that an illuminated TiO$_2$ semiconductor-electrolyte cell electrolyzes water to hydrogen and oxygen.\textsuperscript{12} An electrochemically biased PEC cell was used, which involved chemical and solar energy consumption. Despite superior stability, the utilized TiO$_2$ semiconductor absorbed only a small fraction of incident solar irradiation due to the wide bandgap and therefore the overall efficiency was very low.

Tungsten oxide in form of thin films or nanoparticles was investigated by many groups for several years.\textsuperscript{138-141} This oxide is inexpensive and stable, but has a large bandgap of 2.6 eV, which is limiting its PEC performance. Photocurrent densities around 3 mA/cm$^2$ have been achieved by structured single oxide electrodes.\textsuperscript{142-144} The best-demonstrated STH efficiencies achieved using WO$_3$ in multi-junction photoanode devices, has plateaued in the 3% - 5% range.\textsuperscript{85,145} Current research is mainly focused on reducing the bandgap through doping of tungsten trioxide structures with different ions.\textsuperscript{146-148}

Iron oxide, which is abundant, stable, inexpensive and exhibits a bandgap of 1.8 eV - 2.2 eV, has its limitations due to the position of the conduction-band edge below the reversible hydrogen potential, large recombination rates of the photogenerated charge carriers, and short diffusion length of holes as well as poor electrical conductivity.\textsuperscript{149-150} Current research to overcome these limitations is concentrated on thin films and nanostructured materials as well as bulk doping.\textsuperscript{151-155}
As the predominantly investigated binary oxides Fe$_2$O$_3$, TiO$_2$ and WO$_3$ do not show sufficient stability, suitable bandgaps, efficient light absorption, catalytic activity, and charge carrier lifetimes, the development of more complex metal oxides, such as ternary or quaternary metal oxides, can therefore not be avoided. It was shown that the development of new photoelectrodes made of solid solutions and more complicated multicomponent compositions is promising.\textsuperscript{156}

Many investigated ternary and quaternary metal oxide semiconducting anodes, such as SrTiO$_3$, BaTiO$_3$, CdFe$_2$O$_4$, PbFe$_{12}$O$_{19}$, Pb$_2$Ti$_{1.5}$W$_{0.5}$O$_{6.5}$, Hg$_2$Ta$_2$O$_7$, and Hg$_2$Nb$_2$O$_7$ form a rectifying junction with the electrolyte, but anodic photocurrents were generated only with larger-than-band-gap illumination.

BiVO$_4$ is a promising candidate for tandem PEC cells, as it possesses a bandgap of 2.4 eV.\textsuperscript{157-158} However, separation and collection of photogenerated charge in BiVO$_4$ is inefficient, which results in poor photocurrent response.\textsuperscript{159} To overcome these limitations composite materials like WO$_3$/BiVO$_4$ or alloys with Mo or W were investigated.\textsuperscript{160-161}

Rather complicated compounds, such as Sm$_2$Ti$_2$S$_2$O$_5$, Y$_2$Ta$_2$O$_5$N$_2$ and LaTiO$_2$N were predicted to be suitable for efficient solar water splitting based on calculations using density functional theory.\textsuperscript{162-164} Both, the bandgap and band edge positions were predicted to be optimal and the theoretical efficiency, which could be achieved with these materials, was estimated to be up to 30%. Nevertheless, there are no reports about functioning of these systems without sacrificial reagents in solution. Obviously, without easily oxidizable redox species in solution the materials would corrode by oxidizing non-oxide anions such as nitrogen, sulfur and carbon, causing degradation of the materials.

High throughput combinatorial techniques allowed investigation of new photoactive quaternary oxides containing cobalt, aluminum and iron, which was not previously known.\textsuperscript{32} Thin films of this material contained cobalt, aluminum, and iron in a Co$_3$O$_4$ spinel structure with Fe and Al substituting Co sites. The material had p-type semiconductor properties and an indirect bandgap of around 1.5 eV. The onset of hydrogen evolution was about 0.9 V more positive than the thermodynamic value and the photocurrent was limited by slow kinetics for hydrogen evolution. Recently investigated quaternary n- and p-type Fe, Cr, Al oxides also demonstrated a nearly ideal bandgap of 1.8 eV, but with a high surface recombination of photogenerated charges.\textsuperscript{165}

Although metal oxides seem to be ideal candidate materials for PEC electrodes because of their superior stability and low cost, there are still no known semiconducting metal oxide materials that have the proper set of characteristics for
efficient water photoelectrolysis. It is currently evident, that new materials have to be discovered, and those materials might be complex multinary oxide structures.

3.3.2.1 Synthesis techniques of semiconducting thin films

As the maximum efficiency of a photovoltaic device is defined by the fraction of absorbed solar energy, it is directly related to the bandgaps of the materials in the device. Use of tandem photoelectrolysis systems allows employing lower bandgap materials absorbing photons of lower energy. This results in considerable higher efficiencies in multi-junction devices. Whenever the resulting PEC device will have a monolithic design or exists as two separated electrodes, if it will be biased by buried PV junction or get external bias potential, in all these cases the used absorber(s) consist of thin films each absorbing its own portion of solar radiation.

While silicon with its indirect bandgap has a low absorption coefficient, this fact can be easily overcome by using thicker electrodes, as the diffusion length in Si is long. Materials such as GaAs have quite low diffusion length, but because of the direct bandgap the absorption is high, allowing using thinner electrodes. Transition metal oxides typically have indirect bandgap, with low absorption as a consequence. Simultaneously, metal oxides have short diffusion lengths. From here a concept of an optimal film thickness emerges. The maximum of photoresponse in a semiconductor electrode is expected when the film thickness is roughly equal to the reciprocal of its absorption coefficient:

\[
\chi_f \approx \frac{1}{\alpha} \approx w
\]

Equation 38

\(\chi_f\) is the film thickness, \(\alpha\) is the absorption coefficient of light, and \(w\) is the depletion layer width. As most of the incident irradiation should be absorbed inside the SCR, the film thickness should not exceed the width of the depletion layer.\(^{166}\) For most transition metal oxides the optimal film thickness is in a range from 100 nm to 2.0 \(\mu\)m. To compensate the lack of absorption for extremely thin layers, a multilayer device can be used.\(^{167}\)

There are various methods, which can be employed to make thin films: anodic oxidation, spray pyrolysis, reactive sputtering, and vapor deposition among others. The photoelectrochemical behavior of photoelectrodes is dependent on the way it was fabricated.

Anodic oxides can be obtained by anodic polarization of the respective metal\(^{168}\) or metal alloys\(^{169}\) in aqueous electrolyte solution. However, this method can only be applied to valve metals or alloys containing a large fraction of them, since other
metals do not form oxides, but rather dissolve. The thermal oxidation of metals to form metal oxides is a convenient way to make photosensitive electrodes. Sol-gel deposition involves the transfer of metal ions from a liquid (sol) into a solid (gel) phase, typically followed by a thermal treatment in order to decompose the gel into metal oxide and crystallization thereof. Thin-films can be fabricated by dip coating or spin coating. A big advantage of the method is the possibility to modify the gel by addition of suitable dopants in order to get materials of desired properties. Electrochemically induced gel formation allows high control over the deposition process in terms of composition and thickness. Solid thin films or powders on the substrate surface can be obtained from gaseous molecules by means of chemical vapor deposition (CVD). Thereby, the process of film growth and film properties can be controlled by power density, gas pressure, frequency, gas composition, and substrate temperature. Metal oxides thin films prepared by CVD have shown superior quantum efficiencies in comparison to thermally grown thin films. Sputtering can be used for coating of a variety of substrates with thin films of electrically conductive or insulating materials. Bombardment of a sputtering target surface with plasma-induced ions results in material ejection from the target that becomes the deposited film. Reactive sputtering is deposition of a film formed by chemical reaction between the target material and a gas introduced into the sputtering chamber. Although the synthesis systems and their associated peripheral components are expensive, their maintenance costs are high and high purity materials have to be used, this deposition method presents important advantages. For example, by varying the deposition rates of individual targets and employing a wide variety of materials the thickness and stoichiometry of the films can be precisely controlled.
3.4 Photoelectrochemical characterization of PEC systems

3.4.1 Conversion efficiency determination

There are many efficiency values described in literature that can be reported for PEC devices independent of their construction.\textsuperscript{22, 106, 174-177} In many published works, wrong methods or mathematical expressions were used for efficiency determination, until Chen et al. presented in a review article proper definitions and mathematical expressions for device efficiencies.\textsuperscript{178} Measures of efficiency were split into two main categories: benchmark efficiency and diagnostic efficiencies.

<table>
<thead>
<tr>
<th>Benchmark efficiency (suitable for mainstream reporting)</th>
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<td>• Solar-to-hydrogen conversion efficiency (STH)</td>
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<table>
<thead>
<tr>
<th>Diagnostic efficiencies (to understand material performance)</th>
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</thead>
<tbody>
<tr>
<td>• Applied bias photon-to-current efficiency (ABPE)</td>
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<tr>
<td>• Intrinsic solar to chemical (ISTC) conversion efficiency - internal photovoltaic power multiplied by electrolysis efficiency</td>
</tr>
<tr>
<td>• External quantum efficiency (EQE) - incident photon-to-current efficiency (IPCE)</td>
</tr>
<tr>
<td>• Internal quantum efficiency (IQE) - absorbed photon-to-current efficiency (APCE)</td>
</tr>
</tbody>
</table>

Figure 14. Measures of PEC systems efficiency.

While the STH efficiency is the most important of all efficiency measurements as it describes the overall efficiency of a PEC water-splitting device, diagnostic efficiency measurements, namely IPCE, APCE, ABPE and the recently introduced ISTC\textsuperscript{179} are valuable for understanding and improving materials performance (Figure 14).

3.4.1.1 Solar-to-hydrogen efficiency (STH)

The most important efficiency evaluation method of PEC devices is determination of the STH efficiency. Independent on the device construction or used materials, the STH efficiency is a single value by which all PEC devices can be reliably ranked against one another.\textsuperscript{94} STH efficiency describes the overall efficiency of a PEC water-splitting device exposed to solar Air Mass 1.5 Global (AM1.5\textsubscript{G}) illumination.\textsuperscript{106, 180-181} Important is that there is no applied voltage between the working electrode (WE) and counter electrode (CE), which means the WE and CE should be short-circuited and the STH is measured in a 2-electrode system. Both, the WE and CE need to be immersed in a solution with the same pH value. When the WE and CE are compartmentalized and immersed in solutions with different pH values, a Nernstian bias of 59 mV per pH unit of difference arises from the chemical bias between these two solutions.\textsuperscript{15} Maintaining the pH difference between these two compartments...
requires energy and is therefore not sustainable. The electrolyte should also not contain any sacrificial donors or acceptors because the redox reactions would not reflect the true water splitting process.

The STH conversion efficiency of solar-based hydrogen generating systems is defined as the ratio of energy contained in the amount of hydrogen generated to the total solar energy delivered to the system. In other words, it is the ratio of the output (chemical) power to the input (solar) power. Considering the Gibbs free energy for hydrogen and a solar flux of AM1.5\textsubscript{g} solar irradiation\textsuperscript{177,182} the STH efficiency can be denoted as:

$$ STH(\%) = \frac{\Delta G \times R_H_2}{P_{solar}} = \frac{\Delta G (J_{ph}/2e)}{P_{solar}} \approx 0.123 \times J_{ph} $$

Equation 39

STH is not the only acceptable benchmark for reporting the device efficiency. Other measures can also provide insight into the functionality and limitations of a device. For example, as can be seen from the equation 39 the power output (numerator) of the STH expression can be determined by two generally accepted approaches: the direct measurement of the true H\textsubscript{2} production rate by an analytical method such as gas chromatography or mass spectrometry and the relation that power is the product of voltage and current. While solid-state solar cells are operated at the maximum power point (maximum product of photocurrent and photovoltage)\textsuperscript{183} electrolyzers for the best hydrogen-production performance should be operated at maximum photocurrent, with the minimal required voltage, therefore the current is the short-circuit photocurrent density normalized to the illuminated electrode area and the voltage is 1.23 V, the thermodynamic water-splitting potential. This leads to another efficiency measure – the photocurrent. The faradaic efficiency for hydrogen evolution is considered to be 100\%, otherwise it has to be multiplied by the current and voltage. Direct identification and quantification of H\textsubscript{2} and O\textsubscript{2} can be used to establish faradaic efficiencies. The denominator in the equation is simply the total integrated power density of the incident solar irradiation.

### 3.4.1.2 Applied bias photon-to-current efficiency (ABPE)

If a bias is applied between working and counter electrodes the efficiency cannot be calculated and referred as STH. The simplified expression for so-called applied bias photon-to-current conversion efficiency (ABPE) is given by:\textsuperscript{178}

$$ ABPE = \frac{J_{ph}}{P_{solar}} (V_{redox} - V_{bias}) $$

Equation 40
Here $V_{\text{redox}}$ is the redox potential for water splitting, $V_{\text{bias}}$ is the externally applied bias potential and $P_{\text{solar}}$ is the power of the incident light. Removing bias potential turns the equation back to the STH efficiency. Both, the STH and the ABPE are defined for a two electrode PEC cell, but most of investigations are performed under potentiostatic control using three-electrode cells. The ABPE can still be used in this case if $V_{\text{bias}}$ is replaced by the electrode potential with respect to the reversible potential of the counter electrode.

### 3.4.1.3 Intrinsic solar to chemical (ISTC) conversion efficiency

If it is impossible to define the overall efficiency of the entire PEC device, an alternative definition can be used, which allows estimation of the intrinsic (internal) solar-to-chemical conversion efficiency of the photoelectrode.\(^{179}\) Photocurrent and photovoltage produced by the photoelectrode can be extracted from voltammograms measured in a three-electrode electrochemical set-up in the dark and under illumination. The internal photovoltaic power produced by the photoelectrode is calculated as the photocurrent multiplied by photovoltage; further multiplying by electrolysis efficiency yields the intrinsic solar-to-chemical efficiency. Determination of the effective photovoltage includes the assumption, that the internal resistance of the photoelectrode is small. The photovoltage is calculated as the potential shift between the light current and the dark current, because of photovoltaic effects at the polarized SCLJ.\(^{21}\) Talking about a photoanode, it behaves as an anode connected in series to a potential source (e.g. PV) and the generated potential adds up to that supplied by the potentiostat.\(^{184}\) As the current is a function of the effective potential, it reaches the same level under light at an applied potential lower than under dark. So, if there is a photocurrent density of $X$ mA/cm\(^2\) at an applied potential of $Y$ mV and in the dark a potential of $Z$ mV should be applied in order to reach the current density of $X$ mA/cm\(^2\), the solar irradiation power saves $Z-Y$ mV potential, which is considered as photovoltage. Multiplication of the so calculated photovoltage by the corresponding photocurrent density and division by the incident light power yields ISTC.

\[
\text{ISTC} = \frac{J_{ph} \times V_{ph}}{P_{solar}}
\]

**Equation 41**

However, treating of the photoelectrode as a solar cell providing an internal bias voltage to the electrode is incorrect in most cases.\(^{185}\) As the mechanism of dark current generation at semiconductor electrodes involves minority carriers, for example holes in the case of an $n$-type semiconductor, depending on bandgap value, doping level and thermal generation of minority carriers in the dark the mechanism of dark current generation may be very different, and therefore the dark current of a
photoelectrode is not a reliable quantity for definition of photoelectrolysis efficiencies.

### 3.4.2 Characterization of semiconductor-liquid junction

Characterization of semiconductor-liquid junction based solar-to-hydrogen conversion systems can be divided into two classes: intrinsic properties of semiconducting material and physico-chemical properties of the formed SCLJ. Such semiconducting material properties as conductivity type ($p$- or $n$-), bandgap and corresponding absorption spectrum, CB/VB positions and charge carrier (doping) concentration are considered as intrinsic properties of solid-state semiconducting materials.\textsuperscript{36,48} The flat-band potential, charge separation efficiency, charge carriers mobility, lifetimes, interfacial charge transfer, recombination routes and rates are considered as properties of SCLJ. Furthermore, the surface area of the SC, which could be measured using gas absorption techniques, does not implicitly represent the electrochemical active surface area of the SC in SCLJ, which could be determined using capacitance measurement of the double layer.

![Figure 15. Measurement techniques and obtainable information about SCLJ properties.](image)

#### 3.4.3 Open circuit potential

An open-circuit potential measurement under illumination is the most simple method to detect photoactivity of materials, determine the conductivity type and the flat band potential value.\textsuperscript{47} To define the conductivity type the change of the open-circuit potential ($\Delta$OCP) under illumination is determined. At open circuit conditions the photogenerated holes or electrons accumulate at the surface in case of $n$- and $p$-type semiconducting materials, respectively. The Fermi level (corresponding to the measured OCP value) increases in the case of $n$-type ($\Delta$OCP is negative) and...
decreases in the case of p-type semiconductors (ΔOCP is positive). While the investigated material is intensely illuminated with light having an energy bigger than the semiconductor’s bandgap value, carriers are generated at the interface and separated under influence of the built-in electric field. Since there is no external current flow, charges build up and generate an electrostatic field directed opposite to the built-in electric field of the space-charge region. This accumulation of charges stops if the rate of charge recombination is equal to the rate of charge generation. The resulting potential is then the field free potential, which is the definition of the flat band potential. Of course, samples with a high bulk recombination rate prevent band flattening and therefore the flat band potential cannot be determined correctly using this method. Apart from the measurement of the open circuit potential under intense illumination, there are two more electrochemical techniques which can be used to determine the flat band potential: measurement of the of photocurrent on-set potential and Mott-Schottky plots.

3.4.4 Amperometry
Using classical electrochemical techniques such as cyclic or linear sweep voltammetry the electrochemical stability of materials can be evaluated in the dark. ABPE or ISTC efficiency determination, as described above, can be achieved by recording sequential voltammograms in the dark and upon illumination. Furthermore, the flat band potential and the conductivity type can be determined from the photocurrent on-set potential, which involves current measurement as function of applied potential in light and dark. At a potential equal to the flat band potential there should be no current flow, since there is no electric field for the separation of photogenerated charges. Changing the applied potential results in the occurrence of an electric field, followed by charge separation and current flow in the external circuit. The potential at which the photocurrent begins to flow is taken as the flat band potential. The sign of the photocurrent indicates the conductivity type of the material: cathodic current for p-type and anodic for n-type semiconductors. At an applied bias potential below (for p-type) or above (for n-type) a certain value, the photocurrent saturates indicating maximal extraction of charges into the electrolyte. However, due to interfacial charge transport limitations (kinetics) the photocurrent on-set potential can be determined erroneously. Overpotentials need to be minimized through surface catalyst deposition. Surface recombination of photogenerated charges can be estimated by observation of the time-dependent photocurrent response of a semiconductor electrode to a square illumination pulse. When the electrode is illuminated, a hole current flows into the surface almost instantaneously. If holes are captured by surface states, electrons recombine with these trapped holes. The measured photocurrent in the external circuit decreases from its initial value towards its steady state value as the electron current increases.
3.4.5 Photocurrent spectroscopy

For any potential photocatalyst with initially unknown properties a set of measurements has to be performed in order to assess the conversion efficiency and stability of the material. The first requirement for a material, which could be used as a PEC absorber, is an efficient absorption of sunlight. A very important property of semiconducting materials is its quantum efficiency (QE). The QE is usually measured over a range of different wavelengths and shows the conversion efficiency at each photon energy. Two types of quantum efficiency are usually considered: external quantum efficiency (EQE) and internal quantum efficiency (IQE). The EQE is defined as the ratio of generated charge carriers to the number of incident photons (Equation 42) and the IQE is the ratio of generated charge carriers to the number of absorbed photons (Equation 43). Correspondingly, \( \text{EQE} \geq \text{IQE} \). The EQE of a photoactive film is defined as the ratio of photogenerated charges to the amount of photons hitting the film as a function of illumination wavelength and is also called incident photon to current efficiency. The abbreviation IPCE is also derived from incident photon converted to electron. This measurement provides knowledge about the material’s ability to convert incident photons to collected electrons for a given incident photon energy (using monochromatic light) and reveals the minimal photon energy required to drive water splitting.

\[
\text{EQE} = \frac{\text{electrons}}{\text{incident photons}}
\]

Equation 42

\[
\text{IQE} = \frac{\text{electrons}}{\text{absorbed photons}}
\]

Equation 43

A big advantage of IPCE over STH measurement is that it can be performed with any calibrated, monochromatic illumination source, which does not need to be an AM1.5\text{G} illumination, since the number of incident photons at each wavelength is counted. If broadband solar-simulated illumination is used for the IPCE measurement, the IPCE spectrum could be integrated over the irradiation spectrum to estimate the maximum possible STH efficiency for that device. Thereby the same fundamental conditions as for STH efficiency measurement have to be considered: zero electrical and chemical bias and no sacrificial donors or acceptors. IPCE measured under an applied bias is not a valid estimate for STH, but can give insight into the PEC material properties such as efficiencies of photon absorbance, charge transport to the solid-liquid interface and the efficiency of interfacial charge transfer, when proper experiment design was achieved.
While IPCE/EQE measurements include losses of photons that are reflected or transmitted, the understanding of the intrinsic performance of a material requires subtraction of these losses and measurement of the efficiency based only on absorbed photons. Absorbed photon to current efficiency APCE/IQE describes the photocurrent collected per incident photon absorbed. This value is useful for studying thin films, because the optimum balance between maximal path length for photon absorption versus minimal effective $e/h^*$ transport distance within the material can be determined. Absorbance or light harvesting efficiency (LHE) spectra can be determined experimentally by UV/VIS spectroscopy, which provides a measurement of the number of photons absorbed per incident photon impinging on the sample.

In the absence of surface modifications with catalysts, APCE is calculated from IPCE and the light harvesting efficiency using following equations:

$$APCE = \frac{IPCE}{LHE}$$

Equation 44

$$LHE = 1 - 10^{-Abs(\lambda)}$$

Equation 45

$Abs(\lambda)$ is the materials absorbance value at a given wavelength.\textsuperscript{165} To provide information about the amounts of the various adsorbed species, simultaneous acquisition of IPCE and attenuated total reflectance (ATR) or UV/VIS spectra can be used.\textsuperscript{190} The absorption properties of a material can be also elucidated by measuring a transmission\textsuperscript{192-194} or diffuse reflectance\textsuperscript{195-197} but it will differ from the optical bandgap value obtained from UV/VIS spectroscopy.\textsuperscript{141}

EQE or IQE measurement of solid-state or semiconductor-liquid junctions can be realized by measuring the photocurrent as a function of the irradiation wavelength. The photon flux and exposed surface have to be known. EQE is calculated as:

$$EQE = \frac{e_e n}{s \cdot cm^2} = \frac{I(amp)/cm^2}{s \cdot cm^2} = \frac{e_{ph}N}{N \cdot h \cdot \lambda} = \frac{I(amp)/cm^2}{N \cdot h \cdot \lambda}$$

Equation 46

Thereby $e_e$ is the electron charge, $n$ – is the amount of collected electrons, $e_{ph}$ is the energy of the incident photons, $\lambda$ is the corresponding wavelength, $h$ - is Planck’s constant, $c$ – is the speed of light, and $N$ is the number of incident photons. Photocurrent measurements are external quantum efficiency measurements, which
means, they do not provide data about which portion of the incident photons is absorbed and how much of the photons are reflected back. In order to measure IQE the number of absorbed photons has to be used. Correspondingly, in order to measure the IQE, EQE, transmission and reflection of the thin film have to be measured and combined.\textsuperscript{190} For very thick films, such as used in PV devices, transmission is mostly zero, therefore only reflectance of the film has to be measured. In contrast to PV devices, only those photogenerated charges in SCLJ systems can be considered, which were utilized in electrochemical reactions causing current flow, thus yielding real solar-to-chemical energy conversion efficiency. While for PV devices I-U curve is usually measured, photocurrent spectra acquisition as function of applied bias potential is performed for SCLJ.

A suitable determination method of the bandgap value is using Tauc-type plots. Derived from absorption spectroscopy, which uses Tauc-type plots of \((\alpha h\nu)^s\) versus \(h\nu\), with \(\alpha\) being the measured absorption coefficient to determine the optical bulk bandgap and can distinguish between allowed direct \((s = 2)\), forbidden direct \((s = 2/3)\), allowed indirect \((s = 1/2)\), and forbidden indirect \((s = 1/3)\) transitions.\textsuperscript{198-200} In photoelectrochemistry, the photocurrent \((j_{ph})\) is used instead of the sorption coefficient \((\alpha)\) and plotting \((j_{ph} h\nu)^s\) versus \(h\nu\) can yield the same results. Photocurrent spectra can be better analyzed by means of adopted Tauc plots: the ratio of the current and irradiance (EQE) for each wavelength needs to be calculated and \((\text{EQE}/(1-\text{EQE})^s h\nu)^s\) versus \(h\nu\) plots can be used to determine the transition type and bandgap values of materials with higher precision.\textsuperscript{165,189} For better accuracy wavelength-dependent scattering and reflectance have to be taken into account while interpreting the photocurrent spectra. APCE (IQE) can be obtained when combined with information from UV/VIS measurements and plotting \((\text{IQE}/(1-\text{IQE})^s h\nu)^s\).\textsuperscript{165}

### 3.4.6 Electrochemical impedance spectroscopy

One of the main tasks in characterization of SCLJ is the correct location of the conduction band edge \((E_C)\) and valence band edge \((E_V)\). Knowledge of the absolute position of the Fermi level enables determination of the absolute positions of the conduction band for n-type or the valence band for p-type SC by assessing the majority carrier concentration from a Mott-Schottky measurement. Adding or subtracting the bandgap value from the majority carrier band edge can estimate the position of the conduction band of p-type or the valence band of n-type semiconductors. Importantly, no surface states that pin the Fermi level at the surface have to be present. Capacitance measurements of SCLJ offer most information about the system, but these are also the most difficult measurements to perform and interpret.\textsuperscript{201}
The determination of the flat band potential from capacitance measurements is based on the classical Mott-Schottky relationship, initially derived for a solid-state junction, but later also validated for SCLJ. The SCLJ can be treated as two capacitances connected in series: the Helmholtz layer capacitance within the electrolyte region near the interface and the space charge capacitance inside the semiconductor (3.1.3.2.2). Generally the capacitance of the Helmholtz layer is much larger than that of the SCR. Hence, for the inverse of the total capacitance the double layer capacitance can be neglected. A plot of the inverse square of the capacity as a function of voltage has a linear region. The voltage intercept corresponds to the flat band potential and the slope is proportional to the doping density (charge carrier density). The ideal sample for such measurements would be a single-crystal material possessing high crystallinity and having a moderate doping. Extreme thin and disordered or amorphous structures exhibit non-ideal behavior such as frequency dependence. The theory of amorphous semiconductor Schottky barriers combined with the MS theory allows a rather correct determination of SCLJ properties, but requires the use of rather complex equivalent circuits.

The three described ways of $E_{FB}$ determination may produce different values for the same sample and all three methods may be needed to extract the correct flat band potential.
3.5 Combinatorial techniques for discovery and optimization of photoabsorbers

3.5.1 Combinatorial approaches to materials discovery

In chemistry and materials science it is known, that the performance of a material is determined by its chemical composition and structure. Even small details in processing significantly influence materials performance. Looking for materials with new or optimized specific properties often leads to multicomponent materials. Each specific element of the material performs one of the required roles in the overall functionality and therefore these special materials have to be combined in specific proportions to create the desired synergy. A good example of a special property in a multicomponent material is the high temperature superconducting oxide $\text{Hg}_0.8\text{Tl}_0.2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.33}$ containing five metals. Present theoretical knowledge is insufficient to calculate properties of such complex systems \textit{a priori}. In the absence of a thorough \textit{a priori} understanding of the many interdependent properties and relationships between components, the components are combined in a large number of different ways. From observations of specific properties of the different combinations the fundamental interdependent relationships are inductively determined. Combinatorial chemistry is the synthesis and screening of large numbers of different materials from different combinations of chemical variables in a systematic and deliberate manner to explore their composition-structural-property relationships and discover, empirically, an otherwise unpredictable material with specific desirable properties. High-throughput experimentation methods using robotics and computers allow the use of combinatorial methods at high speed to increase the rate of discovery and understanding of complex materials.

As early as in 1900s, the Italian photochemist Giacomo Ciamician placed hundreds of flasks with different mixtures of materials under the sunlight, observing occurrence of unexpected photochemical reactions. The light bulb discovery in 1879 by Thomas Edison was the result of more than 3000 tests of different materials as filament. Although creating and characterizing of large numbers of materials only based on intuition was strongly criticized, Edison used results of each of the failed tests for understanding of unsatisfactory materials properties and used these in subsequent discoveries. With appearance of automation and robotics, scientists worldwide have used high-throughput methodologies. In 1950s the use of high-throughput screening (HTS) was intensely used in the field of medical testing and commercial systems for synthesis, analysis and data acquisition became available. Joseph Hanak in 1969 introduced a formal strategy for synthesis and testing of large numbers of solid-state materials. He used radio-frequency (RF) co-sputtering technique as the method of synthesis that is capable of depositing a great variety of substances. This allowed preparation of diverse superconducting, ceramic and
luminescent materials as well as photovoltaic materials.\textsuperscript{215-217} Using the HTS methods, Hanak succeeded to optimize doping combinations for photovoltaic semiconductors.\textsuperscript{218} Later, in 1995 Xiang combined physical vapor deposition (PVD) synthesis with masking systems and generated arrays of superconducting and giant-magnetoresistive thin films.\textsuperscript{219} After this work, he created the company Symyx Technologies and used electron-beam evaporation for the preparation of thin-film materials libraries of thousands of inorganic compounds. In search of new luminescent materials SrCeO\textsubscript{3} was found to have unusual properties and unexpected structure.\textsuperscript{220} Combinatorial methodology was applied in many other fields of research, such as determination of phase diagrams,\textsuperscript{221} identification of new shape-memory alloys,\textsuperscript{222} search for catalysts\textsuperscript{223} or optical luminescent materials\textsuperscript{224} and polymer science.\textsuperscript{225}

It has to be clear that finding of new materials by a combinatorial approach needs to be coupled with robotics in order to accelerate the discovery process. Thereby, combinatorics in fabrication can be classified as a method and the robotic systems as a technical instrument. Development and using of combinatorial high-throughput systems for fabrication and characterization of new materials demands a well-defined strategy of fabrication and characterization coupled with feedback.

3.5.2 Combinatorial approach to identification of PEC catalysts

In photoelectrochemistry transition metal oxides are considered to be a very promising class of materials for construction of a long-lasting photoelectrolysis system, primarily because of their stability. The discovery and optimization of metal-oxide based semiconductor materials for photoelectrochemical water splitting that are abundant, stable and non-toxic is one of the most challenging tasks in modern materials science. Despite increasing efforts in recent years, there is still no known material that ideally matches the necessary criteria for efficient water photoelectrolysis. Currently, more than 200 oxides were tested for PEC water splitting systems.\textsuperscript{27} The predominantly investigated binary oxides Fe\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2} and WO\textsubscript{3} do not show sufficient stability, suitable bandgaps, efficient light absorption, catalytic activity or charge carrier lifetimes.\textsuperscript{25} Few oxides show promising properties for solar water splitting but none of them is even close to meeting all the PEC criteria. In consequence, new materials have to be discovered, but there are millions of possibilities. If all possible ternary oxides will be prepared by mixing of N materials three at a time, there are N!/3!(N-3)! permutations. Considering 50 possible candidates from the periodic table, this results in 19,600 combinations. For a quaternary system there are 4,220,000 possible combinations. Even more combinations are possible when also additional elements acting as electrical dopants are considered and very many more, when various structures and relative compositions are considered. The number of combinations to be tested can be
reduced by applying some chemical knowledge. For instance metals can be classified into four categories according to their role in a final PEC material. Elements such as Ti, W, Zr, Ta, Si, Mo and others are structural components, since they form very stable oxides with high formation heat. Other elements such as Fe, Cr, V, Co, Mn, Ni, Cu, and some rare earth elements such as Ce can be classified as light absorbing components, and multiple elements might be combined to absorb light from the overall solar spectrum.\textsuperscript{226-227} The third class is comprised of elements suitable for lowering of overpotential losses in the electrochemical reactions on the absorber surface (i.e. Ru, Rh, Pd, Ni, Pt, Ir, Os, Re).\textsuperscript{32,228} and ionic charge compensators (i.e. Ca, Sr, Ba, Mg, Zn, Cd, Li, Na, K, Rb, Cs) that are often present in such structures as spinels and perovskites to counterbalance the negative oxygen charge in the compounds. This way of chemical design greatly reduces the number of possible combinations. Furthermore toxic metals such as Pb, Tl, Cd and Hg can be excluded since large-scale implementation of any discovered photocatalysts is envisaged and the environmental consequences of these elements should be avoided. Despite this reduction of possible combinations their quantity is still in the tens of thousands range. While an enormous number of semiconductor formulations could be created from earth-abundant non-toxic elements, only a relatively tiny fraction have been synthesized and studied. In order to estimate the identity and quantity of specific metals in resulting oxides for efficient photoelectrolysis of water, empirical methods need to be employed. Thousands of mixed metal oxides have to be produced and tested for their catalytic activity and stability until an effective material is discovered. The prediction of all relevant properties of a multi-component metal oxide material for solar water splitting is still beyond the current capabilities of theoretical models and calculations. Combinatorial material fabrication, with both synthesis and rapid analysis of a large number of compositions in materials libraries and high-throughput characterization, may therefore serve as key method in the discovery and optimization of novel materials compositions and properties.\textsuperscript{229-230} It is evident, that such a large number of possible mixtures needs to be produced and characterized using high-throughput techniques, which also include well-designed strategies in fabrication and characterization of new materials.

### 3.5.2.1 High-throughput synthesis of PEC materials

#### 3.5.2.1.1 Liquid-dispensing robots

A large series of solid-state photocatalyst libraries was synthesized and screened for hydrogen production by Lettmann et al.\textsuperscript{231} The aim of this work was to develop a reliable high-throughput technique for the efficient discovery of new photocatalysts. 45 transparent HPLC glass flasks were arranged in an addressable rack and the potential catalysts were synthesized directly in these flasks by means of a synthesis robot. For synthesis, a sol-gel procedure was applied.
Seyler et al. used a computer-controlled pipetting robot in order to quantitatively dispense precursor solutions into a 5 by 10 array of small vials. After combinatorial pipetting, the samples were shaked for mixing and aging, dried and calcined following specific protocols, thus generating binary and ternary oxides with a big variety of metals.

3.5.2.1.2 Spray pyrolysis
The process of spray pyrolysis consists of spraying a metal-oxide precursor onto a hot substrate in order to decompose the precursor. Control of the resulting film thickness can be achieved by variation of the sprayed amount of the precursor. As precursor metal salts are used. Decomposition thereof results in metal oxides or hydroxides. Following thermal treatment performed at high temperatures enables further decomposition of hydroxides and crystallization of the formed oxides. The main advantage of spray pyrolysis is its simplicity. Using spray-pyrolysis systems a variety of thin-film materials can be deposited. In this way, ZnO and Fe₂O₃ semiconducting metal oxides were prepared by different groups. The challenge is in using spray pyrolysis for an automated high-throughput synthesis system. Only one group succeeded in the application of spray pyrolysis for HTS of materials with variable composition. Although the work was presented at a conference it was not published. The set-up included a liquid delivery system consisting of 19 valves connected to 19 different solutions connected to a spraying nozzle and the heating substrate was fixed on an x-, y-moving stage. Mixing of precursors is easy and therefore synthesis of mixed metal oxides can be achieved. Nonetheless, there are many complications arising from uneven solvent evaporation and temperature gradients of the heated substrate. Furthermore the interaction of the precursor droplets and the substrate has an impact on the morphology and crystallinity of the samples, thus the control over the morphology of the samples is complicated.

3.5.2.1.3 Electrochemical synthesis
Electrochemical synthesis of materials allows variation of the resulting composition and structure/morphology by varying the electrolyte composition and deposition parameter, such as deposition temperature, applied potential, potential profile and others. Fabrication of doped metal oxides can be achieved, when an electrosynthetic method is well established. For instance, the relationship between the concentration of precursors and the resulting solid-state material composition needs to be determined. This can be achieved by mixing precursor solution and evaluating the resulting solid-state materials by EDX or XPS. McFarland reported first the specific utilization of robotic systems for HTS and HTC of solid-state PEC catalysts. Two different HT electrochemical deposition systems were published: the first system performed rapid serial electrochemical deposition of samples by electrochemical methods such as galvanostatic, potentiostatic, pulse deposition and cyclic
voltammograms. The system allowed deposition of up to 120 samples on a single substrate. The second system allowed performing of parallel electrochemical depositions and consisted of an electrode array, a moving block for sample synthesis, electrochemical equipment and software. The parallel deposition results in much higher throughput compared to the previous set-up. Drawback of the system is that all deposition cells have the same applied potential at the working electrodes. In order to have control over conditions for deposition of each individual sample a more complex instrumentation and multiplexing is needed. Using these systems, mixed-metal oxides, with the formula W₆O₂ₓMₓ with M= Ni, Co, Cu, Pt, Ru, Pd and Ag photoelectrochemically and electrochromically active tungsten–molybdenum oxides, mesoporous ZnO, mesoporous TiO₂ thin films, and Zn₁₋ₓCoₓO thin films were synthesized.

3.5.2.1.4 Ink-jet printing

Woodhouse and Parkinson presented a new simple HTS method for the deposition of metal oxide based materials capable of the photoelectrolysis of water. Ink-jet printing was used to pattern nitrate salts as metal oxide precursors onto conductive glass substrates. Subsequent pyrolysis or calcination yields electrodes with patterns of metal oxide compositions. This comparatively simple method was extended to a distributed combinatorial outreach program. The actual version of the deposition method utilizes a Fuji-Dimatix DMP-2810 single channel piezoelectric ink-jet printer to print patterns at a jetting frequency of 5 kHz. The total drop count with the volume of each drop and the ink concentration is used to calculate the stoichiometry of a given sample. Large compositional spaces as triangle-shaped overlaprint and vertex gradient templates were chosen to span specific stoichiometric ranges. Several publications utilizing this deposition method and screening with a HTS set-up are described in the following section, including: effects of Ti, Si, and Al on the performance of hematite photoanodes, PEC properties of spinel Co₃₋ₓMₓO₄ thin films (M=Al, Ga, In), study of binary Bi-V oxides and their improvement by W, Cu, Fe, Mg, and Mn, OER catalysts for acidic electrolytes, photoactive Fe, Cr and Al containing oxides and, recently, optimization of the spinel type Co₃₋ₓMₓO₄ thin films (M=Al, Ga, In).

3.5.2.1.5 CVD and PVD

A wide variety of material types including metal oxides, metal oxynitrides and oxygen-free materials can be deposited using CVD and PVD techniques. High-throughput sample production can be performed when using masking systems, multilayer deposition or special target alignment. A disadvantage of physical vapor deposition is the expensive synthesis system, peripheral equipment and maintenance. However, the high quality and variety of samples makes this technique an excellent method of HTS of thin film materials. The successful
application of reactive co-sputtering fabrication of thin film materials libraries for such applications as shape memory alloys, capacitors, hydrogen storage materials, ORR catalysts, and PEC materials was demonstrated. Many groups used PVD techniques for fabrication of discrete composition variations in libraries of materials, a continuous composition spread (CCS) type of materials library has a continuous compositional variation of the materials across the library, containing much more single samples which amount is only limited by the resolution of the used characterization systems. Commercial systems are available for automated vapor deposition of libraries of materials that could be suitable for the synthesis of photocatalysts.

### 3.5.2.2 High-throughput screening of PEC materials

#### 3.5.2.2.1 Optical, UV/VIS and IR screening

Sun demonstrated a high-throughput screening system for rapid discovery of a photocatalyst for air purification. A system using an infrared microscope equipped with a set of homemade in-situ gas reaction cells and a gas dosing system was described. A La-Nd-TiO$_2$ system of certain composition was claimed as an active photocatalyst for toluene degradation. A scanning spectrometer operating in the UV-visible and near-infrared range was published by the group of Gregoire. The system can simultaneously perform transmission and total reflectance measurements at the rate of one sample per second and was demonstrated as a suitable instrument for screening of new light absorber materials by measuring the spectral absorbance. The same group demonstrated a colorimetric screening system for HT identification of light absorbers. The system was used for qualitative identification of materials within multiple quaternary oxide libraries and compounds with a suitable bandgap for solar applications were identified. An approach to screen the electrocatalytic activities of OER and HER catalysts by imaging the oxygen and hydrogen bubbles in an optical screening system called high-throughput bubble screening method was developed. This parallel screening method can yield much higher throughput as traditional electrochemical characterization via current-voltage measurements. The bubble formation intensity was used as a figure of merit (FOM) representing the reaction rate. Prove of concept was done by screening of 231 compositions from the Ni-Fe-Co-O system. Alternatively, local pH changes in the electrolyte can be used as a measure for the conversion efficiency. As the local concentration of protons increases at sites where water oxidation occurs (oxygen evolution) and decreases at sites of water reduction (hydrogen evolution) pH-dependent fluorescent indicators or molecular sensitizers can be used. The optical detection of a colorcast shift was realized by a CCD camera. While such methods are very rapid, high resolution is not possible and the indicator molecules can easily interfere with the overall redox process occurring in
electrolyte, for instance by being oxidized instead or in parallel with water. Using a fluorescence-based electro-optical high-throughput screening system, 378 compositions from the Cu-Ni-Mn and Co-Ni-Mn systems were investigated with respect to ORR activity. Quantitative measurements of ORR-catalysts were realized by optical fluorescence data acquisition. Rapid identification of areas of interest (compositions which show distinctive properties) in thin film materials libraries by optical and other measurements was demonstrated for the Ni–Al system.

3.5.2.2.2 Direct hydrogen detection
While a number of different methods can be used for efficiently testing of PEC devices, the ideal method would be the direct measurement of hydrogen/oxygen production rates using, for example, gas chromatography. Modern systems for screening of catalytic materials using a scanning mass spectrometer are capable to measure the activity and selectivity of catalysts from materials libraries at rates greater than one composition per minute. Since simple thin film structures do not absorb a large fraction of the incident light, the expected hydrogen generation rate is rather small and the detection thereof is complicated. An interesting combination of both, hydrogen detection and rapid optical detection was achieved in a high-throughput screening system for libraries of hydrogen producing catalytic materials based on the chemo-optical properties of tungsten oxide. For HTS a reactor block housing a 8x12 catalysts array deposited as thin films was assembled with a Pd/WO₃ sensor film covering these 96 micro reactors, thus forming a 96-element two-dimensional hydrogen sensor array. In the presence of hydrogen the reflectance of Pd-coated WO₃ sensors changes. The time-dependent changes in reflectance indicate relative rates of hydrogen production. The system was tested on electrocatalysts synthesized from Ti, Pt, Ni, Au, Pd, Al, Ag, Ge and mixtures thereof. In the work of Seyler the irradiation of catalyst suspensions with a custom illumination setup was followed by fast sequential product gas analysis using gas chromatography.

3.5.2.2.3 Photocurrent screening systems
The most desirable electrochemical characterization requires a three-electrode cell under potentiostatic control. In high throughput screening, a material library can be explored by employing an array of such cells. Based on this approach the first automated system for high throughput screening of catalytic materials was developed and used for investigation of discrete nanoparticulate gold supported on TiO₂. Thereby electrochemical screening was used to characterize the electrocatalytic activity of the supported Au clusters for photoelectrochemical water oxidation. The system consisted of motion hardware, an optical system, an electrochemical probe head, a liquid-delivery system, an electrochemical/electronic subsystem and system software. The system allowed photocurrent and photocurrent
spectrum acquisition with throughput of 120 samples per day. Tungsten oxide and zinc oxide based photocatalysts were characterized using this system as well. Another HTS system for discrete samples was demonstrated by Xiang et al. A special cell architecture and multiplexing allowed high-throughput measurements of PEC materials. External quantum yields of 1819 different compositions from a pseudoquaternary metal oxide library containing Fe, Zn, Sn and Ti were measured at 385 nm. Preliminary results identified a promising ternary composition $\text{Fe}_{0.894}\text{Sn}_{0.103}\text{Ti}_{0.0034}\text{O}_x$, which showed an external quantum yield of 6.7%.

Anderson demonstrated a HTS system for investigation of photovoltaic activity of CuO compounds. A library of 169 solar cells fabricated by pulsed laser deposition (PLD), with varying thickness of sprayed titanium dioxide (TiO$_2$) as the window layer, and varying thickness and composition of binary compounds of copper oxides (Cu-O) as light absorber was used. The screening system was able to measure IQE and was supported by high-throughput techniques for bandgap fitting, composition analysis, and thickness mapping.

Important steps towards a characterization system for CSS type materials libraries were done in the groups of McFarland and Parkinson. Together with the high-throughput liquid phase synthesis method using inkjet printers, a high-throughput screening system was developed which allowed performing PEC materials characterization using direct readout of the photocurrent while a laser was scanned over the materials library surface. The electrochemical cell used FTO conductive glass substrate with the printed CSS type materials library as working electrode and a graphite rod counter electrode. The screening system allows identification of potential leads, but no quantitative performance measurements can be obtained, since only three kinds of lasers with wavelengths of 514.5 nm, 532 nm and 632.8 nm as the source of light were used. Thus, the obtained information does not necessarily represent the behavior of the material under realistic conditions in a PEC-device where the sun is the source of light. Nevertheless this HTP-HTS combination allowed discovery of new potential PEC materials: Fe-, Cr- and Al-containing oxides and spinel type $\text{Co}_{3-x}\text{M}_x\text{O}_4$ thin films ($\text{M=Al, Ga, In}$), as well as new Ce-containing OER catalysts. Arai developed a similar high-throughput screening system and applied it for the development of Fe-Ti, Fe-Nb and Fe-V visible-light-responsive semiconductors for photoelectrodes. For the high-speed evaluation procedure (HEP), the photocurrent of the sample was evaluated by scanning the photoelectrode with focused light, while a constant potential was applied.

In addition to the possibility to use an array of three-electrode electrochemical cells, rastering a single cell over the materials library is another possible approach. To attain this capability, a scanning droplet cell set-up can be used.
Photoelectrochemical scanning droplet cell microscopy (PE-SDCM) arises as an extremely versatile tool for the screening of new solar cell materials, as it was demonstrated by the group of Hassel.\textsuperscript{282} This technique allows the performance of the most important photoelectrochemical experiments within a 100 \(\mu\)m diameter area on CSS type materials libraries. Various light sources are coupled into a multimode fiber to illuminate a small spot that is wetted by the electrolyte from a capillary. Reference electrode, counter electrode, and optical fiber are installed in the capillary system. The performance of this system was firstly demonstrated by photocurrent measurements on \(n\)-doped Si and \(p\)-doped Si as model substrates. First real application of the system was for localized photoelectrochemistry on a tungsten oxide-iron oxide thin film material library fabricated using a vapor phase co-deposition method.\textsuperscript{283} In the following, photoelectrochemical scanning droplet cell microscopy was used for high throughput screening of photoelectrochemical activity of a \(\text{WO}_3\)-CoO thin film combinatorial library. The compositional spread was deposited using co-evaporation of \(\text{WO}_3\) and metallic Co followed by thermal oxidation in pure oxygen.\textsuperscript{284} A modified version of a photoelectrochemical scanning droplet cell microscope (PE-SDCM) was adapted for use with non-aqueous electrolytes containing an optical fiber for localized illumination.\textsuperscript{285,286} The group of Gregoire also employed PEC-SDC for screening of a Ni-Fe-Co-Ce quaternary oxide library as (photo)electrocatalysts for the oxygen evolution reaction. 5456 samples with a throughput of 4 s per sample were explored.\textsuperscript{278,287}

Bard demonstrated rather advanced HTP and HTS of PEC materials. Scanning electrochemical microscopy (SECM) technique modified by replacing a normal ultramicroelectrode with an optical fiber was used for fast screening of various \(n\)-type \(\text{BiVO}_4\) based photocatalyst arrays.\textsuperscript{288} Materials arrays were prepared using a solution dispenser consisting of a stepper-motor-operated \(x\), \(y\), \(z\)-stage with a piezoelectric dispensing tip.
4 Problem identification

Large numbers of multi-component compositions have to be produced and examined with respect to their ability to convert solar into chemical energy.\textsuperscript{31-33} Systematic screening of potential PEC materials is limited by the very small throughput of manual experiments. Combination of high-throughput preparation (HTP) and high-throughput characterization (HTC) of a large number of different materials increases the investigation speed of the compositional and structural effects on materials performance and allows efficient search for materials that fulfill the required specifications.\textsuperscript{33-35, 214} The presently demonstrated HTP techniques have a variety of different limitations. The most advanced HTP method using ink-jet printing has two obstacles towards a more widespread application of this technique for the fabrication of functional metal oxides:\textsuperscript{289} fabrication of uniform and continuous multi-component structures and maintaining stability during post-processing cannot be realized currently. Usually, printed solutions are not mixed at the molecular level on the substrate and the formation probability of real multinary oxides after pyrolysis is rather low.

This project emerged based on a collaboration with the Materials Research Department (MRD),\textsuperscript{290} where reactive magnetron co-sputtering techniques are used for combinatorial materials development. Major advantages of this deposition technique are precise control of the film thickness, control of film stoichiometry by varying the deposition rate of each of the sources, and the possibility of using a wide variety of material types as well as control of film morphology by varying carrier gas pressure. A continuous composition spread (CCS) type of materials library can be made, presenting a continuous compositional variation of the materials across it.\textsuperscript{256, 263-265} Adding masking systems and other automated means of high-throughput sample production, this technique can be extremely rapid. Advanced sputtering equipment allows fabrication of discontinuous changes in surface morphology within a continuous film using special microgradient-heaters.\textsuperscript{291} Magnetron sputtering can be used to create materials suitable for PEC applications.\textsuperscript{250, 292} The magnetron sputtering based HTP at the MRD is supported by non-HT SEM and HTC techniques including EDX, XRD, optical absorption, resistance and thickness measurements.\textsuperscript{256, 273, 293} This set of instruments allows development of suitable functional materials for PEC applications, but there is a lack of HTC systems for evaluation of photoelectrochemical properties of sputtered thin films, which is required for the development of new materials for solar water splitting. Although plenty of robotic systems for high-throughput screening of PEC materials already exist, the available equipment and processes have not been sufficiently optimized. To the best of our knowledge, none of the published systems fulfills the desired requirements, which include: different (photo)electrochemical techniques
implemented, precise control of characterization parameters, high reproducibility of results, adaptability and precise HTC with quantifiable results.

The objective of this work is the development of a versatile HTC system for evaluation of materials with PEC properties within large CCS-type materials libraries prepared by reactive magnetron co-sputtering. The PEC HTC has to be achieved by performing a large variety of localized electrochemical and photoelectrochemical experiments in a fully automated manner. The new system has to be highly robust and precisely calibrated to allow performing of thousands unsupervised highly reliable and reproducible measurements. The characterization has to yield a large number of materials physico-chemical properties, such as photoactivity, type of semiconducting material, its (photo)electrochemical stability, wavelength resolved and integral conversion efficiency of incident light, charge transfer and recombination rates, value of $E_g$, positions of $E_{FB}$, $CB$ and $VB$, existence and positions of surface states, charge carrier density, admittance and active surface area of thin films. This enables direct correlation of compositional, structural, electrical, optical and chemical properties of single materials and discovery of systematics of these dependencies. Finding of new efficient materials is not only accelerated, but also supported by understanding of influencing factors on materials performance. After development and optimization, the system is used for investigations of different binary, ternary and quaternary metal oxide materials libraries.
5 Results and discussion

5.1 Strategies of materials libraries characterization

Combination of the HTP and HTC of a large number of different materials allows efficient search for desired materials. There is a processing loop, which starts with selection of materials combinations, which might provide a desired materials property (Figure 16). Therefore, the best available theory and fundamental knowledge have to be used. Some combinations may be excluded due to knowledge about instability and other basic chemical synthesis rules, or due to different practical constraints such as cost or toxicity.

![Figure 16. Processing loop of combinatorial materials search.](image)

Using HTP, the materials are synthesized as libraries, where one or more properties may be varied along one or more spatial axes. The next step could be the screening of the materials library exclusively for a property of interest. In case of search for materials for solar water splitting, this is the STH conversion efficiency. Once the desired property is not achieved or achieved not at the expected level, the corresponding materials combination is discarded. If the analysis of the screening results identifies materials meeting specific performance metrics, these candidates are then included into the next preparation-characterization loop. This investigation strategy is fast, since materials are only screened for the property of interest but this is also the disadvantage of this strategy, since no correlation of the materials performance with processing parameters can be established. Materials composition and fabrication parameters determine very different intrinsic materials properties, which then determine the material’s solar energy conversion efficiency. The link between the materials composition/processing parameters and performance is missing; hence, the strategy has a particularly blind and brute-force character. Since
the objective is not performing of many pointless experiments, but to do high-quality materials preparation and characterization in an accelerated way, having an advanced feedback in form of understanding the composition-performance coherence, the libraries have to be screened for other properties as well. Results of different characterization experiments are correlated and the hypothesis are re-examined and modified to guide the design of the next preparation-characterization loop. The absolute minimum set of materials properties which have to be considered during thin film PEC materials development includes composition, film thickness, crystal structure and (photo)electrochemical behavior. From the scope of this work the (high-throughput) characterization techniques will be divided into two sub-sets: the first is the characterization of thin films, whereby all techniques and analysis performed at MRD are included; the second “wet” set is the characterization of semiconductor-liquid junction, including all analytical techniques used for PEC materials characterization, which represents a part of this work.
5.2 High-throughput characterization of semiconductor-liquid junctions

5.2.1 Development of the PEC-HTC set-up

This section describes realization of the first objectives of the current work, namely the development of a HTC system for evaluation of materials PEC properties within CCS-type materials libraries.

5.2.1.1 General considerations and aims

In order to get the right construction design and operation mode of the set-up, the envisaged type of measurements and nature of samples to be investigated, have to be taken into account. Commercial systems for reactive magnetron sputter co-deposition of thin films using a variety of target materials, that would be suitable for synthesis of photocatalysts, are available. In order to accelerate materials investigation, the semiconductor samples are prepared not as discrete homogeneous samples, or as small series of discrete samples with systematic variation of their properties, but as material libraries prepared in such a way that the properties of the materials vary continuously over the surface while materials exhibit well resolved property gradients. Since the materials libraries possess continuous properties variation, the effective number of samples is only limited by the possible lateral resolution of the used characterization instruments. High-resolution detection of the sample properties within the materials library is thus vital, because averaging data over a large area can lead to a loss of analytical information. Considering 4 inch wafers as substrates of materials libraries and composition variation in the range of several dozen atomic percent per ML, the variation of composition as function of lateral position is in the range of 0.1 at.%/mm – 1 at.%/mm. In order to collect data from materials with a step of at least 1 at.% the distance between adjacent measurement areas (MA) has to lie in a range of 1 mm – 10 mm. Correspondingly, the size of a single MA has to be as small as 1 mm in order to avoid overlapping of adjacent MA. Using a set-up, which is incapable to screen small spots, the measurement is also possible, however, the low resolution has to be compensated by less steep property gradients. The larger single samples spot within a materials library, the fewer the number of samples the library can have. In consequence, the number of properties of the materials, which can be studied in one measurement cycle, gets smaller.

Measurement techniques for characterization of SCLJ, which have been previously discussed, have to be implemented in the measurement protocol. This requires implementation of small sample spots in a three-electrode measuring arrangement with the sample spot as the working electrode and exposed to light. In order to allow evaluation of specific experimental features, like pH dependence, long-term stability tests or gas extraction, the electrolyte in the cell has to be exchangeable during an
actual measurement. It is imperative to mask the cell such that only the reported active area is illuminated with light in order to avoid edge effects. The sample area has to be illuminated with uniform light intensity. Accurate determination of the light intensity, which illuminates the sample, is essential. An additional challenge is the accurate determination of the geometric surface area of the analyzed sample spot, in order to normalize the measured current, admittance or capacity. Small spots of materials libraries have to be characterized with high accuracy, therefore constancy of the cell surface area after many measurements has to be also guaranteed. Otherwise, reproducible measurements cannot be obtained. Although the working electrode surface area might be as small as 0.785 mm² (1 mm in diameter), it is still big enough to perform regular “macro-scale” electrochemical experiments without any limitations, which could be induced by a micro-electrochemical cell. Moreover, the geometry of the cell and relative positions of electrodes have to be optimized in order to enable high-quality EIS measurements and eliminate the potential drop between counter and working electrodes by minimizing the effective distance between them.

**Figure 17. Requirements to high-throughput PEC characterization set-up.**

Acceleration of the characterization process has not to be achieved via sacrificing the measurement quality by reducing measurement time (for instance shortening of equilibration processes or reducing of measurement points number), but by automation of the measurements and unsupervised continuous operation. Therefore, the system has to be robust enough for performing of thousands of unsupervised experiments. Since the required electrochemical experiments run
automatically, no negative influence of the measurements quality by human factor occurs.

The measurement protocol has to be easily customizable and, ideally, the system has to be able to optimize the characterization process by making decisions concerning change of the measurement protocol on the fly: since the probability to have electrochemically instable or not photoactive samples is high. It does not make sense to perform a complete characterization of such materials. Once the system detects that the given sample is not suitable for the given purpose, the characterization thereof has to be skipped, thus saving valuable time. Figure 17 depicts all the above-listed requirements to the PEC-HTC set-up. The objective is seen in development of a system having all described technical features, which is able to perform many thousands of fully automatized, highly reproducible photoelectrochemical measurements on different but well-known compositions of sputtered CCS-type materials libraries.

5.2.1.2 System basis and aimed construction

Many spatially resolved electrochemical techniques were developed as an answer to the demand for analysis of miniaturized electronic components, mechanical devices or sensors. There was a need to apply the standard 3-electrode arrangement to small surface areas. Scanning electrochemical microscopy (SECM) shows impressive, even excessive resolution for macroscopic materials libraries, but cannot be used for many common macroscopic electrochemical methods. A suitable characterization system should have no restrictions other than in a macro cell concerning the experimental techniques. The need was seen in reducing of the wetted area of the sample. Capillary-based microcells were presented before by Süter and Lohrengel. This type of electrochemical cells could be applied for local investigation of technical surfaces, investigation of wafers or single crystals; or of metal parts of complex shape, addressing of microelectrodes, and investigation of single grains of polycrystalline materials. Furthermore, it could be applied for local electrochemical preparation or modification of materials spots. An automated capillary-based electrochemical cell is known as scanning droplet cell (SDC). Another modification thereof is a flowing scanning droplet cell (F-SDC) or scanning flow cell (SFC), in which fresh electrolyte is continuously supplied on the surface to be examined. Photoelectrochemical scanning droplet cell microscopy used by Hassel’s and Gregoire’s groups has the ability to automatically perform photoelectrochemical measurements in confined areas. In these systems, a glass capillary that is wetting the surface of interest, either with a free-hanging droplet or using silicone seals at its tip, is used. Scanning droplet cells are well suited for performing of a high number of experiments while working in contact-free mode. However, the low reproducibility of the investigated sample
surface area is leading to different wetted measurement areas. Furthermore, most metal oxides are hydrophilic and as a free droplet requires non-wetting surfaces (contact angles close to 90°), it is necessary to use a capillary with a silicone rubber gasket. However, the lifetime of the sealing is limited to several hundred measurements. The replacement of a tip and the necessary recalibration of the system is time consuming and unattended experiments are difficult to perform. The preparation of modified capillaries has low repeatability. This means every new capillary with gasket has a different opening diameter and thus addresses a different surface area. The presence of silicon rubber restricts the possibility to use the glass capillary as a light fiber. Therefore an additional light fiber is needed. Measurement of the effective output light intensity is difficult, since the capillary is clear and does not mask the wetted surface area. Any used power measurement device will detect direct and spilled light and the measured light intensity will be overestimated. Further known disadvantages of droplet cells based on glass capillaries is the need to use a micro-reference electrode, which is not stable for a long time since it dries out. Although the use of a SDC for current research seems to be feasible, many existing limitations have to be overcome by improving the concept of SDC and many new features have to be added into the system design.

The construction of a capillary-based cell has to be improved in order to enhance its durability to allow performing of thousands of reproducible measurements. The working electrode is the materials library, more precisely, the measurement area selected by the droplet cell. The cell has to be supplied with an electrolyte by means of syringe and/or peristaltic pumps via a valves system, which allows exchange of electrolytes and also let an electrolyte to flow through the cell. Precise determination of cell surface area for normalization of obtained currents, capacitance and admittance needs to be enabled. A precise and homogeneous illumination of the wetted area in the cell must be ensured. The existing construction of the reference electrode has to be improved in order to make it stable for long time periods. Finally the system maintaining procedures have to be simplified to allow quick system restoring, once it is damaged or it failed. The set-up includes an enhanced optical-SDC, electrolyte supply system consisting of different pumps and valves, polychromatic and monochromatic light sources, positioning system and measurement equipment. All these components are controlled by a specific software.

5.2.1.3 Hardware components of the OSDC system

Figure 18 depicts a block connection diagram of the components of the designed optical scanning droplet cell (OSDC) set-up. DIO – digital in/out, DAC – digital/analog converter and ADC – analog/digital converter are physically one PCI board. The used LIA – lock-in amplifier as well as SMC – stepper motor controller also have a form factor of PCI boards plugged directly into corresponding ports of the used PC. STM –
stepper motors for x-, y-, z-positioning of the OSDC are connected to the SMC. The MCR - monochromator uses a single stepper motor for wavelength selection; the latter is controlled by a stepper motor controller connected via a RS232 port. LMP – lamp, SRP – syringe pump and FSA – force sensor amplifier communicate with the PC via RS232 ports. The PRP – peristaltic pump is an analogue device and the communication is realized using DAC and DIO. DIO coupled to a relays board (RLB) is used to switch valves (VLS). FRS means force sensor and PST is the potentiostat, connected to the AD/DA and LIA. In the following the components are described in details.


5.2.1.3.1 Optical scanning droplet cell (OSDC)

Two designs of the optical droplet cell were created in the course of the project. While the second design includes improvements and additional features, the original concept of OSDC was realized already in the first version. Instead of a glass capillary with silicone rubber as sealant, a specially designed polytetrafluoroethylene (PTFE) capillary was used. In addition to its chemical stability, factors such as hydrophobicity and plasticity of PTFE were a reason to choose this material for this particular application. The elasticity of PTFE allows obtaining a hermetic seal between the tip and the sample by pressing the tip of the capillary slightly against the sample, which causes a slight reversible deformation of the tip’s PTFE walls. The
diameter of the tip nozzle can be varied over a wide range depending on the application.

Figure 19. a) First generation of OSDC (1) with an optical fiber (2), electrolyte inlet (3), capillary tip (4), miniaturized Ag/AgCl reference electrode (5) and a Pt counter electrode (6). b) PTFE tip (1) with centric adapter (2), sealing O-ring (3), light fiber (4) and Pt-wire as the counter electrode (5).

The cell is filled with the electrolyte inside of the capillary and thus the electrochemical cell is formed with a defined area of the sample acting as working electrode. The geometrical wetted area of the sample is the same as that of the nozzle and is fairly reproducible independent of surface properties. Since electrochemistry occurs at the electrode/electrolyte interface, only the portion of the sample that is in contact with the electrolyte is probed. This allows analysis of small spots within a large library of materials, which possess property gradients. The hydrophobicity of the PTFE tip precludes wetting of the tip, thus ensuring highly reproducible droplet formation and, correspondingly, reproducible surface area of the formed working electrode. The use of this tip is a better alternative to capillaries with silicone rubber gaskets in term of robustness and allows easier technical solutions for light fiber placement. Figure 19a depicts the design of the first OSDC generation. It consists of a body (1) made of polymethylmethacrylat (PMMA) which incorporates an optical fiber (2), electrolyte inlet (3), capillary tip (4), miniaturized Ag/AgCl/3 M KCl reference electrode (5) and a Pt counter electrode (6). An O-ring is used to seal the tip-cell connection. As shown in figure 19b, a special centric adapter (2) inside of the PTFE tip (1) was used for stationing the light fiber (4) exactly against the nozzle. Further openings in the centric adapter are machined for electrolyte flow and Pt-wire as the counter electrode (5). The used light fiber had a core diameter of 1 mm and was made of PMMA. Edge effects due to illumination were avoided by designing the opening diameter to be smaller than the diameter of the light fiber. In this way, the entire active area of the sample was uniformly
illuminated. The chamber in the OSDC body facilitates the cell assembly and allows placing of bigger reference electrode, thus the problem of RE instability is solved.

![Diagram](image)

**Figure 20.** Scheme of the second generation OSDC. Optical fiber 1, integrated double-junction Ag/AgCl/3 M KCl reference electrode 2, electrolyte in- and outlets 3 and a Pt-wire counter electrode 4 incorporated in a PMMA body 5 with a PTFE capillary tip 6.

The second generation of OSDC is depicted in figure 20. The OSDC consists of an optical fiber (1), an integrated double-junction Ag/AgCl/3 M KCl reference electrode (2), electrolyte in- and outlets (3), and a Pt-wire counter electrode (4) incorporated in a PMMA body (5) with a PTFE capillary tip (6). Compared to the previous design of the cell, it possesses both, in- and outlet for electrolyte, allowing continuous replacement of the electrolyte during an actual measurement and collecting of the outgoing electrolyte for additional analysis. The actual volume of the cell was drastically reduced, thus allowing installation of oxygen and hydrogen sensors. Since only a small amount of evolved gases is needed to saturate such small electrolyte volume, less sensitive sensors are required for detection. Another advantage of the small cell volume is the fast complete electrolyte replacement. Furthermore, the cell can be completely evacuated, allowing removal of the electrolyte from the sample’s surface after a measurement, thus avoiding spilling of the electrolyte over the materials library. In the previous design, evacuation of the cell would result in disconnection of the RE because of blockage with an air bubble. The reference electrode in the new design was brought in close proximity of the WE and CE by integration into the cell body. This reduces further internal resistivity of the cell and enhances the quality of EIS acquisition. Finally, the PTFE tip is fixed by a thread and can be easily replaced by hand. Hence, no further O-ring is needed for sealing. Also there is no centric adapter needed, since the PMMA body holds the light fiber and counter electrode precisely and very close to the working electrode.
5.2.1.3.2 Positioning system

5.2.1.3.2.1 Stepper motor controller

The OSDC can be moved in the three space directions by means of stepper motor-driven micrometer screws. The positioning system was based on existing constructions used for SECM and an older SDC set-up, but all three stages (x, y and z) were installed in a way, that the cell is hanging, thus any contamination of moving stages with electrolyte is avoided. Furthermore, it is subjectively more natural to move the cell instead of moving the sample, as in the latter case the x- and y-directions are inverted. An OWIS PS-30 stepper-motor controller and corresponding software modules control the moving stages. If during operation the new z-position lies lower than the previous one, first x- and y-movements are executed followed by the z-movement. Correspondingly, if a new z-target is higher, than the current one, first a z-movement is executed which is followed by x- and y-translations. This avoids sample and cell damage by hitting or scratching the x-, y-plane.

5.2.1.3.2.2 Force sensor

It is important that the applied force on the tip does not lead to any inelastic deformation of the tip to avoid an ill-defined and not reproducible working electrode area and possible electrolyte leakage. A strain gauge based force sensor KD 45-2N was used for controlled approach of the cell to the sample. In this way, the pressure exerted by the cell on the sample surface was kept constant at each point. The typical applied force varied from 50 mN to 400 mN depending on the tip size and geometry. The force sensor utilizes a measuring amplifier for strain gauge sensors GSV-3USB working in a bridge mode. This amplifier communicates with the PC via a RS232 port.

5.2.1.3.3 Light sources

5.2.1.3.3.1 Lamp

Many research groups use a Xe-lamp as a light source for investigation of conversion efficiency of PEC catalysts and report the measured values only indicating the power of the light source. Clearly, such data is not reliable since different lamp models and different measurement arrangements result in different irradiation spectra, although the integral power is identical. The influence of the choice of light source on measured photoconversion efficiencies for semiconductor photoelectrodes was examined, and has shown that the use of a Xe-lamp as light source can lead to a large overestimate of the photoconversion efficiency relative to that obtained at standard AM1.5G solar illumination.\(^{177}\) It was concluded that a reliable estimation of the efficiency under standard conditions is best obtained by measuring the IPCE as a function of wavelength and integrating over the AM1.5G solar spectrum or by measuring under sunlight with a similar zenith angle to that of the AM1.5G spectrum.
Since in case of PEC-HTC many samples are compared to each other, the difference in Xe-lamp spectrum and AM1.5$_G$ does not play a big role, as only internal comparison of results obtained under absolute identical conditions takes place. IPCE measurements, however, can be used for comparison of the obtained results with those of other groups, since this efficiency measure does not depend on light source spectra in a first approximation. A Hamamatsu Hg/Xe visible light source LC8 with a wavelength range from 370 nm to 700 nm was chosen as it employs long lifetime and high intensity mercury-xenon lamps. Light intensity usually varies over time during lamp operation. The LC8 light source, however, constantly maintains the light intensity at a fixed level for stable irradiation as it monitors it with an internal sensor. A further important feature is an electric diaphragm mechanism, which allows variation of the relative light output from 0% to 100% and the integrated shutter. Finally, this unit has a built-in RS232 interface, thus shutter switching and intensity variation can be performed from an external device (PC), thus meeting various kinds of measurement conditions is possible. Lamp irradiation spectrum and intensity as well as the calibration process are discussed in section 5.2.1.5.

5.2.1.3.3.2 Monochromator

The used monochromator Jobin Yvon H10-61 contains just one optical element, an aberration-corrected holographic grating. The focal length of the monochromator is 100 mm and the aperture value is f/3.5. Since its unique design eliminates internal mirrors, the construction of the monochromator has only one moving component, namely the parabolic grating. The used mirror has 1200 gr/mm grating, graduated in 0.2 nm intervals, which allows bypassing of selected wavelengths with the precision of ± 0.25 nm. The dependence of the output wavelength is strongly linear with the rotating angle of the grating, whereby the latter is moved by means of a stepper motor. Initially the assembly did not contain any stepper motor controller and in order to enable the monochromator control by a computer, an Eppendorf stepper motor controller was integrated into the system. The development of corresponding software modules and the calibration procedure of the monochromator are described in following sections. The entrance monochromator tube was fitted and inserted directly in the exit tube of the LC8 Hg/Xe-lamp such that the grating is placed in the focal plane of the lamp’s integrated parabolic mirror, thus maximizing the efficiency. In order to achieve better coupling of the light into the monochromator, the entrance slit of the latter was removed and replaced by a cylindrical lens. The lens condenses the polychromatic light into a narrow bundle and projects it directly on the concave holographic grating. The PMMA light fiber acts as the exit slit, defining the width of the exit by its diameter. The resulting full width at half maximum (FWHM) of the monochromatic irradiation is shown in the calibration section.
5.2.1.3.3 Light fiber

The optical fiber HITRONIC® POF SIMPLEX PE was designed for optical signal transmission in industrial applications. It has a PMMA core of 1 mm diameter and a cladding made of fluoropolymers. The outer diameter is 2.2 mm. The light fiber is very flexible with a bending radius as small as 25 mm. It is very suitable for visible light applications, as the PMMA light fiber is transparent in the whole visible wavelength range. The transmittance spectrum of the light fiber recorded using a UV/VIS spectrometer is depicted in figure 21. At 300 nm the transparency is 95% and increases to almost 100% at 700 nm. The irradiation spectrum of the used Hg/Xe-lamp is depicted as black line referring to the same x-axis.

![Figure 21. Transmittance spectrum of the PMMA light fiber recorded using a UV/VIS spectrometer (red line) and the irradiation spectrum of the used Hg/Xe-lamp (black line).](image)

5.2.1.3.4 Electrolyte supply system

The simple first generation of the OSDC only requires using one syringe pump, which supplies the cell with an electrolyte. However, this also limits the application of the OSDC to short-term experiments and does not allow electrolyte replacement on the fly. The current second generation of the OSDC, which also possesses a flow-through feature, requires a rather complex electrolyte supply system, which is schematically depicted in figure 22.

Solution (S) is supplied by two types of pumps: a peristaltic pump (PP) Gilson Minipuls3 and a syringe pump (SP) Tecan Cavro XLP6000. A PC using the DIO board and a relay array controls the peristaltic pump. This allows switching the pumping process on and off and changing of the pumping direction. A DAC is used to set the pumping rate. A special software feature, described in the next sections, allows variation of the pumping rate during measurements. The syringe pump is controlled via a RS232 port. The used switching (SV) and blocking (BV) valves are solenoid based and are controlled using relays. The mixing unit (M) is a small 1 cm³ vessel with two inlets and an outlet combined with a miniaturized magnetic stirrer. A
membrane degasification unit (DG) allows removing of gases from the solution S1 once needed.

![Figure 22. Schematic representation of electrolyte supply system components.](image)

In a simple „droplet“ mode the syringe pump SP1 forwards working electrolyte solution S1 from the corresponding storage vessel through the optional degasing unit DG and the switching valve SV1 into the cell (C). The blocking valve BV is thereby locked, forming a one-way system: the only exit for the electrolyte is the opening in the PTFE tip of the cell.

The “flow-through” mode allows realization of more complex synthetic and analytical experiments. A first possible application is continuous electrolyte replacement during measurement. Therefore either peristaltic pump PP1 or PP2 are used. Correspondingly, working electrolyte S1 or S2 is used. In this operation mode SV1 connects the S1 to the PP1 and SV2.1 directs the electrolyte into the cell. The BV is opened, letting the used electrolyte to flow to the waste container W. Similarly, for using of electrolyte S2 the chain S2-PP2-SV2.2-C is connected. Electrolyte can also be cycled by putting the cell outlet into S1 or S2, depending on the used route. Using both peristaltic pumps connected to the cell by means of mixing unit M allows variation of the electrolyte composition during a running measurement, e.g. in the measurement of the open circuit potential as a function of electrolyte pH value. S1 might be a stock solution of NaH₂PO₄ and S2 a stock solution of Na₂HPO₄. By varying the pump rates of the individual pumps relative to each other different amounts of each solution will be supplied into the mixing unit M varying the resulting pH value within a certain range. The resulting electrolyte flows through the cell and the actual pH value can be controlled at the cell outlet. Moreover, having two solution vessels allows modification of materials and subsequent characterization. For instance, the cell filled with co-catalyst precursor solution is placed on the sample, which is then decorated with the co-catalyst using an electrochemical methods or by
photochemically induced deposition. Without moving the cell to the waste position for cleaning, the precursor solution is removed from the cell by forward or reverse pumping and then the working electrolyte flushes into the cell in the flow-through mode in order to remove residuals of the co-catalyst precursor solution. Finally, characterization of the modified sample is performed in the working electrolyte.

5.2.1.3.5 ADC/DAC/DIO
To enable data acquisition from an analog potentiostat an analog/digital converter is needed. A digital/analog converter is used to control the potentiostat and peristaltic pump. A PCI-DAS6014 data acquisition board (DAQ board) provided by Measurement Computing Corporation was implemented into the system. The PCI-DAS6014 is a 16-bit DAQ board with 8 digital I/O, 2 analog outputs and 16 ADC channels. It provides an up to 200 kHz data acquisition rate (sampling rate) for analog inputs. Input and output ranges of ±10 V were used, which corresponds to a resolution of ~0.3 mV/bit and thus enables applying smooth potential ramps, which is important for potentiodynamic photocurrent measurements. DIOs of the DAQ board were used to control a relay board, whereby the latter controls peristaltic pump and switches the electrochemical cell between OCP or i-cell mode, depending on the measurement.

5.2.1.3.6 Measurement equipment

5.2.1.3.6.1 Lock-in amplifier
In order to enable EIS data acquisition an Anfatec AMU 2.4 lock-in amplifier was coupled to an analogue potentiostat (Figure 23). The oscillator of the lock-in amplifier (LIA) generates an AC signal with predefined frequency and amplitude. By means of a summing amplifier (SA) the AC signal is joined with the DC bias potential applied by a DAC and the combined AC/DC excitation signal is supplied into the potentiostat (PST).

![Figure 23. Connection diagram for EIS acquisition.](image)
While ADC digitizes the measured DC current from the potentiostat, the values of magnitude and phase shift extracted by the lock-in amplifier from the back coupling with the potentiostat are supplied directly in digital form. Specially developed software modules (section 5.2.1.4) allow both, variation of the applied DC potential in order to perform AC linear sweep voltammetry, as well as the applied frequency and amplitude of the AC signal, thus enabling acquisition of Mott-Schottky plots and full EIS spectra.

5.2.1.3.6.2 Potentiostat
Two kinds of potentiostats were used in the course of the work: an analog mono potentiostat Jaissle 1002 PC.T connected to ADC/DAC/DIO and fully controlled by the developed software and a Gamry Reference 600 potentiostat with a stand-alone software coupled to the OSDC set-up by means of a trigger system. One DAC channel was used to trigger the beginning of a measurement and one ADC channel was used to detect termination of the measurement. While the analog potentiostat was used for most measurements, the Gamry potentiostat was utilized for specific EIS data acquisition, as the data quality of EIS spectra recorded by this potentiostat is better.

5.2.1.4 Software development
Previously discussed characterization techniques of SCLJ have to be implemented into the new system. From the software point of view, the common of all these experiments is the need to record different physical values either as function of time, or other influencing factors. For instance, the OCP value might be recorded as function of time, light intensity or irradiation wavelength. All amperometric experiments, such as photocurrent measurement, photocurrent spectroscopy, etc. include acquisition of the current as function of applied potential, time, light intensity, and irradiation wavelength. Finally, for impedance spectroscopy magnitude and phase as function of applied frequency, amplitude and bias potential are recorded. In all these experiments the influencing factor can be either fixed (for instance applied potential), or varied (for instance time – a-priori, wavelength, bias-potential, etc.).

A software package initially developed for scanning electrochemical microscopy (SECM) was used as basis for the new OSDC set-up. The existing software allows controlling of many different hardware components, such as motor controllers, piezo-electric positioning units, as well as AD-DA converters for data acquisition and control of analog potentiostat. Furthermore, the software has many conventional and specific experimental features implemented, which enable different kinds of SECM measurements. First versions of the SECM software were developed using the programming language Visual Basic 3 (VB3). Since the software was old-fashioned and the programming language is not compatible with most modern hardware
components, the project was completely ported to Visual Basic 6.0 by Dr. Schäfer in 2008. This was a very important step, since it enabled object-oriented programming (OOP). OOP has great advantages over other programming styles: In older programs there is a need to understand all details of code before using it. If an object is created in OOP, no deep knowledge of its implementation is needed for use. Large-object oriented programs have better design and less flaws and are easier to program than non-OOP. Maintenance and modification of OOP is much easier. The newly created SECM program logic was very flexible and could be extended. The whole software was partitioned in small sections – classes and modules. This simplifies design, development and maintenance of the program since these classes and modules are not directly depending on each other and could be therefore designed and modified almost independently. Modularization was the basis of the newly structured software, since there was no need to implement a big set of software modules. Corresponding expansions of the software could be done once needed. The existing SECM software should be further specialized for an OSDC set-up, but its flexibility and all-purpose applicability should be maintained, as it is envisaged to be used not only for the OSDC set-up but also for SECM. Further software development includes development of new program modules for new hardware components and new experimental procedures.

Even though the important step towards modularization was done by partially converting of the software into an OOP project, many modules in the last version of the “SECM” software were not implemented to the OOP basis, but just integrated in the software suite as more or less autonomous software packages. Many configurable software modules in “SECM 2.6” lacked a corresponding graphic user interface (GUI). Editing of special configuration file was needed in order to configure hardware components or experiments. Without having enough experience in software operating, this complicated way of system configuration results in plenty of mistakes. It is inevitable not only to further develop and optimize the software in order to support new hardware components (i.e., light sources, monochromators, pumps and lock-in amplifiers) and enable new experimental features such as photocurrent spectroscopy, light intensity dependent open circuit potential measurement, flexible scans), but also create a clear and usable graphic user interface.

In the course of the work the “SECM 2.6” software was completely converted to an OOP project named “Union”. The name emerged from the fact, that the “SECM 2.6” software contained plenty of different projects with slightly different features optimized for SKP-SECM (project Mojito), shear-force SECM (project Caveman), oxygen permeation SECM (project Flowerpower) and many more, which, nevertheless used same modules and classes. In order to simplify and optimize
software maintenance and further development, all existing projects were unified while keeping and transferring all possible specific features into the “Union” project. Thus, the “Union” is seen to replace all scattered projects in future. To give a general overview of the program development an appendix contains a list of all currently existing modules of the Union project including short descriptions and status signs, which indicate novelty or amount of changes done at each given software module. Newly developed modules, which did not exist before, are marked with a green marker. Modules, which existed before, but were modified by more than 50% are marked with a yellow marker. Modules, which were slightly adapted to the new software structure and/or required some revision and error elimination, are marked with red markers. Black markers indicate modules, which remained unchanged.

5.2.1.4.1 Base objects
The software can be presented as a set of so-called base objects, namely sensors, transducers, ramps and hooks. A sensor allows recording of different data from external devices. Transducers allow applying a signal using external devices, while ramps allow variation of the applied signal in time or as function of different system variables. Finally, hooks allow termination of data acquisition processes if certain conditions are met. Using these four base objects and a framework experiment such as time-trace and/or scan experiment with the corresponding hardware enables performing infinitely complex sequences of measurements, while parameters of these measurements can be automatically adapted depending on acquired values. In order to understand how such complex measurement sequences can be realized, these four base objects are explained in the following sections.

5.2.1.4.1.1 Sensors
Sensors are objects, which record signals from supported external devices and can be used in different experiments and with different feedback controllers. In SECM 2.6 clsSensor used an AD channel to record values, clsLockinSensor queried a lock-in amplifier and clsTempSensor queried a temperature controller for data. In Union the abstract class clsSensor was fully redefined and the following sensor types were improved and created: clsSensorAD - uses any configured AD channel, clsSensorLamp – records the shutter state and/or irradiation intensity of a lamp, clsSensorLockIn records amplitude, frequency, sensitivity, phase, magnitude, x- and y- of any supported lock-in amplifier, clsSensorForce – records values from force sensor amplifier, clsSensorPosition – returns the current position for x-, y- and z- axis in µm. A new sensor types GUI was created and optimized for sensor configuration. By this it is easy to create any kind of sensors by just selecting the desired type and suitable hardware from a corresponding dropdown lists. Depending on sensor type, only suitable hardware and settings will be shown. Most parameters of the newly
created sensors are automatically filled and can be varied depending on the experiment to be performed.

5.2.1.4.1.2 Transducer

In order to enable continuous variation of applied signals during an experiment execution “Union” got a new abstract class called *clsHWTransducer* (hardware transducer). Other software modules use it in order to change the state of different hardware components on-the-fly. Each active hardware component in “Union” is additionally represented as a transducer, as it converts (mostly) electrical signals in another specific type of signal. For instance a lamp emits light with different intensity, a DAC supplies a certain potential, a peristaltic pump pumps with a certain rate. In this way, transducer *lamp* defines the shutter state (0 or 1) and the irradiation intensity (0% - 100%), transducer *DAC* applies a potential in its working range, the transducer *DIO* switches the state of a selected digital output, the transducer *lock-in* applies AC potential with the desired amplitude and frequency in addition to switching sensitivity and bandwidth, the transducer *monochromator* sets the desired wavelength, and so on. The transducers are controlled by ramps.

5.2.1.4.1.3 Ramps

In the “SECM 2.6" software there was one single type of ramps available: the so-called potential ramp. Using potential ramps, complex potential profiles could be applied to up to two fixed DACs. The profiles could consist of many segments, each described as an arbitrary mathematical function. These functions may use a set of variables such as *t*, which is time since start of an experiment; *x*, *y*, and *z*, which are current coordinates in micrometers and also available sensor values. In “Union” an abstract class *clsRamps* was created and many hardware components were implemented as transducers for the ramps. Universal library based DACs, lamps type LC8 and lock-in amplifiers of all implemented types can be used as active transducers in ramps. In case of DAC, the number of active channels is defined by the amount of existing DA channels. For lamps there are two channels defined, whereby the first channel is responsible for the shutter state and the second for the irradiation intensity. The transducer lock-in basically has two channels: frequency and amplitude, but depending on the lock-in amplifier model it can be up to four channels; additionally sensitivity and bandwidth can be varied on-the-fly. The amount of simultaneously active transducers was increased to three. Any configured hardware can be selected and used as transducer. The number of available channels automatically changes depending on the selected component and its configuration.

1.1.1.1.1 Hooks

The core of the hook is an arbitrary mathematical expression, which can use a set of variables exactly as a ramp: e.g. *t* - time since start of experiment in milliseconds; *x*,
y-, z-position coordinates in micrometers and any sensor recorded. If the hook expression becomes 0, the experiment is stopped.

Using of ramps and hooks provides a lot of flexibility. Since there is a possibility to change the parameters of an experiment for each scanning grid point (use of x-, y- and z- in ramps and hooks) for instance a gradient materials electrodeposition can be performed. Use of sensor values (and their change in time) allows detection of equilibration establishment and termination of an equilibration procedure in order to save time.

5.2.1.4.2 Supported hardware
This section describes hardware components, which were newly implemented in the “Union” software.

5.2.1.4.2.1 Hardware implementation
Figure 24 shows existing hardware classes sorted by program classes, as which they are implemented. Pumps, DACs, and digital-out boards can exclusively act as transducers, as they can only apply signals. Lamps, lock-in amplifiers and monochromators can act as both, as transducer as well as sensor. As transducers, these components apply signals; as sensors, they can record signals, for example lamp shutter state, irradiation intensity, phase shift, etc. Hardware components such as ADC, digital-in and force sensors can only supply signals and are therefore sensors. Stepper motor controllers or piezo actuator controllers act as positioners and also as sensors, as one can read the current position as a sensor value.

![Figure 24. Supported hardware classes and their implementation.](image)

5.2.1.4.2.2 DAC/ADC/DIO
Support of universal library based AD/DA cards was already provided in the “SECM 2.6” software. However, for instance, the system could not start if there was no ADDA card installed. Furthermore ADC and DAC were implemented in the same module, which does not allow use of only ADC or DAC, as most old DAQ boards have both integrated. New USB DAQ devices do not necessarily contain both ADC and DAC, thus the use of only ADC or only DAC with the existing software module was
not possible. In “Union” two independent abstract classes clsHWDAC and clsHWADC, for DAC and ADC respectively, were developed. The interface for DAC allows applying an arbitrary potential to an arbitrary channel and also enables saving and reading of all hardware settings, which is important for flawless functioning of the DAC in different experiments. Hence, for instance, the class provides information about the DAC’s potential range, number of DA channels, board identifier, etc. This information is used by other software components to avoid incompatible settings and resulting errors. The same is true for ADC. For Measurement Computing DAQ boards using universal library two specific classes were created: clsHWDACULib and clsHWADCULib. DAC is thereby implemented as a transducer, thus allowing applying of potential ramps. ADC allows signal recording with arbitrary averaging, as well as high-rate data acquisition using the DAQ’s internal memory.

Additionally, an abstract class clsHWDIO and a hardware specific class clsHWDIOULib were developed for control of DIO boards. Using these classes arbitrary DO channel can be activated or deactivated manually or during any scan experiment.

5.2.1.4.2.3 Stepper motor controllers
All software modules responsible for stepper motor controller (SMC) were properly implemented as corresponding software classes into “Union” and error corrections were done. Newly implemented SMCs are Eppendorf SMC and Tecan RSP9000 pipetting robot. Both SMCs can be used as standard SMC for n-dimensional positioning and can be used for arbitrary scan experiments or simple movements. Currently supported SMC models are PI Micos SM32 (clsHWSMCPISM32), Owis PS30 (clsHWSMCOWISPS30), Lang LSTEP (clsHWSMCLangLStep), Eppendorf SMC (clsHWSMCEppendorf) and RSP9000 (clsHWRSP9000). Eppendorf SMC was further modified and implemented into the monochromator software module. The RSP9000 SMC was used for the spray coating robotic device described below. Also piezo actuator controllers PCE665, PCE761 and PCE816 were converted in VB6 classes, corrected and optimized. Thus, for example, real coordinates of a piezo actuator can be obtained from the piezo controller during a scan experiment and saved along with measured values. A resulting heat map is then much more precise as one based on control input. This is very important for high quality SECM measurements, as actual coordinates usually differ from set points.

5.2.1.4.2.4 Force sensor amplifier
The software class for the force sensor amplifier MEGSV was developed by D. Schäfer in „SECM 2.6“ software. In “Union” the abstract class clsHWDMSAmplifier was developed, which has to be implemented in any DMS amplifier used in the system. This interface allows reading of force values from DMS based sensors. The hardware
specific software class developed by D. Schäfer was adapted and called \textit{clsHWDMSEGSV}.

5.2.1.4.2.5 \textbf{Lamps}

For controlling the lamp an abstract class \textit{clsLamp} and a hardware specific class \textit{clsLC8} for the Hamatsu LC8 lamp were created. The abstract class \textit{clsLamp} includes following methods: switch lamp on, switch lamp off, open shutter, close shutter, set intensity, get intensity and get status. The Lamp LC8 was implemented as a transducer and as a sensor. In order to obtain the value of actual irradiation intensity or shutter state, a command is sent to the lamp via a RS232 port. The answer obtained from the lamp is evaluated and the needed values are extracted. Since this process takes some time and implementation of the lamp as a sensor requires fast response (up to several kHz), virtual shutter and virtual intensity read only properties were also added. The virtual values are based on internally stored values of shutter state and lamp intensity and do not use the RS232 interface. Thus shutter and intensity can be obtained from software without any lag time.

5.2.1.4.2.6 \textbf{Monochromators}

For monochromators the abstract class \textit{clsMonochromator} was developed. The interface allows obtaining status (ready, busy, error), setting of a single wavelength, scan within a predefined wavelengths range and with predefined scan speed as well as setting of bypass position, whereby the monochromator lets the full spectrum of the light source through. For the constructed monochromator described in section 5.2.1.3.3.2 \textit{clsHWMonochromatorRS232} was developed. It utilizes a single Eppendorf SMC and allows performing monochromator calibration (section 5.2.1.5.2.2).

5.2.1.4.2.7 \textbf{Pumps}

The “SECM 2.6” software supported Hamilton pumps (in “Union” implemented as \textit{clsHWPumpHamilton}). The pumps Tecan Cavro XLP6000 got support in “Union” software (\textit{clsHWPumpCavroXLP6000}) as \textit{clsHWPump} can pump predefined amounts of liquid in a predefined direction with predefined speed. Additionally, all pumps were implemented as transducers, thus allowing determination of the pump volume by ramps. This development was done especially for the spray-coating set-up in order to deposit films possessing thickness gradients. The amount of liquid (precursor) dispensed at each position within a scanned grid is defined by current x- and y- coordinates. For example, for a one-dimensional gradient the following expression for a ramp can be used:

\[
V = aX + b
\]

\textit{Equation 47}
\( V \) is the dispensed liquid volume, \( a \) is the proportion coefficient defining the steepness of the resulting thickness gradient, \( X \) is the actual coordinate and \( b \) is the offset, which defines the minimal film thickness.

5.2.1.4.2.8 Lock-in amplifiers

Support of lock-in amplifiers Signal Recovery type 5210 and 7280 was inherited from “SECM 2.6” software and improved. The abstract class \( \text{clsHWLockin} \) was extended and allows setting of parameters such as frequency, amplitude, sensitivity, time constant, roll-off filter, hard gain, harmonic and coupling type (AC or DC). These functions were also implemented in existing classes for both above-mentioned lock-in amplifiers and a new class \( \text{clsHWLockinAMU24} \) for the PCI lock-in amplifier Anfatec AMU 2.4 was implemented.

![Graph](image)

**Figure 25.** Finding of optimal amplitude of excitation signal for AC-LSV.

All lock-in amplifiers were also implemented as transducers allowing arbitrary variation of applied frequency, amplitude, sensitivity and other parameters on-the-fly. Figure 25 depicts the result of a simple experiment, in which the amplitude of the excitation signal was increased with time and the resulting magnitude and phase shift were recorded in order to find the optimal excitation signal amplitude. In the same way a frequency sweep can be performed, thus allowing acquisition of EIS spectra. For instance, using of a logarithmic step function for the frequency ramp allows the use of a lock-in amplifier for AC-SECM experiments.

5.2.1.4.3 Graphic user interface

Besides structure optimization, error correction and implementation of a vast number of new hardware components and experiments, a new graphic user interface was created. The new GUI has a multiple document interface (MDI), which means that multiple windows reside under a single parent window (Figure 26).
There is a row of buttons in the upper part of the parent window, which allows showing up of child windows (Figure 26). These buttons are separated in five sections: the first section contains buttons for manual control and configuration of hardware and simple hardware related experiments. The second section of buttons is used for configuration and execution of rather complex experiments, which imply multiple hardware components, sensors and advanced software features, such as ramps and hooks. The third section invokes windows for configuration and execution of scan experiments. The fourth section configures sensors, feedback controllers, ramps and hooks. The last section contains buttons for activation and deactivation of hardware components, calling up a help file and specific script features. It is important to allow easy operation of the software by non-experienced users. Therefore, a script system was developed allowing fully automated execution of preconfigured complex experiments and sequences by a single mouse click. In the bottom part of the mainframe a status bar indicates the current program status, user messages, global coordinates of the OSDC and coordinates of the OSDC within the current array, which is being evaluated during a scan experiment.
All supported hardware classes (positioning units, DACs, DIOs, lamps, pumps, monochromators and lock-in amplifiers) got an interface for control and configuration of the equipment itself and equipment-related experiments (simple actions, section 1.1.1.1.1.2). For instance, the lamp has a window with three tabs (Figure 27).

![Figure 27. Interface for control and configuration of lamps and lamp-related experiments. From left to right: status display and manual control tab, experiments configuration tab and lamp configuration tab.](image)

The first tab contains a display, which shows the current status of the equipment and (if applicable) measurement values and allows manual control of the device (Figure 27a). The display status is continuously updated and shows the actual state of the equipment if it was modified by other experiments/procedures. The second tab allows management and configuration of simple actions (Figure 27b). The third tab allows adding, removing and configuration of hardware components (Figure 27c). Creating and configuration of hardware components has a predictive character, which means, the software automatically selects proper parameters for a given instrument based on its specifications. Hence, there is no need for the user to refer to manuals or technical notes while configuring hardware. Auto correction of input parameters is also implemented in many modules. This feature automatically checks user entered parameters and notifies once these parameters are incorrect or incomplete.

5.2.1.4.4 Characterization protocol

In this section experimental features based on the use of the above-mentioned base objects, as well as specific experiments, such as scan experiments are discussed. Experimental procedures for complete PEC characterization of SCLJ are listed and explained in the order as they should be conducted in accordance to sections 3.4.2 - 3.4.6. Figure 28 depicts the characterization protocol for absorbers materials libraries with initially unknown properties. The first potentiometric analysis reveals properties of the material such as photoactivity, conductivity type, and flat band potential. A potentiodynamic photocurrent measurement provides information about the materials electrochemical stability, photocurrent values, intrinsic solar-to-current efficiency and flat band potential extracted from the photocurrent on-set potential. Potentiostatic photocurrent measurements at selected applied bias
potential indicate materials steady-state ABPE and can be used for the evaluation of materials long-term stability.

<table>
<thead>
<tr>
<th>Potentiometry: Measure OCP in the dark and upon illumination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whether the material is photoactive</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Amperometry: Potentiodynamic photocurrent measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical stability</td>
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<table>
<thead>
<tr>
<th>Amperometry: Potentiostatic photocurrent</th>
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<tbody>
<tr>
<td>Steady-state ABPE</td>
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<table>
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<tr>
<th>Amperometry: Photocurrent spectroscopy</th>
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<tbody>
<tr>
<td>EQE, Eg</td>
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<table>
<thead>
<tr>
<th>EIS</th>
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<tr>
<td>MS-Plot - $E_{FB}$</td>
</tr>
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**Figure 28. Suggested PEC characterization flow chart for a single-absorber material.**

Photocurrent spectroscopy is then used for elucidation of EQE, transition type and extraction of bandgap value. Finally, electrochemical impedance spectroscopy is used for detection of flat band position, estimation of active surface area by capacitance measurement and elucidation of film admittance by evaluation of the real part of measured impedance.

### 1.1.1.1.2 Simple actions

Any active hardware component in “Union” can be manually controlled using a corresponding window. For example, it is easy to switch on or off a lamp, pump a predefined electrolyte amount in a predefined direction or apply a certain potential to a certain channel using a selected DAC. Besides the possibility to manually control hardware components, so-called simple action experiments were developed. Using simple actions, automatic execution of primitive manual procedures involving hardware can be done: movement of a positioner, switching on or off the lamp, simple pumping procedure and others. These simple procedures can be stacked in an experiment sequence, thus performing automatically complex multi-step procedures. The following actions were created: Switch DA ($clsExpSwitchDA$) – applies a desired potential at a selected DA channel, Switch DIO ($clsExpDIOChange$) –
activates or deactivates a desired DIO channel, Switch lock-in (clsExpSwitchLockIn) – applies a predefined AC signal frequency or amplitude, also switches sensitivity of a lock-in amplifier, Switch monochromator (clsExpSpectroscopy) – sets a predefined wavelength or bypass position as well as performs a scan within a predefined wavelength range and scan speed, Pump (clsExpPump) – pumps a predefined electrolyte amount in a predefined direction using a selected pump. Moving procedure (clsExpMovingProcedure) moves any positioning hardware, such as motor or piezo to a predefined position, performs any arbitrary procedure/experiment and brings the positioner to its initial position once needed. An example is a procedure for cell rinsing: called from a scanner experiment, the moving procedure forces the OSDC to move to the waste container, a pump procedure rinses the cell and finally the cell goes back to the current scanner position. One moving procedure can include another one, thus complex moving/experiment sequences can be achieved. All these procedures can be described as “service” procedures, comprising a scan experiment together with actual measurements.

5.2.1.4.4.1 Potentiometry

The very first step of photoabsorbers characterization is to find out if the given material has semiconducting properties and shows some photoactivity and, in case photoactivity is verified, to learn which conductivity type it possesses. Once the sample has no photoactivity, its characterization may be skipped in favor of further materials of the given ML. Combination of open circuit potential measurement with light intensity variation in time reveals both properties about the sample. The $p$- or $n$-behavior of a semiconductor and its flat band potential ($E_{FB}$) are determined by recording the change of the OCP upon illumination. For $p$-type semiconductors the OCP shifts to more anodic potentials while for $n$-type semiconductors OCP shifts to more cathodic potentials upon illumination. If there is no variation of OCP, the sample has no photoactivity. For this purpose a time-trace experiment including a ramp with a lamp as a transducer and a hook have to be used. The time-trace experiment registers values of selected sensors with a defined interval and can include ramps for control of involved transducers and hooks for termination of the experiment. Initially, the OCP value in the dark is measured. Since different materials have different equilibration time, there is a need to monitor the change of the OCP in time. Once the value remains stable over some time, the OCP is considered as stabilized. Here, a hook is used for termination of the OCP acquisition, once the measured potential value is stable. For this, values of the corresponding sensor in time are compared. After stabilization the light intensity is gradually increased using a ramp with a mathematical expression of a straight line with a slope corresponding to the rate of increasing intensity. The value of OCP in the dark and under illumination can be compared using a suitable mathematical expression. If no OCP
shift is observed, the corresponding hook can terminate the characterization of the current sample. Once the OCP is stable under dark conditions, the light intensity (black line) is increased at a rate of 0.5%/s.

![Graph showing relative light intensity and OCP over time](image)

**Figure 29.** Relative light intensity (black) and OCP (red) for determination of the photopotential and the flat band potential.

The absolute light intensity ($I_{\text{Abs}}$) in W/m² is known for each relative light intensity ($I_{\text{Rel}}$) which allows plotting of OCP versus $I_{\text{Abs}}$. At a sufficiently high intensity, OCP becomes constant and represents $E_{\text{FB}}$. A possible error in $E_{\text{FB}}$ determination was discussed in previous sections. However, a big advantage of this method over MS-plot is that the ΔOCP measurement is virtually a non-destructive test, as no bias potential has to be applied and thus the measured sample can be subsequently analyzed with different techniques.

### 5.2.1.4.4.2 Potentiodynamic photocurrent measurements

A classic potentiodynamic photocurrent measurement consists of two steps, a potential sweep in the dark and a potential sweep under illumination. This can be achieved by a simple measurement sequence, namely linear sweep amperometry using a simple potential ramp (Equation 48) followed by a simple action “lamp on” and a second identical linear sweep amperometry.

$$U = U_{\text{start}} + SR \cdot t,$$

$$t_{\text{end}} = \frac{U_{\text{end}} - U_{\text{start}}}{SR}$$

**Equation 48**

$U$ is the applied potential, $U_{\text{start}}$ and $U_{\text{end}}$ are the start and end potentials, respectively. $SR$ is the scan rate and $t_{\text{end}}$ is the (scan) ramp duration. Two recorded voltammograms are then compared. Disadvantage of this method is the double time needed to record two voltammograms and the high probability of electrochemical
altering of the sample during the first sweep. Combined potentiodynamic photocurrent (CPP) measurement includes potential sweep with low scan rate and interrupted illumination (square wave) of the sample. For this, two transducers are simultaneously used: DAC for potential ramp and lamp for switching on and off the shutter. The mathematical expression for the DAC is the same as above. Expression for the transducer lamp includes a \( \sin \) function and a logical expression. As the value of \( \sin \) function can continuously vary between \(-1\) and \(1\) and the lamp shutter can only have two states \(0\) (closed) and \(1\) (opened), the logical operator “\(<\)” was added, thus converting the expression into a logical expression, which can only have two values as a result: 0 or 1 (false or true):

\[
S = \sin \left(\frac{t}{a}\right) < b
\]

**Equation 49**

\( S \) is the shutter state, \( t \) is the time, \( a \) is a coefficient which defines the frequency of the shutter switching, and \( b \) defines the ratio between shutter opened and shutter closed periods lengths. Understanding of the function is simple: if the \( \sin \) value is larger than \( b \), then the expression is \textit{true} and the shutter is opened, otherwise the expression is \textit{false} and the shutter is closed. Since the \( \sin \) function is quasi-symmetrical relative to \( x \)-axis for \( b=0 \) the durations of the shutter closed and shutter open periods are equal. The optimal potential range starts at OCP and the potential sweep goes anodic for an assumed \( n \)-type semiconductor and cathodic for an assumed \( p \)-type semiconductor.

\[ \text{Figure 30. From left to right: Linear sweep photocurrent voltammogram (scan rate 1 mV/s) from 1.5 V to 0.35 V. The current is continuously recorded while the light beam is chopped at 0.2 Hz. b) Magnification of the potential range between 1445 mV and 1370 mV. The dotted line shows the trigger signal of the lamp shutter. The transient current spikes are caused by charge recombination. c) Dark current, current under illumination and peak current as function of applied potential extracted from a).} \]

Besides saving time by recording one voltammogram instead of two, this method has further advantages. Even if the sample corrodes at a certain potential the corrosion
current can be differentiated from the photocurrent. Figure 30a shows a typical current response curve recorded using an n-type semiconductor with conduction band energy below the H+/H₂ redox potential. For this example, the material generates anodic photocurrents under illumination with a photocurrent on-set potential of around 850 mV vs. RHE. Below 750 mV bias-potential the material starts to corrode. Extracting current values (Figure 30b) immediately after shutter opening (yellow), just before shutter closing (red), immediately after shutter closing (blue) and just before shutter opening (black) allows obtaining (peak)photo- and dark currents at different bias-potentials as well as their on-set potentials (Figure 30c) and allows estimating surface recombination rates.

Among photocurrent as function of applied potential, and thereby photocurrent on-set potential, potential windows of sample stability can be determined and the surface recombination rate can be evaluated by observing the profile of the photocurrent response. The time-dependent photocurrent response of a semiconductor electrode to a square illumination pulse has to be observed. As the current stabilization process can be fast, it is important to have a very high rate of data acquisition. Therefore an experiment “Fast data acquisition” (clsExpFastDAQ) was newly programed. It utilizes the DAQ's internal memory for fast data acquisition (up to 200 kS/s) and the acquired data are transferred to the computer and evaluated after enough data are collected or if the buffer of the DAQ is full.

![Figure 31. Processing of current response acquired at 100 kHz data acquisition rate.](image)

Compared to the version in “SECM 2.6” this experiment is more flexible with respect to settings. It automatically takes different parameters of existing sensors such as current range, factors, units if applicable and also plots data on-the-fly. Figure 31 depicts data processing after data acquisition at 100 kHz for 1000 ms (100,000 data points).
5.2.1.4.4.3 Potentiostatic photocurrent measurements

For quantitative photocurrent mapping, amperometric detection with enough time for equilibration has to be employed. The simplest measuring procedure consists of measuring the dark current followed by measuring the current upon illumination (Figure 30d). The photocurrent is calculated as the difference between the currents measured in the dark and under illumination. Since the time for reaching steady state differs from material to material, it makes sense to imply a hook for experiment termination once the steady-state current is reached. The current is recorded and the slope of the current with time \( (\frac{di}{dt}) \) is determined.

![Graph showing photocurrent measurement](image)

Figure 32. Steady-state photocurrent measurement: dark current (black) and current measured under illumination (red).

Long-term experiments can be performed in many ways: continuous illumination and observation of the photocurrent at fixed potential, altering acquisition of potentiostatic dark current and current under illumination, recording of dark and illumination CV and others. In any case, it is important to replace the electrolyte in the cell, as its quantity continuously decreases because of water splitting. The formed gas bubbles block the nozzle of the OSDC. In case of photocatalyst degradation hydrogen and oxygen form in a non-stoichiometric ratio. This means that the pH value of the electrolyte changes, which influences both, kinetics and thermodynamics of the water splitting process. Electrolyte replacement without cell movement can be realized in two ways: either by use of a syringe pump, pumping electrolyte through the cell at certain intervals or by use of a peristaltic pump, pumping the electrolyte continuously. In the latter case, hydrodynamic electrochemical measurements are performed. The results might be different as compared to (quasi-)hydrostatic experiments performed with or without occasional electrolyte change.
5.2.1.4.4.4 Photocurrent spectroscopy measurements

In order to perform photocurrent spectroscopy measurements monochromatic light is used. A time-trace experiment uses monochromator as transducer and records current as function of time. As the start and end wavelengths as well as the scan rate are known, current versus wavelength can be plotted and evaluated. Photocurrent spectroscopy measurements can be performed in two ways. Method 1 starts with applying a predefined bias-potential and the system waits until a steady-state dark current <0.1 nA/measurement area (<10 nA/cm²) is attained. After dark current equilibration the measurement area is illuminated with light at a fixed wavelength in the range from 350 nm to 700 nm with a monochromator scan speed of 1 nm/s. This method is suitable for samples lacking dark current flow or with a constant dark current flow. Once the dark current values are not constant in time, method 2 is used: after applying the bias potential the measurement area is illuminated with monochromatic light of certain wavelengths for 10 s following 10 s dark phase. This is done for the selected wavelength range with a predefined increment between the used wavelengths. The difference between the current under illumination and the dark current yields the photocurrent for a given wavelength. As a matter of fact, the photocurrent spectrum is light-source specific and it is only suitable for a rough estimation of the photoelectrochemical materials properties. The light source independent photocurrent action spectra as a function of the wavelength can be displayed as the IPCE, obtained by normalizing the photocurrent with the photon flux at each wavelength.

5.2.1.4.4.5 EIS

Electrochemical impedance spectroscopy was implemented in the system in two ways. The first way is using of a lock-in amplifier coupled to a potentiostat as described in section 5.2.1.3.6.1. In order to perform Mott-Schottky plots, DAC is implemented in a time-trace experiment as transducer. The ramp includes sweep of bias potential (DC), whereby frequency and amplitude of the AC signal are fixed. Phase shift and magnitude obtained from the lock-in amplifier are recorded as function of the applied bias potential. In order to record the frequency response the lock-in amplifier is implemented as transducer in the time-trace experiment and phase shift and magnitude are recorded as function of applied frequency. Implementing both DAC and lock-in amplifier as transducers allows performing rather complex EIS experiments, such as e.g. CV impedance.

5.2.1.4.4.6 Scan experiments

A scan experiment (clsExpScan) uses a so-called scanner to move the OSDC in x-, y-, z-directions line by line. The given increments and length define a matrix-like grid of points. At each point a user-defined sequence of experiments is performed. This
sequence can be long and may contain any experiment, including a \textit{clsExpScan}. Therefore it is possible to integrate scans into scans.

5.2.1.4.4.6.1 Array scanner
The “SECM 2.6” software had one scanner implemented: \textit{clsScannerArrayComb}, which only allows scanning of an orthogonal grid. This scanner was improved in order to allow repeating of the scan many times, to allow increments smaller than 1 µm and a special “end line hook” was added, allowing lifting of the OSDC or SECM tip at the end of each line scan before moving to the beginning of the line. This is very important for SECM measurements running in feedback mode, as for tilted surfaces tip damaging may occur by moving to the beginning of a line.

Already in “SECM 2.6” an existing experiment “Single value” (\textit{clsExpSingleValue}) was used for acquisition of a single value at each point of the grid. This experiment was mostly used for SECM measurements. It was enhanced by the following features: Display – the acquired values can be false color-coded displayed during an actual measurement. Up to four sensors can be displayed in four heat maps. Many Single value (SV) experiments can be put in a single scan experiment sequentially and the resulting data are recorded as independent ASCII files along with \textit{x}, \textit{y}, and \textit{z}-coordinates. For PEC measurements this feature is very useful for fast data treatment. For example, during photocurrent measurement, first the dark current is recorded (time-trace experiment). After equilibration, a single value of steady-state current is recorded and stored in a file. The following measurement of the current under illumination also results in a single value recorded along with the actual position. After finishing of the scan experiments two files exist: dark current map and current under illumination map. Both files can be easily imported in Origin and plotted as heat maps. An application example for AC-SECM is setting of a SV experiment after a “Switch lock-in” experiment, whereby the latter applies an excitation signal with predefined frequency and lets the system equilibrate. This set can be repeated many times with different excitation frequencies at each grid point. After the scan is finished, current response maps for each applied frequency are created and a plot of heat maps as function of position for each applied frequency can be easily done.

5.2.1.4.4.6.2 Free scanner
Despite an orthogonal grid is the most common layout for the evaluation of a materials library, the \textit{x}, \textit{y}-coordinates at which the measurements should be sequentially performed can be drawn using a mouse and saved as a text file containing the coordinates of the resulting points, thus allowing any arbitrary sequence of positions to be addressed. The cell moves to the first pre-defined position, collects local data and after rinsing the cell with new electrolyte solution
moves to the next position in the list. Figure 33 depicts the window of the “Free scan” experiment utilizing the newly developed class “clsExpFreeScan” and the scanner class “clsScannerFree”. In order to create a new array with arbitrary form the x- and y-increments as well as maximal array dimensions have to be indicated.

![Figure 33. Free scanner experiment GUI](image)

The program generates a grid with corresponding size and number of points. The user picks those points, which need to be evaluated. The selected points are then saved as a list of coordinates and can be loaded again at any time and used for different free scan experiments. Figure 33 shows the array which is evaluated. Green dots show points already measured, while red dots symbolize points to be characterized. Picking any of existing experiments and placing those into the list forms the list of procedures performed at any point of any complex grid.

### 5.2.1.5 System assembly and calibration

#### 5.2.1.5.1 OSDC assembly

The optical scanning droplet cell has to be assembled prior to its fixing on the positioning system. The construction of the positioning system is described elsewhere.\(^{169,213}\) The built-in reference electrode (RE) consists of a AgCl coated Ag wire fixed in a \(\frac{1}{4}\)" fitting, the reference electrode container with \(\frac{1}{4}\)" thread and a ceramic frit of 2 mm diameter melted into a 2.5 mm glass capillary. The prepared capillary is glued into a PMMA body. A 5 cm long piece of Ag wire is soldered to a 2 mm Hirschmann MKU 1 jack. The jack is then inserted into a pre-drilled \(\frac{1}{4}\)" fitting and fixed by two component glue. The glue also acts as insulator of the soldering, thus only the Ag wire can contact the electrolyte. In order to coat Ag with AgCl a very simple method can be used. The Ag wire of the assembly is polished, degreased and put into *aqua regia* for 3 min to be coated with AgCl. After chloridization the wire is cleaned with distilled water. The reference electrode container is screwed into the PMMA body, which already has the integrated ceramic frit. The container is filled
with 3 M KCl and the assembly of the fitting, including jack and AgCl coated Ag wire is screwed into the container. If impedance measurements are performed, it is better to use such a mono-junction reference electrode (Figure 34a). If the working electrolyte is a highly concentrated acid or base, then a double-junction reference electrode is preferred (Figure 34b). For this, two reference electrode containers have to be used, whereby the one possessing the integrated ceramic frit is screwed into the other one, which is fixed in the PMMA body. The lower container is usually filled with working electrolyte with reduced concentration or with 1:1 vol. mixture of the working electrolyte and 3 M KCl solution. The upper container containing the Ag/AgCl wire is filled with 3 M KCl solution.

Figure 34. Schematic representation of reference electrode constructions, left: mono-junction reference electrode, right: double-junction reference electrode.

Assembly of the OSDC continues with removal of 15 mm cladding from the light fiber, placing it into an adapter and screwing the latter in the PMMA body of the OSDC. Thereby, the light fiber sticks out several millimeters at the bottom of the PMMA body. Prior to installing, the light fiber end is polished with different sand papers finishing with 1 μm grain size. Then, identically to the preparation of the reference electrode, a 3 cm long piece of Pt wire is soldered to a 2 mm Hirschmann MKU 1 jack, which is then inserted into a pre-drilled ¼” fitting and fixed by two component glue. Also here the glue insulates the soldering position, thus only Pt wire contacts the electrolyte. The assembly of the fitting, jack and Pt wire is screwed into corresponding opening of the PMMA body. The Pt wire is then coiled around the light fiber. Thus, the counter electrode coil is placed exactly opposite the future working electrode. After installing of light fiber, RE and CE, a pre-drilled PTFE capillary is screwed onto the PMMA body. The assembled OSDC is fixed at a force sensor and electrolyte lines are connected to the OSDC. In order to avoid leakage of the electrolyte during measurements, the front plane of the PTFE tip has to be polished using lubricated 1 μm sandpaper to get the tip surface smooth and exactly parallel to the sample plane. The optimized polishing procedures starts with an
approach of the cell to the sand paper achieving 10% of the working force. For a PMMA tip with 1 mm opening the optimal working pressure was found to be 400 mN (40 g). A first approach reaches a force of 40 mN. The sand paper is moved to the front and back thereby polishing the tip until the pressure drops to almost zero. During the next approach, 20% of the working pressure has to be reached and the polishing has to be repeated. This approach-polish procedure has to be repeated several times with a 10% increment until 90% of the working pressure is reached. Then the OSDC is prepared to work.

5.2.1.5.2 Cell surface area
In order to determine precisely the surface area of a single measurement spot, a polished Cu plate is connected as working electrode. Upon approaching the droplet cell to a tight seal with a predefined force, Cu is electrochemically etched (Figure 35a). An optical microscope enables the accurate determination of the surface area of the etched region. After repeating this procedure 20 times at different positions (Figure 35b), the measured surface area was averaged. For the used 0.4 mm tip an area of 0.125 mm² with a standard deviation of 0.0012 mm² or 0.93% was obtained. The determination of the surface area exhibited practically no significant change after the full characterization of a standard materials library (342 points), which corresponds to about 1000 measurements. This proves the high stability and robustness of the PTFE tip as well as the effectiveness of the cleaning system.

![Normalized current vs. time](image)

**Figure 35.** Top: 20 normalized i(t) curves recorded during electrochemical etching of a Cu plate using the OSDC, bottom: microscopic image of the etched Cu spots. The distance between the spots is 2 mm.
5.2.1.5.2.1 Lamp calibration

It is important to measure the energy output directly at the capillary opening in order to consider all losses in the light fiber and the PTFE capillary. Correct measurement of the incident light power at the sample demands considering the influence of the electrolyte, as it influences the light propagation in the cell acting as a light fiber. In order to measure the polychromatic irradiation power a specially modified power sensor set-up was developed (Figure 36).

Figure 36. Modified thermopile for measurement of OSDC output irradiation intensity.

A thermopile-based power meter Ophir 3A-SH was protected with a quartz glass shield. By this, the cell can be approached and set on top of the protected sensor, as it would be at the sample. The illuminated thermopile transforms the irradiation into heat and then into electricity, which is evaluated by an external measuring device, a NOVA II Meter. Another reference thermopile installed in the measuring head is not illuminated and acts as a compensator of thermal drift. The OSDC is filled with working electrolyte and placed on the modified sensor. First, the dark power value is measured until the measuring device indicates a stable power value. After setting the background power value as zero point, the shutter of the used lamp is opened until a stable power value is indicated again. This process can be repeated several times to improve accuracy of the measurement. Furthermore, the cell has to be removed from the sensor and approached again prior to each measurement. If dispersion of the measured values is low, the average value of the output power can be used. After each PTFE tip replacement, the system needs to be recalibrated. For monitoring the measured lamp irradiation power, the output power is maintained at 100 mW/cm², considering the surface area of PTFE tip used.

5.2.1.5.2.2 Monochromator calibration

Calibration of monochromator consists of two procedures: compilation of calibration curve and acquisition of wavelength resolved power spectrum. The monochromator uses a stepper motor for moving the grating and selection of the desired wavelength. The output wavelength is strongly linearly correlated with the position of the stepper motor (step). Thus, the calibration curve indicating the wavelength as a function of the stepper motor position follows a straight line:
\[ \lambda(nm) = a \left( \frac{nm}{steps} \right) \cdot x(steps) + b(nm) \]

**Equation 50**

The programmed class for monochromator control uses the factors \(a\), \(x\) and \(b\) in order to correctly set the desired wavelength. In order to obtain these factors the stepper motor of the monochromator can be set in any known arbitrary position using the calibration interface of “Union”. The resulting output wavelength is measured at the OASD capillary using any calibrated spectrometer. The measured wavelength values are plotted against a set of stepper motor positions and the equation is obtained by linear fitting (Figure 37).

![Figure 37. Calibration curve of the monochromator.](image)

An additional parameter to the calibration curve is the position of the grating for total reflection of the incident light. Moving the grating with small steps using the software and measuring the output light intensity by means of the above-described power sensor allows determination of this position. The motor position at which maximal light intensity is observed is saved with other monochromator parameters and used by the program to set the bypass position.

The next calibration procedure is the determination of the actual output lamp spectrum. First, the monochromator is set into bypass position and the lamp intensity is set to 100 mW/cm\(^2\). After this the output power at each wavelength has to be measured. A highly sensitive photodiode-based sensor was used for calibration of the monochromatic light since the intensity of a single monochromatic light fraction is very low (\(\mu W\) range). The photodiode-based sensor was also protected with a glass shield and the measurement of monochromatic irradiation was performed in the same way as with the thermopile based power sensor. For each wavelength, the power is measured and then converted into a photon flux as the photon energy for each wavelength is known.
Figure 38 depicts the spectrum of the used Xe-lamp at the OSDC exit comprised of 350 single measurements, each at one wavelength in a range from 350 nm to 700 nm (red line). AM1.5g spectrum is shown for comparison as a red line. There is no need to perform full recalibration of monochromator after each PTFE tip or light bulb replacement, as it was found out that the lamp spectrum and correspondingly the spectral power distribution does not significantly change in time.

![Figure 38. Irradiation spectra of the used Hg/Xe lamp (blue) and AM 1.5g solar irradiation (red).](image)

Therefore it is sufficient to verify two parameters for two or three preselected wavelengths (e.g. 400 nm, 500 nm and 600 nm): 1. using a spectrometer, if the wavelengths selected by the software are actually irradiated, and 2. using a power meter, if the photon flux of the selected wavelengths correspond to the values obtained by the initial full calibration. Only in case of big discrepancies a full recalibration is recommended.

![Figure 39. Determination of peak position and FWHM.](image)

Figure 39 (black line) depicts a peak form of the output irradiation at a wavelength of 365 nm. In order to calculate the full width at half maximum (FWHM) value the
peak was fitted using a Gaussian distribution (Figure 39, red line). This also allows precise determination of the peak wavelength, as the emitted peak has slight asymmetry. While the set wavelength was 365 nm, the intensity peak is located at 365.9 nm, which is considered as acceptable ($\Delta\lambda < 1$ nm). The FWHM value is 6.67 nm.

It is important to keep in mind, that the integration of the obtained spectrum does not resemble the input power of 100 mW/cm$^2$, as losses of the light intensity due to reflection from the grating at each wavelength are included. This is not important for IPCE spectra calculation, as in this case the actual photon flux is known and used, but the attempt to derive the integral conversion efficiency for AM1.5G irradiation without considering these losses is erroneous.

5.2.1.5.3 Cell resistance
The uncompensated resistance of a three-electrode electrochemical cell can be described as the resistance between the working electrode surface and the tip of the reference electrode. The ohmic drop depends on this ohmic resistance and is a function of the cell geometry and the conductivity of the used electrolyte.$^{308}$ Since the conductivity of the electrolyte is usually known and the cell geometry can be considered as simple, the ohmic drop can be calculated. For a planar electrode with uniform current density across its surface the ohmic resistance $R$ can be calculated as:

$$R = \rho \cdot \frac{l}{A} = 2.715 \, \Omega \text{cm} \cdot \left(\frac{0.3 \, \text{cm}}{0.00785 \, \text{cm}^2}\right) = 103.75 \, \Omega$$

Equation 51

$\rho$ is the solution specific resistance ($2.715 \, \Omega \text{cm}$ for 1 M HClO$_4$),$^{309}$ $l$ the distance between reference and working electrode, $A$ the surface area of the working electrode.

The cell resistance is determined by acquisition of EIS in a frequency range from 500 kHz to 0.1 Hz at OCP. The Nyquist plot in figure 40 shows almost ideal impedance: a semicircle with a diameter corresponding to the charge transfer resistance and the intersection of the impedance data with the real part of the axis at the high frequency end gives the ohmic resistance. The Nyquist plot obtained from measurements performed on sputtered Pt electrodes using a tip with a 0.785 mm$^2$ surface area and 1 M HClO$_4$ solution is depicted in figure 40. The resistivity of the cell with 1 mm opening diameter (0.785 mm$^2$) was found to be 91.62 Ohm using a Pt working electrode in 1 M HClO$_4$ solution as electrolyte. Normalization reveals a resistance of 0.72 Ohm/cm$^2$, which is absolutely acceptable for the given purpose and could be even neglected in some cases.
The EIS spectrum shows no artifacts, neither in the high- nor in the low-frequency region, which proves suitability of the cell for EIS. Nevertheless it is important to keep all cable lengths as short as possible to reduce parasitic capacitances as well as to use proper shielding, which was available, since the OSDC set-up was assembled in a Faraday cage.

5.2.1.5.4 Operation of the OSDC

Once the OSDC system is assembled and calibrated it is ready for operation. The system can perform automated characterization after few preparation steps: sample installation, definition of sample format/measurement array and characterization protocol. The characterization protocol is comprised of the experimental procedures described above as an arbitrary set. For characterization, which does not include any preparation or modification of samples the set-up is operated in a simple stop-and-go mode, i.e. the cell moves to the first measurement area of the materials library, collects local data according to the predefined characterization procedures set and then moves to a new position, until the whole measurement array is evaluated. It is important, that the measurement of each MA starts while the cell is empty, to avoid any contamination with any liquid. The x- and y-coordinates of each MA are predefined within a scan experiment and the z-position is determined during auto-approach in a feedback loop. Once the z-position is determined, the x-, y-, z-coordinates are saved and the cell is moved to the predefined waste position and is
rinsed with fresh electrolyte using the syringe pump prior to a new measurement. Hydrophobicity of the PTFE plays an important role in forming electrolyte droplets with reproducible size: after rinsing, the OSDC is moved 0.2 mm above the polycarbonate Petri dish used as waste container. Since the hydrophilicity of polycarbonate is higher than that of PTFE, the remaining drop is reproducibly removed during crossing the edge of the dish. After each data acquisition the electrolyte is sucked back using the syringe pump, thus applying an under-pressure before retracting the cell for refilling. Hence, spreading of the remaining electrolyte droplet over the possibly hydrophilic sample surface at the measurement area is avoided.

Rather complicated characterization schemes, which also include sample preparation or modification, employ a peristaltic pump as well. In this case, the empty cell approach the surface, moves toward “waste” position, gets fresh electrolyte and goes back to the surface. Then the electrolyte can be continuously purged through the cell during a synthesis/characterization procedure or replaced with any other electrolyte/precursor solution, as explained in section 5.2.1.3.4.

5.2.1.5.5 Reproducibility control
The reproducibility of the photocurrent determination was evaluated using OCP and photocurrent measurements at multiple positions of a homogeneous WO₃ sample (Figure 41a). The average OCP value under irradiation was 661.6 mV ± 7.9 mV (1.2%) standard deviation.

![Figure 41. Reproducibility of the OCP and photocurrent determination using multiple measuring sites of a homogeneous sputtered WO₃ thin film sample: top - OCP in the dark (black), OCP under polychromatic irradiation (red) and ΔOCP (blue), bottom - dark current (black) and current under polychromatic irradiation (red).](image)

The average OCP value in the dark was 746.4 mV ± 8.8 mV (1.2% SD); the resulting ΔOCP was -84 mV ±3.5 mV (4.12% SD). The current was recorded at a bias-potential of 1475 mV vs. RHE (Figure 41b) in the dark and under illumination. The average
photocurrent value was 6.3 μA/cm² (standard deviation 0.1 μA/cm² or 1.6%). The homogeneous WO₃ is supposed to be used for system calibration from time to time or after replacing one of the components, such as the PTFE tip, to ensure known and unchanged system parameters.
5.3 PEC HTC of thin film materials libraries

5.3.1 W-O system

Even though the binary W-O system was studied by many groups\textsuperscript{139, 311-313} and cannot be used as efficient single junction photoanode material because it does not show sufficient stability, suitable bandgaps, efficient light absorption, catalytic activity and charge carrier lifetimes, this material can be successfully used as host material for hybrid structures as well as absorber in multijunction systems.\textsuperscript{145, 160, 261, 314-315}

In previous studies of sputtered WO\textsubscript{3} films the influence of deposition pressure and film thickness were evaluated. The work of Marsen showed a dependence of film composition on sputtering pressure.\textsuperscript{142} At low oxygen partial pressure the films were sub-stoichiometric and showed increased disorder. At partial pressures of 1.4 mTorr and higher, stoichiometric WO\textsubscript{3} films were produced and exhibited higher photocurrents as compared to WO\textsubscript{3-x} films. Furthermore, it was shown that sub-stoichiometric films suffer from poor carrier collection. In addition to different Ar/O\textsubscript{2} gas pressures Vidyarthi et al. varied the film thickness and studied the effect of both parameters on the photoelectrochemical behavior of the films.\textsuperscript{144} The variation of the sputter pressure led to the formation of different microstructures of the thin films. The films fabricated at 2 mTorr sputter pressure were dense and showed diminished PEC properties, while the films fabricated at 20 mTorr and 30 mTorr were less dense and exhibited enhanced water photooxidation efficiency (Figure 42). The enhanced photooxidation was attributed to the coexistence of the porous microstructure and a SCR enabling improved charge carrier transfer to the electrolyte and back contact.

5.3.1.1 Verification of PEC performance

Due to the fact, that the output power of the light source used in the PEC experiments by Vidyarthi was underestimated, the claimed photocurrent densities are strongly overestimated. The materials libraries used in ref.\textsuperscript{144} were available for further experiments. The photocurrent density values depicted in figure 42 were determined using the OSDC set-up. As the used mask had some edge effect on the resulting samples 5 photocurrent measurements were performed at each of the 9 samples comprising the materials libraries. These 5 photocurrent acquisitions are comprised of 4 measurements performed in corners of the square-shaped samples and one in the center.

The obtained photocurrent values were averaged and the deviations were used for estimating error bars. While the obtained photocurrent densities are almost 3.5
times lower than those published by Vidyarthi et al., the photocurrent dependence on film thickness and deposition pressure was verified.

![Figure 42](image)

**Figure 42.** Thickness dependent photocurrent response of WO₃ thin film photoanodes fabricated at different sputter pressures; 2, 10, 20 and 30 mTorr. The photocurrent was measured in 0.5 M NaClO₄ (pH 4.5) solution at a bias potential of 1 V (vs. Ag/AgCl/3M KCl) and a Hg/Xe lamp light intensity of 100 mW/cm².

Further characterization of sputtered WO₃ thin film samples was done using photocurrent spectroscopy and electrochemical impedance spectroscopy in order to demonstrate functionality of these measuring methods in the OSDC and to find out, whether film thickness and sputtering pressure influence further properties of the resulting materials apart from morphology and photocurrent density.

### 5.3.1.2 Electrochemical impedance spectroscopy

Here and further in text the interpretation of the impedance data was performed considering possible faradaic and non-faradaic processes, that occur at the surface and in the bulk of semiconducting electrodes and relating them to a modified Randles circuit.³¹⁶ The first component of the circuit is the resistance $R_S$ representing the voltage drop in the electrolyte owing to the passage of current in an electrochemical cell. As the OSDC has a fixed geometry, the $R_S$ only depends on the used electrolyte and remains constant within a given series of measurements. Since impedance measurements were performed in the dark, the only possible faradaic process could be charge transfer caused by corrosion of the semiconducting material. Considering the selection of impedance acquisition parameters excluding any damage of electrodes, the $R_{CT}$ in the Randles circuit equals to infinity and can be therefore ignored. The Warburg impedance $Z_W$ in series with $R_{CT}$ takes into account diffusion of electroactive species towards the electrode. As this term is mostly significant at low frequencies and only single frequency impedance (SFI) is recorded at a frequency of 1 kHz this term can be also ignored. Furthermore it does not play any role, as it is connected serially to an infinite resistance. Since there are no
faradaic processes, variation of the applied potential solely influences the width of
the depletion layer. The non-faradaic electrode capacitance in parallel to \( R_{CT} \) and \( Z_W \)
is caused by the build-up of charge at the semiconducting electrode (double layer
capacitance). In order to take into account non-homogeneity of the semiconductor
surface, for example, surface roughness the double-layer capacitance is replaced by a
constant-phase element (CPE). Also here, since the SFI are acquired, this element can
be simplified and is represented by an ideal capacitance (\( C_{DL} \)). \( C_{SCR} \) represents
the capacitance of the space-charge region within the semiconductor. Typical values for
\( C_{SCR} \) are 10 nF/cm² to 100 nF/cm². As \( C_{SCR} \) is a function of the depletion layer width,
which can be affected by the applied bias potential, \( C_{SCR} \) elimination at sufficiently
negative bias potential indicates absence of band bending. This is the underlying
effect for MS-type plots. The \( C_{DL} \) is much larger than the \( C_{SCR} \), therefore any change in
the applied bias potential falls across the depletion layer of the semiconductor and
\( C_{DL} \) will remain constant.

Figure 43. Modified Randles circuit used to model a semiconducting electrode interface.

The film resistance is then represented by \( R_{SC} \), which is the resistance of the
semiconductor film not affected by SCR. Considering all possible simplifications, the
equivalent circuit consists of the serially connected \( R_S \), \( C_{DL} \) and \( C_{SCR} \). Since the
capacitance of SCR is much lower than that of the double layer, it can be neglected
during \( C_{DL} \) estimation. The imaginary part of the impedance can be used for
estimation of the double layer capacitance. Its relation to the reactance \( X_C \) is given
by:

\[
C = -\frac{1}{2\pi f X_C}
\]

Equation 52

\( f \) is applied AC frequency. Since the double layer capacitance is proportional to the
exposed active surface area, the latter can be estimated and compared between
samples using SFI data.

5.3.1.2.1 Estimation of film resistance by SFI
WO₃ samples deposited at 2, 5, 10 and 30 mTorr with a thickness of 300 nm were
analyzed by SFI at fixed AC frequency of 1 kHz in a potential range from 500 mV to
-500 mV vs. Ag/AgCl/3 M KCl reference electrode in 0.5 M NaClO₄ at pH 4.5. The
potential sweep was started in the anodic region, as it was known that these films are irreversibly reduced at a certain cathodic potential. Applying of potentials lower than or close to OCP (200 mV) causes film degradation due to proton injection into WO₃ followed by HₓWO₃ formation. The presence of Na⁺ ions causes irreversible degeneration of WO₃ films, since the formed sodium tungstates possess high solubility.

![Figure 44](image_url) Real part of impedance as function of the applied bias potential recorded at 1 kHz. SFI were measured in 0.5M NaClO₄ at pH 4.5, potentials are indicated vs. Ag/AgCl/3 M KCl reference electrode.

The real part of the impedance as function of the applied potential is depicted in figure 44. Since the probe diameter (1 mm) is much larger than the film thickness the influence of lateral film conductivity on the obtained resistance values can be neglected. At potentials where the WO₃ films remain stable, the measured resistance does not depend substantially on the applied bias potential representing R_math(_{SC}). While films deposited at 2, 5 and 10 mTorr have nearly the same resistance of about 300 Ohm, the 30 mTorr sample has twice less resistance. This can be explained by the rather porous structure of the latter film (Figure 46) effectively reducing the averaged film thickness and therefore the measured resistance R_math(_{SC}). Below 200 mV the resistance increases for films deposited at 2, 5 and 10 mTorr with values of ΔR = 600 Ohm, 300 Ohm and 30 Ohm, respectively, and then drops to a finite value. No resistance increase was observed for the 30 mTorr film (Figure 44). This behavior could be explained by degradation of the films, whereby initially WO₃^-x is formed at SCLJ resulting in an increased resistance followed by film dissolution, effectively reducing its thickness and hence R_math(_{SC}).

5.3.1.2.2 Estimation of double layer capacitance by SFI
Considering SEM images (Figure 46) the apparent surface area of different WO₃ films increases with increasing deposition pressure, as a rather open structure is evolved at higher sputter pressures.
Figure 45. Film capacitance extracted from the imaginary part of the impedance plotted as function of the applied bias potential measured on WO$_3$ thin films deposited at different sputter pressures. SFI were acquired in 0.5M NaClO$_4$ at pH 4.5, potentials are indicated vs. Ag/AgCl/3 M KCl reference electrode.

Quantification of the surface area was performed by elucidation of the double layer capacitance obtained from the imaginary part of the impedance according to Equation 52. At potentials above OCP the capacitance is constant, as expected for stable oxide films and represents the double layer capacitance, proportional to the film surface area.

![Figure 45: Graph showing capacitance extracted from the imaginary part of the impedance as a function of potential for different sputter pressures.](image)

Figure 46. SEM images of WO$_3$ films fabricated at a sputter pressure of: a) 30 mTorr, b) 20 mTorr, c) 10 mTorr and d) 2 mTorr. 

The obtained capacitance values are 90 nF, 175 nF, 500 nF, 4 µF for films grown at 2, 5, 10 and 30 mTorr, respectively, indicating nearly exponential growth of the surface area with increasing sputter pressure. Below OCP dissolution of the films occurs leading to an increasing measured capacitance, which can be explained by evolution of the rather porous structure during leaching.

5.3.1.3 Photocurrent spectroscopy

As can be seen from previous resistance and capacitance measurements, the enhanced conversion efficiency of WO$_3$ films deposited at higher chamber pressures can be explained by a lower film resistance and larger surface area. The next question to be answered is, whether the absorption spectra of WO$_3$ thin films are also depending on the film deposition parameters. Therefore continuous
photon spectra of the four WO\textsubscript{3} films each at 300 nm thickness were acquired in the wavelength range from 390 nm to 700 nm by scanning at 1 nm/s. 0.5 M NaClO\textsubscript{4} solution at pH 4.5 was used as electrolyte. Figure 47 left depicts photocurrent spectra recorded from the 2 mTorr WO\textsubscript{3} sample at different applied bias potentials of 875 mV, 1075 mV, 1275 mV and 1475 mV vs. RHE. The given absorption spectra are light source specific. The spectrum of the used Xe-Lamp is shown as black dashed line. The photocurrent spectra have been converted into IPCE spectra by dividing the electron flux determined from the photocurrent values by the incident photon flux for each wavelength. Two absorption bands can be clearly observed: the first (I) has an absorption maximum at 390 nm and the second (II) at 450 nm. Considering WO\textsubscript{3} as indirect bandgap semiconductor, (EQE/(1-EQE)*hv)s vs. hv plots with s = 0.5 were used for determination of bandgap values.

Figure 47. From left to right: Photocurrent spectra of WO\textsubscript{3} thin film deposited at 2 mTorr recorded at different bias potentials in 0.5 M NaClO\textsubscript{4} solution at pH 4.5 (potentials are indicated vs. Ag/AgCl/3 M KCl) and lamp spectrum (black dotted line), IPCE spectra calculated from the photocurrent spectra and irradiation spectrum, Tauc-type plots considering indirect transition.

The obtained value of the $E_g$ I was 2.9 eV, which can be related to pure WO\textsubscript{3} and that of $E_g$ II was 2.41 eV. While the band I can be attributed to the allowed indirect transition in WO\textsubscript{3}, the nature of the band II is unknown. The phenomenon of the IPCE drop between 410 nm and 450 nm could not be explained, nevertheless this effect could not be observed for other films. Co-existence of two semiconducting structures is assumed. The primary semiconductor is “regular” WO\textsubscript{3} with the absorption band I yielding the expected bandgap value. The CB of the secondary semiconductor might originate from localized states within the existing bandgap of WO\textsubscript{3} due to disordered and/or amorphous structures. While band I is observable already at the lowest applied bias potential, band II appears and gets more distinct at higher bias potentials. External biasing increases the width of the depletion layer and allows separation of excitons generated deeper in the bulk by longer wavelengths, as the absorption coefficient and therefore penetration depth of photons increases with a decrease in their energy. Furthermore, this can be a sign
that the second absorption band arises from a rather disordered structure. By enhancement of the built-in electric field charge recombination it is suppressed resulting in higher photocurrent. The tail width below the edge of band II was determined using a logarithmic plot of the IPCE \( vs. \ h\nu \). The slope below 2.55 eV became linear and the reciprocal value of the gradient of this line is the Urbach energy. For the WO\(_3\) sample \( E_\text{u} = 0.1 \) eV has been obtained. The value indicates low crystallinity of the material with intensive blurring of the energy bands. Very good low defects samples of for instance amorphous Si have an Urbach energy of around 0.05 eV, indicating a sharp absorption edge, thus augmenting the assumption of the coexistence of crystalline and amorphous or strongly disordered WO\(_3\).

Figure 48. IPCE spectra (top) and Tauc type plots for allowed indirect transitions (bottom) of WO\(_3\) films deposited at (from left to right) 2, 10 and 30 mTorr chamber pressure.

Figure 48 depicts IPCE spectra and Tauc-type plots for direct and indirect allowed transitions of films deposited at 2, 10 and 30 mTorr obtained from photocurrent spectra acquired at 1475 mV vs. RHE. A similar effect was observed for all three films: In addition to the primary absorption band ascribed to crystalline WO\(_3\) a secondary absorption band at lower energy appears. Interestingly, as more disordered the film is (as higher the deposition pressure was), as more distinct the second absorption band is. This is also in agreement with the considered nature of
the second absorption band – amorphous/disordered WO$_3$. The fraction of the disordered WO$_3$ gets larger with increasing deposition pressure. Alongside with the growth of the absorption band intensity, the estimated bandgap value for the secondary transition increases for more disordered films (2.30 eV, 2.41 eV and 2.68 eV for films deposited at 2, 10 and 30 mTorr, respectively) and both absorption bands merge. Thus, for the film deposited at 30 mTorr it is already difficult to differentiate the two bands. Correlation of the absorption spectra with films morphology yields an additional possible explanation for these secondary absorption bands and the intensity distribution among films deposited at different pressure. In absence of band bending it is suggested that the charge separation in the nanocrystalline films is controlled by the charge transfer kinetics to the redox species in the solution.\textsuperscript{318} The deeper in the bulk these charges are generated, the higher is the probability of their recombination since there is no driving force for their separation other than the redox reaction at SCLJ, which is very slow for water oxidation. With increasing wavelength the absorption coefficient drops, thus, low energy photons can be absorbed much deeper in the bulk as compared to high energy photons.\textsuperscript{312} Therefore, they will not contribute to the photocurrent. The films deposited at 2 and 20 mTorr consist of large crystallites (350 nm – 400 nm) embedded in a matrix of smaller grains (50 nm – 70 nm). Considering the size of the big crystallites the possibility of SCR formation cannot be excluded, as the typical width of the SCR is 5 nm – 500 nm. Applying higher bias potentials increases the width of SCR, thus charge recombination is suppressed as excitons are separated by the built-in electric field. This results in an increase in their life-time, thus compensating slow kinetics of the water oxidation reaction at the semiconductor surface. This is proven by an increase in the IPCE in the short wavelength range (compare Figure 47). Importantly, the formation of the SCR also allows charges which are generated deeper in the bulk to diffuse to the SCLJ. Thus, the charges generated by absorption of low energy irradiation participate in the water oxidation reaction. Considering disappearing of the big crystallites for the films deposited at higher pressures, the probability of SCR formation drops and less of long wavelength irradiation can be utilized.

5.3.1.4 Characterization of polycrystalline WO$_3$ film with thickness gradient

Vidyarthi demonstrated the dependence of the evolving crystal structure on film thickness for a WO$_3$ film deposited at 30 mTorr, but the influence of the preferred crystal orientation on WO$_3$ thin film PEC properties was not discussed. Dependence of the film resistance, capacitance, flat band potential and charge carrier concentration on film thickness and preferred crystal orientation were studied by impedance spectroscopy. Figure 49 shows XRD patterns from the thickness gradient WO$_3$ materials library deposited at 30 mTorr chamber pressure. The films consist of polycrystalline WO$_3$. The reflections at 2Theta 23.03°, 23.59° and 24.14° could be
assigned to 002, 020 and 200 reflections of the monoclinic and/or orthorhombic WO$_3$ phase.$^{311,319-320}$

Figure 49. X-ray diffraction patterns (Cu-K$_\alpha$, $\lambda = 0.154$ nm) recorded from WO$_3$ thickness-gradient ML on Pt coated Si-substrate (30 mTorr, Ar/O$_2$ mass flow ratio 1:3, substrate temperature 350 °C), XRD raw data provided by MRD (R. Meyer).

The intensity of the 020 and 200 reflections vanishes for thinner films. Electrochemical characterization was performed along the thickness gradient and the obtained properties are correlated with the film thickness and preferred crystal orientation. As shown above, polarization of the semiconducting electrode causing injection of electrons into the film results in a reduction of WO$_3$. The presence of metal cations induces formation of soluble tungstate salts reducing the potential stability window of the semiconducting material because of irreversible dissolution of thin film. In order to exclude the presence of metal cations and extend the electrochemical stability window in the cathodic region, for the determination of the flat band potential pure acid was used as electrolyte. Furthermore, a double junction reference electrode was used for these measurements. The color change of the measured areas after applying bias potentials below OCP was still observed, which indicates formation of tungsten bronze. Formation of tungsten bronze could also be observed due to the change of the film resistance. This process is considered quasi-reversible: back formation of WO$_3$ occurs at 0.958 V vs. SHE.$^{317}$ Nevertheless, the newly formed WO$_3$ does not necessarily possess the same crystal structure as before.

5.3.1.4.1 Estimation of the film resistance by SFI

The real part of impedance recorded at 1 kHz in the potential range from 800 mV to -200 mV vs. RHE has a similar behavior for films of all thicknesses: the maximal resistance is observed at positive potentials and it decays gradually with descending bias. As the WO$_3$ electrode is typically positively biased during operation, only the film resistance at positive potentials is important. Figure 50 shows the resistance of a WO$_3$ film at 800 mV vs. RHE. As the resistance of a stable homogeneous
semiconducting film is expected to decay with decreasing film thickness and the observed behavior does not correlate with this assumption, a preferred crystal orientation and surface morphology were taken into account.

Even though the film thickness increases as measured by the profilometer, the film resistance between 40 nm and 200 nm decreases. This might be explained by evolution of a porous film with increasing measured film thickness (compare Figure 51) resulting in an effectively lower thickness. Furthermore, the resistance drop between 40 nm and 200 nm also coincides with increasing of the (002) reflection having its maximal value between 200 nm and 300 nm, where the film resistance remains constant. Between 300 nm and 400 nm the behavior conforms to the expectation: with increasing film thickness the resistance increases too. The resistance drop between 400 nm and 600 nm could be also explained by the evolution of a rather porous structure as confirmed by capacitance measurements.

5.3.1.4.2 Estimation of double layer capacitance by SFI

Figure 52 depicts the double layer capacitance calculated from the imaginary part of impedance as function of film thickness. The trend is clear and is well correlated with film morphology shown in Figure 51.

Figure 50. Left: WO$_3$ film resistance at 800 mV vs. RHE as function of film thickness. Right: Reflection intensity as function of WO$_3$ film thickness. XRD raw data provided by MRD (R. Meyer).

Figure 51. SEM images of the surface topography of WO$_3$ films deposited at 30 mTorr with thicknesses of: a) 606 nm, b) 210 nm and c) 55 nm.
Figure 52. Capacitance calculated from the imaginary part of impedance as function of film thickness.

5.3.1.4.3 Estimation of flat band potential and charge carrier concentration

Flat band potentials of WO$_3$, published by different groups, vary in a range from 450 mV to 953 mV vs. RHE. $^{139, 145, 311, 321}$ While first fundamental work were performed on WO$_3$ single crystals, more recently the effort is concentrated on nanocrystalline thin films. While in the first case the reported flat band potential values are close to 1 V, the values obtained for nanocrystalline films are rather small. Since the flat band potential directly reflects the extent of bend bending, this discrepancy can be explained. In large single crystals the formation of SCR is not hindered and the band bending can be as high as 1 V if a deep depletion layer is formed, which is fairly common in photoelectrode materials with a relatively large bandgap. The maximal width of the depletion layer is limited by the physical size of semiconducting particles. With decreasing particles size or dense film thickness the probability of SCR formation decreases and corresponding flat band value decreases too. In nanoparticulate films the band bending cannot exist, thus it is already at flat band conditions. $E_{FB}$ values extracted from MS-type plots for WO$_3$ thin films are plotted against the film thickness in Figure 53. Three distinct regions with similar $E_{FB}$ values can be distinguished: from 40 nm to 290 nm the estimated flat band value is 175 mV vs. RHE. Between 300 nm and 400 nm there is a transition to the second region (400 nm – 500 nm) showing a flat band potential of 138 mV. From 500 nm to 550 nm the flat band potential increases again until it reaches the value of 160 mV and remains constant from 550 nm till 640 nm. There is a correlation of the observed trend with the film resistances distribution: the drop of the flat band potential between 300 nm and 550 nm coincides with the increase in the film resistance. In polycrystalline WO$_3$ films many crystal planes are exposed, suggesting that the different $E_{FB}$ values arise as a result of conductivity differences along different crystallographic planes.
The small $E_{FB}$ values compared to those published for thicker films or single crystals are in agreement with the suggestion of low bend bending. Nevertheless, the estimation of flat band potential by MS-plot can be erroneous as this method is very sensitive to surface states, which existence is very probable for polycrystalline films. Thus, the presented values could represent the energetic position of surface states and the actual flat band potentials values could be larger. In order to prove, whether the obtained values do really represent flat band potentials the latter was determined by means of potentiodynamic photocurrent measurement. The current was measured under polychromatic irradiation in the potential range from 40 mV to 1000 mV vs. RHE with a potential sweep rate of 1 mV/s at WO$_3$ films with different thicknesses. After base line subtraction the photocurrent on-set potentials were determined by extrapolation of the apparently linear region of the i(U) curve versus film thickness. Even though this method is very rough and introduces a certain offset into the obtained values it is not that important, since the estimated values also include the kinetic overpotential of water oxidation. Considering $\eta = 960$ mV$^{322}$ the potential axis was corrected correspondingly. The photocurrent on-set potential is shown in Figure 84 right. With increasing potential both photocurrent and photocurrent on-set potential increase. On the one hand, this seems to be feasible since a thicker semiconducting film may have a larger SCR and separation of photogenerated charges is rather efficient leading to larger photocurrent values. On the other hand, the overpotential is not constant but increases with the current density. Thus, for thicker films generating more photocurrent a larger $\eta$ has to be considered, which might result in a different dependence of the photocurrent on-set potential on film thickness. Nevertheless, the effect of increasing overpotential could be neglected considering a larger surface area of the thicker film as shown by capacitance measurements. Thus, the effective photocurrent density does not change too much. Based on this assumption it can be asserted, that the flat band potential increases with increasing film thickness. Though the calculated values might not
represent absolute values due to a certain off-set, the qualitative trend can be considered as correct. Furthermore, EFB does not drop at 450 nm as it was the case for the values of EFB as determined by MS-type plots.

![Graph](image1)

Figure 54. Left: linear sweep voltammograms recorded under 100 mW irradiation on WO₃ films deposited at 30 mTorr with different film thicknesses. Right: Photocurrent on-set potential determined by extrapolation of the apparently linear region of the i(U) curve versus film thickness.

This indicates, that the drop was caused by surface states. Figure 55 depicts the slope of the linear regions of MS-type plots as function of film thickness. From the slope the concentration of charge carriers can be calculated.

![Graph](image2)

Figure 55. Slopes of linear regions of MS-type plots and estimated charge carrier concentration considering the dielectric constant of pure sputtered WO₃.

While the flat band potential estimated from MS-type plots can be strongly influenced by surface states, the charge carrier concentration is exclusively a bulk property. Therefore, there is no discontinuity in the plot of charge concentration versus film thickness and the preferred crystal orientation. Concentration of charge carriers varies over 14 orders of magnitude being negligibly small at 60 nm film thickness and increasing almost exponentially until it reaches the value of 1.9x10¹⁴ cm⁻³.
5.3.2 Ti-W-O system

The most studied \textit{n}-type semiconductors WO$_3$ and TiO$_2$ are sufficiently stable in aqueous electrolytes under continuous solar radiation, relatively abundant and cheap. Common drawbacks are the large bandgaps of WO$_3$ and TiO$_2$, which limit the fraction of the absorbed solar spectrum. By combining WO$_3$ and TiO$_2$ in the Ti-W-O system, these disadvantages might be overcome. By changing the short- and long-range order the electronic structure might improve towards higher conversion efficiency. Photoelectrochemical characterization of samples with different Ti/W ratio may lead to discovery of new ternary oxide phases exhibiting interesting properties and provide both qualitative and quantitative trends for further in-depth analysis of hits obtained during the characterization.

5.3.2.1 Photocurrent pre-screening

A mixture of W and Ti oxides was deposited by magnetron co-sputtering on three 4-inch thermally oxidized Si wafers pre-coated with a 100 nm Pt layer as back electrode (MRD; M. Hofmann). Two adjacent W and Ti cathodes were used for film deposition on a stationary substrate. The position of the cathodes was adjusted to obtain materials library possessing both a material- as well as a thickness gradient. The composition range from 10 at.% to 96 at.% Ti was covered by these three materials libraries. EDX mappings of square-shaped regions of the 4-inch wafers are shown in Figure 56. Since it was not possible to determine the metal to oxygen ratio by energy dispersive X-ray (EDX) analysis, the given compositional data is limited to the binary Ti to W ratio.

![Figure 56](image)

Figure 56. EDX mapping of square shaped arrays within 4-inch Ti-W-O materials libraries. From left to right: materials library 1 to 3. Raw data provided by MRD (M. Hofmann).

The film thickness was not determined but considering the sputter rates a range from 200 nm to 600 nm can be assumed, whereby the film is thin at the bottom of the MLs and thicker at the top. In order to achieve a low W content in the third ML its sputter rate was much lower than that of Ti. Therefore, the thickness of the
semiconductor film is higher at the bottom right edge and drops towards the left upper edge. This could be also seen from light interference color fringes.

In order to obtain comparable results from different screening procedures (i.e. EDX and PEC) different measured data sets were saved with respect to a position index allowing comparison of the different properties at one measurement area. Using a square shaped raster of 15 x 15 measurement areas the highest bias-potential, which does not cause any current flow in the dark was determined by means of potential sweep in the dark. Subsequently steady-state photocurrent screening was performed at 250 mW/cm² irradiation intensity and 1000 mV vs. Ag/AgCl/3 M KCl bias potential at pH 4.5 (1475 mV vs. RHE). Measuring the current upon illumination followed dark current acquisition. The photocurrent was calculated as the difference between the currents measured in the dark and under illumination. The obtained photocurrent density maps of the screened regions are depicted in Figure 57 (logarithmic scale).

![Photocurrent density map](chart)

**Figure 57.** Photocurrent mapping of square shaped arrays within the 4-inch materials libraries. From left to right: materials library 1 to 3.

At films with Ti contents below 20 at.% the photocurrent density is 7 µA/cm². No thickness dependence could be observed. Between 20 at.% and 30 at.% Ti the photocurrent density decreases to 1 µA/cm² – 3 µA/cm². With thinner films higher photocurrent is obtained. Above 30 at.% Ti both materials library 1 and 2 show a direct correlation of the observed photocurrents and the Ti content: with increasing Ti content the photocurrent increases too. At 30 at.% – 40 at.% Ti in ML1 the photocurrent density increases with increasing film thickness by ten times from about 3 µA/cm² to up to 30 µA/cm². A rather interesting behavior is observed for materials library 3, where almost exponential photocurrent increase with decreasing W-content was observed in the composition range from 90 at.% to 96 at.% Ti. Furthermore, two distinct regions with enhanced photocurrent could be derived: a small local photocurrent peak at around 85 at.% Ti (best seen in the linear plot of $i_{ph}$)
and the global photocurrent peak at around 95 at.% Ti. These peaks are also isolated in y-direction (coordinates as drawn), which corresponds to the thickness gradient. In order to elucidate compositional-thickness-PEC properties correlation materials library 3 was screened completely using a 342 points pattern (Figure 58) using the “Free scan” experiment. For elucidation of the influence of the film thickness on the PEC performance ML3 was cut in four equal pieces and the film thickness was evaluated using SEM of cross sections. The characterization of the materials library was comprised of OCP and photocurrent mappings as well as photocurrent spectroscopy. Full EDX data is presented as color-coded diagram in Figure 58 showing the variation of the Ti-content from 80.7 at.% to 96.2 at.%.

5.3.2.2 Open circuit potential

OCP in dark and under illumination was recorded at each of the 342 points. Figure 58 shows the dark OCP distribution, which could not be directly correlated to the film composition. The ΔOCP map shows random values distribution between -150 mV and -230 mV indication n-type semiconductor behavior.

5.3.2.3 Integral conversion efficiency

A steady-state photocurrent mapping of the Ti-W-O materials library was performed at each of the 342 measurements areas at 1475 mV vs. RHE bias potential and 100 mW/cm² irradiation intensity. The measured photocurrents are shown in Figure 58. The two previously identified regions with enhanced photocurrents were found at 82 at.% - 87 at.% and 93 at.% - 97 at.% Ti. While the first local maximum peak photocurrent of 40.0 μA/cm² was generated at a composition of 84.4 at.% Ti, the global maximum peak photocurrent value was 70.3 μA/cm² at 94.4 at.% Ti. It is not possible to fully explain the photoelectrochemical behavior only by the elemental...
composition. However, surface morphology is one key factor with a major impact on light absorption and charge transfer through the SCLJ.

In order to interpret the photocurrent behavior including the morphological impact, SEM images of the materials library provided by MRD were studied. Figure 59 shows SEM micrographs of selected compositions of Ti-W-O showing nanocrystalline films consisting of small pyramidal crystallites in the composition range from 81 at.% to 92 at.% Ti. The particles size linearly increases from about 60 nm at 81 at.% Ti to about 70 nm at 92 at.% Ti with an interparticular distance of about 70% of the particles size. The formation of a space charge layer is unlikely due to the small crystallite size suggesting comparatively small photocurrent values due to the absence of band bending impeding efficient electron/hole separation and electron transfer to the back contact. Hence, the observed photocurrent is predominantly governed by the efficiency of the photogenerated charge transfer at the semiconductor/electrolyte interface. Growth of rose-shaped oxide grains of about 300 nm in size was observed in the composition range between 82 at.% to 87 at.% Ti, which coincides with the local maximum of the photocurrent. On the other hand, this morphology increases the semiconductor/electrolyte interface. On the other hand, a depletion region may be formed limiting the photocurrent by the potential gradient over the SCR. From about 93 at.% Ti the film morphology changes strongly to 200 nm pyramidal crystallites and a dense underlying layer comprised of
spherical particles of around 50 nm in diameter. This change in morphology leads to the observed increase in the photocurrent. Composition, morphology, structure and film thickness may have an influence on the primary light absorption process, however, only those charge carriers which are generated either in the depletion region or in the diffusion layer contribute to the photocurrent. The holes generated in the diffusion layer have to diffuse to the depletion region. Therefore, in the case of n-type semiconductors the photocurrent decreases for films having thicknesses exceeding the width of the depletion region. If the film thickness exceeds the electron diffusion length the photogenerated charges do not reach the back contact and recombine. The global maximum of the photocurrent was observed at the lower right area of the materials library where the film thickness is maximal (around 600 nm) which indicates good electronic conductivity of the material.

5.3.2.4 Photocurrent spectroscopy and bandgap determination

Photocurrent spectroscopy measurements were carried out at three measurement areas of the materials library at 94.4 at.% Ti (MA1), 84.4 at.% Ti (MA2) and 89.4 at.% Ti (MA3) representing the two above-mentioned local photocurrent maxima and the area in between using method 2 with a resolution of 5 nm at four different bias potentials equal to OCP, 1.0 V, 1.5 V and 2.0 V vs. RHE. OCP values were 0.78 V, 0.75 V and 0.8 V for MA1, MA2, and MA3 respectively. In all cases there are no detectable photocurrents at λ > 500 nm. The calculated quantum efficiencies for the three measurement areas are displayed in Figure 60. Within the wavelength range from 340 nm to 425 nm, the maximum quantum efficiency of 37.5% at 350 nm was observed for MA1, which also generated maximal photocurrent under polychromatic irradiation (Figure 58). MA2 representing the second local photocurrent maximum had a maximum IPCE of 16% at 350 nm. Above 1500 mV the IPCE does not increase indicating photocurrent saturation, which is limited by the rate of generation and separation of excitons.

![Figure 60. IPCE spectra of MA1, MA2 and MA3 calculated from corresponding photocurrent spectra.](image-url)
The less active MA3 between both local maxima showed 12% quantum efficiency at 350 nm in a potential range from 1000 mV to 2000 mV, whereby the IPCE at 1500 mV was slightly higher (13.5%). There is no explanation for the phenomenon and the discrepancy is attributed to limited precision of the photocurrent measurement. The ratio of the current and irradiance for each wavelength was calculated and \((\text{EQE}/(1-\text{EQE})^4 \times h\nu)\) vs. \(h\nu\) plots with \(s = 0.5\) and \(s = 2\) were used to determine the transition type and bandgap values of the materials. The plots of \((\text{EQE}/(1-\text{EQE})^4 \times h\nu)^{1/2}\) vs. \(h\nu\) were linear over two ranges of photon energies from 2.3 eV to 3.0 eV and 3.1 eV to 3.4 eV. The plots of \((\text{EQE}/(1-\text{EQE})^2 \times h\nu)^{1/2}\) vs. \(h\nu\) were linear over one range of photon energies from 3.21 eV to 3.64 eV. Estimation of the corresponding bandgap energies was performed by extrapolation of these linear regions to the x-intercept. The bandgap energies obtained for different transition types at different bias potentials are listed in Table 1. Generally all three materials behaved very similarly and corresponding bandgap values could be averaged as following: indirect \(E_g\ I = 2.98 \pm 0.02\) eV, indirect \(E_g\ II = 2.18 \pm 0.01\) eV and direct \(E_g\ I = 3.23 \pm 0.02\) eV. The indirect \(E_g\ I\) could be attributed to pure \(\text{WO}_3\) (reported band-gap energy varies from 2.6 eV to 3.0 eV).

\[ I = 2.98 \pm 0.02 \text{ eV}, \quad I = 2.18 \pm 0.01 \text{ eV}, \quad I = 3.23 \pm 0.02 \text{ eV} \]

\[ \text{WO}_3 \text{ (reported band-gap energy varies from 2.6 eV to 3.0 eV)} \]

**Figure 61.** Tauc plots top: considering indirect, and bottom: direct allowed transitions.
The origin of the indirect $E_g$ II might be attributed to a newly formed phase, since the value is rather small as compared with the bandgap values of either of the pure TiO$_2$ or WO$_3$. It is worth noting, that at a bias potential of 0.75 V this transition does not occur. This can be explained either a by low depth of the SCR which extends with increasing bias potential, or by a too low position of the corresponding CB, such that the reduction of protons cannot take place because of insufficient energy of photogenerated electrons. The value of the direct $E_g$ I coincides with the reported value of anatase (3.23 eV) TiO$_2$. However, from literature it is well known, that rutile has a direct bandgap at 3.06 eV and an indirect bandgap at 3.10 eV, whereas anatase exhibits only an indirect bandgap at 3.23 eV.$^{325}$ Nevertheless, for sol-gel deposited anatase a direct bandgap with an energy of 3.25 eV was also reported.$^{326}$

Table 1. Bandgap values extracted from Tauc-type plots for three different MAs at four different bias potentials and averaged values.

<table>
<thead>
<tr>
<th>Ti content</th>
<th>Eg</th>
<th>0.75 V</th>
<th>1.0 V</th>
<th>1.5 V</th>
<th>2.0 V</th>
<th>Average</th>
<th>St.Dev.</th>
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<td>84.4 at.%</td>
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<td>2.96</td>
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<td></td>
<td>indirect II</td>
<td>-</td>
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<td>2.19</td>
<td>2.22</td>
<td>2.18</td>
<td>0.04</td>
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<td></td>
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<td>3.27</td>
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<td>3.23</td>
<td>3.25</td>
<td>0.02</td>
</tr>
<tr>
<td>89.4 at.%</td>
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<td>3.00</td>
<td>2.99</td>
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<td>3.01</td>
<td>3.00</td>
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<tr>
<td></td>
<td>indirect II</td>
<td>-</td>
<td>2.19</td>
<td>2.20</td>
<td>2.16</td>
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</tr>
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5.3.3 Fe-W-O system

Identically to the approach of the Ti-W-O system combining WO₃ and Fe₂O₃ into a Fe-W-O system might reveal new materials, potentially overcoming the inherent limitations of hematite such as the position of the conduction-band edge below the reversible hydrogen potential, large recombination rates of the photogenerated charge carriers, short diffusion lengths of holes and poor electrical conductivity.

A continuous mixed Fe-W-O thin films materials library was fabricated by means of reactive co-sputtering from elemental Fe and W targets in Ar/O₂ and local SEM and EDX measurements of the materials library were performed at MRD (M. Hofmann). The automated EDX screening and SEM imaging of the materials library provided the basis to correlate composition and microstructure with the photoelectrochemical properties. Figure 62 depicts a photographic image of the materials library and the film composition along the materials gradient. The Fe content was varied in the range from Fe₃₂W₆₈Oₓ to Fe₈₁W₁₉Oₓ.

![Figure 62. Photographic image of the Fe-W-O materials library and film composition. EDX raw data provided by MRD (M. Hofmann).](image)

Figure 63 shows a series of top-view SEM micrographs of the deposited thin film materials library at different Fe/W ratios. There is a strong dependence of the structure (shape and size of crystallites or grains) of the material on its composition. At low sputter pressures compact grains are formed while at high sputter pressures porous microstructures were observed. Despite the deposition parameters were kept constant, a variety of structures were obtained in dependence of the materials composition. Since the substrate was kept at 400°C during deposition, the obtained structures are most likely thermodynamically favored. Materials with lower Fe content (35 at.%) consist of fine columnar grains of about 50 nm in diameter and very few bigger sharp grains of 100 nm to 200 nm in size. At 40 at.% Fe an increasing number of fine grains is growing together forming larger crystallites. At
45 at.% Fe the structure is dominated by sharp grains with a size from 100 nm to 250 nm.

Vidyarthi et al. reported a similar morphology for sputtered WO$_3$ films. At 55 at.% Fe a more porous structure is obtained with more spherical grains with increasing Fe content. Starting with 60 at.% Fe the round shaped grains grow together forming denser structures until at 65 at.% Fe a flat dense surface is obtained. The latter structure with a grain size of about 50 nm resembles sputtered Fe$_2$O$_3$.

In order to correlate composition, morphology and PEC performance of the materials within the ML it was characterized by potentiometry, amperometry, photocurrent spectroscopy and SFI using the OSDC set-up.

**5.3.3.1 Open circuit potential**

In order to elucidate the band structure of different materials within the Fe-W-O thin film ML, the OCP shift under illumination was measured. The OCP in the dark and under illumination was locally measured using OSDC and the OCP shift (ΔOCP) at 100 mW/cm$^2$ was determined (Figure 64). The OCP shifts upon illumination are negative indicating $n$-type semiconducting behavior. No OCP shift was observed for materials compositions with a Fe content below 45 at.%.

With increasing Fe content the OCP shift increases up to 125 mV at 56 at.% Fe. At higher Fe content the OCP shift decreases.
5.3.3.2 Electrochemical stability
To determine the bias potentials window, which can be applied without invoking corrosion of the Fe-W-O thin films, a linear sweep voltammogram was performed in the dark. The applied potential was swept between 1470 mV and 470 mV vs. RHE at a scan rate of 10 mV/s. All compositions were stable between 900 mV and 1470 mV showing negligible anodic currents of maximal 0.03 µA/cm². Below 900 mV films with Fe contents < 70 at.% corrode cathodically with the highest corrosion currents being measured at Fe contents between 70 at.% and 50 at.. Irreversible reduction of the Fe(III) to Fe(II) is assumed.

5.3.3.3 Integral conversion efficiency
Figure 65 shows the steady-state photocurrent densities measured at fixed illumination intensity (100 mW/cm²) and an applied bias potential of 1400 mV vs. RHE in dependence of the composition. While materials compositions containing 32 at.% to 45 at.% Fe are not photoactive, enhanced photocurrents are detected at compositions between 45 at.% and 72 at.% Fe. The maximum photocurrent is observed at a composition of 55 at.% Fe, which coincides with the composition showing maximum delta OCP as well as the most porous surface morphology.
In dense compact films the thickness beyond the depletion region acts as an ohmic barrier for the transport of electrons which increases the probability of their recombination with diffusing holes.\textsuperscript{327} The porous structure enhances the photoconversion efficiency by rendering the path of the holes into the solution shorter and thereby reducing recombination probability. Thus, in this case the electron diffusion length mainly limits the photocurrent response. Furthermore the porous structure of the films leads to an increase in the overall efficiency because the photocurrent density is proportional to the specific electrode surface. For instance by using a host scaffold, guest absorber approach a 20\% increase in photocurrent was observed.\textsuperscript{315} The improvement was attributed to an increase in the absorbed photon conversion efficiency because of the host/guest architecture. Moreover, the porosity may increase light absorption due to light scattering inside the porous film.

### 5.3.3.4 Photocurrent spectroscopy and bandgap determination

Photocurrent spectroscopy measurements were performed at 35 selected measurement areas and the IPCE values were calculated as the quotient of the number of transferred electrons and incident photon flux for each wavelength. Photocurrent spectra for materials compositions with Fe contents > 75 at.% were not recorded since the dark current values were too high and not constant. Compositions with Fe contents < 45 at.% show negligible light absorption, while materials with higher Fe contents show two absorption bands (Figure 66).
Figure 66. IPCE of Fe-W-O films as function of Fe content and irradiation wavelength.

Figure 67 displays the derived bandgap energies estimated by extrapolation of the linear ranges of \((\text{EQE}/(1-\text{EQE})*hv)^s\) vs. \(hv\) plots with \(s = 0.5\) considering indirect transition as function of the Fe content. Two linear ranges were obtained and related to two coexisting semiconducting materials further denoted as SC I and SC II with corresponding bandgap values \(E_g\) I and \(E_g\) II. Below 45 at% Fe the \(E_g\) I and \(E_g\) II values are constant at about 2.54 eV and 2.33 eV, respectively. At 50 at.% Fe the bandgap values increase to up to 2.68 eV and 2.4 eV for SC I and SC II which might correspond to a binary WO₃ and a ternary FeWₓOᵧ phase, respectively, and then decrease almost linearly with increasing Fe content eventually approaching the bandgap of pure hematite. The magnitude of the absorption band II is constantly growing with increasing Fe content so that the ratio of the absorption bands magnitudes decreased. Above 62 at.% Fe the absorption band of SC I could not be distinguished from that of SC II. For materials compositions with a Fe-content > 68 at.% a third absorption band with an averaged corresponding bandgap value of 1.98 eV was detected which can be attributed to the Fe₂O₃ phase (not shown). There is no direct correlation between the bandgap values and the photocurrent density, but, the bandgap values are affected by the composition leading to an unpredicted interesting material composition at a Fe content of about 55 at%.
5.3.3.5 Single frequency impedance

Similarities in the dependence of OCP and photocurrent density on the composition are observed. Film composition defines its crystal structure and intrinsic properties of the resulting semiconductor such as its conductivity. Also morphology and correspondingly the active surface area is a function of film composition, thickness and structure. In order to determine resistance and active surface area of the Fe-W-O films and elucidate the correlation between these parameters and the conversion efficiency SFI was performed at MAs lying within the compositional range from 47 at.% to 65 at.% Fe, where the photocurrent density peak was found. SFI values were acquired at a fixed frequency of 1 kHz in a bias potential range from 1500 mV to 0 mV vs. RHE in 0.1 M phosphate buffer at pH 7. A neutral electrolyte was chosen since Fe-W-O film is labile in acids at higher bias potentials (oxidation of Fe$^{2+}$) and in bases at bias potentials below OCP (reduction of W$^{6+}$). In addition to the determination of the film resistance and capacitance it was intended to make Mott-Schottky-type plots in order to determine flat band potentials of Fe-W-O films and compare the obtained values with those derived from OCP measurements under illumination. This measurement could not be performed since the Fe-W-O films were irreversibly reduced at potentials below 700 mV - 900 mV. Figure 68 shows the resistance of the Fe-W-O films as function of the Fe content and the photocurrent density. The resistance lies in the kOhm range, which particularly explains comparably low photocurrents.
Figure 68. Fe-W-O film resistance as function of Fe content (black markers) and inversely plotted photocurrent density (red markers).

A minimal resistance value of 5 kOhm was observed for the films with Fe content between 54 at.% and 56 at.%, which precisely coincides with the position of the photocurrent maximum of 3 μA/cm².

Figure 69. Fe-W-O film capacitance as function of Fe content (black markers) and photocurrent density (red markers).

Furthermore, the photocurrent density follows the films resistance. At ~13 kOhm film resistance the photocurrent values are about 1 μA/cm² irrespective of the film composition. Obviously, the photocurrent distribution is governed by the film conductivity rather than the film composition. A direct correlation between the film composition and the conductivity cannot be excluded. Figure 69 depicts the capacitance of the film extracted from the imaginary part of the impedance. The surface area can be well correlated with the obtained photocurrent density as well as with the film morphology derived from SEM figures.
5.3.4 Fe-W-O composites prepared by co-precipitation

The identified Fe-W-O material found at 55 at.% Fe might correspond to a ternary FeW₆O₉ phase. The most likely compositions are iron tungstate (Fe₂W₀₆) included into a matrix of amorphous WO₃ or Fe₂WO₆ with Fe substituted by W. Different Fe₂WO₆/WO₃ composites were synthesized by a co-precipitation method followed by high-temperature annealing and characterization by means of photocurrent spectroscopy. In 1982 Leiva et al. reported the preparation of α-iron tungstate. Among crystallographic, magnetic and electric properties, photoelectrochemical properties have been characterized. Photoanodes were prepared by evaporating thin films of gold on the back of sintered Fe₂WO₆ disks. Under illumination these photoanodes showed a photoresponse between those of α-Fe₂O₃ and WO₃, but the flat band potential was still too positive. In 1992 Walczak et al. studied conditions for the synthesis of Fe₂WO₆ in the solid state and found a new polymorphic modification. Among amorphous metastable Fe₂(WO₄)₃ three different high-temperature polymorphic modifications of iron tungstate were obtained. There are several reports concerning the energy diagram of Fe(II)-tungstate compounds. The one in the ref. used a synthesis method for iron tungstate based on sintering of WO₃ and Fe₂O₃ powders resulting in pure stoichiometric compounds possessing crystal structures with low defectivity. These materials are intrinsic semiconductors with low or absent doping. Correspondingly, no high PEC activity could be expected. Sintering could be replaced by hydrothermal synthesis or co-precipitation of WO₄²⁻ and Fe³⁺ ions followed by high-temperature annealing. The latter method resulted in an iron tungstate phase embedded in a WO₃ matrix, similarly, as it was observed for the sputtered Fe-W-O system.

5.3.4.1 Synthesis and characterization of iron tungstates

By adding of iron nitrate into sodium tungstate solution an amorphous metastable phase is formed:

\[
2Fe^{3+} + 3WO_4^{2-} \rightarrow Fe_2W_3O_{12}
\]

Equation 53

Heat treatment induces decomposition of the meta-stable phase into iron(III)-tungstate and WO₃ at a ratio of 1 to 2:

\[
Fe_2W_3O_{12} \xrightarrow{\Delta} Fe_2WO_6 + 2WO_3
\]

Equation 54

Depending on the heat-treatment parameters the formed iron tungstates possess different crystal structures. Four different phases were prepared: amorphous Fe₂(WO₄)₃, α-, β- and γ-Fe₂WO₆.
Compared to yellow Fe$_2$(WO$_4$)$_3$, the other phases had a red-brown color and were very distinct from each other (Figure 70) in their optical appearance as well as in their crystal shape. SEM images of the as-prepared Fe$_2$(WO$_4$)$_3$ and the three phases after corresponding temperature treatments are shown in Figure 70 at two different magnifications.

While Fe$_2$(WO$_4$)$_3$ is known to be amorphous, the α-, β-, and γ-phases seem to be crystalline. The XRD pattern of Fe$_2$(WO$_4$)$_3$ did not show any reflections. The XRD patterns of the obtained α-, β-, and γ-phases were difficult to interpret, because of low signal quality, however, several peaks were observed and could be assigned to
reflections as previously shown in ref. and WO₃. Two different sorts of crystals could be clearly distinguished for each high-temperature phase (Figure 70, red arrows). Using EDX-mapping (Figure 71) the large crystals were assigned to be WO₃, while small crystallites are the corresponding Fe₂WO₆ phases, as they showed more intense signals for Fe.

5.3.4.2 Automated spray-coating set-up

In addition to the synthesis of the powder PEC materials, the preparation of photoelectrodes needs to be performed. The evaporation of thin gold films onto sintered tungstate disks, fusion inside a platinum crucible or investigation of single crystals do not seem to be convenient. Therefore, spray-coating was chosen for photoelectrode preparation. Paints, including inorganic suspensions may be deposited by a variety of spray guns. An air spray gun is a simple device that operates at normal conditions and is based on the Venturi effect: a stream of high-velocity gas passed through a tube connected to the paint reservoir, lowers the pressure in the Venturi and by this draws suspension from the reservoir and converts it in to fine spray which is propelled towards the substrate. The spray gun can be fed by gravity or by a pump. Based on this technique a special automated micro-dispensing spray system, which is able to reproducibly deposit well-controlled amounts of dispersed powders or liquids on flat surfaces, was designed and built. The deposition set-up is based on a motorized robotic arm with a custom-made spray nozzle supplied with catalyst material suspension by means of a syringe pump. A compressor continuously supplies the nozzle with air as a carrier gas. The spray-coating set-up is schematically shown in figure 72. It consists of a robotic arm, a spray nozzle, an air-compressor and a syringe pump. The magnified image of the spray nozzle shows that it consists of two one-way plastic pipette tips of different size. The inner pipettes tip supplies suspension to be sprayed, while the outer tip supplies and directs compressed air. The airflow meets the suspension at the exit of the inner tip, draws small droplets of the suspension from its edge and nebulizes it. This results in fine homogeneous aerosol. The used pipette tips can be easily replaced once blocked or contaminated. The catalysts suspension is supplied by means of a syringe pump with a practical precision limited to 1 µL. For positioning the spray nozzle is fixed on the industrial robotic arm. This allows formation of a computer controlled spray raster (array) consisting of spray points in x- and y-directions. At each of these points a well-defined amount of the suspension can be sprayed. Different substrate sizes and shapes can be used, since the array can be varied using the “Union” software. The highlight of the system as compared to classic automatized spray-coating systems is the ability of dosing of well-defined portions of the suspension at fixed substrate positions while the spray nozzle is moved. This decreases the overall coating speed, but makes the coating much more controlled and reproducible. Even though the suspension covers the substrates in discrete
points proper coating parameters result in overlap of the formed coating islands leading to homogeneous layers.

Figure 72. Schematic representation of the automated spray-coating set-up.

Figure 73 schematically shows the distribution of a suspension on a substrate as function of nozzle-to-substrate distance. The thickness profile has a normal distribution profile described by a Gauss curve. The smaller the nozzle to substrate distance is, the smaller is the spot and higher is the profile. With increasing nozzle-to-substrate distance the profile gets wider and lower.

Figure 73. Simulated profile of a single solid spot deposited by spray coating as function of tip to substrate distance. A normal Gauss distribution was considered.

Once a series of depositions is performed along a straight line in that way, that the profiles are overlapping, the resulting profile gets flat (Figure 74 right). Also here it is important to keep the optimal distance between the spray nozzle and the
substrate. The smaller the nozzle-to-substrate distance is, the finer the spraying array has to be in order to obtain a smooth surface. The spraying array has to be larger than the substrate, otherwise edge effects occur.

![Graph](image)

*Figure 74. Simulated profile of overlapping solid spots deposited by spray coating at fixed tip to substrate distance.*

Maintaining the nozzle-to-substrate distance and linearly varying the amount of the sprayed suspension results in a thickness gradient (Figure 75). Also in this case the spray array has to be larger than the substrate in order to avoid edge effects.

![Graph](image)

*Figure 75. Simulated thickness gradient profile of overlapping solid spots deposited by spray coating at fixed tip-to-substrate distance and linearly varied quantity of the sprayed material.*

Based on limitations of the used hardware components (minimum spray volume per point is 5 µL) and by trying to minimize deposition time, optimal distance between adjacent raster points (resolution r) was found to be 2.5 mm. Having these parameters as framework conditions, the suspension concentration and spray volume can be varied in order to obtain the desired coating thickness. Since the concentration of the suspension can only be varied in a limited window because of the suspension stability, the number of coating layers can be varied as well.
Figure 76. Schematic representation of overlapping spots deposited by spray coating. Green spots are lying within the surface unit. Orange spots belong to the given surface unit to 50%, blue spot, deposited at the corner of the surface unit belongs to it to 25%.

Figure 76 shows one surface unit (SU) which has a length unit (LU) = 4 \( r \). The suspension sprayed on the edge between two adjacent SUs (orange) is shared between them and therefore only half of it belongs to the given SU. The suspension sprayed at the corner of a SU (blue) is shared by 4 SUs and belongs to the given one only by one quarter. All spots sprayed within the given SU belong exclusively to it (green). Knowing the raster parameters and the amount of sprayed suspension per SU the effective volume per SU can be calculated as:

\[
V_{eff, SU} = \left( \frac{LU}{r} + 1 \right)^2 V_{rp} - 4 \left( \frac{LU}{r} - 1 \right) \frac{V_{rp}}{2} - 4 \frac{3 V_{rp}}{4}
\]

Equation 55

with \( r \) the array resolution in mm, \( V_{rp} \) the volume of the suspension sprayed at one raster point. The first term of the right part of the equation represents the number of sprayed spots landing on one SU independent from the extent they belong to it. The second term represents the number of spots belonging to the given SU for 50% and the third term – amount of spots belonging to the given SU for 25%. These two terms are subtracted from the first one resulting in the effective number of spots belonging to the given SU. For a SU with a \( LU = 1 \) cm and \( r = 2.5 \) mm:

\[
V_{eff, cm^{-2}} = \left( \frac{10 \text{ mm}}{2.5 \text{ mm}} + 1 \right)^2 V_{rp} - 4 \left( \frac{10 \text{ mm}}{2.5 \text{ mm}} - 1 \right) \frac{V_{rp}}{2} - 4 \frac{3 V_{rp}}{4}
\]

\[
V_{eff, cm^{-2}} = 25 V_{rp} - 12 \frac{V_{rp}}{2} - 12 \frac{V_{rp}}{4}
\]

\[
V_{eff, cm^{-2}} = (25 - 6 - 3) V_{rp} = 16 V_{rp}
\]

Equation 56
Knowing the effective suspension volume per cm$^2$, the desired film thickness and density of the solid in the suspension, it is easy to calculate the needed mass concentration of the suspension using the following equation:

$$c = \frac{m}{V} = \frac{\rho AS_D}{V}$$

Equation 57

Here $m$ is the mass of the powder material possessing a density $\rho$ deposited on a surface area $A$ as a layer with thickness $S_D$. $V$ is the volume of suspension sprayed onto surface area $A$. Correspondingly the sum volume equals to the volume $V$ multiplied by the number of points to be spray coated.

5.3.4.3 Fabrication and evaluation of iron tungstate photoelectrodes

After synthesis iron tungstate powders were ground using an agate mortar and suspended in water. The resulting suspensions were stabilized with sodium polyacrylate (Figure 77). Four electrodes ($\text{Fe}_2\text{(WO}_4\text{)}_3\cdot\text{xH}_2\text{O}$, $\alpha$, $\beta$- and $\gamma$-$\text{Fe}_2\text{WO}_6$) were fabricated as homogeneous films on FTO substrates. Considering limited conductivity of the tungstate powders the film thickness to investigate was 1 µm. Cyclic voltammetry was performed to determine the bias potential range, which could be applied during ABPE measurements without causing sample damage (Figure 78). Below 250 mV vs. RHE several reduction peaks can be observed. The reduction mechanism involves the initial reduction of $\text{Fe}^{3+}/\text{Fe}^{2+}$ via insertion of
sodium ions from solution and is followed by tungsten reduction (W^{6+}/W^{4+}) and possibly to the “extrusion” of metallic iron and the concurrent formation of WO₂. Above 1800 mV vs. RHE exponential current growth is observed for every sample which may be due to water oxidation either on tungstate or on an exposed FTO surface. This anodic current overlaps with other anodic peaks most probably caused by oxidation of tungstate compounds. For the α-form the corrosion on-set potential lies just below 1450 mV, for the β-form at 1750 mV, and for the γ-form at 1600 mV. The amorphous tungstate starts to get oxidized at 1500 mV. Hence, a meaningful range of bias potentials, which could be applied lies between 715 mV (flat band condition of the intrinsic SC) and 1450 mV (onset of corrosion).

![Figure 78. Cyclic voltammograms recorded on amorphous-, α-, β- and γ-Fe₂WO₆ electrodes. Potentials are indicated vs. RHE.](image)

Photocurrent measurements under polychromatic irradiation with arbitrary but fixed intensity revealed negligible photoactivity for all samples. Solely for the α-phase a photocurrent of 1.5 µA/cm² at 1250 mV could be observed, which is much smaller as that measured using the reference WO₃ sample with the same loading (16 µA/cm²). No thickness dependence could be observed. This allows the assumption that only those photocatalyst particles are contributing to the photocurrent which have direct electric contact to the substrate. Moreover, the low photoactivity of the prepared electrodes can be explained by limitations associated with low mobility of charge carriers in the formed tungstate compounds as a consequence of low electronic conductivity. The α-Fe₂WO₆ particles, which showed at least some photoactivity, are the smallest within the materials set. Hence, the path of photogenerated charges gets shorter and recombination probability decreases. Furthermore, all electrodes showed poor mechanical stability. Bad adhesion to the substrate results in an increased distance between the particles and the FTO substrate, thus decreasing the probability of electron transfer.
5.3.4.4 Fabrication and evaluation of composite photoelectrodes

Bockris proposed a possible solution of the first problem by using ultrathin films in a stacked formation to increase the proximity of the photogenerated charges to the SCLJ. An increased photoresponse could be obtained by coating absorber thin films on a suitable nanostructured surface, in analogy to the dye-sensitized solar cells. This solution could resolve the issue, but it is difficult to implement for absorber materials with high formation temperature while maintaining its desired crystal structure. As solution to the second problem Kojin coated tungsten oxide photocatalysts with carbon by carbonization with poly(vinyl alcohol) (PVA) as carbon precursor, which increased the efficiency of the resulting composite material. This route was followed by Andel, who applied this technique to Fe(II)-tungstate. In addition to better electrical interconnection of catalysts particles and improved interparticular charge transfer, the high-temperature treatment in presence of carbon caused a reduction of the oxide structures introducing oxygen vacancies and thus doping the material. This method has the disadvantage that the carbon coating absorbs a substantial portion of the incident light converting it exclusively into the heat.

The proposed strategy to circumvent these limitations is embedding of the tungstate particles into a transparent conductive matrix, which allows more efficient charge transfer and improves mechanical stability of the electrode. The matrix should be composed of a wide bandgap metal oxide possessing good charge carrier transport properties. While tungstates act as light absorbers harvesting visible light, the wide bandgap semiconductor acts as charge collector and conductor. Since tungstate particles are directly incorporated into the conductive matrix, the photogenerated electrons can be directly injected into the CB of the matrix and therefore the path of the electrons within tungstates is minimized. The electric field induces a SCR over the whole composite material thickness and induces charge separation. This strategy is slightly similar to the widely used host scaffold/guest absorber (HS-GA) approach, but the main difference is that the absorber particles are not exposed to the solution. Thus, the matrix plays the role of a hole conductor as well as the reaction site. While TiO₂ and SnO₂ are well known materials for HS-GA structures, it is difficult to prepare a dense matrix of this materials using the suggested spray-coating deposition. A ZnO₂ matrix, however, can be easily prepared by pyrolysis of Zn(NO₃)₂. Spray pyrolysis is an alternative hybrid process, in which a liquid precursor, in this case a suspension of tungstate particles in a Zn(NO₃)₂ solution, is deposited by air spraying and then heated to induce pyrolysis. ZnO has a very similar bandgap as TiO₂ (3.2 eV for ZnO versus 3.0 eV for TiO₂) and as well similar band positions (CB = -4.3 eV for ZnO versus -4.5 eV for TiO₂ both vs. vacuum level). Also ZnO exhibits superior electrical properties as compared with TiO₂, since it has a much higher electron mobility. This is considered another
requirement for a good matrix. Furthermore, ZnO is more efficient than TiO$_2$ for a variety of photocatalytic reactions because of its surface consistency, which is important in the given case as well. Finally it was already demonstrated that combinations of ZnO with other semiconductors, such as Fe$_2$O$_3$ and WO$_3$ result in photocatalysts at which degradation of organic compounds occurs with enhanced rates.

Figure 79a shows microscopic image of a ZnO layer on a FTO substrate obtained by pyrolysis of spray coated Zn(NO$_3$)$_2$ at 500°C. Figure 79b shows spray coated γ-Fe$_2$WO$_6$ and figure 79c shows a composite material obtained by spraying of a Zn(NO$_3$)$_2$ solution over γ-iron(III)-tungstate particles previously deposited on the FTO substrate and successive pyrolysed in air at 500°C.

Figure 79. From left to right: ZnO/FTO obtained by pyrolysis of sprayed Zn(NO$_3$)$_2$, Fe$_2$WO$_6$ spray coated FTO, ZnO/Fe$_2$WO$_6$ composite obtained by pyrolysis of over Fe$_2$WO$_6$sprayed Zn(NO$_3$)$_2$.

Figure 80 left depicts a SEM image of the ZnO/γ-Fe$_2$WO$_6$ composite material and EDX mapping including the elements Zn, Fe and W. Micrometer sized γ-Fe$_2$WO$_6$ agglomerates are densely coated by ZnO, which is proven by corresponding the CV shown in Figure 80b. The black curve shows the CV recorded using a γ-Fe$_2$WO$_6$ coated electrode.

Figure 80. Left: SEM image and EDX mapping of ZnO/Fe$_2$WO$_6$ composite, right: CV recorded using γ-Fe$_2$WO$_6$ and ZnO/γ-Fe$_2$WO$_6$ composite electrodes (potential indicated vs. RHE).
The reduction and oxidation peaks, as discussed above, are absent in the CV acquired from the ZnO/γ-Fe₂WO₆ composite coated electrode. It is expected, that the ZnO matrix contributes to the measured photocurrent in the short wavelength range. Therefore, a reference sample exclusively consisting of pyrolized ZnO was investigated using photocurrent spectroscopy at different bias potentials (Figure 81). Hence, the matrix photocurrent contribution could be subtracted from the photocurrent spectra of the composite electrodes. The absorption edge is located at around 380 nm - 390 nm which nicely corresponds to the ZnO bandgap of 3.2 eV. A photocurrent can be observed at a bias potential of 625 mV (OCP). Above 1125 mV the photocurrents do not increase with applied bias potential as it is limited by the charge generation rate.

![Graph](image)

**Figure 81.** Photocurrent spectra of a ZnO modified electrode at different applied bias potentials (indicated vs. RHE).

Comparing the photocurrent spectra of the pure ZnO matrix with that of the composite material at 1625 mV reveals an extension of the absorption spectra for the composite materials. While the absorption edge of ZnO lies at 450 nm, the γ-composite absorbs up to 475 nm, while both α- and β-composites absorb up to 690 nm. Amorphous iron tungstate embedded into ZnO matrix has a negative influence on efficiency of the resulting composite material, most probably acting as recombination sites (Figure 82a). Adding of β- and γ-phases into the ZnO matrix does not only extend the absorption range but also enhances the conversion efficiency between 240 nm and 400 nm as compared with pure ZnO. At 350 nm the photocurrent generated by the β-composite is twice higher than that obtained with ZnO. With increased bias potential the effective absorption edge of the composite material shifts towards longer wavelengths: 450 nm at 620 mV, 510 nm at 1120 mV and 650 nm at 1620 mV (Figure 82b). Most probably the charge recombination in the bulk of the Fe-tungstate is high because of low mobility of majority carriers. Increasing of bias potential enhances the built-in electric field, thus making charge
separation more efficient. Furthermore, the enhanced width of SCR allows separation of charges generated deeper in the iron tungstate bulk, thus the resulting absorption range extends with increasing bias potential.

Figure 82. Left: comparison of photocurrent spectra recorded from a pure ZnO matrix, amorphous-α-, β- and γ-Fe₂W₆O₂₃ at 1625 mV vs. RHE. Right: photocurrent spectrum of α-Fe₂W₆O₂₃ at different bias potentials (indicated vs. RHE).
5.3.5 Extended Fe-W-O system

In order to investigate the Fe-W-O system further as well as to elucidate unequivocally influence of the film thickness on PEC performance three materials libraries covering Fe content from 6 at.% - 61 at.% and film thicknesses ranging from 220 nm to 1160 nm were deposited and characterized by profilometry, EDX and XRD at MRD (M. Hofmann and R. Mayer). The OSDC set-up was used for acquisition of photocurrent density at each of 1026 measurement areas as well as photocurrent and electrochemical impedance spectroscopy from selected compositions.

5.3.5.1 Integral conversion efficiency

The steady-state photocurrent was recorded at 1475 mV vs. RHE in 0.5 M NaClO₄ solution at pH 4.5 under polychromatic irradiation of Hg/Xe-lamp (5.2.1.3.3.1) at an output power density of 100 mW/cm². The photocurrent was calculated as the difference between the currents measured in the dark and under illumination (5.2.1.4.4.3).

The correlations of the measured photocurrent values with film thickness, composition and crystal structure are shown in Figure 83. XRD analysis (R. Meyer) revealed the existence of three different crystalline phases and an amorphous region in the investigated Fe-W-O composition range. Taking into account the crystal structure information, the diagram was divided in five sections (I – V).

Materials in the region I showed exclusively WO₃ (002), (020), (111), (200) and (220) reflections. Thus, the phase was considered to be Fe-doped W-O. A local maximum of photocurrent (49 µA/cm²) was present at 5 at.% - 6 at.% Fe and thicknesses between 700 nm and 800 nm. Here the photocurrent density is gradually increasing until the maximum thickness (765 nm). It cannot be excluded that the optimal thickness was not reached and the maximum photocurrent density for this phase is located at even higher thicknesses, indicating low defectivity and good electronic conductivity of the material. With increasing film thickness absorption of the incident irradiation is improved, while due to high film crystallinity the recombination rate of photogenerated charges is low.

Region II consisting of a WO₃/W₅O₁₄ mixture displays a lower photocurrent density compared to the Fe-doped WO₃, but also here the maximum available film thickness is 700 nm. It is possible, that at higher film thicknesses the photocurrent density still increases until the optimum thickness is reached.

The region III consisting of W₅O₁₄ displayed the highest photocurrent density values with an absolute maximum of about 65 µA/cm² at around 15 at.% – 17 at.% Fe and thicknesses ranging from 900 nm to 1060 nm. Region IV seems to be amorphous and shows minimal photocurrents within the whole materials set. Region V shows (200)
and (061) reflections for the ternary Fe₂WO₆ phase and has a local photocurrent density maximum located at about 51 at.% Fe and a thickness of 345 nm.

Figure 83. Color-coded map showing the correlations between thickness, Fe-content and measured photocurrent density acquired for 1026 measurement areas from 3 MLs. The map is divided in five phase regions (I - V) by black dashed lines indicating the Fe content and thickness for which the measurement areas exhibit the according phase. Magenta lines trace the measurement areas SEM micrographs shown in Figure 90. Adopted from ref.352 Red line on ML3 indicates positions, where SFI were acquired.

The absolute value of 15 µA/cm² is low compared to the binary phase photocurrents. This finding resembles the finding described in the section 5.3.3, where the photocurrent peak at 55 at.% Fe was found. The photocurrent densities recorded from different MLs at measurement areas with similar composition and thickness exhibited comparable values and showed the same trends for all MLs. Nevertheless within the Fe₂WO₆ region ML2 and ML3 a deviation in photocurrent density occured. In both cases the trend of increasing photocurrent density for increasing crystallinity (starting at 44 at.% Fe) is consistent, but the absolute photocurrent density values for ML3 is lower than for ML2 at measurement areas with similar composition and thickness. Furthermore, measurement areas on ML3 show an increase in photocurrent density for increasing thickness, whereas this is not apparent in this ternary region for ML2. R. Meyer related these differences to the morphology of the MLs:352 for the ternary Fe₂WO₆ phase > 44 at.% Fe ML3 shows a relatively smooth and homogeneous surface with only few inclusions of bigger grains. ML2, however, shows a morphology consisting of two grain types for compositions equal or higher 49 at.% Fe. An EDX intensity map revealed no difference in composition for the large grains and the surrounding matrix. The morphology difference was explained by the fact, that the deposition time for ML3 was 60% longer than for ML2, giving an equivalent of 60% more thermal power
applied during growth. The morphological difference might lead to higher photocurrent densities due to the increased specific surface area for ML3.

5.3.5.2 Photocurrent spectroscopy and bandgap determination

Two measurement areas within ML1 representing regions I and III, corresponding to Fe:WO₃ and W₅O₁₄, respectively, were analyzed by means of photocurrent spectroscopy in order to investigate absorption range and bandgap values of these materials. The first question to be answered was whether Fe-doping actually influences semiconducting properties of WO₃, and, for instance, alters its bandgap energy and correspondingly absorption range compared to pure WO₃. The photocurrent densities obtained from Fe:WO₃ and W₅O₁₄ with identical film thickness are equal. Thus the integral conversion efficiency is identical.

![Logarithmic color maps of the relative intensities of the main XRD peaks for ML1 and the absolute thickness (right bottom). Adapted from ref.252](image)

The second aim was to compare IPCE spectra of Fe:WO₃ and W₅O₁₄ films possessing identical thickness in order to evaluate whether the lack of oxygen in W₅O₁₄ alters its absorption spectrum compared to that of Fe:WO₃. Or if it is a matter of two identical materials with a slight difference in composition/structure, which do not have much influence on PEC performance. Figure 84 left depicts logarithmic color maps of the relative intensities of the (002) and (111) peaks for the Fe:WO₃ phase and (001) peaks for the W₅O₁₄ phase. Two measurement areas within ML1 were selected in this way, that they possess identical thickness and include films with mostly pronounced (001) W₅O₁₄ peak and (111) Fe:WO₃ peak, respectively. Photocurrent spectroscopy was performed on these MAs in a wavelength range from 240 nm to 700 nm with an increment of 5 nm and a bias potential range from 775 mV to 2075 mV vs. RHE with an increment of 100 mV using acquisition method II as described in the section 5.2.1.4.4.4. After applying the bias potential and equilibration of the dark current the measurement area is illuminated with monochromatic light of a certain wavelengths until the current under illumination is stabilized. By this, it can be guaranteed that steady-state currents are recorded. Figure 85 depicts two cutouts from selected amperograms in order to elucidate possible recombination pathways and the influence of the applied bias potential.
Figure 85. Left: current recorded from measurement areas comprised of Fe:WO₃ and W₅O₁₄ at 1075 mV and 1775 mV vs. RHE in a wavelength range from 440 nm to 540 nm using acquisition method 2. Right: comparison of current transients recorded from measurement areas comprised of Fe:WO₃ and W₅O₁₄ at 1075 mV and 1775 mV vs. RHE.

Figure 85 left shows, that the absorption range of both the Fe:WO₃ and the W₅O₁₄ phases extends at higher applied bias potentials. While at 1075 mV no photocurrent could be observed at wavelengths longer than 465 nm, at 1775 mV the absorption was extended beyond 540 nm. Thus, kinetic overpotentials do not play a major role and the charge transfer through the solid/liquid interface is fast enough to avoid charge recombination in the bulk. The explanation is simple: the current transients clearly indicate dominating bulk recombination. As the irradiation with longer wavelengths can penetrate deeper into the semiconductor than high-energy irradiation, the penetration depth can exceed the size of the SCR. Therefore, charges generated by absorption of longer wavelengths recombine, as they are generated too deep and there is no driving force to separate them. By applying of higher bias potential the SCR gets wider and these photogenerated charges are additionally separated and contribute to the photocurrent. From the amperograms depicted in Figure 85 it is seen that at lower bias potentials no bulk recombination is visible in the current transients. This is the consequence of the low current flow through the bulk of the semiconductor. The flow of the photogenerated charges is small enough that there is no concurrence in occupation of charge transfer pathways in the bulk. Furthermore, the number of photogenerated holes at the semiconductor surface and the number of photogenerated electrons at the counter electrode surface is small. Therefore, the current density is also small. Considering stoichiometry, it can be assumed that the W₅O₁₄ phase has more oxygen deficiency sites than Fe:WO₃ and therefore a higher doping level resulting in improved electronic conductivity. The comparison of current transients of Fe:WO₃ and W₅O₁₄ reveals no difference in charge recombination rates. The conductivity for the photognerated charges of the
both materials has to be identical. Therefore the situation does not change for thicker films and the optimal thickness for Fe:WO\textsubscript{3} and W\textsubscript{5}O\textsubscript{14} is the same.

Figure 86. Left: IPCE spectra of a MA with predominant Fe:WO\textsubscript{3} phase as function of applied bias potential. Right: selected IPCE spectra of two selected MAs with Fe content of 8 at.% and 6 at.% consisting of the Fe:WO\textsubscript{3} and the W\textsubscript{5}O\textsubscript{14} phases, respectively.

Photocurrent spectra recorded on both MAs are surprisingly similar in the whole wavelength and bias-potential range. The resulting IPCE spectra are identical as well. Figure 86 left shows IPCE spectra of the Fe:WO\textsubscript{3} phase as function of the applied bias potential. A maximum IPCE value of 50 \% is recorded at wavelengths of below 250 nm and bias potentials above 1975 mV. At potentials above 1175 mV the SCR width does not influence absorption spectrum of the semiconductor anymore. Between 1475 mV and 2075 mV the photocurrent gets saturated. Figure 86 right shows four selected IPCE spectra recorded from Fe:WO\textsubscript{3} and W\textsubscript{5}O\textsubscript{14} at 1175 mV and 2075 mV. There is no visible difference in the spectra recorded at identical bias potentials. Since the obtained IPCE spectra are identical for both materials, a Tauc-type plot was constructed for only one of them. Figure 87 depicts a Tauc-type plot obtained by plotting of \((\text{EQE}/(1-\text{EQE})*\text{hv})^s\) vs. \text{hv} with \(s = 0.5\) considering indirect transition. On a first glance two linear regions can be distinguished: 2.75 eV – 3.4 eV and 4.0 eV and 4.6 eV. However, both of them intersect the \(x\)-axis at nearly the same value. Therefore the curve was fitted in the whole photon energy region from 2.75 eV to 3.4 eV and a bandgap value of 2.6 eV was derived. As the span of bandgap values published for pure tungsten oxide is huge and covers values from about 2.6 eV to 3.0 eV,\textsuperscript{139, 323-324} it is difficult to make any assertions concerning influence of Fe doping on the intrinsic properties of the resulting material. Since the Fe:WO\textsubscript{3} and W\textsubscript{5}O\textsubscript{14} phases were found in regions with different Fe-content but show no difference in their photoelectrochemical behaviors, it can be assumed that Fe exists solely as a solid solution and does not function as a doping component. It has to be noted, that the WO\textsubscript{3} and the W\textsubscript{5}O\textsubscript{14} phases are likely to coexist over a large compositional range, where the more pronounced XRD signals are covering the less

\[2.075 \, \text{V (WO}_3)\]
\[2.075 \, \text{V (W}_5\text{O}_{14})\]
\[1.175 \, \text{V (WO}_3)\]
\[1.175 \, \text{V (W}_5\text{O}_{14})\]
pronounced signals of the other phase, especially in the range between 11 at.% and 15 at.% Fe. However, this does not cancel the assumption, that the Fe does not influence intrinsic properties of the semiconducting materials in this compositional range.

![Figure 87. Tauc plot reveals a bandgap value of 2.6 eV.](image)

### 5.3.5.3 Single frequency impedance measurement

According to R. Meyer, the morphology of Fe-W-O films has a smaller influence on the photoelectrochemical properties than crystal structure and thickness. The influence of the thickness on PEC performance is predictable and was discussed above. Thus, the aim was to identify to which extent which parameter defines the PEC performance of the films: phase, composition and morphology. Since composition defines phase and morphology at given fabrication conditions, the amount of variables could be reduced to two: crystal structure and morphology. Among other properties, the crystal structure influences films conductivity. Hence, considering both influencing factors a simple assumption is made: the lower the film resistance and the larger the surface area of a materials film is, the higher photocurrent density can be expected. Therefore, film resistances and surface areas were elucidated. ML3 was further investigated as it possesses three phase regions, in which the Fe-W-O films exhibit different predominant phases (Figure 83 and Figure 88). Starting at about 20 at.% Fe the W5O14 peak intensity (region III) is decreasing and disappears at around 27 at.% - 29 at.% Fe. Measurement areas with Fe contents between 29 at.% and 44 at.% Fe (region IV) are X-ray amorphous. Recording of the potential-dependent impedance was performed at measurement areas possessing identical film thickness of around 530 nm according to Figure 83 (red line). The measurement areas were chosen in that way to characterize films from regions III to V corresponding to the W5O14 phase, amorphous Fe-W-O composite/mixture and crystalline Fe2WO6 phase. SFI were acquired at fixed frequency of 1 kHz in a potential range from 1500 mV to 0 mV vs. RHE in 0.1 M phosphate buffer at pH 7. A
neutral electrolyte was chosen since the Fe-W-O film is unstable in acids at elevated bias potentials (oxidation of Fe$^{2+}$) and in bases at bias potentials below OCP (reduction of W$^{6+}$).

5.3.5.3.1 Estimation of film resistance by SFI

Resistance values of Fe-W-O films were extracted from the real part of impedance. The extracted values showed no dependence on applied bias potential and can be well correlated with the crystallinity of films (Figure 88). Crystalline Fe-W-O films lying in region III, where W$_5$O$_{14}$ reflections were observed show relatively low resistance of about 1.5 kOhm. From 20 at.% to 32 at.% Fe the resistance was constant. This means that the resistance is not a function of film composition but of its crystallinity. Between 33 at.% and 37 at.% Fe, the region in which the transition to amorphous Fe-W-O occurs, the resistance increases by two orders of magnitude to 100 kOhm for amorphous films lying in the region IV (37 at.% - 45 at.%). Also in this region the resistance does not depend on film composition.

With appearance of the Fe$_2$WO$_6$ phase (200 and 061 reflections) the resistance drops to 10 kOhm. This value is similar to that observed for Fe-W-O films in section 5.3.3.5 (5 kOhm – 13 kOhm depending on film morphology). The film resistance can be well correlated with the PEC efficiency of the films: W$_5$O$_{14}$ exhibits a relatively low resistance generates up to 35 $\mu$A/cm$^2$ photocurrent, while the amorphous phase with the large resistance generates almost no photocurrent. The iron tungstate phase generates up to 12 $\mu$A/cm$^2$ photocurrent. There is no linear correlation between films resistance and photocurrent density: a tenfold increase in the film resistance (W$_5$O$_{14}$ vs. Fe$_2$WO$_6$) decreases the photocurrent density only by three
times. A hundredfold increase in the resistance ($W_{5}O_{14}$ vs. amorphous) diminishes the photocurrent by 30 times. The Fe$_2$WO$_6$ phase usually has a well defined crystal structure with only few defects and correspondingly low impurity concentration. Therefore charge transfer through the tungstates has a very low efficiency. In other words, iron tungstates are bad conductors. The nature of the high resistance of amorphous phases has a different reason. The structures are very defective providing many sites for charge recombination. The observed logarithmic dependence might be explained by the connection between effective charge carrier mobility and film resistance, as it was done previously for Si and GaAs. However, since the nature of the Fe-W-O films resistance is rather complicated, as compared with the cases of Si or GaAs for which the resistance was a function of impurity concentration, it is not possible to make draw final conclusions here.

5.3.5.3.2 Estimation of the double layer capacitance by SFI

Figure 90 shows the capacitances of Fe-W-O films with different Fe contents. The trend is similar to the resistance curve: the crystalline $W_{5}O_{14}$ phase has a larger capacitance and, correspondingly, surface area which decreases during the transition to the amorphous phase and increases again for the Fe$_2$WO$_6$ film. Unlike the amorphous and partially the ternary phase with their flat and dense surfaces region (III) contains cavities which can be seen in Figure 90. The W-rich part shows a much higher specific surface area than the amorphous and ternary parts of the MLs. It was not possible to directly correlate the determined film surface areas with the film morphologies, as there are no SEM micrographs available exactly for those measurement areas, where SFI was acquired.

Figure 89. Fe-W-O film capacitance (black markers) and photocurrent density values (red markers) as function of Fe content.
Therefore, available SEM images taken from MAs possessing identical composition as those MAs, where SFI was acquired, were used for the comparison (magenta lines in Figure 83). Figure 90 shows selected SEM micrographs of MAs within ML2 and ML3 with Fe contents from 21 at.% to 50 at.%. Since MAs of ML2 and ML3 in the range from 21 at.% to 35 at.% possess a different morphology at identical compositions, these distinct micrographs were combined. Micrographs taken from ML2 are highlighted with a red frame. Assuming similar morphology development with increasing film thickness as discussed previously in the case of WO$_3$ films, it was supposed that the MAs with a compositional range of 30 at.% - 33 at.% analyzed by SFI have intermediate morphology between a smooth and homogeneous surface as can be seen for ML2 and bigger grains as can be seen for ML3. Large capacitance of films with a Fe content from 20 at.% to 32 at.% can be well correlated with film morphology. The film consists of small grains (90 nm-120 nm) resulting in a large surface area. Furthermore, the films evaluated by means of SFI have morphologies as shown for ML3 rather than for ML2. The capacitance is almost constant in the composition range between 20 at.% - 25 at.% and slowly drops between 25 at.% and 32 at.%, which exactly coincides with the apparent film surface area as seen from SEM micrographs. Between 25 at.% and 32 at.% the film consists of large crystallites (180 nm – 250 nm) embedded in a matrix of smaller grains (50 nm –70 nm). The number of larger grains decreases with increasing Fe content and the film capacitance drops between 32 at.% and 39 at.% Fe by about 5000 times, showing a minimum of only 400 pF. Between 39 at.% and 49 at.% Fe the capacitance increases again by 20 times.

Figure 90. SEM micrographs of selected measurement areas of ML2 (red frame) and ML3. Adapted from ref.352

Capacitance measurements also revealed a clear correlation between the apparent film surface area and the photocurrent density. The influence of the surface area on the PEC performance is less strong than that of the film resistance: a 110 times smaller surface area (Fe$_2$WO$_6$ vs. W$_5$O$_{14}$) reduces the photocurrent density by about three times, while a 5000 times reduced surface area (amorphous vs. W$_5$O$_{14}$) reduced the photocurrent density by only 30 times. The morphology has a weaker influence on the photoelectrochemical properties than the crystal structure and the
film thickness, as these two factors influence the film resistivity mostly. Thus, in order to achieve high PEC efficiency, the semiconducting film has to possess a high degree of crystallinity in order to reduce the number of recombination sites. Simultaneously, the film has to be defective on the atomic level in order to provide good electronic conductivity. The morphology of the film plays a rather minor role in the overall performance. Increasing of the surface area can be beneficial, as current density and therefore overpotential is reduced, as well as disadvantageous, since the photopotential decreases with increasing surface area.
5.3.6 Fe-Cr-Al-O system

B. Parkinson reported the discovery of a new class of semiconducting oxides consisting of Co, Al, Ga, In\textsuperscript{246} and Fe, Cr, Al\textsuperscript{165} using ink-jet printing of the related metal nitrate salts. In the first case, the mixed $p$-type semiconducting oxide exhibiting a spinel structure showed a five-fold photocurrent enhancement as compared to pure $\text{Co}_3\text{O}_4$. The ternary metal oxide materials library consisting of co-deposited Al, Fe and Cr revealed photoactive $p$- and $n$-type semiconductors. The $p$-type material has a composition of $\text{Fe}_{0.84}\text{Cr}_{1.0}\text{Al}_{0.16}\text{O}_3$ and a bandgap of 1.8 eV.

A thin film materials library of Fe-Cr-Al-O on FTO was prepared at MRD (H. Stein and C. Khare) by reactive magnetron co-sputtering and an array of 17 x 17 (289) samples was analyzed with automatic EDX to elucidate compositional properties. EDX screening of the Fe-Cr-Al-O ML revealed a composition spread with 20 at.% - 56 at.% Cr, 19 at.% - 59 at.% Fe and 0.8 at.% - 11.4 at.% Al (Figure 91).

![EDX mappings of Al, Fe and Cr](image)

The OSDC was used to perform photoelectrochemical characterization of the corresponding 289 measurement regions of the materials library. The photoactivity was elucidated by OCP measurement in the dark and under illumination, electrochemical stability and potentiodynamic photocurrents were extracted from potentiodynamic (photo)current measurements and photocurrent spectroscopy was applied to selected measurement areas to determine bandgap values. 0.5 M $\text{NaClO}_4$ solution at pH 4.5 was used as working electrolyte.

5.3.6.1 Open circuit potential

In order to assess the band structure of different materials within the ML, the OCP shift under illumination can be measured (3.4.3). The dark open circuit potential and
OCP shift under illumination (at 100 mW/cm²) were locally measured using the OSDC. The OCP shift was determined as the difference between the OCP under illumination and in the dark. A remarkable similarity of dark OCP and ΔOCP maps with the optical appearance of the ML is observed. Several sharp transitions of OCP values between differently colored regions of the materials library are seen. Since there is a smooth continuous variation of the composition but a sharp OCP transition, it is presumed that the dark OCP is mainly governed by the crystallinity of the materials. In order to assess this assumption 277 measurement areas (excluding the corners of the ternary metal-oxide library) were analyzed by XRD (H. Stein). Based on the identified phases, the ML was divided into 5 regions (I-V) suggested by similar XRD patterns. A remarkable correlation of phase distribution with the optical appearance of the ML could be observed as shown by the colored regions in the optical image of Figure 92.

The diffraction peaks in the magenta region I are attributed to a non-stoichiometric Al-doped Cr₂₋ₓFeₓAlₓO₄ spinel structure. Close to a Cr/Fe ratio of ~2:1 the crystallinity of the films improves, making a spinel type structure plausible. The cyan region II shows the same diffraction peaks but with lower intensities. A lower Al content results in smaller peaks in this region. Region III shows only diffraction peaks from the substrate. Region IV and V have less than 5 at.% Al and the XRD peaks are from a FeCrO₃ structure with a substitution with Al. Region IV shows higher XRD peak intensities from the same structure indicating a higher crystallinity. This phase region is in agreement with previous observations from Rowley et al., who detected the same structure in samples made by ink-jet printing of metal-nitrate salts.¹⁶⁵

In Figure 93 a color-coded ternary diagram of the identified phases is shown, where the colors represent regions I-V (black frame), the corresponding open circuit
potentials in the dark (blue frame) and ΔOCP (red frame). Figure 92 and Figure 93a share the same color code for illustrating the phase areas in the ML.

![Figure 93. Color-coded visualization and corresponding color scales of: phase regions from XRD maps - black frame, dark OCP - blue frame, ΔOCP - red frame.](image)

The distribution of dark OCPs as shown in Figure 93 correlates with the identified dominant phases of the ML: regions IV and V having < 5 at.% Al show OCP values in the range of 600 mV and 750 mV and are easier to oxidize as compared to materials with an Al content > 12 at.%.. Regions I-III display dark OCP values between 850 mV and 950 mV. Transitions of dark OCP values between regions I-III and IV-V are very sharp and are mainly governed by the film crystallinity.

A color-coded ΔOCP ternary diagram shown in Figure 93c also correlates with the phase constitution of the ML. Regions IV and V show negative ΔOCP values indicating n-type semiconducting properties. The ΔOCP values in these regions vary between -35 mV and -170 mV. A sharp change in ΔOCP values is observed between regions IV-V and I-III. In regions II and III a negligible influence of illumination on the OCP values was observed. Region I, with < 10 at.% Al showed p-type semiconductor behavior: the ΔOCP was positive in the range from 120 mV to 180 mV. The part of region I with > 10 at.% Al showed no OCP shift upon illumination.

5.3.6.2 Potentiodynamic photocurrent measurements

Potentiodynamic (photo)current measurements with a sweep rate of 1 mV/s with simultaneous light chopping at 0.2 Hz from a starting potential of 1475 mV to an end potential of -525 mV vs. RHE were performed. The current values were measured immediately after opening of the lamp shutter, just before closing of the shutter, immediately after closing of the shutter, and just before opening of the shutter.
allowing the determination of the peak-photocurrent, steady state photocurrent, peak-dark current, and steady-state dark current during one potential scan.

Figure 94. Selected voltammograms recorded within the measurement areas a) IV, b) III, c) II and d) I. Dark current (black lines), peak of transient dark current (blue lines), current under illumination (red lines) and peak of transient photocurrent (orange lines).

These current measurements allow the determination of i) whether the material at a certain measurement area is an n- or p-type semiconductor, ii) the peak photocurrent on-set potential, iii) the steady-state photocurrent on-set potential, iv) the potential dependence of the photocurrent, v) the surface recombination rate and vi) possible photo- or potential-induced corrosion processes. Potentiodynamic photocurrent measurements were performed at each measurement area. Figure 94 shows four selected voltammograms recorded on region IV - Al:FeCrO₃ (Figure 94a), region III - non crystalline Cr₂FeO₄ (Figure 94b), region II - non crystalline phase with increased Al content (Figure 94c) and region I - Al:Cr₂FeO₄ with a spinel structure (Figure 94d). Each combined voltammogram shows the dark current (black line), the current under illumination (red line), the peak transient dark current (blue line) and the peak of the photocurrent transient (orange line) as function of the applied bias potential. The voltammogram recorded on a selected measurement area in region IV - Al:FeCrO₃ depicted in Figure 94a shows a behavior typical for a n-type semiconductor. The anodic photocurrent onset potential is 1025 mV and the transient photocurrent onset potential is 650 mV. No anodic dark
current was detected in the scanned potential range. The cathodic current at -425 mV may indicate reduction of metal sites in the structure. At least three redox peaks were observed at +165 mV, -240 mV and -400 mV. XRD data of the materials in region III suggest non-crystallinity and no photoactivity was detected over the entire range of applied bias potentials (Figure 94b). Similar to region IV, a dark cathodic current was observed at bias potentials < 0.425 V. Anodic currents were observed at potentials > 1.38 V possibly due to oxidation of the material. Voltammograms recorded in the non-crystalline region II showed negligible photoactivity, whereas strong cathodic currents were observed at potentials < 250 mV most probably caused by reduction of metal ions in the structure (Figure 94c). Region V showed identical corrosion behavior at bias potentials < 250 mV, but was photoactive at potentials between -140 mV and 1250 mV. The maximum photocurrent was recorded at a bias potential of 220 mV. Interestingly, the photoactivity decreased at 575 mV but increased again at 750 mV (Figure 94d).

Extracting the photo- and dark current densities at certain potentials for all measured areas is the basis of a map of the current density values within a ternary composition diagram. This was done for three bias potentials: 1475 mV, where the n-type semiconductor materials in regions IV and V showed high photocurrent values (see Figure 94a for region V), as well as at 750 mV and 220 mV, two potentials at which the material of the composition Fe<sub>36.5</sub>Cr<sub>55.5</sub>Al<sub>8</sub>O<sub>x</sub> (Region V - Al:Cr<sub>2</sub>FeO<sub>4</sub>) showed maximum photoactivity. The dark current mapping for three bias potentials is shown in Figure 95.

![Figure 95. Dark current density maps recorded at: 1450 mV – black frame, 750 mV – blue frame and 220 mV – red frame.](image)

At 1475 mV region I showed high anodic dark currents (Figure 95) similar to the corresponding voltammogram (Figure 94d). Regions III and II also corroded anodically. At 750 mV, small cathodic currents were measured in region II at a Cr concentration > 50 at.% (Figure 95). At 220 mV only region I showed low currents,
while all other compositions exhibited cathodic currents that increase with increasing Al content (from blue to violet in Figure 95). Since, the reduction of Al\(_2\)O\(_3\) at these potentials can be excluded; we assume that Al does not exist as oxide but in a ternary phase or substitution in the crystal lattice of the Fe/Cr oxides that can be reduced from higher to lower oxidation states at acidic conditions.

Figure 96 shows color-coded photocurrent maps for different applied bias-potentials in the ternary composition diagrams. At 1475 mV regions IV and V generated photocurrents of up to 130 \(\mu\)A/cm\(^2\), while all other regions showed negligible photoactivity. The cathodic current appearing in region I was considered to be noise caused by high dark currents at 1475 mV. Region I was photoactive at 750 mV (see also Figure 94d) and generated photocurrents of up to -15 \(\mu\)A/cm\(^2\). All other regions of the ML were not photoactive. At a bias potential of 220 mV a stable photocurrent was generated in region I that increases to up to -60 \(\mu\)A/cm\(^2\) (Figure 96). The photocurrent maps correspond well to the \(\Delta\)OCP map where regions IV and V have \(n\)-type semiconductor properties and region I has \(p\)-type semiconductor properties, whereas no photoactivity was detected in the other regions.

![Figure 96. Photocurrent density maps recorded at: 1450 mV - black frame, 750 mV - blue frame and 220 mV - red frame.](image)

### 5.3.6.3 Photocurrent spectroscopy and bandgap determination

Photocurrent spectra on selected measurement regions were recorded using a tunable monochromatic light source (Instytut Fotonowy) equipped with a 150 W Xe lamp, a grating monochromator and appropriate cut-off filters. The photocurrent response was measured by the difference between average currents for 20 s in the dark and 20 s illuminated at wavelengths between 300 nm and 700 nm with 5 nm increments at different bias potentials. The external quantum efficiency (EQE) values for each wavelength were calculated as the ratio of the photocurrent density and the irradiation power density.
The measurement areas that generated the highest photocurrent densities from regions IV-V with the composition Fe_{50.8}Cr_{47.3}Al_{1.9}O_{x} and from region I with the composition Fe_{36.5}Cr_{55.5}Al_{8}O_{x} (n- and p-type semiconductors, respectively) were selected for further photocurrent spectroscopy studies. The best performing p-type semiconductors were found in a relatively narrow compositional range. The n-type materials, however, show similar high photocurrents over a broad composition range (Fe_{36-68}Cr_{62-26}Al_{2-6}, refer to Figure 96).

Photocurrent spectra were recorded at different applied bias potentials within the corresponding electrochemical stability windows determined from the potential dependent photocurrent measurements (Figure 94). The n-type semiconductor potential window was between 550 mV and 1650 V, while the p-type semiconductor was investigated in a potential range between 1300 mV and 0 mV. The incident photon to current efficiency (IPCE) spectra of the selected p- and n-type semiconductors are shown in Figure 97 and Figure 98 as function of wavelength and applied bias potential. The ratio of the current and irradiance for each wavelength was calculated and \((\text{EQE}/(1-\text{EQE})^*h\nu)^{1/2}\) vs. \(h\nu\) plots with \(s = 0.5\) and \(s = 2\) were used to determine the transition type and bandgap values of the materials.

5.3.6.3.1 n-type semiconductor

Figure 97 shows the external quantum efficiency (EQE) as a function of wavelength and applied bias potential. Below 700 mV no photoactivity was observed. Between 750 mV and 1250 mV the photocurrent onset was between 350 nm and 375 nm, while at bias potentials > 1250 mV the photocurrent onsets shifts between 475 nm and 500 nm.

Figure 97. Left: EQE spectra of the n-type semiconducting material calculated from photocurrent spectra acquired at different bias potentials. Right: Tauc-type plots \((\text{EQE}/(1-\text{EQE})^*h\nu)^{1/2}\) vs. \(h\nu\) of the n-type semiconducting material.
The maximum observed EQE at 1650 mV and 240 nm was about 8.2%. The carriers with very short diffusion lengths generated deeper in the material cannot be collected unless the space charge layer is expanded into the material by application of rather high bias potential values. This explains the apparent extension of the absorption spectrum at higher applied bias potentials. The shape of the \((\text{EQE}/(1-\text{EQE})^*h\nu)^{1/2}\) vs. \(h\nu\) plot strongly depends on the applied bias potential: below 1150 mV only one linear region can be distinguished and extrapolation thereof indicates indirect bandgap values of 2.72 eV at 650 V bias potential, 3.13 eV at 1250 mV and 2.5 eV at 1650 mV, resulting in an averaged bandgap value of 2.82±0.43 eV (Figure 97). At higher bias potentials a second linear region gets more pronounced. Extrapolation of this region leads to an indirect bandgap of 1.97±0.07 eV.

5.3.6.3.2  \(p\)-type semiconductor

Prior to spectra acquisition, the photoelectrochemical cell has been purged with Ar and it was continuously purged with \(H_2\) during the measurement in order to maintain the reduction potential of the protons. In correspondence to observations of Rowley et al., the steady-state photocurrent was not completely reached after 20 s illumination, whereby the initial peak transient current was 100 times higher as after 20 s, which clearly indicates significant charge recombination occurring in this material that is not surprising given that the surface has no catalyst for hydrogen evolution.

This explains the much lower EQE of the \(p\)-type material as compared to that of the \(n\)-type material even though the photocurrents estimated by potentiodynamic current measurement were comparable. EQE values in dependence from the wavelength and applied bias potential for the selected \(p\)-type semiconducting
material is shown in Figure 98. This material composition exhibits a broad absorption range. At 500 mV the absorption range extends to 450 nm, however, between 200 mV and 700 mV the absorption range extends to 650 nm (compare also Figure 94d). The sharp onset of the EQE spectrum at 400 mV in Figure 98 could be explained by Fermi level pinning from where a space charge layer grows again. The drop in EQE at 200 mV could be attributed to photoelectrochemical self-reduction of most probably Fe(III) to Fe(II). From the Tauc-type plot two bandgap values of 1.55±0.05 eV and 2.42±0.01 eV could be extracted. In contrast to the n-type semiconductor two linear ranges are observed at all bias potentials (Figure 98).
6 Conclusions

An automated optical scanning droplet cell (OSDC) with an integrated optical fiber for high-throughput investigation of semiconductor material libraries (ML) for solar water splitting was designed and built. Corresponding software was developed allowing the system to automatically perform potentiometry, potentiostatic and potentiodynamic photocurrent and photocurrent spectroscopy as well as electrochemical impedance spectroscopy measurements. The setup was advantageously used for high-throughput screening of sputtered metal oxide-based semiconductor materials and delivered highly reproducible and, owing to careful system calibration, quantitative results. Using the built system binary W-O, ternary Ti-W-O, Fe-W-O and quaternary Fe-Cr-Al-O systems were investigated.

By means of photocurrent measurements, efficiency of W-O films deposited at different chamber pressures was reviewed and by resistance and capacitance measurements it was experimentally proven, that WO₃ films deposited at high pressures have larger active surface area and have less electric resistance. Using photocurrent spectroscopy absorption spectra of these films were elucidated and it could be demonstrated how films morphology affects the wavelength resolved photoresponse of WO₃-films. Finally variation of film resistance and surface area with film thickness was studied for thickness gradient WO₃ materials library. Using MS-type plot and photocurrent on-set potential measurements thickness dependent flat band values were determined. Charge carrier concentration was elucidated as well.

A ternary Ti-W-O system was characterized by potentiometry, photocurrent and photocurrent spectroscopy and in addition to a predictable photoelectrochemical behavior new phases were found that exhibit unexpected photoelectrochemical properties.

Fe-W-O system with Fe content from 35 at.% to 86 at.% Fe was characterized in terms of composition, morphology and photoelectrochemical properties. Correlating the structural and compositional data with photoelectrochemical measurements resulted in the finding of a previously unknown and non-predictable materials composition at about 55 at.% Fe exhibiting substantially increased photocurrent and photopotential. By means of photocurrent spectroscopy it could be shown, that the bandgap values of Fe-W-O semiconducting materials are strongly affected by the composition. SFI measurement revealed strong correlation of films composition, morphology, resistance and surface area.

The Fe-W-O system was further studied in Fe content range from 5 at.% to 60 at.%. More than 1000 different materials possessing different thickness, compositions and crystal structures were characterized by photocurrent measurement. The screening
revealed correlations between increased photocurrent density and crystallinity, especially for the phases WO$_3$ and W$_5$O$_{14}$ and less distinct but still apparent for the Fe$_2$WO$_6$ phase. Influence of the film structure and morphology on its intrinsic properties was studied by electrochemical impedance spectroscopy. It could be further shown, that the WO$_3$ and W$_5$O$_{14}$ films show no difference in PEC performance.

Three different polymorphic modifications of Fe$_2$WO$_6$ were prepared using co-precipitation and subsequent annealing. An automated spraying system was designed and built for deposition of powders onto conductive substrates. The developed software allows deposition of well-controlled amounts of suspended powders on flat surfaces both as homogeneous films and thickness gradients. Composite photoelectrodes comprised of iron tungstates embedded in a ZnO matrix were fabricated by spray pyrolysis and photocurrent spectroscopy was used for efficiency elucidation of the prepared electrodes. The material showed an extended absorption spectrum and enhanced photocurrent efficiency compared to pure ZnO and pure iron tungstates.

Fe-Cr-Al-O system was studied by means of potentiometry and potentiodynamic photocurrent measurements. $n$- and $p$-type semiconducting areas were identified and showed promising photocurrent onset potentials and high OCP values. Using photocurrent spectroscopy bandgaps of the identified materials were determined and revealed values of 1.94 eV for $n$- and 1.6 eV for $p$-type semiconductors.
7 Outlook

In order to extend the capabilities of the OSDC system additional hardware allowing acquisition of intensity modulated photocurrent spectra (IMPS) could be implemented. This is a powerful tool for measuring the rate constants for charge transfer and recombination. Using this method in a high throughput way would deliver useful information about materials allowing rather precise elucidation of composition-structure-performance dependencies.

A further possibility to expand system functionality is integration of micro electrochemical sensors for detection of evolved oxygen and hydrogen gases allowing STH efficiency determination.

The existing measurement techniques could be further optimized by using electrolytes with readily oxidizable (reducible) reagents for evaluation of n- and p-type materials, respectively. Since the water oxidation reaction is a very complex process accompanied by large kinetic overpotentials, screening of photoabsorbers which are not modified with an OER catalyst by means of photocurrent measurements could lead to overlooking of good photoabsorbers.

Considering the knowledge obtained in the course of this thesis it may be predicted, that highly crystalline sub-stoichiometric oxide materials having low long-range and enhanced short-range defectivity might possess suitable properties for being interesting candidate for solar water splitting photoelectrodes.
8 Experimental part

8.1 Materials

8.1.1 Analytical reagents

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<td>Potassium chloride (KCl)</td>
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<td>Iron(III)-nitrate nonahydrate (Fe(NO₃)₃•9 H₂O)</td>
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<tr>
<td>Sodium tungstate dihydrate (Na₂WO₄•2 H₂O)</td>
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<td>Sodium polyacrylate (NaPa)</td>
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8.1.2 Consumables

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<td>Silver wire (Ø = 0.5 mm)</td>
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8.1.3 Instrumentation

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### 8.1.4 Software

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<td>PalmSense Lite</td>
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<td>Union 2.6.9</td>
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<td>Visual basic 6.0</td>
<td>Microsoft GmbH, Unterschließheim, D</td>
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8.2 Fabrication of materials libraries (WDM)\textsuperscript{290}

The substrates for all sputtered thin film materials libraries were prepared separately; a 100 nm Pt (10 nm Ti adhesion layer) was coated by magnetron sputtering on thermally oxidized Si wafers (1.5 µm SiO\textsubscript{2}) at room temperature and an Ar pressure of 5 mTorr. A radio-frequency (RF) power supply was used for Pt (250 W) and Ti (200 W).

8.2.1 W-O system\textsuperscript{144}

WO\textsubscript{3} thin films were fabricated by reactive magnetron sputtering from a metallic W target (99.99% purity) in a sputter system (AJA International ATC2200V). To suppress arcing during reactive sputtering, units for pulsed direct current (DC) (35 kHz, duty cycle ~95.8%) and an arc suppression unit (Advanced Energy Pinnacle) are connected between the power supply and the W target. The W target was inclined at an angle of 47° with respect to the substrate normal. The films were deposited in a reactive (Ar/O\textsubscript{2} gas mixture) environment. The sputter pressure was varied between 2 mTorr and 30 mTorr, while the Ar/O\textsubscript{2} ratio was kept 1:3 for all W-O films. The substrate was heated up to 350 °C and was kept stationary in order to produce wedge-type WO\textsubscript{3} films with a thickness gradient. The deposition time was adjusted in such a way to deposit around 600 nm thickness of the film at the end closer to the target.

8.2.2 Ti-W-O system\textsuperscript{353}

Continuous Ti-W-O thin film MLs were fabricated using reactive magnetron sputtering of elemental Ti and W (99.99% purity) targets. The sputter system (AJA International ATC2200V) consisted of four confocal aligned cathodes. Depositions were performed at a substrate temperature of 400 °C and a chamber pressure of 10 mTorr. The flows of sputter gas (Ar) and reactive gas (O\textsubscript{2}) were 30 sccm and 90 sccm, respectively. Sputter power and process time were adjusted such to obtain libraries with an approximate thickness of 400 nm at the center of the wafer. A pulsed DC power supply was used for sputtering Ti and a radio frequency (RF) power supply was used for W.

8.2.3 Fe-W-O system\textsuperscript{354}

A continuous Fe-W-O thin-film materials library was fabricated by using reactive magnetron sputtering from elemental Fe and W (99.99% purity) targets. The sputter system (AJA International ATC2200V) consisted of four confocal-aligned cathodes. Deposition was performed at a substrate temperature of 400 °C and a chamber pressure of 10 mTorr. The flows of sputter gas (Ar) and reactive gas (O\textsubscript{2}) were 30 sccm and 90 sccm, respectively. A pulsed direct-current (DC) power supply was used for sputtering Fe (300 W) and a radio-frequency (RF) power supply was used.
for W (300 W). Sputtering powers and process time (5 h) were adjusted to yield libraries with an approximate thickness of 400 nm at the center of the substrate.

8.2.4 Extended Fe-W-O system

The Fe-W-O thin-film MLs were fabricated by co-deposition using reactive magnetron sputtering from elemental metallic targets in an AJA International ATC2200V sputter system. The sputter configuration was chosen to obtain MLs with composition- and thickness gradients almost perpendicular to each other. Fe (99.99% purity) was sputtered using pulsed direct current (DC-p) magnetron sputtering with a frequency \( f = 35 \text{ kHz} \) and a reverse time \( r = 1.2 \text{ ms} \). W (99.99% purity) was deposited by radio frequency (RF) magnetron sputtering. The MLs were deposited at a substrate temperature of 400°C. The gas pressure was 1.33 Pa with an Ar/O\(_2\) ratio of 1:3. The deposition times and powers as well as the composition and thickness ranges for the three MLs are listed in Table 2

<table>
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<tr>
<th>Materials library</th>
<th>Binary content Fe content (at.%)</th>
<th>Thickness (nm)</th>
<th>Deposition power RF / Fe (DC-p) (W)</th>
<th>Deposition time (min)</th>
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<tr>
<td>ML1</td>
<td>6 - 34</td>
<td>220 - 800</td>
<td>460 / 70</td>
<td>214</td>
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<tr>
<td>ML2</td>
<td>17 - 61</td>
<td>220 - 730</td>
<td>330 / 140</td>
<td>250</td>
</tr>
<tr>
<td>ML3</td>
<td>15 - 56</td>
<td>360 - 1160</td>
<td>330 / 140</td>
<td>400</td>
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</table>

8.2.5 Fe–Cr–Al–O system

The Fe–Cr–Al–O ML was fabricated in a magnetron sputtering system (AJA International ATC2200J). The deposition was performed on a square-shaped 7 mm × 75 mm fluorine doped tin oxide (FTO) coated glass substrate by co-sputtering from elemental Fe, Cr, and Al targets (99.99% purity) confocally positioned in the deposition chamber. The deposition was performed at a constant pressure of 10 mTorr with continuous flows of sputter gas (Ar) and reactive gas (O\(_2\)) 40 sccm and 2 sccm respectively. In the cylindrical deposition chamber the azimuthal angle between the sputter targets was 90°, with the Cr and Al targets opposing each other, while the Fe target was positioned in between them. The deposition of Cr and Fe was performed by direct current (DC) magnetron sputtering with a power of 150 W. Al was sputtered with a radio frequency (RF) source at 100 W. There was no intentional substrate heating during deposition. After deposition, the materials library was annealed in air at 525 °C for 90 min with a heating rate of 16 °C/min and a slow cooling rate of 4 °C/min.
8.3 Characterization of sputtered materials libraries (WDM)\textsuperscript{290}  

8.3.1.1 Thickness measurements  
The thickness of fabricated films was determined by a mechanical profilometer Ambios XP2 measuring the step between the Pt surface and sputtered film surface created by depositing through openings of the Si-shadow mask or by lift-off structure.

8.3.1.2 SEM and EDX measurements  
Morphology of materials library was examined by means of a Carl Zeiss LEO Supra 55 FEG scanning electron microscope at different locations.

Compositional analysis was performed by high-throughput energy dispersive X-ray spectroscopy (EDX) at 20 kV acceleration voltage with 100 μm aperture in a JEOL JSM 5800LV equipped with an Oxford Inca system. Compositional data was determined in the center of each measurement area (approximately 400 μm x 600 μm) and presumed to be constant for each sample (accuracy about 0.5 at %). When using a Si-drift-detector (SDD), quantification of very light (i.e. O) and very heavy (i.e. W) elements at the same time is not accurate. Therefore, the presented compositional data are always provided for binary or ternary ratios in case of Fe-W-O/Ti-W-O and Fe-Cr-Al-O systems respectively. Materials library deposited with high O\textsubscript{2} excess at elevated temperature were expected to be stoichiometric.

8.3.1.3 X-ray diffraction (XRD) measurements  
Structural characterization of the samples was carried out by wide-angle X-ray diffraction (XRD) technique using a PANalytical X’Pert PRO X-ray diffractometer system with Nickel-filtered Cu-K\textsubscript{α} radiation equipped with a PIXcel detector in Bragg-Brentano geometry. The area illuminated by the X-ray beam (2θ dependent) was of elliptic shape with a size of about 3 mm x 3 mm. The identification of the phases was based on data from the “Pauling File” database. Phase region identification analysis was performed using the CombiView software.

8.3.2 Preparation and characterization of iron(III)-tungstate photoelectrodes  

8.3.2.1 Cleaning of FTO substrates  
Used FTO coated glass substrates (10 cm x 2 cm) were cleaned using industrial glassware washer supplied with deionized water. The cleaning procedure consists of treatment with a detergent at elevated temperature, rinsing with deionized water, treatment with a phosphoric acid solution, repeated rinsing with deionized water and drying. Resulting substrates were found to be very clean without any residuals.
8.3.2.2 Synthesis of iron(III)-tungstate powder photocatalysts

Three different polymorphic modifications of iron tungstate were prepared by co-precipitation method with subsequent annealing at different temperatures and purification. Fe₂(WO₄)₃•XH₂O precipitate was obtained by dropwise addition of 150 ml 0.3 M sodium tungstate into 100 ml continuously ultrasonicated 0.3 M aqueous Fe(NO₃)₃ solution. The adding rate was around 3 ml/min. The precipitates were subsequently washed twice with water and twice with ethanol, dried and then calcined at different temperatures in order to obtain different Fe₂WO₆ phases according to ref.329. The annealing parameters are summarized in Table 3.

<table>
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<th>Phase</th>
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<td>α-Fe₂WO₆</td>
<td>840</td>
<td>2</td>
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<tr>
<td>β-Fe₂WO₆</td>
<td>850</td>
<td>72</td>
</tr>
<tr>
<td>γ-Fe₂WO₆</td>
<td>950</td>
<td>24</td>
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8.3.2.3 Deposition of iron(III)-tungstate powders

Each suspension was formulated from catalyst powder dispersed in water after addition of 1 wt.% sodium polyacrylate as a surfactant. Table 4 lists the used mass concentrations of different iron tungstate phases. In the cases of Fe₂W₃O₁₂, β-FeWO₆ und γ-Fe₂WO₆ the suspensions were stable at lower mass concentrations. The amount of sprayed suspension was adjusted for each sample. Each mixture was vigorously stirred for 5 min and immediately transferred into the supply line of the spray system. The suspension was continuously stirred in the storage tank of the set-up by means of a shaker, while the spray nozzle was continuously supplied with compressed air at a fixed flow rate (pressure control).

<table>
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<tr>
<th>Catalyst</th>
<th>Density (g/cm³)</th>
<th>Concentration (g/ml)</th>
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<td>Zn(NO₃)₂</td>
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<td>Fe₂W₃O₁₂</td>
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<td>α-Fe₂WO₆</td>
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<td>β-Fe₂WO₆</td>
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<td>0.005</td>
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<td>γ-Fe₂WO₆</td>
<td>12.4</td>
<td>0.005</td>
<td>12</td>
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</table>
First, around 1 ml of the suspension was sprayed into the waste container to assure that the set-up is completely filled and generates a stable spray. During deposition precise amounts of the suspension have been pumped in to the nozzle on demand. Suspensions were sprayed onto FTO/glass substrates fixed on the hotplate heated to 120°C. For composite electrodes Zn(NO₃)₂ solution was sprayed on the top of the freshly deposited tungstate layer at max. 80 °C.

Calcination of photoelectrodes was performed using two different temperature profiles depending on electrode composition. Samples exclusively consisting of iron tungstates were heated up at a rate of 10 °C/min up to 500 °C and kept at the temperature for 6 h in O₂/Ar 1:1 atmosphere. Temperature profile for composite photoelectrodes is depicted in Figure 99.

\[
\text{Figure 99. Temperature profile for heat-treatment of composite photoelectrodes.}
\]

8.3.2.4 Characterization of iron(III)-tungstate photoelectrodes

8.3.2.4.1 SEM and EDX measurements

Energy dispersive X-ray (EDX) maps and scanning electron microscope (SEM) images were obtained with a Quanta 3D FEG microscope from FEI (Eindhoven, The Netherlands).

8.3.2.4.2 Cyclic voltammetry

Cyclic voltammetry was performed in the dark in a potential range from -1.5 V to 1.5 V vs. Ag/AgCl/3 M KCl reference electrode in 0.1 M phosphate buffer at pH 7. Start potential was OCP. Potential sweep rate was 100 mV/s.

8.3.2.4.3 Photocurrent spectroscopy

Photocurrent spectra on selected measurement areas were recorded using a tunable monochromatic light source (Instytut Fotonowy) equipped with a 150 W Xe lamp, a grating monochromator and appropriate cut-off filters. The photocurrent response was measured as the difference between the averaged current values recorded during 20 s in the dark and the averaged current values recorded during 20 s with an illumination at wavelengths between 300 nm and 700 nm with 10 nm increments at different bias potentials.
9 References
42. Frumkin, A.; Damaskin, B., Real free solvation energy of an electron in a solution in equilibrium with the electrode and its dependence on the solvent nature. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry 1977, 79 (2), 259-266.


91. James, B. D.; Baum, G. N.; Perez, J. *Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production*; **2009**.


207. La Mantia, F.; Santamaria, M.; Habazaki, H.; Di Quarto, F., The influence of thermal treatment on the electronic properties of a-Nb$_2$O$_5$. 2009, 411-422.


211. Albini, A.; Fagnoni, M., Green chemistry and photochemistry were born at the same time. *Green Chemistry* 2004, 6 (1), 1-6.


244. Anunson, P. N.; Winlder, G. R.; Winkler, J. R.; Parkinson, B. A.; Christus, J. D. S., Involving students in a collaborative project to help discover inexpensive, stable materials for solar photoelectrolysis. Journal of Chemical Education 2013, 90 (10), 1333-1340.
245. He, J.; Parkinson, B. A., Combinatorial investigation of the effects of the incorporation of Ti, Si, and Al on the performance of alpha-Fe₂O₃ photoanodes. ACS combinatorial science 2011, 13 (4), 399-404.
246. Newhouse, P. F.; Parkinson, B. A., Combinatorial optimization of spinel Co₃₋ₓMₓO₄M = (Al, Ga, In) alloyed thin films prepared by ink jet printing:
photoelectrochemical, optical, and structural properties. *J. Mater. Chem. A* 2015, 3 (11), 5901-5907.


290. mrd@rub.de MATERIALS RESEARCH DEPARTMENT. http://www.mrd.ruhr-uni-bochum.de.


302. Schafer, D. Elektrochemische rastermikroskopie bei variablen temperaturen. Ruhr-Universität Bochum, **2008**.


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343. Preparation of carbon coated FeWO$_4$ and its photocatalytic activity under visible light.


10 Appendix

10.1 Technical drawings
OSDC version 1: general view/assembly
OSDC Version 2: Reference electrode enclosure

OSDC Version 2: PTFE tip
Spray-casting set-up: Modified robotic arm/spray nozzle

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### 10.2 Software classes

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10.3 List of publications


10.4 Oral and poster presentations

10.4.1 Oral presentations


10.4.2 Poster presentations


10.5 Curriculum Vitae

Kirill Sliozberg

Date and place of birth: 28.07.1985, Ukraine, Dnipropetrowsk

Nationality: ukrainian

e-mail: elan@kirillhome.de

**Doctoral Studies (PhD) in** Analytical Chemistry (06/2011 – 09/2015)

Analytical Chemistry - Center for Electrochemical Sciences (CES), Faculty of Chemistry and Biochemistry, Ruhr-Universität Bochum, Bochum, Germany

Supervisor: Prof. Dr. Wolfgang Schuhmann

**Master of Science (MSc) in** Analytical Chemistry (05/2009 – 05/2011)

Analytical Chemistry - Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum, Bochum, Germany

Supervisor: Prof. Dr. W. Schuhmann

Title of thesis: „Hochdurchsatzscreening der photoelektrochemischen Eigenschaften von Materialbibliotheken mittels einer Rastertropfenzelle“

**Bachelor of Science (BSc) in** Physical Chemistry (04/2006 – 05/2009)

Faculty of Physical Chemistry, Ruhr-Universität Bochum, Bochum, Germany

Supervisor: Prof. Dr. M. Havenith-Newen

Title of thesis: “Einlagerung von molekularen Aggregaten in He-Nanotröpfchen”

**Scientific courses**

T 1 Basic concepts in materials science; T 2 Physical chemistry of surfaces and interfaces
T 3 Multiscale modeling; T 4 Deposition and properties of thin films and SAMs

**Fellowships and grants**

Research fellowship by International Max-Plank Research School SurMat (07/2011– 06/2014)

Research School+