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New methods of preparing third generation solar cells

Doctoral Thesis

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Academic Achievements

List of Papers

- **D. Augustowski**, P. Kwaśnicki, J. Dziedzic, and J. Rysz, Magnetron Sputtered Electron Blocking Layer as an Efficient Method to Improve Dye-Sensitized Solar Cell Performance, *Energies*, vol. 13, no. 11, p. 2690, 2020, doi:10.3390/en13112690.
- K. A. Bogdanowicz, **D. Augustowski**, J. Dziedzic, P. Kwaśnicki, W. Malej, and A. Iwan, Preparation and Characterization of Novel Polymer-Based Gel Electrolyte for Dye-Sensitized Solar Cells Based on poly(vinylidene fluoride-co-hexafluoropropylene) and poly(acrylonitrile-co-butadiene) or poly(dimethyl-siloxane) bis(3-aminopropyl) Copolymers, *Materials*, vol. 13, no. 12, p. 2721, 2020, doi:10.3390/ma13122721.
- **D. Augustowski**, M. Gala, P. Kwaśnicki, and J. Rysz, Efficiency Boost in Dye-Sensitized Solar Cells by Post- Annealing UV-Ozone Treatment of TiO₂ Mesoporous Layer, *Materials*, vol. 14, no. 16, p. 4698, 2021, doi:10.3390/ma14164698.
- **D. Augustowski**, M. Michalik, J. Wilgocki-Ślęzak, P. Kwaśnicki, J. Rysz, Scalable method for horizontal-dipping electrodeposition of platinum nanoparticles in application to dye-sensitized solar cells, *Electrochimica Acta*, submitted, dx.doi.org/10.2139/ssrn.4097923.

List of Patents

- A. Budkowski, J. Rysz, K. Awsiuk, P. Dąbczyński, **D. Augustowski**, Sposób wytwarzania warstw aktywnych polimerowych urządzeń optoelektronicznych, *PL Patent P.425043*, August 1, 2022.

Conference Contributions

- **D. Augustowski**, Organiczne ogniwa słoneczne tworzone metodą rozciągania roztworu, X Seminarium "Badania prowadzone metodami skaningowej mikroskopii bliskich oddziaływań STM/AFM", poster, December 2018, Zakopane.
- **D. Augustowski**, Metody tworzenia nanostruktur w zastosowaniu do ogniw słonecznych III generacji, 6th Scientific Conference "Energy Security - Pillars and Development Perspective", September 2021, oral presentation, Rzeszów.
- **D. Augustowski**, M. Gala, J. Rysz, P. Kwaśnicki, Efficiency Improvement of Dye-Sensitized Solar Cells by UV-Ozone Treatment of TiO₂ Mesoporous Layer, 18th International Conference on Nanosciences & Nanotechnologies, poster, July 2021, Thessaloniki.
- **D. Augustowski**, J. Rysz, P. Kwaśnicki, Efficiency Improvement of Dye-Sensitized Solar Cells by UV-Ozone Treatment of TiO₂ Mesoporous Layer, 11th International Conference on Advanced Vibrational Spectroscopy, flash presentation, August 2021, Cracow.
- **D. Augustowski**, Scalable method for platinum nanoparticles electrodeposition on conductive substrates, VII Scientific Conference "Energy Security – Pillars and Development Perspective", September 2022, oral presentation, Rzeszów

Symbols

• e	Elementary Charge
• E_g	Energy Band Gap
• FF	Fill Factor
• $h\nu$	Photon Energy
• I_{sc}	Short Circuit Current
• k_B	Boltzmann Constant
• m/z	Mass to Charge Ratio
• PCE/η	Power Conversion Efficiency
• P_{max}	Maximal Power Point
• q	Electric Charge
• R_s	Series Resistance
• R_{sh}	Shunt Resistance
• U_{oc}	Open Circuit Voltage
• λ	Wavelength
• λ_{emis}	Emission Peak Wavelength
• λ_{exc}	Excitation Peak Wavelength

Abbreviations

AFM	Atomic Force Microscopy
AM1.5	Air Mass Coefficient
ATR	Attenuated Total Reflectance
BSE	Backscattered Electron
CCD	Charge Coupled Device
CE	Counter Electrode
CV	Cyclic Voltammetry
DC	Direct Current
DSSC	Dye-Sensitised Solar Cell
EBL	Electron Blocking Layer
ECSA	Electrochemically Active Surface Area
EDS	Energy Dispersive X-ray Spectroscopy
FTIR	Fourier-Transform Infrared Spectroscopy
FTO	Fluorine-doped tin oxide
HOMO	Highest Occupied Molecular Orbital
I(U)	Current-Voltage Characteristic
IR	Infrared Light
IRRAS	Infrared Reflection Absorption Spectroscopy
ITO	Indium Tin Oxide
LUMO	Lowest Unoccupied Molecular Orbital
PET	Polyethyleneterephthalat
PAB	Poly(Acrylonitrile-co-Butadiene)
PDES-bAP	Poly(Dimethylsiloxane) bis(3-Aminopropyl)-Terminated
PVD	Physical Vapour Deposition
PVDF-HFP	Poly(Vinylidene Fluoride-co-Hexafluoropropylene)
RE	Reference Electrode
RF	Radio Frequency
SE	Secondary Electron
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectrometry
TCO	Transparent Conducting Oxide
ToF	Time of Flight
UV	Ultraviolet Light
VIS	Visible Light
WE	Working Electrode
WF	Work Function
WLI	White Light Interferometry

Theses

The aim of this dissertation is to develop and investigate new methods for the preparation of dye-sensitised solar cells. The thesis will focus of both scientific and technological aspects of their enhanced performance and applicability in mass production. The main research questions addressed in this dissertation are as follows.

1. Does organic impurities still present in the mesoporous layer of titanium(IV) oxide despite its annealing at high temperature?
2. Is the UV-induced ozone treatment efficient in removing organic residuals from the surface of mesoporous TiO_2 ?
3. How does UV-ozone treatment of mesoporous TiO_2 affect the performance of fabricated dye-sensitised solar cells?
4. Is it possible to use the magnetron sputtering PVD method to prepare an effective electron blocking layer?
5. How does a nanometre-thick coating of TiO_2 deposited directly on the FTO photoanode affect the performance of dye-sensitised solar cells?
6. Is the electron blocking layer effective in up-scaled solar cells?
7. Is it possible to implement the novel method of electrodeposition in sliding meniscus to produce a platinum-coated cathode for application to dye-sensitised solar cells?
8. What is the performance of electrodeposited platinum nanoparticles compared to commonly used screen-printed nanoparticles prepared from platinum paste?
9. Whether novel polymer-based electrolytes can replace typically used liquid electrolytes?

Abstract

The growing population on Earth consumes more and more electricity. Currently, the main source of power are conventional power plants, which burn fossil fuels to generate the electrical energy. As a result, we irretrievably deplete Earth's natural resources, devastate the environment and produce an excessive amount of carbon dioxide responsible for global warming. All of these factors lead to climatic changes that could have catastrophic consequences in our lifetime – melting glaciers, shrinking drinking water supplies, high temperatures and more frequent hurricanes. To stop the changes, we need to implement new green sources that are not so destructive to the Earth's ecosystem. One of the fastest growing methods of green power production in recent years is photovoltaics. The Sun provides our planet a large amount of energy, which we can convert to meet global electricity demand. To do this, further investment and research into solar cells is needed.

At least several approaches can be adopted to increase the cost-effectiveness of photovoltaic devices. Increasing the efficiency of solar-to-energy conversion is the simplest of these. However, taking a practical approach, we also need to reduce the production cost, develop new scalable manufacturing methods and improve their durability. Taking these factors into account, I focused on implementing them in my research on dye-sensitised solar cells, which belong to the third generation of solar devices.

The first chapter presents the results of increasing the power conversion efficiency. The adhesion of the dye molecules was significantly improved without changing the typical dye-sensitised solar cell architecture proposed originally by M. Grätzel. This was a consequence of an additional preparation step in which UV-induced ozone was used to clean the mesoporous titanium(IV) oxide layer of organic residuals from the platinum paste. The presence of organic residues was confirmed by Raman and FTIR spectroscopies, while the increase of dye adhesion was proven by absorbance and photoluminescence measurements. Furthermore, it was shown by secondary ion mass spectrometry that the adhesion was enhanced mainly in the subsurface layers of mesoporous TiO_2 . As a result of UV-ozone treatment, the efficiency of fabricated solar cells increased from 4.59 to 5.89%.

The next research was focused on the implementation of electron blocking layer. Its role was to reduce the recombination process at the interface of the FTO electrode and the electrolyte, which decreases the number of charge carriers that reach the external electrode and, as a result, has a negative impact on the efficiency of solar cells. The layer was deposited by magnetron sputtering, an example of physical vapour deposition (PVD) method. It is a widely used technique in industry and science that is able to produce nanocoatings with high precision and be scaled up to large formats. The TiO_2 layer deposited in this research was approximately 30 nm thick. It was characterised by optical profilometry, X-ray energy dispersive spectroscopy, scanning electron microscopy, atomic force microscopy and Raman spectroscopy. The presence of electron blocking layer increased the efficiency of laboratory-size devices from 4.67% to 6.07%.

Third chapter presents a novel deposition method for platinum nanoparticles. They act as catalysts in the reversible redox reaction in iodide electrolyte. The presented method is based

on electrodeposition in sliding meniscus. It can be up-scaled to large areas and enables control of the degree of platinum coverage within the substrate. The structures obtained were characterised by scanning electron microscopy and X-ray energy dispersive spectroscopy. Nanoparticles were almost perfectly spherical, but their size distribution was very wide. The electrocatalytic properties of FTO/Pt cathodes were investigated by cyclic voltamperometry. It was shown that electrodeposited samples exhibited superior catalytic efficiency in comparison to reference samples, which were prepared by platinum paste. Fabricated solar cells containing cathodes prepared with different deposition currents had comparable or even higher power conversion efficiencies (4.84-5.45%) compared to cathodes prepared by screen-printing method (5.14%).

The last chapter focused on replacing a liquid iodine-based electrolyte that is difficult in commercial use due to its high vapour pressure. Novel polymer-based gel electrolytes were prepared by the Military Institute of Engineering Technology in Wrocław. They were used to fill the dye-sensitised solar cell chamber to provide an electrical contact between the electrodes. Among various mixtures, the best performing one (5.07%) was composed of PVDF-HFP:PAB copolymers with a weight ratio of 9:1. According to the ageing tests, its efficiency decreased only by 7% in six weeks and then reached the plateau.

Streszczenie

Rosnąca populacja Ziemi zużywa coraz większe ilości energii elektrycznej. Aktualnie, głównym źródłem prądu są elektrownie konwencjonalne, których działanie opiera się na spalaniu paliw kopalnych. Efektem tego jest bezpowrotne zużywanie się zasobów naturalnych ziemi, dewastacja środowiska, a także nadmierna produkcja CO₂ odpowiadającego za ocieplanie się klimatu. Wszystkie te czynniki prowadzą do zmian na Ziemi, które mogą mieć katastrofalne skutki jeszcze za naszego życia – topienie się lodowców, kurczenie się zasobów wody pitnej, wysokie temperatury czy coraz częstsze huragany. Żeby zatrzymać postęp tych zmian potrzebne są nowe źródła energii, które będą źródłami odnawialnymi, dzięki czemu nie będą w tak dużym stopniu ingerować w środowisko. Jedną z najszybciej rozwijających się metod generacji prądu w ostatnich latach jest fotowoltaika. Wykorzystanie energii wysyłanej na Ziemię przez najbliższą nam gwiazdę w postaci promieniowania elektromagnetycznego może całkowicie zaspokoić globalne zapotrzebowanie na elektryczność. Aby mogło się tak stać, potrzebne są kolejne inwestycje i badania nad ogniwami słonecznymi.

Zwiększenie efektywności urządzeń fotowoltaicznych pod względem kosztów można uzyskać na wiele sposobów. Pierwszym przychodzącym na myśl jest oczywiście zwiększenie sprawności konwersji energii słonecznej w elektryczną. Jednakże, podchodząc do sprawy praktycznie, należy także obniżyć koszty produkcji, zapewnić skalowalne metody tworzenia ogniw, a także zwiększyć ich żywotność. Biorąc pod uwagę wszystkie te czynniki, skupiłem się na wdrożeniu ich w badaniach nad ogniwami barwnikowymi, należących do trzeciej generacji ogniw słonecznych.

Na początku przedstawione zostaną wyniki badań nad zwiększeniem sprawności ogniw. Nie zmieniając oryginalnej architektury ogniwa zaproponowanej przez jego twórcę – M. Grätzela, udało się znacznie podnieść adhezję barwnika do mezoporowatej warstwy tlenku tytanu(IV). Efekt ten uzyskano czyszcząc ją za pomocą ozonu indukowanego światłem UV, który usunął z jego powierzchni zanieczyszczenia organiczne pozostałe po procesie wypalania pasty tytanowej. Obecność pozostałości organicznych potwierdzona została metodami spektroskopii Ramana i spektroskopii FTIR. Zwiększenie przyłączonych molekuł barwnika wyznaczono za pomocą pomiarów absorbancji i fotoluminescencji wybarwionych warstw TiO₂. Ponadto, dzięki metodzie spektrometrii mas jonów wtórnych pokazano, że zwiększenie adsorpcji molekuł barwnika dotyczy głównie warstw przypowierzchniowych. W wyniku zastosowania czyszczenia metodą ozonowania, sprawność ogniw zwiększyła się średnio z 4,59 do 5,89%.

Następne badania dotyczyły zastosowania warstwy blokującej elektrony, która zapobiega rekombinacji nośników ładunku na granicy FTO i elektrolitu. Ten niekorzystny proces prowadzi do zmniejszenia ilości elektronów, które docierają do elektrody zbierającej, a co za tym idzie – do pogorszenia sprawności ogniwa. W celu depozycji nanometrycznej grubości powłoki wybrano metodę napyłania magnetronowego, będącego przykładem metody fizycznego osadzania z fazy gazowej (PVD). Technika jest dobrze znana w przemyśle i nauce. Jej zaletami są m.in. wysoka precyzja grubości i jakości powłok, a także możliwość skalowania na duże powierzchnie. Przed depozycją pasty tytanowej podłoża FTO pokryte zostały ok. 30 nano-

metrową powłoką TiO_2 , która scharakteryzowana została metodami profilometrii optycznej, spektroskopii dyspersji energii promieniowania rentgenowskiego, spektroskopii Ramana, skaningową mikroskopią elektronową czy mikroskopią sił atomowych. Dzięki zastosowaniu warstwy blokującej elektrony, sprawność ogniw o rozmiarach laboratoryjnych zwiększyła się średnio z 4,67 do 6,07%.

W kolejnym rozdziale skupiono się na nowatorskiej metodzie depozycji nanocząstek platyny, których funkcja w ogniwach barwnikowych polega na katalizowaniu odwracalnej reakcji redoks w elektrolicie ciekłym. Przedstawiona metoda jest połączeniem depozycji w przesuwym menisku oraz elektrodopozycji. Co istotne, daje się skalować na duże powierzchnie i umożliwia łatwą kontrolę stopnia pokrycia substratu platyną. Otrzymane struktury zobrażowane zostały metodami skaningowej mikroskopii elektronowej a także spektroskopii dyspersji energii promieniowania rentgenowskiego. Otrzymane nanocząstki były niemalże idealnie sferyczne, lecz posiadały duży rozrzut wielkości. Właściwości elektrokatalityczne zbadano za pomocą woltamperometrii cyklicznej. Wykazano, że zwiększenie stopnia pokrycia zwiększa efektywność katalityczną układu FTO/Pt w szczególności w porównaniu do nanocząstek przygotowanych tradycyjną metodą sitodruku z zastosowaniem pasty platynowej. Gotowe ogniwa słoneczne zawierające katody wykonane z różnymi prądami elektrodopozycji wykazały porównywalne, a nawet wyższe sprawności (4,84-5,45%) w porównaniu z katodami przygotowanymi metodą sitodruku (5,14%).

Ostatni rozdział poświęcony został wymianie elektrolitu ciekłego, który ze względu na dużą prężność par jest niepraktyczny do zastosowań komercyjnych. Nowatorskie polimerowe elektrolity żelowe przygotowane zostały przez Wojskowy Instytut Techniki Inżynierskiej z Wrocławia a następnie wykorzystane do przygotowania laboratoryjnych rozmiarów ogniw barwnikowych. Spośród wszystkich z nich najwyższą sprawność 5,07% wykazał ten bazujący na mieszaninie PVDF-HFP:PAB w stosunku wagowym 9:1. W trakcie testów starzeniowych pokazano, że sprawność elektrolitu w ciągu sześciu tygodni zmalała jedynie o ok. 7% a następnie ustabilizowała się.

Chapter 1

Introduction

The Earth is our common home, where all humans live together. No other planet has been found and settled by humankind yet. Therefore, this is the only place capable of accommodating about 7.9 billion people^[1] and guaranteeing good living conditions for everyone. Sometimes, people forget about that fact and overuse the global resources at a rapid pace, leading to earth pollution, environmental destruction, shortage of natural wealth, global warming and so on^[2]. On the other hand, the present society needs not only food, water and a place to live, as it was in the past centuries. The modern lifestyle forces us to use electrical devices to function normally. Card payments, communication, electric vehicles, internet use, mass production – all of that and many more activities like these need electricity to be used properly.

According to many studies^[3], global energy consumption increases year by year. In 2021, the produced energy was estimated at 557 exajoules (154,846 TWh), where *exa* is a unit prefix equal to 10^{18} . This number contains commercially traded fuels, including modern renewables that used to generate electricity^[4]. If we correlate the increasing earth population with the increasing demand for electric energy, we can expect that this value to rise exponentially over subsequent years. Surely, there will appear negative effects of that production. A great part of the energy is now produced from conventional fuels like coal, gas and oil^[4]. By the effect of their extraction, processing and combustion, we pollute our planet and make non-reversible damage to the environment we live in. To manage that scientists and engineers around the world are looking for more eco-friendly methods to produce electricity. One of the first ways to produce energy from renewable sources was the use of water flow in the rivers. There were about 200 working hydroelectric power plants in the United States^[5] by the end of the 19th century. Nowadays, countries with access to many waterfalls, like e.g. Norway or Switzerland, are able to produce up to 95% of their energy in that way^[6]. Another example is the power of the wind, which is well-known to conventional sailors. The first reported wind turbine used for the production of electricity was built in Scotland in 1887. This solution became popular in windy countries, such as Denmark or Holland, where today there are hundreds of wind power plants located on the land and in the sea, generating about 40-45% of the total energy used by them^[7]. The third most popular method is the photovoltaic effect. This phenomenon was discovered in 1839 by Edmond Becquerel and described in Nature^[8]. After more than a century of additional studies on the photovoltaic effect and novel photosensitive materials, researches from the Bell Laboratories were able to present in 1954 the first practical photovoltaic solar cell based on silicon^[9]. From then, the conversion efficiency of solar radiation to electric power was augmented from 6% to 30% in 2020^[10].

But why has the solar market been on the rise (see Figure 1.1) for the last years^[11]? At the beginning, we need to consider the amount of energy that the Sun provides to the surface of the Earth every day. The power density of solar radiation^[12] before it reaches the atmosphere is about 1360 W/m^2 . After absorption and reflection from atmospheric gases and pollutants, the solar power density near the surface is reduced to the average value of 1000 W/m^2 . Both

values vary, of course, because they change as a function of the Sun to Earth distance, cloudiness of the sky or localization on the Earth's surface. However, the total amount of solar radiation that reaches our planet globally is 3,850,000 exajoules (1,070,300,000 TWh)^[13]. It exceeds 8,000 times the total electrical energy consumed by the whole population^[14]. Thus, it is clearly visible that this substantial amount of energy is much more than what is produced and used every year. Similar contemplations encourage people to the development of solar market by granting research on novel photovoltaic materials, devices and production methods. All these efforts are focused on increasing the efficiency of solar cells, simplifying their production and lowering the fabrication costs.

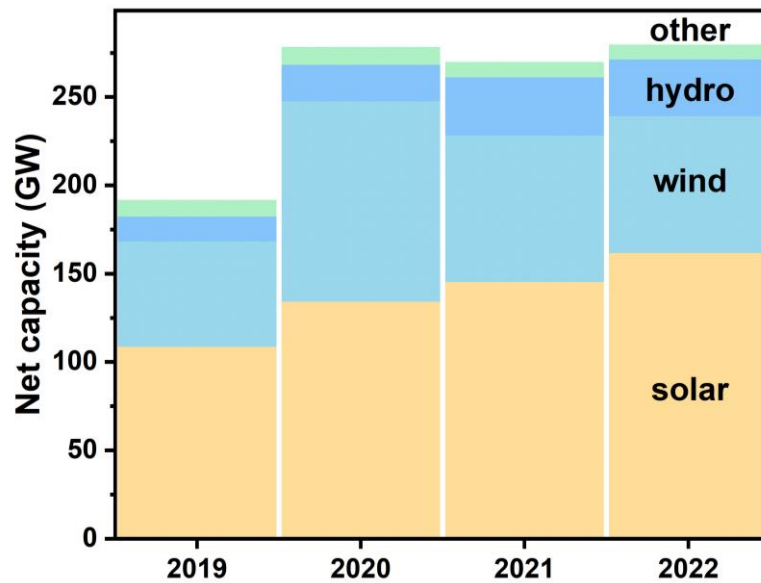


Figure 1.1. Net renewable capacity additions by technology^[15].

After centuries of studies, there is still much to discover and improve in the field of solar energy production. Scientists distinguish three generations of solar cells^[14]. The first one is well-known silicon-based photovoltaics. The solar market is totally dominated by this type of devices, which include mono- and polycrystalline materials. Another group is the second generation of solar cells. Here, we can enumerate the photovoltaics based on, for example, amorphous silicon, cadmium telluride (known as CdTe) or CIGS (a material composed of copper, indium, gallium and selenium in proper stoichiometry). These devices are much thinner than the first generation, which makes them cheaper in production. However, some companies that tried to commercialise those products failed and, in a few cases, went bankrupt^[16]. There is also a third generation, which is the youngest and has the greatest chance to be commercialized in the following years. This group includes dozens of possible materials and architectures. Therefore, the third generation is classified into several subgroups^[17], of which the most important are: CZTS (thin films based on copper, zinc, tin and sulphide), organic solar cells (blends of *n*- and *p*-type organic materials, such as conductive polymers, fullerenes and other small molecules), quantum dot solar cells (based on zero-dimensional semiconductor nanoparticles with a diameter below 10 nm), perovskite solar cells (materials with perovskite structure) and dye-sensitized solar cells (dye-sensitized semiconductors with a proper electrolyte).

Presented in this dissertation studies are focused on solving an essential problems, which typically occur in third generation solar cells. Among them we should mention the most important ones. The first thing comes to mind is the power conversion efficiency. The whole scientific world is competing now for new solutions to increase the rate of the light that could be converted to electricity. Thus, year by year, they report new world records^[18]. Secondly, this generation of solar cells is still sensitive to atmospheric conditions, like e.g. moisture, oxygen, ultraviolet light and temperature. Therefore, commercialization is still impossible, due to the low durability of such devices, which necessarily has to be improved. Another issue that is brought up in this dissertation is the mass production techniques of photovoltaic devices. Commercially available methods still correspond to high preparation cost, long deposition times and the need for high-tech systems, such as processes carried out in high vacuum or reactions using hazardous precursors. I place my hope that the results presented in this dissertation will help to create cheap and available for everyone well-performing photovoltaics. Perhaps one day, solar energy combined with other renewable sources will provide 100% of the energy for the population. Due to that, we will become independent of the fossil fuels that pollute the Earth, our planet, so much.

Chapter 2

Theoretical Background

2.1 Dye-sensitised solar cell – working principle

The concept of dye-sensitised solar cell was developed after discovery in late 1960s that organic dyes could be utilized to generate electricity from the sunlight^[19]. As a result of cooperation of M. Grätzel and B. O'Regan, the new type of photovoltaic device was invented in 1991^[20]. It was based on highly porous titanium(IV) oxide and dyes with an appropriate light absorption spectrum. Their invention was ten further developed by many scientists across the globe. It was described as economically and technically credible alternative for traditional photovoltaic devices based on *p-n* junction. There are four key elements of DSSC – the working electrode, photo-sensitizer, redox-mediator and counter electrode.

Generally, the FTO glass is used as a substrate for the DSSC fabrication. Its role is to pass the light through and collect the charge carriers. Because of that, any substrate for DSSC should has high transparency and possibly low resistance to reduce the energy loss in electric circuit. Deposited on the substrate *n*-type semiconductor should be cheap, transparent and conductive. Titanium(IV) oxide fulfils all these requirements, thus, it is widely used due to its easy availability, low cost, high energy band gap (3.2 eV) and relatively good electronic conductivity^[19]. Typically, the anatase phase is preferred^[21], because of a few factors. The first one is the energy band gap. The anatase has the gap of 3.2 eV, whereas the rutile form has a gap of 3.0 eV^[22]. This small difference cause that rutile absorbs more incident light, due to that less solar radiation is able to reach the dye and generate the photocurrent. After the chemical bath in the dye solution, the dyes covalently bond to the surface of TiO₂. As a consequence of the highly porous structure and, thus, a wide surface area, a large number of molecules are allowed to get attached, so the light absorption across the layer increases.

The dye is the most important element in the DSSC structure. It absorbs the visible light and makes it possible to convert the solar radiation to the electricity. According to Sharma et al.^[19], good dye for photovoltaic application should have a few key properties. Firstly, the molecule need to behave a luminescent effect. Its absorption spectrum shall cover the near UV, visible and near IR region. Secondly, the dye's LUMO level should be located possibly close, but be slightly higher, to the TiO₂'s conductive bands, whereas the HOMO should be located far from valence band. On the other hand, the HOMO shall lie lower than the redox potential level of the electrolyte. The dye must also be hydrophobic to provide a good operation and long-term stability. This is due to the fact that deformation of the dye from the TiO₂ surface can occur under the influence of water, which can reduce the durability of the solar cells. Finally, it should avoid aggregation over the TiO₂ surface, because the aggregation will lead to increased recombination effect^[23].

The third key element is the electrolyte, which is an electric mediator between two electrodes. Basically, it is composed of redox couple, solvent, additives, ionic liquids and cations. The first ingredient should be able to regenerate the oxidized state of the dye. Of course, it need to be stable in time under the solar radiation and be non-corrosive to other DSSC components.

Furthermore, it should not overlap with dye absorbance spectrum and exhibit a good ionic conductivity. Commonly, the redox iodine-based (I^-/I_3^-) electrolytes are utilized, but recently, they are replaced by other types, such as liquid, gel or solid electrolytes^[24].

The fourth element is the counter electrode. In most cases it is composed of FTO glass covered by platinum nanoparticles. When the photoanode and cathode are sealed together and the electrolyte fills the space between them, the platinum catalyses the reduction of ions in liquid electrolyte. Due to the presence of catalyst, the DSSC demonstrates augmented efficiencies. High cost of platinum inspired scientists to study at least few different cheaper materials that could replace it, for example, carbon^[25] or WO_3 ^[26].

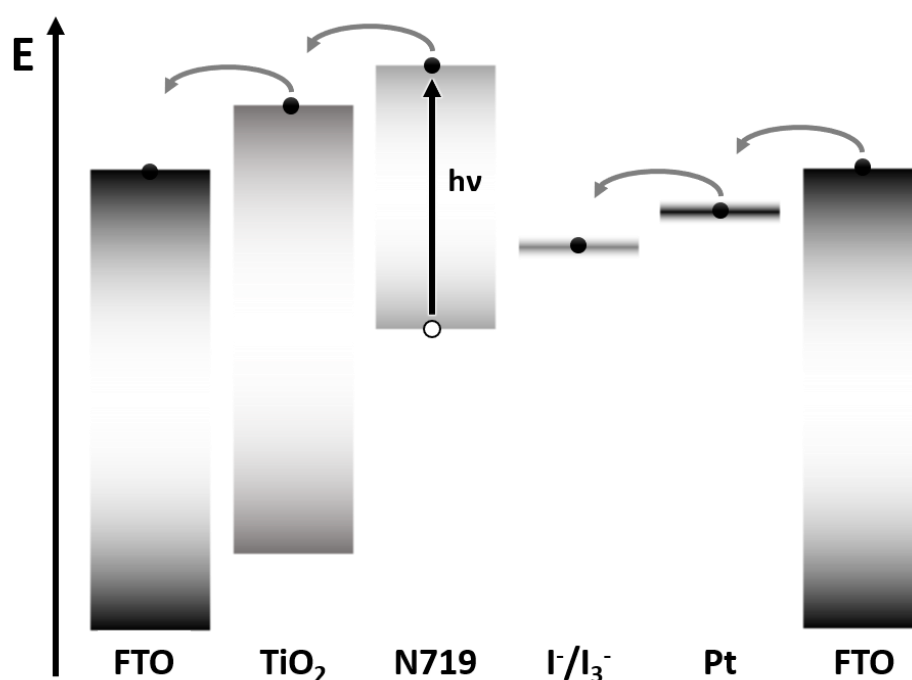
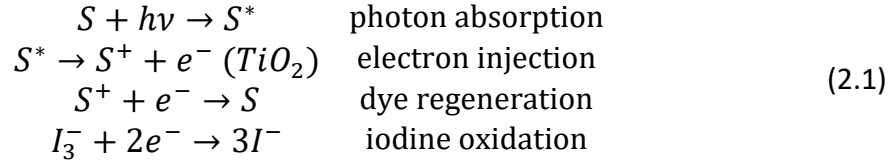


Figure 2.1. Working principle of DSSC shown on the energy level diagram.

Assembled as described device is then ready to perform as a solar cell. The working principle of DSSC could be divided to four basic steps: photon absorption, electron injection, charge carrier transport and collection^[19]. When the device is illuminated under the solar radiation, the incident photons are absorbed by dye molecules. As a result, electrons are promoted from the ground state to the excited state. The lifetime of such excited electron is reported to be in the range of nanoseconds^[19]. The energy between these two states is approximately equal or slightly lower to the energy of absorbed photon. Subsequently, the electron is injected into the conduction band of TiO_2 , which is placed below the excited state of the dye. In effect of that transition, the dye molecule gets oxidised. The injected electron is then transported through the TiO_2 to the collecting electrode (FTO layer). The electric current flows through the external circuit to the counter electrode, where the electrons are able to reduce I_3^- to I^- with a support of catalyst. Due to the acceptance of electrons from I^- redox mediator, the dyes are regenerated and the ions get oxidised back to the I_3^- form. After that, the ion is able to diffuse toward the counter electrode and reduce to the form of I^- . Overall, all those steps could be described as follows



where S and S^* corresponds to ground and excited state of a dye, respectively.

2.2 Equivalent electrical circuit of photovoltaic device

The solar cell device is typically represented by an equivalent circuit. An ideal model of such circuit is presented in Figure 2.2. It consists of a current source, a diode and an external load. When the solar cell is under illumination, the device works as a current source^[27], which provide a current I_{ph} . Some of that current counteracts the junction current of the diode and the residual current flow to the load. The junction current of the p - n diode, according to the Shockley's theory, could be described by the following equation^[28]

$$I_d = I_0 \exp\left(\frac{qV}{nk_B T} - 1\right), \tag{2.2}$$

where k_B is Boltzmann constant, T is temperature, I_0 is the reverse saturation current, q is the charge of electron and V is the output voltage, which could be understood as an applied voltage during the solar cell test^[27]. The n parameter is the ideality factor. When there is no carrier recombination and the diffusion current is dominant, it is equal to 1. However, in real solar cells its value varies on many parameters, such as solar cell type. In case of typical silicon-based photovoltaics it ranges from 1 to 2^[27], but for DSSC or OPV devices, it is typically higher than 2^[29].

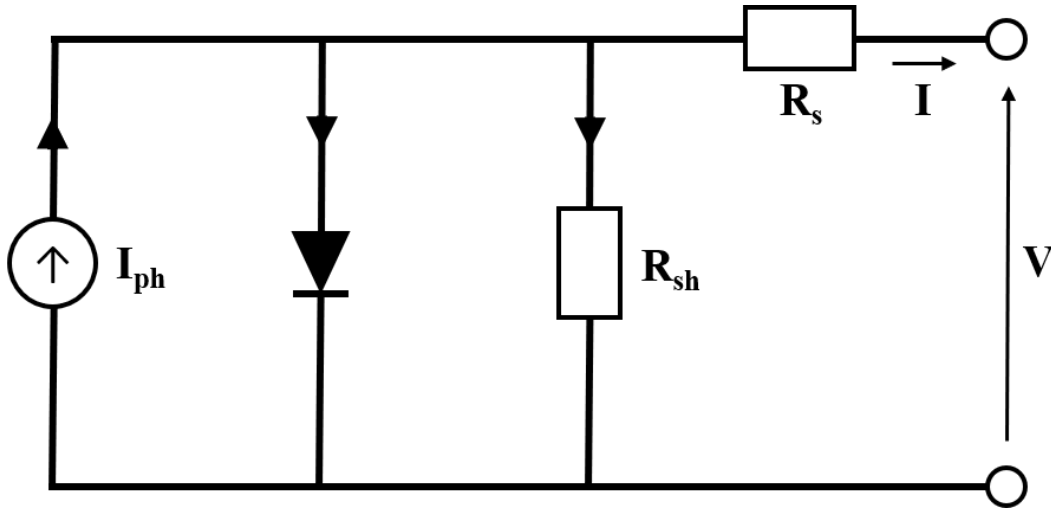


Figure 2.2. Solar cell equivalent circuit model.

Presented in the schematic model are also two important factors – series resistance R_s and shunt resistance R_{sh} . The first one corresponds to the sum of the resistive elements in DSSC structure^[30], such as collecting electrodes or photoanode semiconductor. The second one originates from various kinds of current leakage within the device. Taking into account all mentioned parameters, the current in photovoltaic device could be given by a following equation^[27]

$$I = \frac{R_{sh}}{R_{sh} + R_s} \left(I_0 \left[\exp \left(\frac{q(V - IR_s)}{nk_B T} \right) - 1 \right] + \frac{V}{R_{sh}} \right) - I_{ph} . \quad (2.3)$$

The equation is useful in the characterisation of solar cells. Once the current-voltage curves have been determined, it is possible to fit this equation to the measurement points. As a result, we obtain the photovoltaic parameters that are crucial to understand the performance of solar cell device.

Chapter 3

Experimental

3.1 Materials

3.1.1 TCO glass

Transparent conductive oxides (TCO) are a type of functional thin-film materials. TCOs are typically highly conductive and highly transparent metal oxides. They are usually prepared on glass substrates, but recently it became popular to prepare TCO on flexible substrates, such as PET foils. This unique pair of features makes them useful in a wide range of applications. For instance, they found an application in LCD displays^[31], touch panel contacts^[32], electronic inks^[33], antireflection coatings^[34], but also in photovoltaic devices^[35] as a transparent, conductive electrode. There are at least a few different coatings in TCO, but the most popular and commercially available are ITO and FTO.

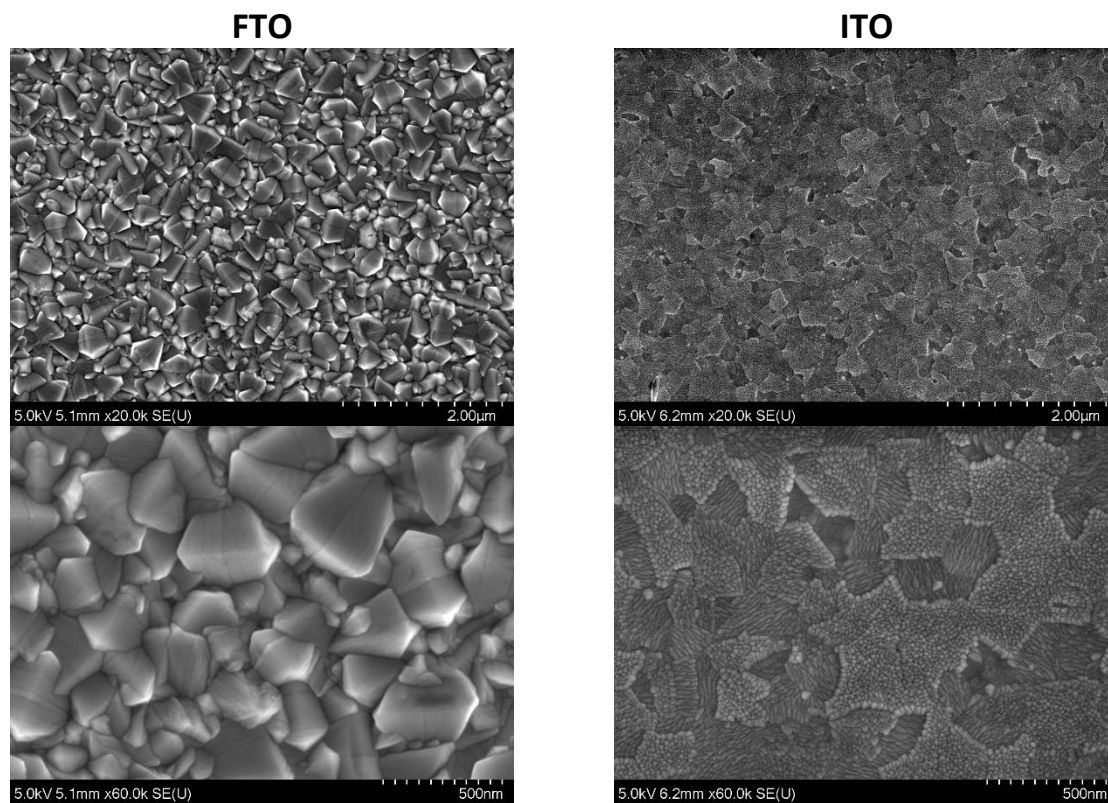


Figure 3.1. SEM images of FTO and ITO coatings in different magnifications.

The shortcut ITO stands for indium tin oxide. It is a material composed of indium and tin oxides with a percentage weight ratio of 90:10 ($\text{In}_2\text{O}_3:\text{SnO}_2$)^[36]. The electrical conductivity and optical transparency of ITO are relatively high. It has a transmittance of about 80-90% in the visible region^[37] and sheet resistance of 5 Ω /square for a thickness of more than 200 nm^[38]. The structure of ITO is typically represented by small grains connected together, which each of them is composed of smaller subgrains oriented in the same direction. One of the main disadvantage of this material is its instability at high temperatures. After annealing at temperatures higher than 150 °C, the resistivity of ITO increases significantly^[39]. Another

example of TCO is a fluorine-doped tin oxide (FTO, $\text{SnO}_2:\text{F}$). It is slightly less transparent than ITO^[40], but has similar electrical conductivity. It is widely used in DSSC devices, because FTO coating is more resistant to high temperatures^[39] used in the solar cell preparation process. It is also noteworthy that those coatings are soft, so it is really easy to damage them mechanically, e.g. by scratching the surface. Under the SEM microscope, as shown in Figure 3.1, the FTO layer is composed of various sizes of sintered grains.

3.1.2 Mesoporous TiO_2

Titanium(IV) oxide (TiO_2) is one of the most studied materials. It is a transition metal oxide, which occurs naturally. The colour of TiO_2 is white, thus it is widely used as an additive to paints, printing inks, plastics, ceramics, pigments and cosmetics^[41]. It exists in three crystalline forms: anatase, rutile and brookite^[42]. Each of them has different properties, such as energy band gap. For example, the rutile has the E_g of 3.0 eV, while the anatase 3.2 eV^[43].

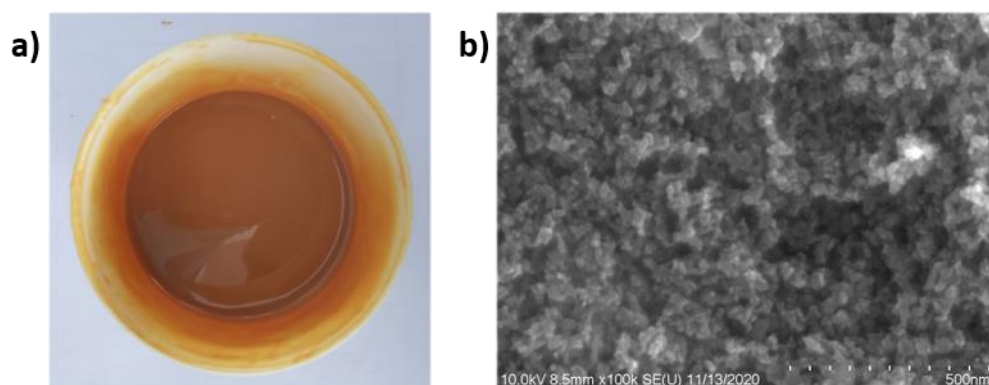


Figure 3.2. The photography of a) titania paste and b) SEM image of mesoporous TiO_2 morphology.

The anatase TiO_2 is a *n*-type semiconductor that is popular in photovoltaics as an electron transport layer (ETL). In the case of DSSC, it is used as a mesoporous layer – a structure with a very large surface area. Compared to the continuous layer of TiO_2 , the mesoporous structure increases the number of sites where dye molecules could adsorb. A titania paste (Figure 3.2a) is commonly used to produce such layer. It is a mixture of titanium(IV) oxide nanoparticles (with a specific dimension distribution) dispersed in organic suspension, which is often based on α -terpineol. After the deposition of the titania paste on the substrate, a wet layer has to be annealed at temperature above 500 °C to remove the organic fraction and receive a sintered mesoporous layer of TiO_2 (Figure 3.2b).

3.1.3 N719 dye

The N719 is a ruthenium-based dye, which is a modification of the popular N3 dye^[44]. The full name of this molecule is di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II). In comparison to the previous dyes, it is more stable, has a deeper HOMO energy level and exhibits an increased electrostatic binding to the TiO_2 surface^[45]. The N719 found an application as an efficient light absorber in DSSCs, where it can achieve U_{oc} of around 700 mV^[46]. The TiO_2 layers are commonly dye-sensitised by a chemical bath in ethylic solution of N719 in low concentration (e.g. 10^{-4} M).

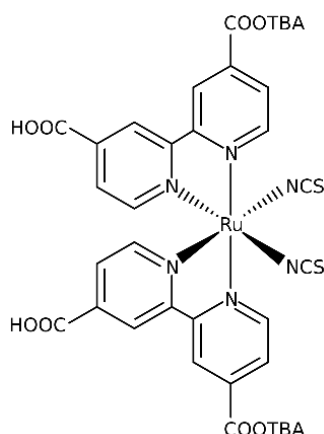


Figure 3.3. Schematic representation of N719 molecule.

3.1.4 Iodine-based electrolyte

To close the electric circuit between two solid parts in DSSC devices, liquid electrolytes are commonly used. One of the best performing is the iodine-based electrolyte, with a commercial name EL-HPE. It is a mixture of acetonitrile, valeronitrile, 1-butyl-3-methylimidazolium iodine, 4-tert-butyl-pyridine, guanidium, thiocyanate and iodine^[47]. This electrolyte is characterised by low viscosity, high conductivity and low boiling point. The latter feature is problematic as it leads to electrolyte leakage in the DSSCs after the long solar exposure, which is caused by the rise of the solvent pressure^[48]. The working principle of iodine electrolyte is based on a redox reaction of iodide (the ion of iodine, I^-), which is fully reversible.

3.1.5 Platinum nanoparticles

Platinum (Pt) is a transition metal, which is nowadays one of the most expensive and precious materials on the earth. Its unique properties are often used in many fields of science. For instance, it found an application in biomedicine, electrode systems or anticancer drugs. The platinum is a ductile material, but it is highly unreactive. Thus, it is widely used in electrochemistry as a counter electrode, because it does not react with most chemicals under ambient conditions^[49]. It has also found an application as a catalyst. For instance, platinum could be used as an electrocatalyst in different types of fuel cells^[50]. In photovoltaics, especially in DSSCs, it was applied to catalyse the redox reaction in the electrolyte, to provide a higher ion conductance in the circuit. In this case, the platinum nanoparticles are deposited on the FTO glass by the screen printing method from platinum paste. In contrast to titania paste, it does not contain platinum nanoparticles, but a small fraction (3-5%) of hexachloroplatinic acid in α -terpineol^[51]. At high temperature ($>500\text{ }^{\circ}\text{C}$) during the annealing process, the organic fraction is removed and the platinum in the H_2PtCl_6 is thermally reduced to Pt^0 and forms Pt nanoparticles.

3.2 Dye-sensitized solar cell preparation

3.2.1 Deposition of TiO_2 layer

The FTO glass sheet was cut into smaller parts with a specific dimension, typically $20 \times 20\text{ mm}^2$. The presence of impurities, such as dust or fatty oils, could affect further charge transport between other layers. To remove them from the surface, the substrates were cleaned in

an ultrasonic bath in acetone and isopropanol, sequentially for 15 minutes, and then dried under a dry nitrogen flow. The role of acetone is to remove organic contaminants, whereas isopropanol removes other physisorbed species. Firstly, to prepare the mesoporous TiO_2 layers, the titania paste (18-NRT) was mixed in a speedmixer for at least 5 minutes with a rotation speed of 2000 rpm. The substrates were then placed on the screen-printer platform. The screen with designed architecture was then positioned a few millimetres above the FTO glasses and the paste was applied to its surface. After the rubber squeegee pressed the screen, it started to move horizontally backward and forward to print the titania paste on the substrates. Afterward, the printed paste was left for a few minutes to settle and, thus, remove air bubbles from the bulk. When the air was no longer visible in the layers, the substrates were loaded into the tunnel dryer with four chambers with subsequent temperatures: 60, 90, 120 and 90 °C. This additional preheating step leads to solvent evaporation and slight solidification of the titania paste. These printing and drying steps were repeated thrice to obtain the appropriate thickness of the layer.

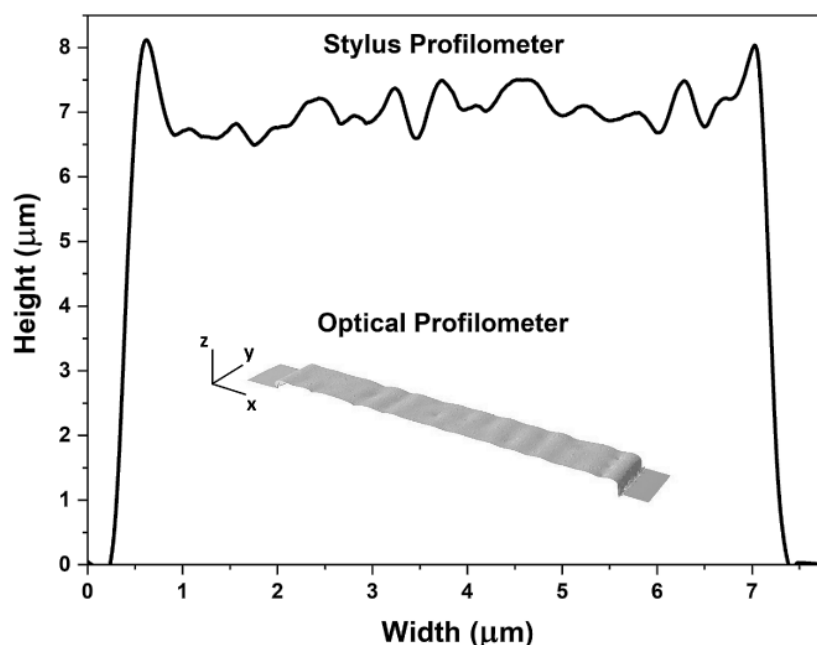


Figure 3.4. The height profiles of annealed TiO_2 mesoporous layer obtained by stylus and optical profilometers. The average thickness was approximately 7 μm .

Finally, the substrates with the deposited paste were annealed in the oven at high temperature. The maximal temperature was set to 565 °C to avoid the phase transition from anatase to rutile, which occurs at approximately 600 °C^[52]. The heating ramp was 200 °C per hour and the maximum temperature was held for 15 minutes. As a result, the organic compounds of the paste were completely removed, because only the inorganic part could withstand such temperature. The residuals evaporated in the form of carbon dioxide, water and other volatile molecules. Hence, TiO_2 nanoparticles were able to sinter together and form a few micrometres thick mesoporous layer of titanium(IV) oxide. An example of a height profiles for a 7 μm thick sample, obtained by a stylus and optical profilometers, are shown in Figure 3.4.

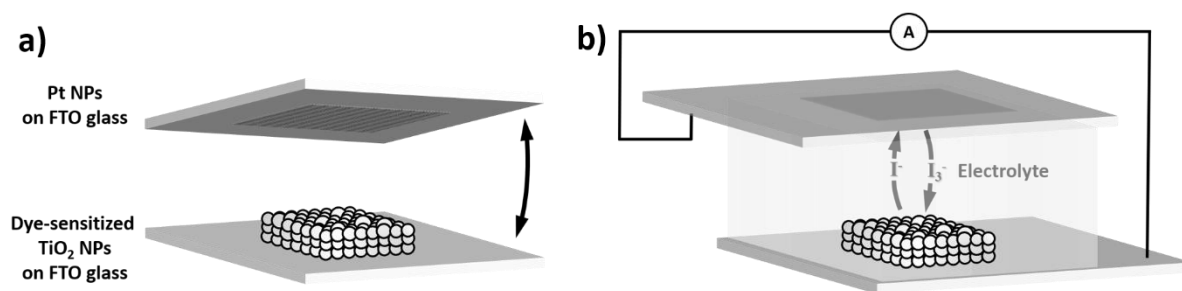


Figure 3.5. Schematic representation of a) photoanode and cathode, b) architecture of completed dye-sensitised solar cell.

3.2.2 Dye-sensitising of TiO₂ layer

The 10^{-4} M dye solution was prepared from the powder of N719 dye and pure ethanol (99.8%). It was mixed overnight on a horizontal mixer to receive a homogeneous solution. When the TiO₂ layers cooled down after annealing, they were immediately immersed in the dye solution. In effect of humid air, water molecules may be trapped in the mesoporous structure of TiO₂, which could affect the efficiency of solar cells by increasing the desorption and degradation of the dye^[53]. Thus, the time that readily formed layers are exposed to ambient air should be as short as possible. To obtain a good sensitization rate of the dye, the substrates should be immersed in the solution for at least 24 hours. The container with solution was additionally placed on the horizontal mixer with a slow rotation speed of 80 rpm, to enhance the dye molecules penetration within the mesoporous layer. After that, to remove any unadhered dye molecules, the substrates were rinsed with ethanol and dried with dry nitrogen stream. Thereafter, the sensitized photoanodes were immediately sealed with the cathode, because ambient conditions, such as UV light, moisture or oxygen, could lead to the dye degradation, which significantly reduces the solar cell's efficiency^[54].

3.2.3 Deposition of platinum nanoparticles

Another part of cleaned FTO glasses was covered by platinum nanoparticles. Its role is to catalyse the redox reactions of the electrolyte on the cathode. As it was in the case of titania paste, the platinum paste was deposited by screen printing method. The paste was first mixed in the speedmixer, printed through the screen with proper architecture, preheated in tunnel dryer and, finally, annealed at high temperature to remove the organic compound. As a result, nanoparticles were able to cover the FTO surface. Prepared as described platinum layer typically contains chaotically distributed nanoparticles. The particles have no contact with each other and each of them is an active centre for redox reaction for the surrounding iodide ions.

3.2.4 Electrodes sealing and electrolyte filling

To seal both the photoanode and the cathode, lamination foil with a thickness of 60 μm , was used as a sealant. After the assembly of the anode, foil and cathode in a sandwich-like structure, they were placed in the laminator. As a result of high temperature (about 120 °C) and pressure, the lamination foil melted and stuck to both surfaces, adjoining them together. Before cleaning, a small hole was drilled in the cathode FTO glass. Therefore, after the lamination, the space between the electrodes was filled through those holes with liquid

iodine-based or gel electrolyte, depending on the experiment. It was important to remove any air bubbles from the inside, because air decreases the efficiency of the DSSC, e.g. by disturbing the ion current through the electrolyte. When the drilled holes were already sealed by an additional glass cover to prevent the leakage, the solar cells were then ready for further measurements.

Chapter 4

Measurement Methods

In this dissertation a variety of analytical methods were used to better understand the nature of the samples and investigate the changes in them. This chapter will present the main techniques that were applied in the research. In general, they can be divided into three principal groups: imaging, spectroscopic and electrical methods. As all of them are well-known and commonly used, they are only briefly overviewed within this chapter.

4.1 Stylus profilometer

The profilometry is a simple method of measuring the surface profile of a sample. Typically, its function is to receive a profile, which is then used to quantify the roughness, the curvature or the flatness of the tested surface^[55]. In some cases, for instance, when the coating is not present on the whole sample, it is possible to calculate the thickness of the material by measuring the step height between the substrate and the coating.

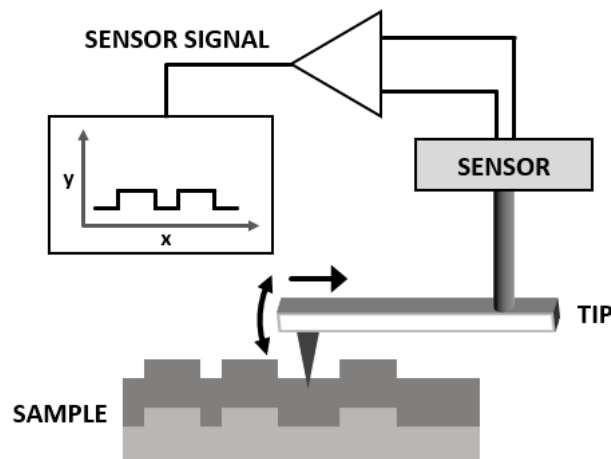


Figure 4.1. Schematic diagram of the stylus profilometer instrumentation.

A common representative of such devices is a stylus profilometer. In simplicity, it contains a stylus probe which is able to move horizontally along the sample surface^[56]. The contact force should be constant during the measurement, and, in case of soft samples, should be previously adjusted to avoid the material's damage. The stylus is attached to the scanner that can measure the level of the probe deflection, typically ranging from ten nanometres to few millimetres, depending on a device. The scanner generates signal, which is subsequently analysed by a computer and then displayed on the screen. Standard diagram contains the scan distance on the horizontal axis and sample height profile on the vertical axis. Contrary to atomic force microscopy, where the probe end is atomically sharp, the stylus in profilometer is typically round and has the radius dimension from tens of nanometres to even tens of micrometers.

4.2 Optical profilometer

In contrast to the stylus profilometry, the optical profilometry is a non-contact method of surface characterization, thus, it is a safe technique with a low probability of damaging the

sample^[57]. As in the previous case, it is possible to measure a step height, a sample roughness or convexity. To obtain the topography map, it uses an electromagnetic wave within the range of visible light. Typically used in this method is the white light interferometry (WLI) mode^[58].

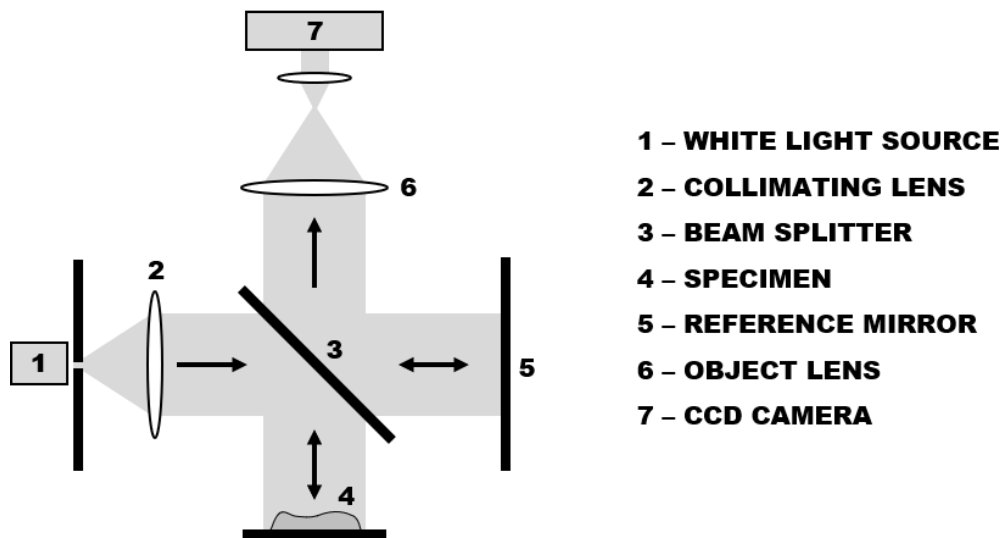


Figure 4.2. The working principle of optical profilometer.

When two light beams of the same wavelength combine, the resultant electromagnetic wave's amplitude depends on the phase difference between them and the initial amplitudes. For instance, if two waves of the same amplitudes are 180 degrees out of phase, there is a destructive interference, which means that the wave is cancelled^[59]. On the other hand, when the waves are in phase, the constructively interfered wave will have the doubled amplitude. In WLI mode we use a wide range of visible wavelengths, which causes that the light has white colour. One of the light beams is reflected from a sample and the second one is reflected from the built-in reference mirror. As a result of their mixing, the phase of reflected light is changing. The shift is a function of the path length – the height of the sample, thus, at a given location on the surface the constructive and destructive interference corresponds to a different height. The interference fringes – observed in the camera patterns of bright and dark areas, are collected while varying the distance between the lens and the sample. An appropriate algorithm is able to calculate the absolute height differences and determine a topography map – a matrix of height values for X and Y coordinates. This method is characterised by fast imaging and high resolution (up to 0.1 nm). Unfortunately, not every sample could be measured by an optical profilometer. The main requirement is that the sample's surface has to be highly reflective, smooth and not to be optically active.

4.3 Atomic Force Microscopy

The atomic force microscopy (AFM) is a type of scanning probe microscopy (SPM). The history of AFM began in 1985, when G. Binnig and his co-workers built the first prototype^[60]. They declared that their device is capable to measure the forces up to 10^{-18} N and create a topography maps with a lateral resolution of 3 nm and vertical resolution of 0.1 nm. Nowadays, the atomic force microscopy is a popular and precise method to observe nanostructures, calculate a roughness parameters^[61] in nanoscale or manipulate nanoobjects with the use of atomically sharp tip^[62].

The operation of AFM is based on well-known Hooke's law, which describes the sample surface interactions with a very sharp tip^[63]. The tip is located on a flexible cantilever. When its end touch the sample, the cantilever bends. The deviation level could be analysed by a simple laser beam system. Firstly, the incident light illuminates the end of the cantilever, which is highly reflective. The reflected light is detected on the photodetector with four independent segments. Each one measures the intensity of incident light. When the cantilever is in a neutral position, segments detect the same signal, because each one is illuminated with the same intensity. But when the cantilever bends, the light beam shifts its position on a detector, so the signal on each segment is different. By a simple analyse, we are then able to verify, if the cantilever bends vertically

$$S_{vertical} = \frac{(A + B) - (C + D)}{A + B + C + D} \quad (4.1)$$

or horizontally

$$S_{horizontal} = \frac{(A + C) - (B + D)}{A + B + C + D} \quad (4.2)$$

where the A , B , C and D are the signals measured on respective segments sketched in Figure 4.3. The second case is often use when the lateral force is measured, e.g. in a friction measurements. A very precise relative movement of the sample and the tip is realised by a piezoelectric scanner. When a voltage is applied, a piezoelement extends or contracts, hence, move the sample in X/Y directions. After acquiring signals in many coordinates, it possible to receive a heights matrix, which could be drawn as topography map.

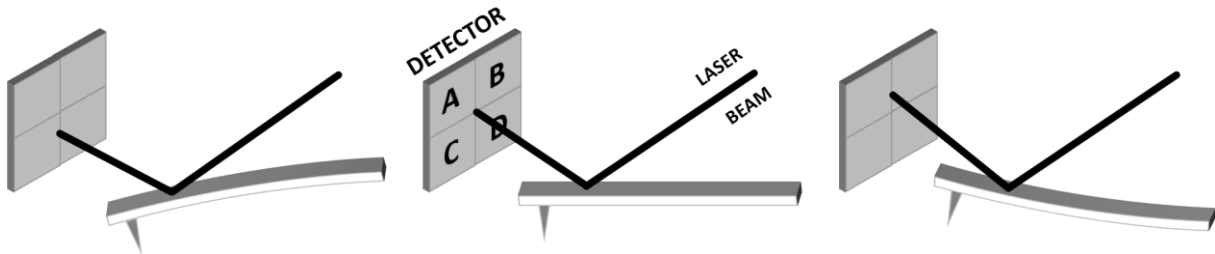


Figure 4.3. Schematic representation the cantilever deflection measurement using a photodetector with four independent segments.

There are three basic modes of operation to conduct the measurement by AFM^{[64]-[65]}. In the simplest, contact mode (C-AFM), the tip is in contact with the sample surface. The distance between them is only a few angstroms ($1 \text{ \AA}$ is equal to $10^{-10} \text{ m} = 0.1 \text{ nm}$), so only the repulsion forces are measured. If the microscope is working at constant force mode, the feedback system changes the sample height during the scan, thus, the built-in software analyses the signal changes to draw a topography map. When the C-AFM is used, there is a high risk of sample or tip mechanical damage. For this reason, this mode is rarely used to examine soft samples, like e.g. biological tissues or polymer coatings.

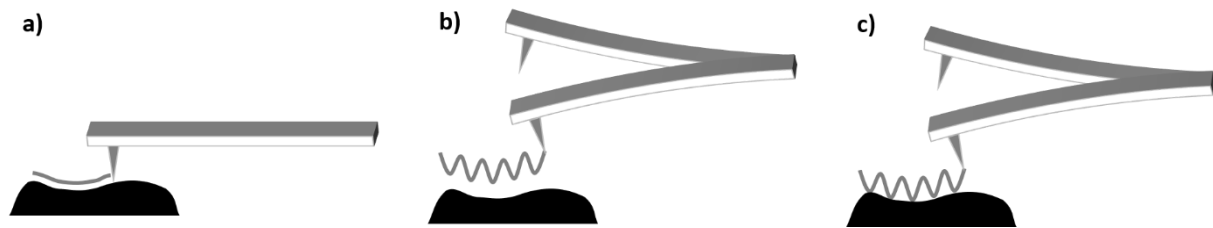


Figure 4.4. Three basic AFM modes: a) contact mode (C-AFM), b) non-contact mode (NC-AFM) and c) tapping mode (TM-AFM).

The next mode is a non-contact mode (NC-AFM). In this case, the tip moves above the sample surface at a height of tens nanometres and oscillates quickly. Attractive forces, mainly the van der Waals forces, attract the tip which causes the change in cantilever oscillation. The electronic feedback tries to keep the constant force, understood as maintaining a stable oscillation parameters. This mode enables to distinguish two different materials, when the sample surface is relatively flat. It is possible, because the tip could be attracted with different force by each material, what is manifested as a change in oscillation phase. The third mode is a combination of two described above methods and it is known as tapping mode (TM-AFM). Here, the cantilever is oscillating with a high amplitude (10-100 nm). As a result, the tip is tapping the sample continuously during the measurement. While the scanner is scanning the surface, the software analyse the change in oscillation amplitude or oscillation phase shift. Due to the short contact between the tip and the sample, the TM-AFM is capable to provide a high-resolution topography maps and not destroy soft materials^[66]. Thus, it is commonly use to examine sensitive samples, which are easy to damage by hard and sharp tip's end.

4.4 Scanning Electron Microscopy

The scanning electron microscopy (SEM) is similar to optical microscopy to some extent. Traditional optical microscope uses visible light to image the sample, while SEM uses a focused accelerated electron beam. The resolution of the first one is limited by electromagnetic wave's diffraction properties, which is a function of wavelength. Electron microscopy has significantly higher resolution, because electrons have a shorter wavelength. Due to that they are more energetic than photons in the visible range and the diffraction effect occurs at much smaller physical dimension. Thus, the SEM is capable to produce an image from micro- to nanoscale with a magnification up to 3,000,000 times^[67]. Its history began in 1931, as a result of the work of M. Knoll and E. Ruska, which was based on new de Broglie's hypothesis of the "material wave"^[68]. The first microscope was finished in 1935^[69]. Since then, many technical limits had to be overcome. Today, electron microscopy is a popular, efficient and well-known method to observe the world in nano and even atomic scale. It is widely used to provide high resolution images in materials science^[70], biology^[71], geology^[72], microchip production, semiconductor inspection^[73] and many more fields of science and industry.

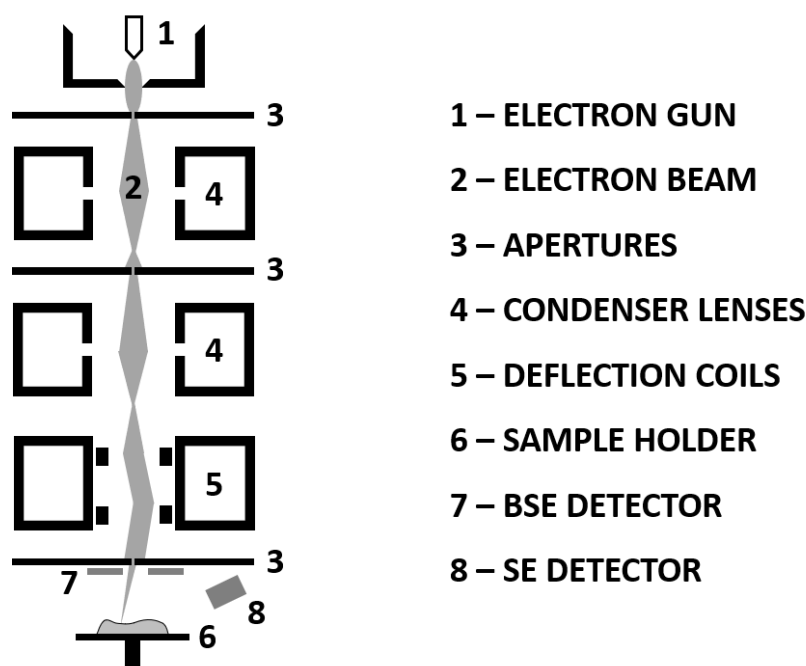


Figure 4.5. Schematic diagram of electron beam formation in SEM.

As mentioned above, in SEM a beam of accelerated electron is used^[74]. Firstly, the electrons are emitted from a source, such as thermionic filament (typically a heated to high temperature tungsten cathode) or field emission gun (FEG), which generates a strong electrical field that pulls the electrons away from their atoms. The electrons could be accelerated to low (0.2 eV) or high (up to 40 keV) energy and then the beam passes through the lenses and scanning coils. Their role is to form highly focused spot, which size is below 5 nm in diameter. The best microscopes are able to reduce its size to 0.4 nm to provide a high resolution images. The last lens deflects the beam in XY plane, thus, the build-in software is able to control the direction of the scanning beam over the sample's surface with a high precision. When electron reaches the analysed material, its energy decrease in effect of repeated random scattering within a teardrop-shaped volume, which size depends on electron energy, sample density and few other specimen parameters. After the energy transfer, secondary (SE) or backscattered (BSE) electrons are emitted. They are a result of inelastic and elastic scattering, respectively, and both of them could be independently detected.

The secondary electrons come from a layer within a few nanometres below the sample surface. These electrons are ejected from the sample atoms after the energy transfer from accelerated primary electrons. Their energy is low, typically it does not exceed 50 eV. The SE are very sensitive to the surface structure, thus, they provide topographic information with a resolution of even 0.5 nm. Another type of possibility to detect electrons is the BSE mode. Their energy is higher than SE (>50 eV). As a result of elastic scattering, primary electrons reflect on the specimen atoms, losing a small amount of their energy. They originate from the deeper layers of the sample – up to few micrometres below the surface. Because elements with high atomic number backscatter these electrons more strongly than elements with low atomic number, the BSE provide information about a chemical composition, which is visible as a contrast on the image. In comparison to SE mode, the BSE images have lower resolution.

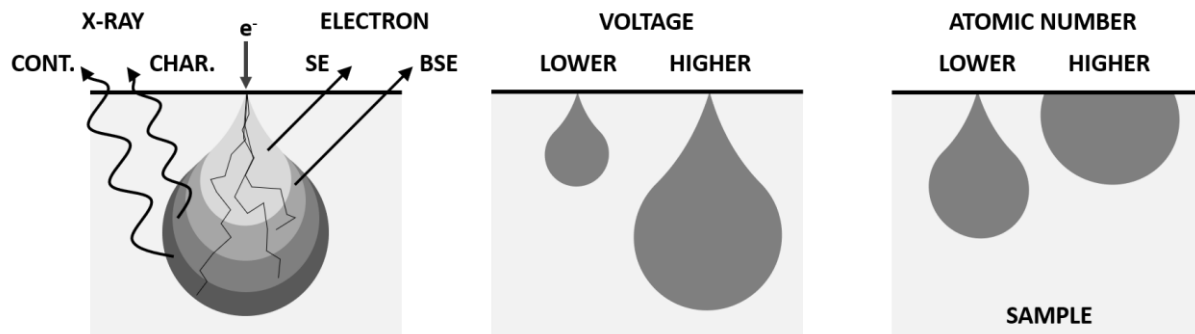


Figure 4.6. The teardrop interaction volume of electrons with a sample. The secondary electrons (SE), backscattered electrons (BSE), characteristic X-ray (CHAR) and continuous X-ray (CONT) are released in different depths. The volume shape varies depending on e.g. primary electrons acceleration voltage or the atomic number of the sample elements.

4.5 Energy Dispersive X-Ray Spectroscopy

The energy dispersive X-ray spectroscopy (EDS or EDX) and SEM are often utilised together, because they can use the same source of electrons^[75]. In this method the Röntgen rays, created by the interaction of accelerated electrons and sample atoms, are analysed. The EDS provides information about the elemental composition of the specimen with a detection limit of 1000 ppm. It is a powerful technique for quick analysis of materials that are composed of elements with an atomic number greater than boron ($Z > 5$). It could be applied to various types of measurements, such as material identification, contamination analysis or even the creation of two-dimension maps of element distribution^[76].

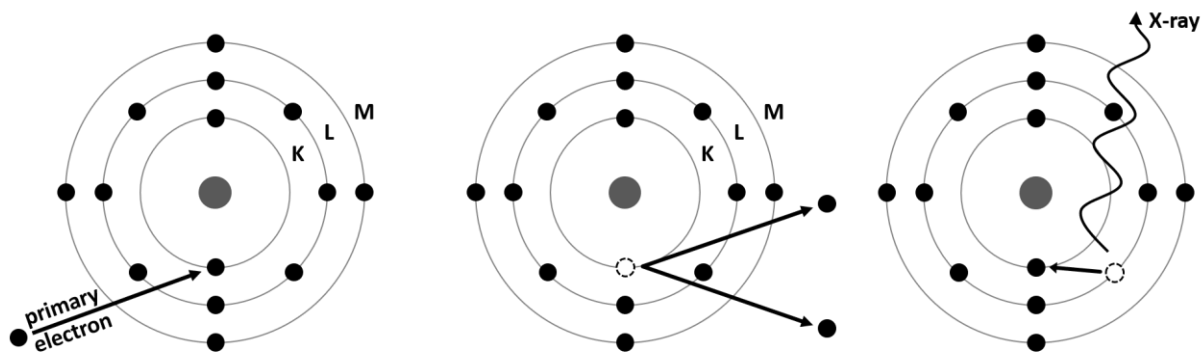


Figure 4.7. The mechanism of creating X-rays in the sample as a result of electrons bombardment.

Characteristic X-ray radiation is, like in SEM, generated by a highly accelerated electron beam, which reaches the sample. As a result, the shell electrons are ejected from the inner shells – orbitals that are closest to the nucleus. The electron hole, created in the position of the removed shell electron, is then filled by the electron from an outer, higher-energy shell. It is due to the fact, that every system in the universe is trying to reach its energetic minimum, because it is thermodynamically preferable. After the relaxation, the difference in energy between these two shells is released in the form of an X-ray. The energy of radiation is characteristic for every element, like an energetic fingerprint, and could be analysed to provide the elemental composition of the sample. The primary electrons that do not interact

with the sample are going deeper. An effect of their rapid deceleration in the crystal lattice is the electromagnetic radiation in the wavelength range of X-rays, which is known as Bremsstrahlung. It is typically seen in the EDS spectrum as a background and it is not further analysed. This method is recommended for the analysis of flat samples, because the surface structures in rough samples could completely absorb the X-rays before they reach a detector. It is also not suitable for thin coatings below 100 nm, due to the fact that the radiation is mainly generated in the deeper part of the sample. This depth is strictly related to the energy of the primary electrons and the atomic number of the elements present in the specimen. The phenomenon of material penetration of energetic electrons was described by the K. Kanaya and S. Okayama^[77]. They formulated the empirical formula for the penetration depth, which is

$$R_{KO} = \frac{0.0276A}{Z^{0.89}\rho} E_0^{1.67} \quad (4.3)$$

where A is atomic mass number, ρ is a material density (g/cm^3) and E_0 is the energy of the electron. Typically, for higher energies (>10 keV), its value ranges from 1 to 5 microns. Every element has its own characteristic X-ray energy, which is related to the energy difference between the shell electrons. Heavier atoms could have a plenty of different lines. The first shell, the closest one to the atomic nucleus, is marked by K letter, the second L, the third M and so on. In EDS method, the characteristic lines are defined by the one Latin and one Greek letter. The first one describes at which shell the electron vacancy occurred (K, L, M etc.) and the second gives the information about at which shell was the vacancy-filling electron that have dropped down (α , β , γ etc.). For example, if the electron was removed from the K shell and filled by the electron from the L shell, then the line is $K\alpha$. But when the vacancy is filled by the electron from M shell, then the line is labelled as $K\beta$. The graphical explanation is shown in Figure 4.8.

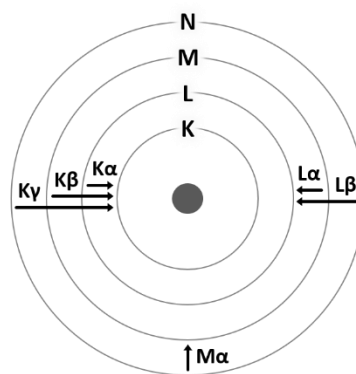


Figure 4.8. Schematic representation of the description of the characteristic lines in EDS method. First letter represents the shell with electron vacancy, while second describes at which shell was the vacancy-filling electron.

4.6 UV-VIS-NIR Spectrophotometry

Light could interact with the matter in various ways. We can distinguish the light absorption, transmission and reflection^[78]. Each of these phenomena depends on the electromagnetic wavelength, which analysis provides valuable information about the sample's properties. The

first device –spectrophotometer – for such measurements was built by A. Beckman^[79] in 1940. This product was then developed to measure better characteristics in ultraviolet and a method became very popular to characterise different kinds of materials. There are three simple measurement modes. In each of them, the device calculates the difference between the power of light beam with and without a sample. Commonly, spectrophotometry is used in science, for instance, to determine the optical parameters of different materials^[80], calculate an optical band gap^[81] or solution concentration^[82]. It is also a popular technique in industry, e.g. widely used in production quality control^[83].

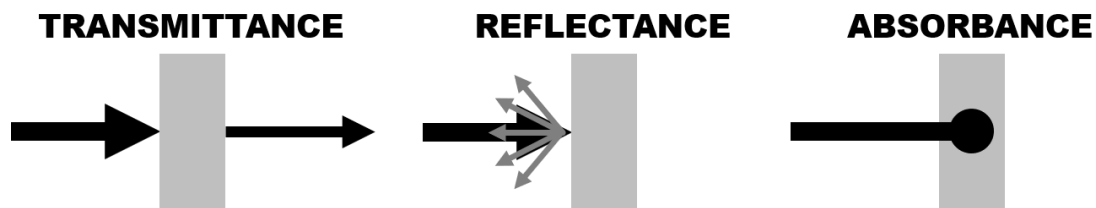


Figure 4.9. Three possible mechanism of light interaction with a material: transmission, reflection, absorption and three spectrophotometric modes: transmittance, reflectance and absorbance.

The first mode is reflectance. In this case, the incident light reflects from a sample surface, and then the light spectrum of the reflected beam is measured by a photodetector. This measurement can be carried out at different angles. When the bunch of optical fibre is used – the cable with several fibre optics in one tube, the reflectance could be measured with zero angle. The easiest way is the measurement with specific angle (5-85°). The light beam reflects on the sample surface and then reaches the detector. The most comprehensive method is to use a integration sphere to measure almost all of the reflected photons. In this case the light beam goes through the small hole in the sphere and is directed to the sample on the opposite side. The light, which is not reflected, goes through the sample, but the reflected photons are collected by the integration sphere wall, thus, the light spectrum could be measured by a photodetector. This technique is known as absolute reflectance measurement, because we are able to collect all of the reflected light in an angle range of 5-90°.

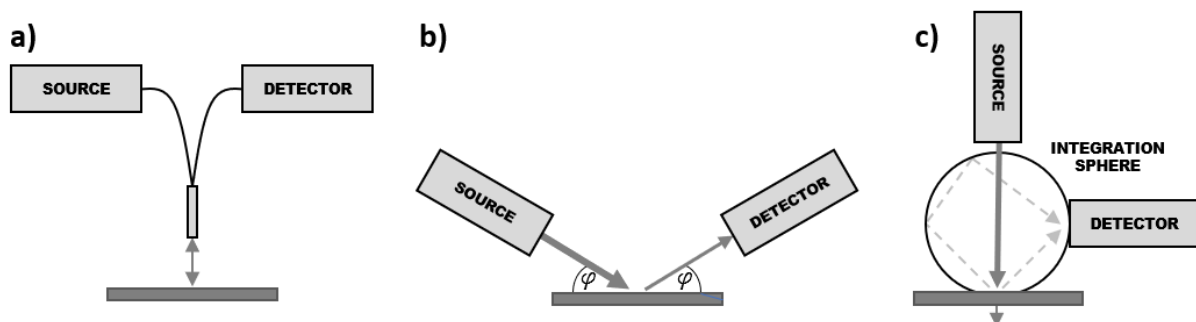


Figure 4.10. Three methods of reflectance measurements: a) zero angle with a optic fibre, b) specific angle and c) absolute reflectance with integration sphere.

To describe this phenomenon the term of reflectance is commonly used. Its value (in percent) is the ratio of the incident light power (P_i) and the power of reflected light (P_r)

$$R(\lambda)\% = \frac{P_r}{P_i} \cdot 100\% . \quad (4.4)$$

Obviously, due to some losses, not 100% of the light is acquired. Some light is backscattered through the hole and the material, which coats the integration sphere inner wall could absorb some range of wavelengths.

Two other modes – the transmittance and absorption, are closely correlated. Here, the light passes through the sample and the light power is detected on the opposite site. Those measurements are typically conducted with the incident angle of zero. The transmittance is a percentage ratio of incident and transmitted (P_t) light powers, described by the following equation

$$T(\lambda)\% = \frac{P_t}{P_i} \cdot 100\% , \quad (4.5)$$

while the absorbance – the value, which gives information on what amount of light was absorbed by the sample, is correlated with the transmittance and equal to

$$A = \log_{10} \frac{P_i}{P_t} = -\log_{10} T(\lambda) . \quad (4.6)$$

The typical spectrophotometric spectrum consists absorbance, reflectance or transmittance on vertical axis and the wavelength on the horizontal axis. Such analysis is possible, because every spectrophotometer has the built-in monochromator (typically it is a grazing diffraction grating), which disperse the white light beam to the specific wavelengths^[84]. Thus, the device is able to characterise optical properties of sample at every particular wavelength, which commonly is done in the range of ultraviolet, through the visible, up to the infrared light. Good quality devices are capable to carry out the measurements from 200 to 2500 nm, which is mainly determined by included lamps, which have to emit the continuous light spectrum from UV to IR.

4.7 Spectrofluorometry

The spectrofluorometer, known also as a fluorescence spectrometer, is a device, which was designed to measure a luminescence effect. Spectrofluorometry is a variation of electromagnetic spectroscopy, where the fluorescence and phosphorescence could be analysed. This method is widely used in biological^[85] and chemical^[86] analysis. In the field of environmental measurements, it is sometime used to monitor the water quality by detecting bacterial contamination^[87] or organic pollutants^[88].

The luminescence effect can be divided into a few steps. Firstly, a molecule absorbs a photon (A) of specific energy ($h\nu$). After that, the molecule excites from a ground electronic state (S_0) to one of the singlet excited states ($S_{i \neq 0}$), which is determined by the selection rules. Every excited state has its own individual vibrational states. To reach the possibly lowest state, the vibrational energy is lost in a form of thermal energy. This process is typically known as vibrational relaxation (VR). When the molecule is already in the lowest vibrational state, the relaxation process occurs, which means that the molecule drops down to the ground state. During that process, the molecule emits a photon with an energy equal to the difference between the excited and ground state levels, which is known as fluorescence (F). Described

above phenomenon is often visualised by a Jabłoński diagram^[89], named after a polish scientist A. Jabłoński, who published his concept in Nature in 1933.

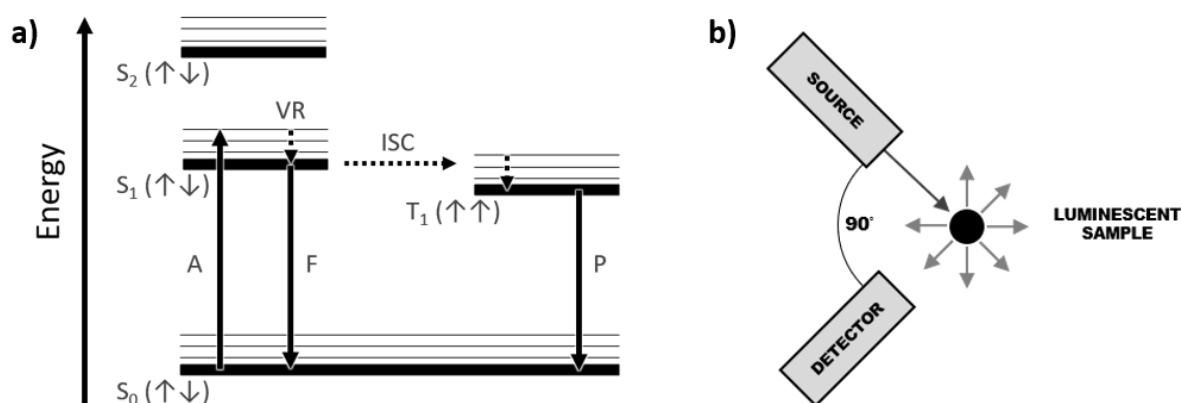


Figure 4.11. Schematic representation of a) Jabłoński diagram and b) spectrofluorometer instrumentation.

The diagram illustrates also a phosphorescence effect (*P*). In this case, after the photon absorption, the molecule excited firstly to the one of the singlet state. The materials, which exhibit phosphorescence effect, can then transit to the excited triplet state (T_1) by an intersystem crossing (*ISC*) transition. After losing its vibrational energy, in the same way as described above, the possibly lowest state is reached and then the molecule drops down to the ground state with simultaneous photon emission. However, at this condition, the relaxation process last longer. To distinguish that two phenomenon in macroworld, the scientists described the typical relaxation times of phosphorescence as higher and fluorescence as lower than few microseconds, but there is no a specific value.

In most instances, the spectrofluorometer instrumentation consists a light source, a sample holder, a diffraction grating monochromator and a detector. After mounting the sample, the slit from the light source is open. The incident light is absorbed by the tested material and the molecules starts to emit the specific electromagnetic waves. Typically, the fluorescent light is emitted in all directions, thus we can use an integrating sphere to collect it absolutely and calculate the fluorescence quantum yield. However, whenever only the distribution of wavelengths of emitted lights has to be measured, then the device has a single slit, where just a small amount of emitted light is detected. In that case, the angle between the incident and emitted light is set to 90 degrees to minimize the risk of collecting the reflected or transmitted light. The built-in diffraction grating enable to characterise the sample by every light wavelength, hence, the result of spectrofluorimetric measurement is a spectrum, which consists the light intensity as a function of wavelength. Generally, to carry out a test, firstly the excitation spectrum is collected. The researcher has to receive an absorbance spectrum to find the most intensive absorbance wavelength. After that, the emission spectrum could be obtained with the use of proper wavelength. For instance, when the sample has the maximum of absorbance in 330 nm, the emission spectrum is collected under the illumination of that specific wavelength and measured in interested range of UV, VIS or IR light.

4.8 Fourier Transform Infrared Spectroscopy

One of the variation of the spectroscopy in infrared range of electromagnetic waves (IR) is the Fourier transform infrared spectroscopy (FTIR). It is widely used in chemical identification of functional groups in materials. This technique is based on the absorption of IR radiation by chemical bonds present in the sample molecules^[90]. Mostly, the measurement is carried out in a range of $4000\text{--}400\text{ cm}^{-1}$ which is absorbable by various types of materials, including solid, liquid and gas phases. The first commercially available FTIR spectrometer was produced in 1957 by the Perkin-Elmer company^[91]. Today, due to the fast analysis and high sensitivity, it finds an applications in chemistry, geology, biology and materials science. As an example, if the database is available, this method is capable to identify many materials within seconds. What is more, it is able to monitor the chemical reaction process, because it is possible to record a time-dependent change in the intensity of each peak, thus, analyse if specific chemical bonds appear or disappear in the spectrum^[92].

The FTIR instrumentation is based on the Michelson interferometer. The IR beam from the source passes through the beam splitter, which is a mirror with a 50% of reflectance. One of the splitted beams reflects on a fixed mirror and the second on the movable mirror. Then, two beams are recombined by the splitting mirror. The constructive interference occurs if the light path distance between two mirrors is equal to $n\lambda$, where n is a natural number. But if the path length difference is equal to $n\lambda + \lambda/2$, the result is destructive interference. In FTIR, the output light is reaching the surface of the sample. Depending on the measurement mode, we can analyse the reflected or transmitted beam. Subsequently, the interferograms – plots of the dependence of intensity (in volts) versus the optical path difference (OPD), are determined. This plot is measured in terms of centimetre (cm) domain, thus, after the Fourier transformation it is possible to obtain the intensity versus wave number plot, which converted to the terms of inverse centimetre (cm^{-1}) domain and is known as the FTIR spectrum. In comparison with the traditional IR spectroscopy method, where the sample is scanned sequentially by every wavelength, FTIR is significantly faster, but need more precise instrumentation.

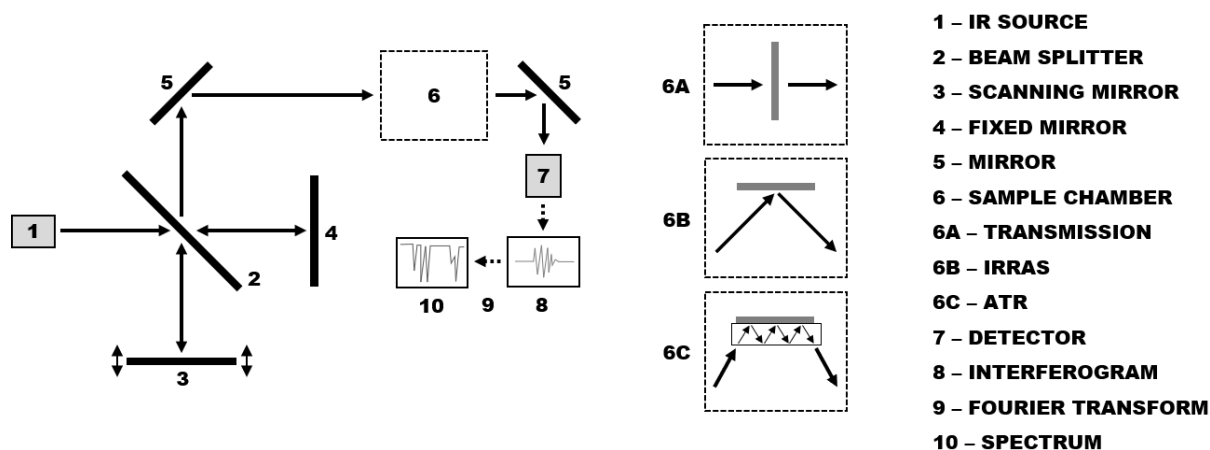


Figure 4.12. Schematic representation of the FTIR instrumentation. The sample could be analysed by different methods, such as (6A) transmission spectroscopy, (6B) IRRAS – infrared reflection absorption spectroscopy or (6C) ATR – attenuated total reflectance^[93].

The infrared light is a type of low-energy radiation, especially, when it is compared to the UV or even VIS light. Thus, these electromagnetic wavelengths are not able to cause the molecule or atom excitation, however, it can activate the vibrational modes in a chemical bonds presented in the sample. This is an example of a quantised process, because molecule could absorb only the selected frequency that is matched with the bond's natural vibrational frequency, which causes stretching and bending vibrations of different bonds. Other frequencies are just passing through and do not interact with the sample. Not every molecule is IR active. In order for a vibrational mode to absorb the IR light, it must cause the periodic change in its dipole moment. In general, the greater the bond polarity, the stronger absorption is observed in the spectrum. Hence, it is impossible to measure completely symmetrical molecules containing double or triple bond, such as 1,2-butadiene or 2-butyne. The number of possible vibrational modes, known as degrees of freedom (*DoF*), for a molecule with *N* atoms is equal to

$$DoF = 3N - 6 \quad (4.7)$$

for nonlinear and

$$DoF = 3N - 5 \quad (4.8)$$

for linear molecules. As an example, water (H₂O), which is nonlinear, has 3 different vibrational modes. The simplest molecules (e.g. HCl) contain only two modes of vibration: stretching and bending. But in the case of more complex types, the list of possible vibrations is extended to: symmetric and asymmetric vibrations, characterised as stretching vibrations, and wagging, rocking, twisting and scissoring, which are the types of bending vibrations.

4.9 Raman Spectroscopy

The Raman and IR spectroscopies are complementary, which means that vibrational information received from both methods is complete, but each method characterises the material in a different way^[94]. It is a non-destructive technique for chemical analysis that provides comprehensive data about chemical structure^[95], phase^[96], polymorph^[97], crystallinity^[98] and molecular interactions^[99]. The principle of working is based on the phenomenon of Raman scattering^[100] of monochromatic laser beam on the sample. There is no restriction to analyse solid, liquid or gaseous samples. However, it is not suitable for metals and their alloys. The Raman spectroscopy finds an application in many fields, such as archaeology^[101], chemistry^[102], geology^[103] and semiconductor industry for quality control^[104]. A very interesting example is the use of Raman by pharmaceutical companies, where the distribution of active chemical ingredients may be mapped in a pills^[105], which is a very useful information for the medicine producers.

The effect of Raman scattering, contrary to Rayleigh scattering, is an example of inelastic light scattering. In this case, the scattered photon has the frequency composed of the sum of frequency of incident photon (ν_0) and the frequency corresponding to molecular vibration (ν_R). As shown in Figure 4.13, the final frequency could be a sum ($\nu_0 + \nu_R$) or a difference ($\nu_0 - \nu_R$). These lines are known as anti-Stokes and Stokes, respectively. They are a result of sample excitation caused by incident photon, where the molecule is excited for a short time to virtual

energy state and then photon is reemitted. After that, the sample is in a different rotational or vibrational state and the photon receives or loses the small amount of energy ($\nu_0 \pm \nu_R$).

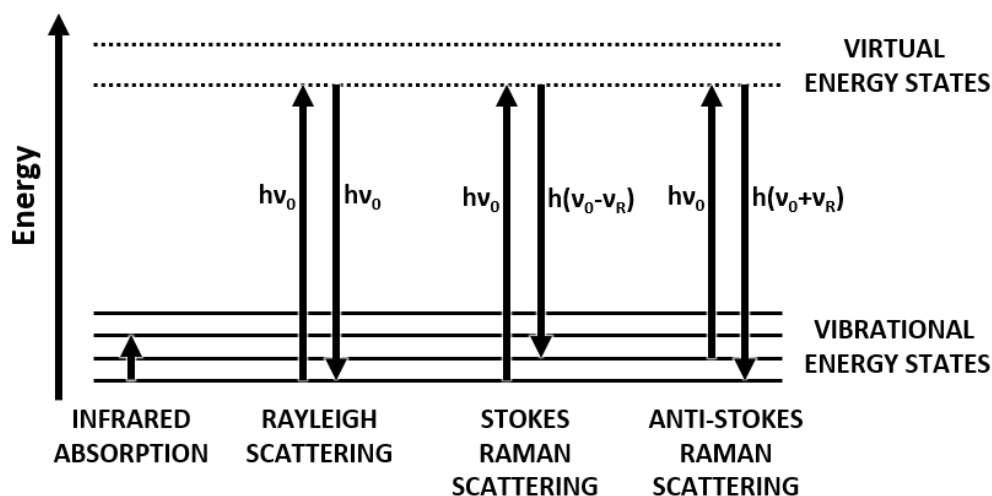


Figure 4.13. Energy level diagram presenting the principle of IR absorption, Rayleigh, Stokes and anti-Stokes scattering.

The Raman effect strongly correlates with the change of polarizability of the electrons in a molecule. Due to that the intensity of such scattering is proportional to the polarizability. It is noteworthy that this phenomenon shall not be confused with fluorescence, where the molecules are excited to electronic states and then dropped down to ground state. Here the sample is excited to the virtual state, which is not energetically available for the electron. It also differs with the IR spectroscopy, because there the electromagnetic wave is absorbed by the sample and its energy is equal to the difference between initial and vibrational states. As previously mentioned, the Raman scattering occurs, when the molecule is able to change its polarizability (α)^[106]. Thus, it could be described as

$$\left(\frac{d\alpha}{dq}\right)_{eq} \neq 0, \quad (4.9)$$

where q is the normal coordinate and eq is equilibrium position. In simple words, the electron density within the molecule decreases or increases in time. Thus, for instance, an asymmetric stretch of carbon dioxide (CO_2) is Raman inactive (IR active), because it does not change the polarizability, while the symmetric stretch is Raman active (IR inactive). This is also a good example, why the Raman and IR spectroscopies are called complementary.

Typical Raman spectrum is represented by a plot of signal intensity versus Raman shift ($\Delta\nu$). This shift is typically reported in inverse centimetres (cm^{-1}). To calculate this value, we need to know wavelength of excitation light (λ_0) and the Raman spectrum wavelengths (λ_i), which is given by the equation

$$\Delta\nu = \frac{1}{\lambda_0} - \frac{1}{\lambda_i}. \quad (4.10)$$

In short, it could be consider as a difference between the energies of incident and scattered photon. Modern Raman spectrometers uses the monochromatic light generated by a lasers. Typical laser wavelengths are e.g. 405, 533, 633 or 832 nm. It is important to choose the proper laser wavelength. The UV light could damage the sample during long-lasting illumination and the IR laser may not generate detectable signal, because the signal intensity is correlated with cross section for Raman scattering, which is proportional to the factor of λ^{-4} . Thus, the lower the excitation wavelength, the more intensive is the Raman scattering and the higher signal could be detected. It is also very important to choose the laser wavelength, which would not induce a fluorescence of the sample. Typical configuration of Raman spectrometers consists the microscope, from which the laser light is directed onto the sample surface. Then the light is reflected back to the objective and then diffracted by the diffraction grating and analysed by a detector, e.g. CCD camera.

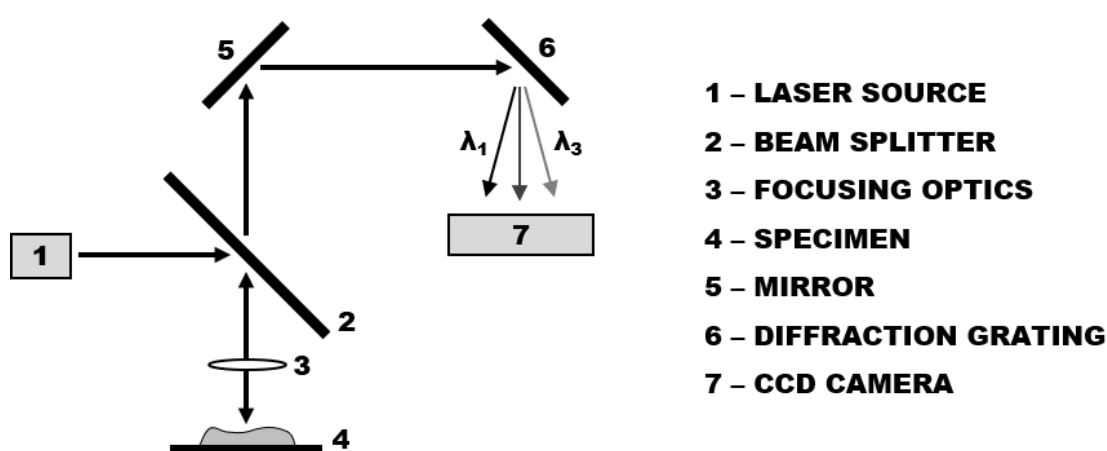


Figure 4.14. Schematic representation of the Raman spectrometer instrumentation.

4.10 Secondary Ion Mass Spectrometry

The secondary ion mass spectrometry (SIMS) is a powerful technique to analyse the chemical composition of solid materials. The history of SIMS began in 1910, when J. Thomson observed that when the solid surface is bombarded by energetic ions, the sample release a positive ions and neutral atoms^[107]. Nowadays, it is known that as a result of bombardment also electrons, specific radiation and whole neutral and ionised clusters are released. In the case of SIMS method, only the ionized species are analysed by the mass to charge ratio (m/z). Modern devices are able to give not only the information about the surface chemical composition, but also to characterise materials by imagining a secondary ions distribution as a two (2D) and three dimensional (3D) maps^[108]. This method is often use in semiconductor industry in quality control measurements.

The primary ions are ionized atoms or clusters that are bombarding the sample, which is called a target in SIMS nomenclature. Commonly used ions are, for instance, Ar_n^+ , Bi_n^+ , O_2^+ , Cs^+ or C_{60}^+ . As shown, the projectile could be e.g. a noble gas, oxygen, molecule and cluster^[109]. The last one could contain from a few to even a hundreds of clustered particles. Every single impact defects a small area of the target surface, which ranges from one to over a dozen nanometres and depends on primary ion's mass and energy. In effect of using a single atom, the penetration depth will be significant and the released particles will be highly ionised.

On the other hand, if the cluster projectile is used, the sputtering efficiency is higher and the penetration depth is lower.

As a result of collision of accelerated primary ion and the target, in the consequence of energy and momentum transfer, the secondary ions are released. Their current could be described by following equation

$$I = I_p Y \alpha^{\pm} T c \quad (4.11)$$

where I_p is a primary ion current, Y is a number of emitted species (ionized and neutral) per number of a primary projectile, so called sputtering yield of species, $\alpha^{\pm}$ is a positive or negative ionization probability, T is the transmission of the analysis system and c is a fractional concentration of species in the target. This theoretic equation is difficult to maintain in real measurement, because there are dozens of parameters, which could change the secondary ion current, for example, the vacuum chamber pressure or the matrix effects. Hence, it could be only useful when the reference samples with a high purity are examined.

Most of the sensitive mass spectrometers are equipped with time of flight (ToF) analyser. It measures the mass to charge ratio (m/z), which is determined by the time that is required for specific ion to fly through the device's chamber. When the ions are sputtered from the surface, they fly through the analyser slit. Then, the electrodes system accelerates them in the electric field until they reach the same kinetic energy. The time that is required for the particular ion to reach the detector at a known distance (l) is given by the simple equation

$$t = \sqrt{\frac{l^2 m}{2 U_0 z}} \quad (4.12)$$

where m is the mass of an ion, U_0 is an accelerating voltage and z is an ion's charge^[110]. It is worth to notice that despite its simplicity, the ToF is a very sensitive technique. For instance, modern devices are capable to distinguish Si^- (27.98 u) and CO^- (27.99 u) ions. This is a very good result, especially, when it is compared with the mass of the hydrogen atom ($m_H = 1.008$ u).

We can distinguish two basic operating modes in SIMS measurements^[109]. The simplest one is static SIMS (sSIMS), where only the first material's monolayer is analysed. It is possible, when the primary ion dose do not exceed 10^{12} ions per cm^2 for organic and 10^{14} ions per cm^2 for inorganic materials. With this values we could assume that the secondary ions are sputtered from non-damaged area. If the information about the subsurface layer composition is required, the dynamic SIMS (dSIMS) mode is used. In that case, the ion dose is much more higher than in sSIMS. Increased dose is able to sputter the successive sample layers and get the secondary ions from the bulk. The eroded area is getting deeper and deeper in time, while the ions are continuously analysed. Due to that it is possible to create a depth profiles, where the sputtering rate (f) depends at least on a few factors: primary ion current (I_p), total sputtering yield (Y_{tot}) and target's atomic density (ρ). It is given by the following equation

$$f = \frac{I_p Y_{tot}}{e \rho}, \quad (4.13)$$

where e is the elementary charge. The sputtering rate could be considered as a material parameter, assuming the consistency of experimental conditions, such as projectile type, energy and incidence angle. Typically, the depth profiles are presented as a signal intensity versus sputtering time. However, it is possible to recalculate the time to depth, if only the sputtering rate is known or the crater's depth is measured by other method (e.g. profilometer). Nowadays, a dual beam system is commonly deployed to carry out dSIMS measurements. In such case, the first gun sputters the sample, while the second gun analyses exposed layers. For the analysis, we have to choose the ion, which is a molecule's fingerprint. For instance, if the structure with titanium dioxide and N719 molecule ($C_{58}H_{86}N_8O_8RuS_2$) is examined, we can assume that the TiO^- and the NCS^- ions are fingerprints for TiO_2 and N719, respectively.

4.11 Current-Voltage Characteristics

The current-voltage characteristics were developed to test electrical devices. In simple words, when the voltage is applied, the current flow is measured and draw as a graph $I(U)$. The obtained curve is characteristic for every electronic element: resistors, batteries, transistors, diodes and solar cells. Based on the curve, it is possible to obtain the specific electrical parameters for each device.

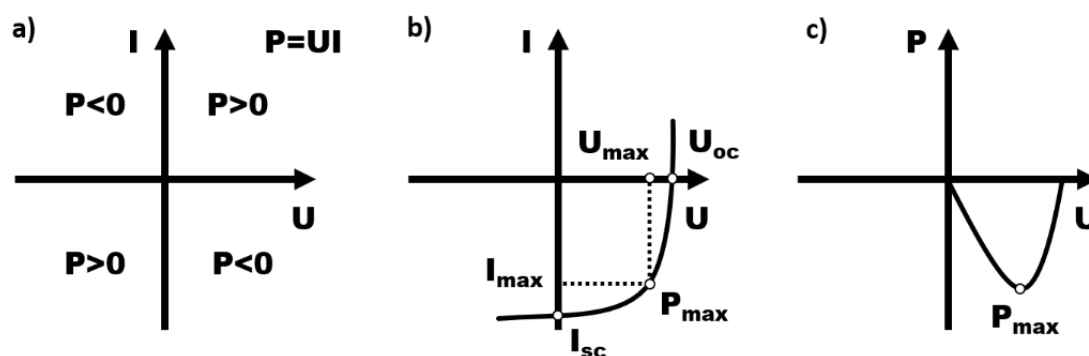


Figure 4.15. Schematic diagrams of a) the four quadrants, where the power is generated ($P < 0$) or consumed ($P > 0$) by the device, b) the exemplary solar cell curve with characteristic points and c) the localization of maximal power point.

When a solar cell without illumination is electrically characterised, the U - I shall look like the diode curve^[111]. However, if the sunlight illuminates the photovoltaic device, the curve should be shifted down along the current axis, because the additional photocurrent is generated. At the $I(U)$ graph we can point out a few specific points^[112]. The first is the open-circuit voltage (U_{oc}), which is the maximum voltage available from the solar cell and occurs at the current equal to zero. It corresponds to the amount of forward bias caused by the bias of the solar cell with the light-generated current. Another parameter is the short-circuit current (I_{sc}), which is the current of collected light-generated carriers. In an ideal model, where the resistive loss is negligible, the I_{sc} and light-generated current are equal. That parameter significantly depends on a few main factors, such as the solar cell's area, but also the intensity and the spectrum of incident light. When the values of corresponding currents and voltages are multiplied, the obtain graph presents the device's power dependence on the applied voltage $P(U)$. The

minimum of that curve is the maximal power point (P_{max} or *MPP*), which is characterised by *MPP* voltage U_{max} and *MPP* current I_{max} values.

According to described values, we are able to calculate two following parameters: fill factor (FF) and power conversion efficiency (PCE), which is often marked with a Greek letter η . The first one describes the ratio of P_{max} to I_{sc} and U_{oc}

$$FF = \frac{P_{max}}{I_{sc}U_{oc}} = \frac{I_{max}U_{max}}{I_{sc}U_{oc}}. \quad (4.14)$$

Graphically, the FF is a measure of the squareness of the solar cell characteristic and is also the area of the largest rectangle which would fit the $I(U)$ curve. Ideally, the FF value should be close to 1. In real, it ranges from 0.3 to 0.9^[113], depending on the solar cell's type. The most popular is the PCE parameter, because it directly describes how much light power is converted into the electrical power. It helps to compare the performance of one solar cell to another. The efficiency here is simply defined as the ratio of incident light power (P_{in}) to energy output from the solar cell (P_{max}) and could be easily correlated with described above photovoltaic parameters as follow

$$\eta = \frac{P_{max}}{P_{in}} = \frac{I_{sc}U_{oc}FF}{P_{in}}. \quad (4.15)$$

The power conversion efficiency is commonly investigated under standardised conditions. Nowadays, the most popular standard is AM1.5^[114], which is a simulated Sun's light spectrum on the surface of Earth. It was determined assuming that the Sun is shining 41.81° above the horizon, the solar cell is tilted 37° from the horizon, the pressure is 1013.25 mbar and the CO₂ level is 370 ppm. The light power is standardised as well, thus, presented in equation 3.15 P_{in} should be equal to 1 SUN what corresponds to the value of 100 mW/cm² or 1000 W/m².

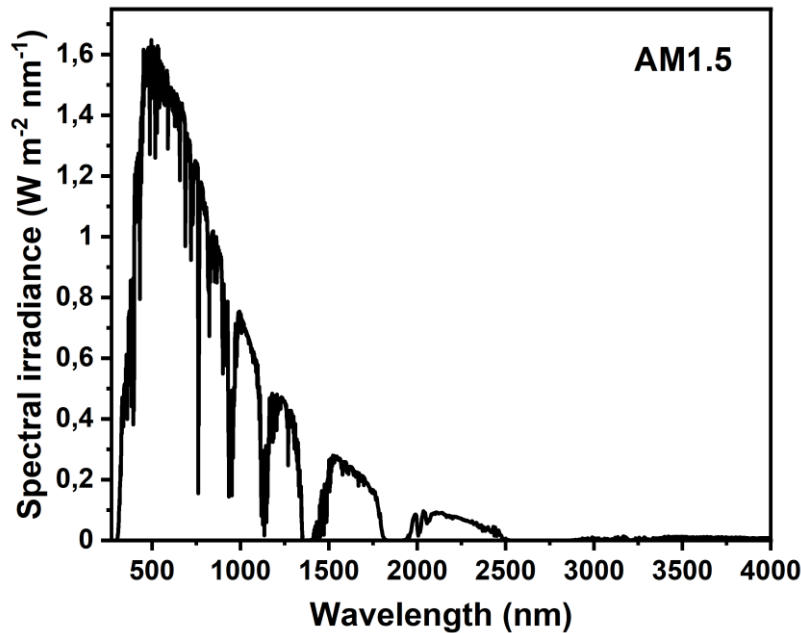


Figure 4.16. Spectral irradiance of the AM1.5 spectrum.

4.12 Kelvin Probe

To electrically characterise the sample surface, the Kelvin probe method is frequently used. This technique enables to calculate the material's work function (WF), which, in definition, is a minimum potential that is necessary to remove an electron from the bulk material through a given surface^[115]. Besides the science (surface charging^[116], adsorption-desorption process^[117]), it also finds an application in industry. For example, when the WF is measured, we are able to assess if the material is highly corrosive or not^[118]. On the other hand, when the measurement are conducted in time, it is possible to calculate the time-dependent corrosion rate, because the surficial corrosion layer, which typically is an metal oxide, has higher WF if compared to pure, non-corroded metal. In photovoltaics, it found an application in measuring the metallic electrode WF. Its value strongly impacts on the solar cell efficiency, because unmatched energy levels of the inner layer and the electrode could block the electrons on the interface and, thus, decrease the PCE.

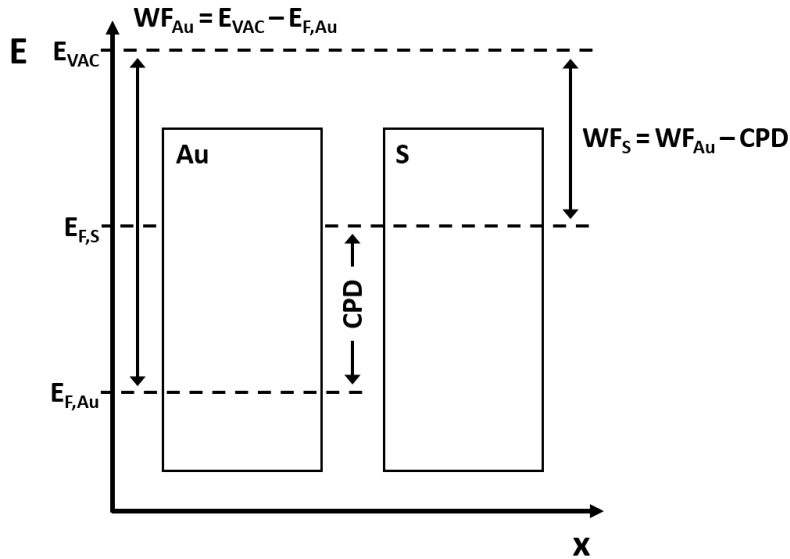


Figure 4.17. Energy level diagram presenting the principle of CPD between the gold probe and the sample. The E_{VAC} , $E_{F,S}$, $E_{F,Au}$ are the vacuum level, the Fermi level of the sample and the Fermi level of the gold probe.

The measurement is non-contact. It involves an oscillating capacitor – one electrode is a sample, the other is an oscillating reference electrode (see Figure 4.18) made of gold (Au). Hence, the measure is referenced to the gold's WF, which is equal to 5.1 eV and stable in time^[119], even at ambient conditions. To calculate the WF, firstly the contact potential difference (*CPD*) has to be measured. The *CPD* is an electrostatic potential that exists between samples of two dissimilar conductive materials, which are brought into thermal equilibrium with each other. Typically, it means two materials with different WFs that are in direct physical contact.

The general formula for capacitance (C) contains a charge (Q) and a voltage (V) between two flat electrodes. In this case, the voltage is related to *CPD*

$$C = \frac{Q}{V} = \frac{Q}{CPD}. \quad (4.16)$$

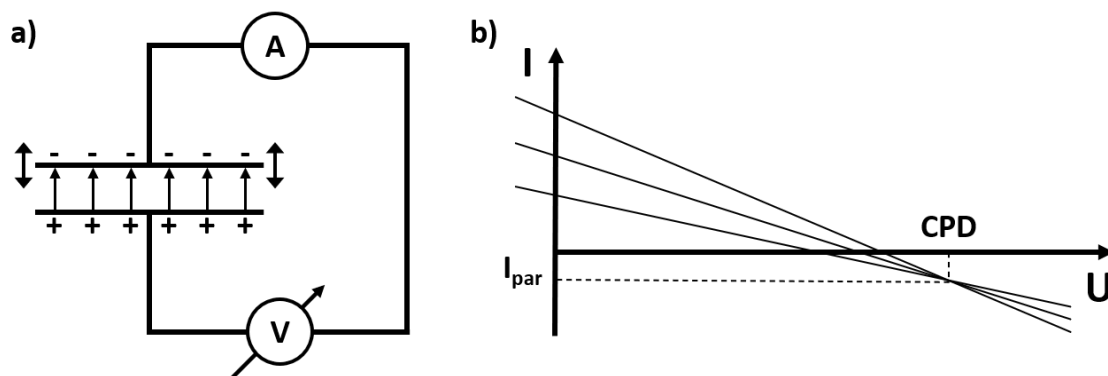


Figure 4.18. Schematic representation of a) Kelvin probe circuit and b) exemplary current-voltage characteristic for three different heights.

When one electrode oscillates, the capacitance is changing in time, thus, the charge accumulated on electrodes changes too. The change in charge over time by definition is a current (I)

$$Q = C \cdot CPD \quad (4.17)$$

$$\frac{dQ}{dt} \equiv I = \frac{dC}{dt} CPD. \quad (4.18)$$

If an additional voltage source is appended, we are able to calculate the CPD value, which is equal to applied voltage (V_0), by finding the zero current point on the $I(U)$ plot

$$\frac{dQ}{dt} = I = \frac{dC}{dt} (CPD - V_0). \quad (4.19)$$

Unfortunately, during the experiments the current amplitude reaches zero for different potentials at different distances between the sample and the tip. It is caused by the parasitic currents (I_{par}) induced in the Kelvin probe circuit. An exemplary source of such current is the oscillating driving circuit that couples to the circuit. Thus, more accurate is the following equation

$$\frac{dQ}{dt} = I = \frac{dC}{dt} (CPD - V_0) + I_{par}. \quad (4.20)$$

In order to determine I_{par} we should perform a potential scans at least for three different sample to tip distances. All received lines cross each other in one point, which coordinates correspond to the I_{par} and CPD . If the reference electrode was made of gold, the sample's WF is then given by a simple equation

$$WF_{sample} = CPD + WF_{Au}. \quad (4.21)$$

4.13 Cyclic Voltammetry

Voltammetry is a widely used electroanalytical method to probe reactions, which involve an electron transfers. It relates to chemical changes caused by the flow of electrons, that are often associated with reduction and oxidation. The cyclic voltammetry (CV) measurements are generally used to examine the electrochemical properties of a given analyte in solution

or electrocatalytic properties of a material, which is interconnected as a working electrode. In science, it is often used to determine thermodynamic and kinetic parameters^[120] of voltage induced reactions that can be easily controlled by the driving force.

Cyclic voltammetry measurements are typically carried out in a three-electrode system^[121]. The first one is the counter electrode (CE). Its role is just to pass all the current needed to balance the current observed at the working electrode (WE). In most cases, platinum is used, as a chemically inert good electrical conductor, because CE is often swung to extreme potentials in order to accomplish this task. The function of WE is to carry out the electrochemical event of interest; thus, it must facilitate the charge transfer to and from the analyte. Because the reactions occur at this electrode, it needs to be noticed that the chemical species could adsorb on its surface, which can influence the measurements. The last one is the reference electrode (RE), which role is to control and maintain the constant potential at the working electrode. It must have a well-defined and stable equilibrium electropotential. Applied during the measurement voltage is typically presented in relation to the RE's potential. Generally, the RE is separated from the solution by a porous frit, which is necessary to mitigate junction potentials by matching the solvent and electrolyte in the reference compartment to the one used in the experiment.

When a three-electrode cell is assembled, the electrocatalytic experiment could be run. All the electrodes have to be connected to the potentiostat, which is an electronic hardware used to maintain a constant potential at WE with respect to the RE. It simply adjusts the current at a CE to keep the stable voltage level. After setting the measurement parameters, such as scanning potential range, scan rate and number of scans, the device is scanning the currents as a function of applied voltage. As a result, the voltammograms are received.

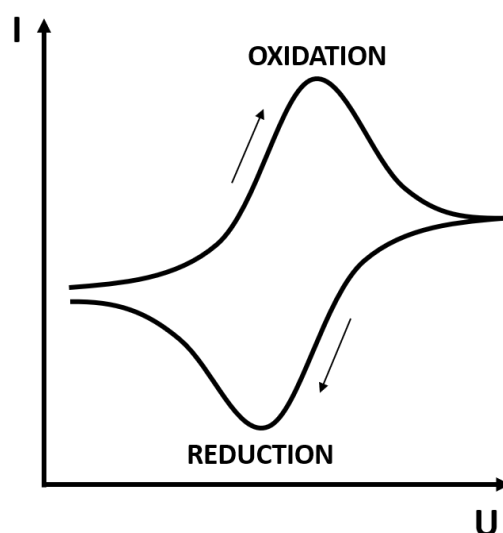
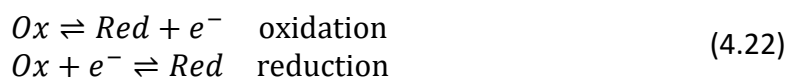


Figure 4.19. The example of voltammogram for a simple reversible redox reaction.

In a situation where no electrochemical reaction occurred, the current would linearly increase in the whole range of potential. However, in the case of an electron transfer reaction, the voltammogram will present a local minima or maxima. Their location is strictly related to the specific type of

reaction mechanism. In the simplest example, analyte could undergo a reversible redox reaction, that occurs at different potentials, what is described by following equations



where *Ox* is an oxidant (electron acceptor) and *Red* is a reducer (electron donor). The analysis of the obtained voltammograms could provide an interesting information about the reaction reversibility or kinetics of the analyte. Furthermore, it could be useful in a study of electrocatalysis, molecule and adsorption/desorption at the working electrode.

Chapter 5

Effect of Post-Annealing UV-Ozone Treatment of TiO₂ Mesoporous Layer

5.1 Introduction

The original DSSC architecture designed by M. Grätzel and B. O'Regan was modified by many scientific groups, because this device is susceptible to modifications. Thus, a dozen scientific papers were published, where authors focused on changing the original materials used by M. Grätzel. For instance, the titanium(IV) oxide as the photoanode material, was replaced by other *n*-type and even *p*-type semiconductors, such as zinc oxide (ZnO)^[122] or nickel(II) oxide (NiO)^[123]. In some articles, to enhance the properties of TiO₂ nanoparticles, the doping effect was also studied. Different dopants have been reported, for example, tungsten (W)^[124], sulphur (S)^[125] or copper (Cu)^[126]. Recently, also the plasmonic effect was applied in the DSSCs. Quantum-size metal nanoparticles are able to increase the solar cell performance by improving the charge transport through the semiconductor layer^[127]. Additionally, it was reported that plasmonic particles exhibit an enhanced scattering effect within the active layer^[128]. In this case, the scattered light is harvested more efficiently by the dye, due to increased cross section of absorbance.

In this dissertation, another important aspect that has a great influence on dye-sensitized solar cell performance will be pointed out. As previously described, the mesoporous TiO₂ layer is commonly prepared from titania paste by screen printing method^[129]. This paste contains not only the inorganic titanium(IV) oxide nanoparticles, but also a relevant amount of organic ingredients. Despite the annealing of the wet layer at high temperature, which reaches almost 600 °C, organic contaminations are still present within the nanoporous TiO₂ film^[130]. It is not easy to remove them by a chemical bath, because the solvent may be adsorbed deep into the mesoporous structure as a result of the capillary action. It would be then necessary to remove the trapped solvent, for the reason that its presence would disturb the dye-sensitising process and performance of the electrolyte. Besides, the higher temperature should not be considered to remove the organic residues, because the temperature above 600 °C would change the titania phase to rutile^[52]. The most time- and cost-efficient method is to apply the reactive gas. The use of a gaseous state of matter guarantees that the molecules would penetrate deep into the micro- and nanostructure of TiO₂. Thus, this chapter will focus on the application of highly reactive gas – the ozone (O₃), to remove organic residuals from TiO₂ surface.

There are some studies showing that ozone, induced by a high-power UV radiation from the O₂ molecules, is capable of changing the surface properties of TiO₂. For instance, some reports show that the ozone-treated layers had increased dye adsorption compared to the untreated ones, which caused the higher photocurrent in DSSCs^{[131]-[132]}. Authors of these reports focused on stoichiometry, wettability and roughness. Reported by them reduction of Ti⁴⁺ to Ti³⁺ generated more negative charge carriers in the layer, what led to higher conductivity and lower electron-hole recombination. Due to the better wettability, in the sense of lower solvent contact angle, the dye solution was able to penetrate deeper within the TiO₂

mesoporous layer. For that reason the dye sensitising process was more efficient. In the last case, it was reported that UV-ozone treatment decreased the titania layer roughness in submicroscale, what – according to the authors' statement – improved the incident light harvesting across the active layer. It is worth noting that even the authors have suggested that additional research is needed to understand the effect of UV-ozone treatment of TiO₂ on the performance of dye-sensitized solar cells. Therefore, this chapter presents the results from UV-ozone cleaning, which, in contrast to plasma-based methods, seems to be an energy-effective process to increase the efficiency of DSSCs. The data obtained show that ozone is able to clean the surface of mesoporous TiO₂ from any organic residuals. As a result, more bonding sites were available for dye molecules, which enhanced the dye-sensitisation and consequently the solar cell efficiency.

5.2 Experimental

5.2.1 UV-ozone generation

Ozone is an inorganic molecule, which consists three oxygen atoms (O₃). The oxygen occurs naturally in a diatomic form (O₂), because it is more thermodynamically preferable. Thus, ozone is an unstable gas, which is difficult to store for long time under normal conditions. When triatomic forms decay to diatomic ones, a free oxygen atoms create activated hydroxyl radicals (*OH), which exhibit a strong oxidizing effect^[133]. Such radicals can break carbon bonds in organic molecules and form two types of molecules – carbon dioxide (CO₂) and water (H₂O).

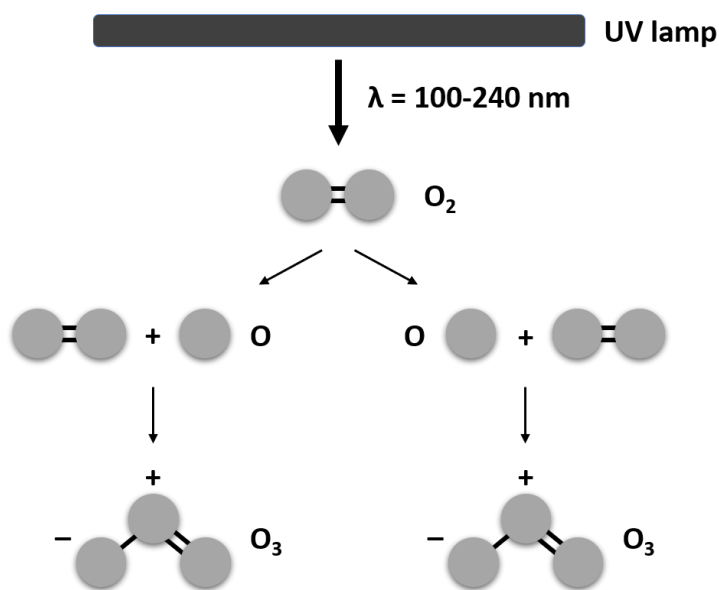


Figure 5.1. Ozone generation process: UV light splits the diatomic oxygen into two single molecules that attach to other diatomic oxygens and form triatomic ozone.

One of the most popular methods to generate an O₃ molecules is based on UV radiation (see Figure 5.1). The generation process begins, when the high-energy UV-C photons are absorbed by oxygen. Because of this, the diatomic form splits into two separate oxygen atoms. These two atoms attempt to attach to surrounding oxygen molecules. Accordingly, the attachment of that third atom creates the ozone. This highly reactive molecule is then able to break the bonds in organic compounds, such as oils or lipids, and decompose their chemical

structure^[134]. As a result, volatile products, in particular carbon dioxide and water molecules, are produced (see Figure 5.2).

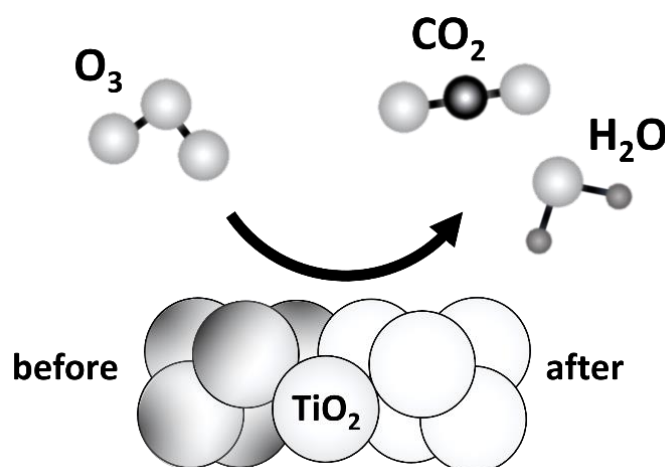


Figure 5.2. Schematic representation of the UV-ozone cleaning process of TiO₂ particles.

5.2.2 Preparation of dye-sensitized solar cells

Reference samples were prepared as previously described. To study the effect of ozonisation, an additional step was introduced into the preparation process. After annealing at a high temperature, when the mesoporous TiO₂ layers were already cooled down, one part of the substrates was placed in the vacuum chamber to avoid contact of the sample with an ambient conditions – moisture, UV light, CO₂ etc. The second part was transferred to the UV-ozone cleaner (ZoneSEM II, Sanyu Ltd.) presented in Figure 5.3.



Figure 5.3. Tabletop specimen cleaner (ZoneSEM II^[135]) used in ML System laboratory.

The vacuum level was set to 5%, which means that the inside pressure was twenty times lower than the atmospheric pressure. Then, after a 5 minutes of pressure stabilization and sample's dehumidification, the UV lamp was turned on for 20 minutes. As a consequence of UV radiation and the presence of oxygen molecules, light-induced ozone reacted with organic impurities and adsorbed contaminants. The reaction products, such as CO₂ and H₂O

molecules, were continuously extracted from the device chamber by the built-in vacuum pump. The samples were stored inside for another 5 minutes after the lamp was turned off to clean the chamber of any reaction products, because they and O₃ may be hazardous to people and environment. One part of the samples was left for further characterisation. The second part of reference and ozonised TiO₂ layers was immersed in a dye solution and finally sealed with cathode substrates to complete the DSSC devices.

5.3 Results and discussion

5.3.1 Contamination effect

The UV-ozone treated and untreated (reference) samples were transferred to the SEM vacuum chamber. Images were obtained with the use of SE detector, acceleration voltage of 10 keV and beam current of 4.7 μ A. As shown in Figure 5.4, the TiO₂ layers had a typical structure of sintered nanoparticles. No differences in the nanostructure were observed between the reference and UV-ozonised samples.

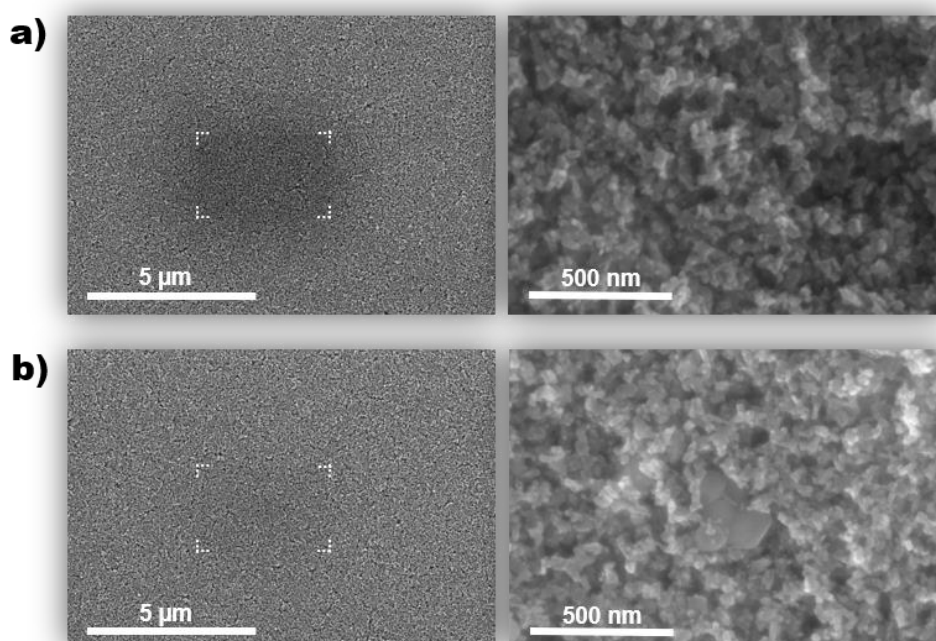


Figure 5.4. SEM images of a) reference and b) UV-ozone treated TiO₂ mesoporous layer. Marked areas presents the surface area, which was exposed to electron beam for two minutes.

To show the effect of contamination, the samples were exposed locally to the electron beam for two minutes. These areas were marked with white symbols in the images. The contamination phenomenon is well known to SEM users. If the sample surface is covered by organic molecules, in effect of interaction with high energy electrons, the molecules start to aggregate and polymerise. The irradiated areas became darker and blurred on the screen. As reported here, in the case of an untreated sample, the images of electron exposed areas became darker than those of the surrounding, unexposed ones. However, if we look at the images received from UV-ozonised TiO₂, we can notice that the exposed areas did not change significantly.

5.3.2 Spectroscopic determination of organic residuals

Two spectroscopic methods, Raman and FTIR, give subsurface information about the chemical composition of the analysed sample. However, the probing depth of both techniques differs significantly. In case of Raman spectroscopy, the information is obtained from less than 1 millimeter, while IR spectroscopy characterises the material up to 1 centimetre underneath the surface^[136]. In this dissertation, both methods were applied to study the residuals in the TiO₂ layer immediately after the sintering process.

Presented in Figure 5.5 FTIR spectra correspond to pure titania paste, annealed paste (sintered layer of TiO₂) and sintered layer after the UV-ozone treatment, respectively. The measurements were carried out in ATR mode for the paste and in IRRAS mode for annealed samples. As previously mentioned, TiO₂ paste is composed of titanium(IV) oxide nanoparticles and a mixture of organic compounds, thus, the respective spectrum contained strong peaks that point to the presence of organic components. They are, for example, C-H (2900 cm⁻¹), O-H (1600 cm⁻¹) bands and multipeak region from 800 to 1500 cm⁻¹, which is correlated with C-O, C=C, C-H bending and stretching bands. The data received for annealed sample showed characteristic Ti-O stretching band (900 cm⁻¹). Furthermore, the O-H stretching (1600 cm⁻¹) and bending (3500 cm⁻¹) modes were present in the spectrum. After detailed analysis, a weak multipeak signal was visible in the range of 2800-3000 cm⁻¹. These peaks are associated with C-H stretching vibrational modes. When we look at the same region in the case of UV-ozonised sample, these peaks were no more present in the spectrum. Thus, it can be assumed that the organic residuals were successfully removed from the sample.

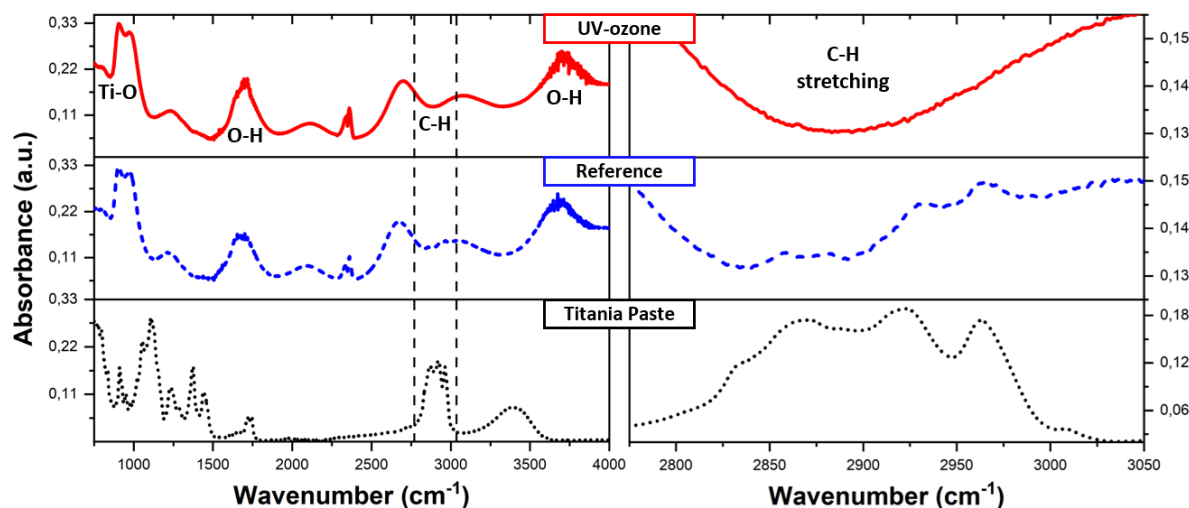


Figure 5.5. FTIR spectra of titania paste (dotted black), mesoporous TiO₂ before (dashed blue) and after (solid red) UV-ozone treatment. The C-H stretching region disappeared as a result of ozone cleaning.

All the samples were also analysed by Raman spectrometry. The He-Ne laser (wavelength 633 nm) and the objective of $\times 100$ magnification were used to acquire the data. The spectra obtained are shown in Figure 5.6. The spectrum received for the fresh layer of titania paste was a superposition of characteristic signals for TiO₂ and other organic compounds. In the first case, the typical bands are located at 144 cm⁻¹ (E_g), 197 cm⁻¹ (E_g), 399 cm⁻¹ (B_{1g}), 519 cm⁻¹

(A_{1g}), and 639 cm⁻¹ (E_g). These vibrational modes are characteristic for the anatase form of titanium(IV) oxide^[137]. Additional peaks were located at 237 cm⁻¹, 448 cm⁻¹, and 609 cm⁻¹. They definitely correspond to the organic components, which are present in the paste. Because it is a mixture containing at least a few different chemical constituents, it is impossible to distinguish each of them. However, we can assume that visible peaks can be associated with $\delta(\text{CC})$ and $\nu(\text{CC})$ vibrations in aliphatic chains. After a detailed analysis, it is possible to point out additional weak signals corresponding to $\nu(\text{CC})$ vibrations in alicyclic/aliphatic chains or aromatic rings, which are located at 969 cm⁻¹ and 1033 cm⁻¹. These two signals transformed into one in the annealed sample (1002 cm⁻¹). This change may be difficult to explain, but with a great probability, it could be a result of the conformation change of organic compounds due to the high temperature treatment. It is noteworthy that all signals presented previously in this spectrum range disappeared after the UV-ozone cleaning.

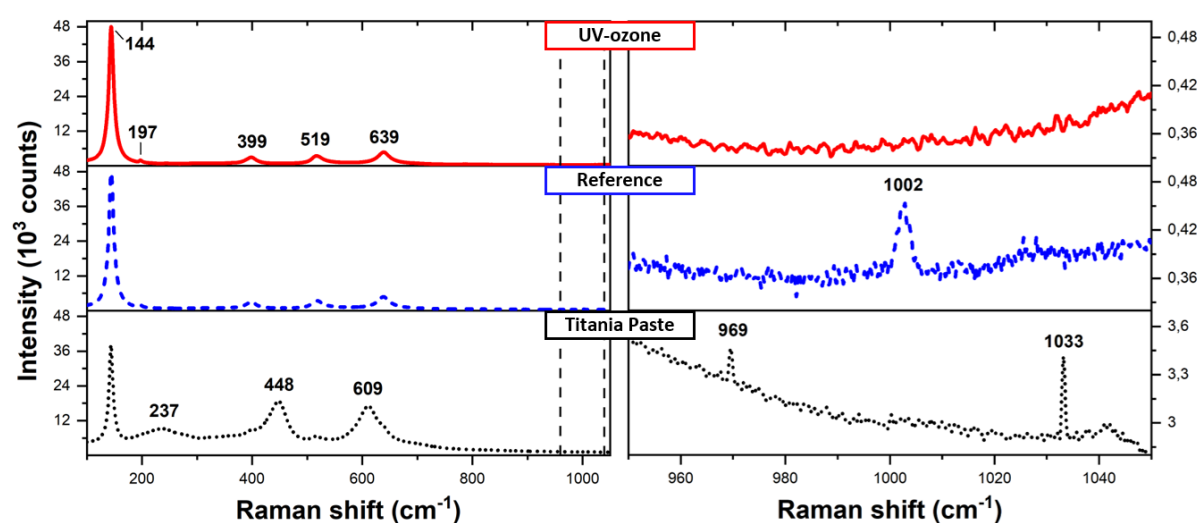


Figure 5.6. Raman spectra of titania paste (dotted black), mesoporous TiO₂ before (dashed blue) and after (solid red) UV-ozone treatment. The peaks corresponding to $\nu(\text{CC})$ disappeared after ozone cleaning.

5.3.3 Influence of UV-ozone treatment on TiO₂ properties

The annealed TiO₂ mesoporous layers were analysed by UV-VIS-NIR spectrophotometry prior to the dye-sensitising process. As a result, the optical energy band gaps were calculated for UV-ozone treated and untreated samples. The absorbance spectra obtained were recalculated to Tauc plot, a graph of $(\alpha h\nu)^{1/2}$ versus $h\nu$, where α is an absorption coefficient and $h\nu$ is a photon energy^[138]. To calculate the value of the optical band gap, the linear region of the graph has to be extrapolated, as shown in Figure 5.7.

As expected, the band gap calculated for the treated and untreated samples was the same and was equal to 3.22 ± 0.02 eV. It is consistent with E_g values for the anatase form of TiO₂ crystals, which were reported by other researchers^[139]. Ozone molecules are not able to penetrate the bulk of titanium(IV) oxide. Thus, the ozonisation did not affect its inner structure and bulk properties. Any change, such as crystal structure or stoichiometry, would be seen in shifted E_g values.

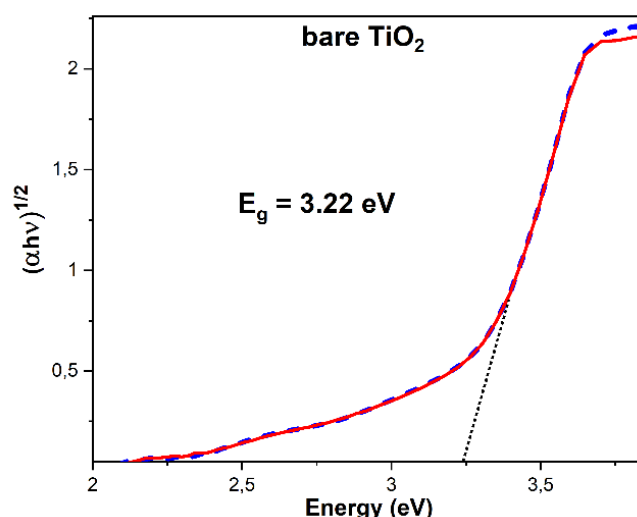


Figure 5.7. Tauc plot of mesoporous TiO₂ before (dashed blue) and after (solid red) UV-ozone treatment. The linear extrapolation (dotted black) presents the optical band gap.

Nonetheless, the cleaning effect was visible in the change of work function, which was measured by the Kelvin probe method in the air. The work function of TiO₂ depends on at least a few parameters. They could be, for example, preparation method, annealing atmosphere, crystal structure, annealing temperature, etc. However, one of the most reported value for the TiO₂ crystal, which is stoichiometric and annealed, is 5.0 eV^[140]. The WF for the untreated sample was equal to 5.56±0.03 eV, but after UV-ozone cleaning this value turned to 5.06±0.02 eV. These numbers were calculated for three different samples and then averaged. The effect of decreasing work function can be explained by slight oxidization of the material surface. According to other studies^[140], in the case of titanium(IV) oxide, a surface oxidation process results in a higher WF. However, taking into consideration the previously data obtained by FTIR and Raman spectroscopies, we could assumed with a high degree of certainty that the change in WF was caused by the removal of organic residues.

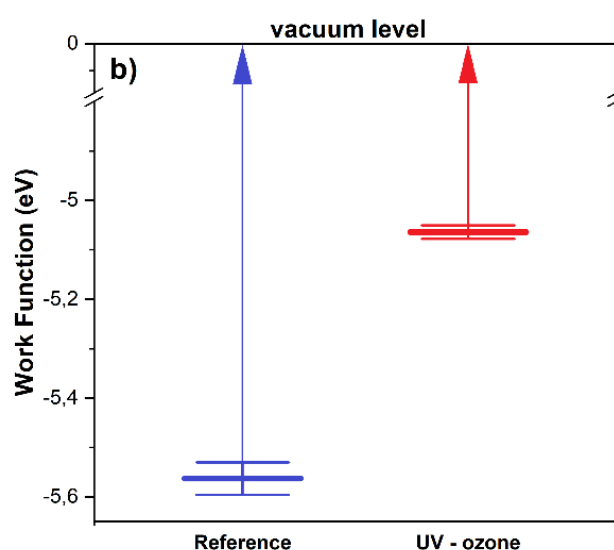


Figure 5.8. Work function for mesoporous TiO₂ before (blue) and after (red) UV-ozone treatment obtained by Kelvin probe measurements in air.

The value of the work function is a potential that is needed to be applied to extract the electron from the sample. Thus, if any additional layer is present on the surface of the sample, especially when it is an insulating material, this value increases. It could be easily explained by the presence of an extra potential barrier on the electron's way to the probe. In simple words – the higher is the barrier, the greater potential is needed to eject the electron from the sample. Furthermore, the change in work function in the effect of oxidation is more relevant, when TiO₂ is treated by the oxygen plasma^[141] rather than a low-power UV-induced ozone.

5.3.4 Enhanced dye-sensitising efficiency

The two parts of UV-treated and untreated substrates were then dye-sensitized in a solution of N719 for 24 h. After that, the samples were characterised by spectrophotometric measurements. Firstly, the absorbance spectra were acquired for the sensitized TiO₂. The N719 molecule has its peak at $\lambda_{\text{ABS}} = 540$ nm. It is clearly visible in Figure 5.9a that the absorbance around that peak was noticeably higher in case of UV-ozonised layer. Similarly, the same result was affirmed by the photoluminescence effect. Presented in Figure 5.9b. spectra show an emission peak at $\lambda_{\text{emis}} = 650$ nm. The signal was acquired at an excitation wavelength of $\lambda_{\text{exc}} = 540$ nm. Once again the signal was higher for the UV-treated sample (see Figure 5.9b). Both results could be explained by an enhanced dye-sensitising efficiency. When the surface of TiO₂ was free of organic impurities, more dye molecules were able to bond covalently within the mesoporous layer. Thus, both the absorbance and the luminescence signals were considerably augmented.

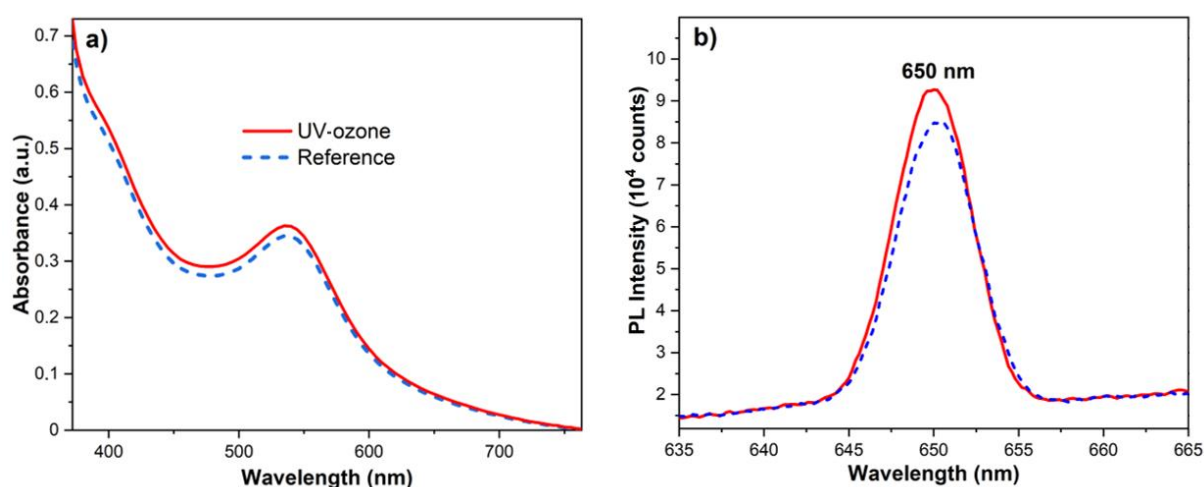


Figure 5.9. Spectra of a) absorbance and b) photoluminescence of N719-sensitized TiO₂, which were treated (solid red) and untreated (dashed blue) by UV-ozone.

The dynamic mode of SIMS was used to analyse the subsurface adhesion of the N719 dye molecules. Dual-beam measurements were carried out with the ToF analyser in a depth profiling mode. The samples were sputtered with a caesium beam (Cs⁺, 1 keV, 75 nA) and analysed with a bismuth cluster beam (Bi₃⁺, 30 keV, 0.4 pA). To avoid the so-called edge effect, the sample was sputtered from an area of 500×500 μm², while the analysis was performed at its centre with a smaller area of 250×250 μm². The obtained depth profiles are presented in Figure 5.10. During the analysis, two characteristic ions were chosen as sample fingerprint. The first one – TiO₂⁻ ion, was used as a characteristic signal for TiO₂ layer and the second –

NCS⁻ ion, was selected for N719. The NCS⁻ ion was chosen, because it is one of the ligands in N719 molecule, which is bonded to the central atom (Ru). It is relatively easy to break the covalent bond between Ru and NCS group and, additionally, sulphur (S) is a unique element in the composition of N719-sensitized TiO₂. These characteristic ions were then analysed as a function of sputter time. The data obtained showed that more dye molecules were able to adsorb deeper within the subsurface TiO₂ structure in case of UV-ozone treated sample. It was directly observed as an increased intensity, in the sense of higher ion counts at specific depth, of NCS⁻ ions in the time range of 50-600 s. After that time both signals reached the plateau. Thus, based on the collected data, we can assume that the effect of UV-ozone treatment is effective not only on the surface, but also in the subsurface layers.

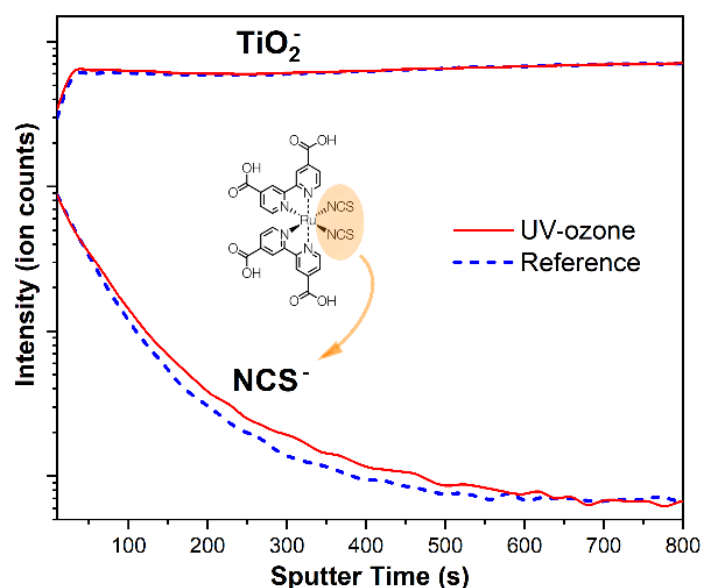


Figure 5.10. Depth profiles of N719-sensitized TiO₂, which were treated (solid red) and untreated (dashed blue) by UV-ozone. The analysed ions: NCS⁻ for N719 molecule and TiO₂⁻ for TiO₂ layer.

5.3.5 Performance of dye-sensitized solar cells

Completed dye-sensitized solar cells were then characterised by current-voltage measurements. Five devices of each type (treated and untreated by UV-ozone) were measured under a solar simulator. Figure 5.11 shows an exemplary U-I curves. As seen in the graph, the photocurrent was higher in the case of UV-ozonised samples. If we look closer to the horizontal axis, we can observe that the open-circuit voltage was also shifted slightly to higher values. On the basis of the curves obtained, the photovoltaic parameters were calculated and presented in Table 5.1. The UV-ozone treatment increased the short-circuit current from 10.3 ± 1.0 to 12.3 ± 0.7 mA/cm², the same as open-circuit voltage (from 667 ± 10 to 679 ± 10 mV) and fill factor (from 0.67 ± 0.01 to 0.70 ± 0.01). The change in photocurrent should be related to a higher adsorption of the N719 dye. When more molecules were able to bond to the surface, incident light flux was harvested more efficiently to generate the photocarriers. Overall, as a consequence of the change of these parameters, the efficiency of these devices was enhanced from $4.59 \pm 0.45\%$ to $5.89 \pm 0.38\%$, what gives a total improvement rate of approximately 28%.

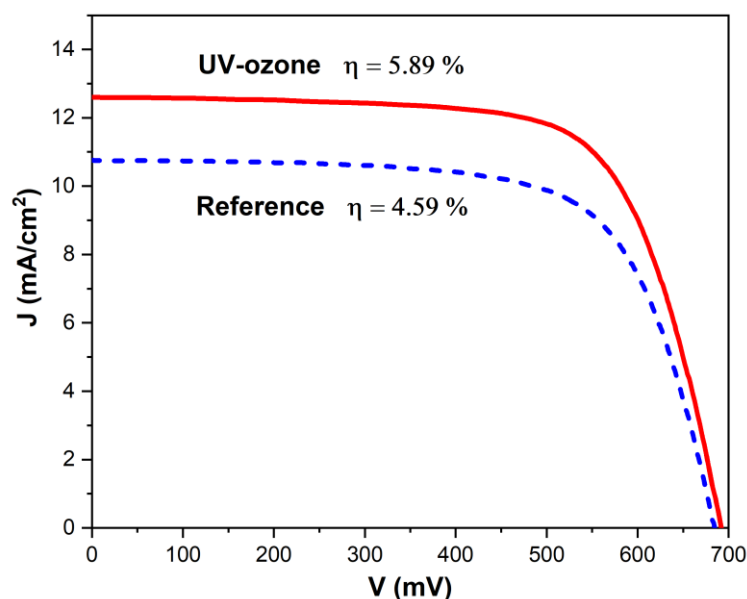


Figure 5.11. Current-voltage characteristics of treated (solid red) and untreated (dashed blue) by UV-ozone DSSCs.

The fill factor is directly related with the series and shunt resistances. The first one decreased from 58.1 ± 4.3 to 49.1 ± 3.9 Ω , while the second increased from 22.0 ± 5.3 to 39 ± 4.8 k Ω . With a high probability, their change was the result of a reduced recombination process in UV-ozone treated DSSCs. Thus, the photogenerated charge carriers were collected more efficiently by electrode, before they get recombined after the excitation, when the TiO₂ surface was free of the organic residuals. Additionally, according to SIMS results, we can imply that increased amount of N719 absorbers inside the TiO₂ structure may also be responsible for decreasing R_s . It could be caused by a shorter way that photogenerated carriers had to travel before they were collected by the electrode.

Table 5.1. Parameters obtained by current-voltage characteristics for treated and untreated by UV-ozone DSSCs.

DSSC	U_{oc} (mV)	J_{sc} (mA/cm ²)	FF	PCE (%)	R_s (Ω)	R_{sh} (k Ω)
Reference	667 ± 10	10.3 ± 1.0	0.67 ± 0.01	4.59 ± 0.45	58.1 ± 4.3	22.0 ± 5.3
UV-ozone	679 ± 10	12.3 ± 0.7	0.70 ± 0.01	5.89 ± 0.38	49.1 ± 3.9	39.0 ± 4.8

5.4 Conclusions

The UV-induced ozone was used to remove the organic residues from the surface of TiO₂ nanoparticles, which formed the mesoporous layer of titanium(IV) oxide. The presence of organic contaminations was proven by spectroscopic methods. A 20-minute process of low-power ozonisation was applied to clear the photoanode substrates prior to the dye-sensitisation. FTIR and Raman spectroscopies were used to find the differences between the UV-treated and untreated samples. The acquired spectra for the samples before cleaning contained low signals, which were associated with C-C and C-H vibrational modes. They were no more present in the spectra after the UV-ozonisation. The cleaning effect was also

correlated with enhanced dye-sensitising process. The obtained absorbance and photoluminescence signals were noticeably higher for ozonised samples. Additionally, obtained by secondary ion mass spectroscopy depth profiles provided information on the higher signal from N719 molecule in the subsurface depth of dye-sensitized TiO₂. All these results allow us to conclude that, due to the removal of organic impurities, more dye molecules were able to covalently bond to the surface of mesoporous TiO₂. Therefore, in increased amount of N719 absorber molecules led to a higher photocurrent generated by completed dye-sensitized solar cells. All of the reported photovoltaic parameters were enhanced. Overall, the base efficiency of $4.59 \pm 0.45\%$ was improved to $5.89 \pm 0.38\%$. It was possible mainly due to an increase in the short-circuit current and slight improvement in both open-circuit voltage and fill factor.

Chapter 6

Effect of Magnetron Sputtered TiO₂ Electron Blocking Layer

6.1 Introduction

Dye-sensitised solar cells were modified in many ways to improve their performance. Some attempts were focused on changing its typical structure. For instance, novel wide band gap semiconductors with various structures were developed to replace the titanium(IV) oxide nanoparticles, from which we can mention nanotubes, nanowires and nanospheres that have been tested in DSSCs^[142]. At the same time, scientists developed the performance of various dyes. A dozen of new molecules were synthesised to enhance the absorbance spectrum in the visible range of light^{[143]-[144]}. However, besides introducing new materials and solving other technical problems, like the time-dependent drop in power conversion efficiency^[145] or the electrolyte leakage^[146], some physical problems still have to be solved^[147]. One of the frequently reported mechanisms that decrease the DSSC efficiency is the electron-electrolyte recombination process.

Typically, in an ideal model, after the photon absorption the dye gets to the excited state. The exciton is then splitted into the hole and the electron. The latter is subsequently injected into *n*-type semiconductor (TiO₂) and transferred to the collecting electrode (FTO). At this moment, the charge carrier should be directed to the external circuit and be able to power any electronic device. Unfortunately, there are at least a few possible paths through which electrons could recombine. Two of them are the most significant – recombination at TiO₂/electrolyte and FTO/electrolyte interfaces. To reduce these effects, the electron blocking layer (EBL) was introduced. As it was shown in Figure 6.1, their function is to prevent charge carriers from being injected back into the electrolyte. It is possible because the additional layer is able to provide more preferable transport along the FTO due to the appropriate band structure.

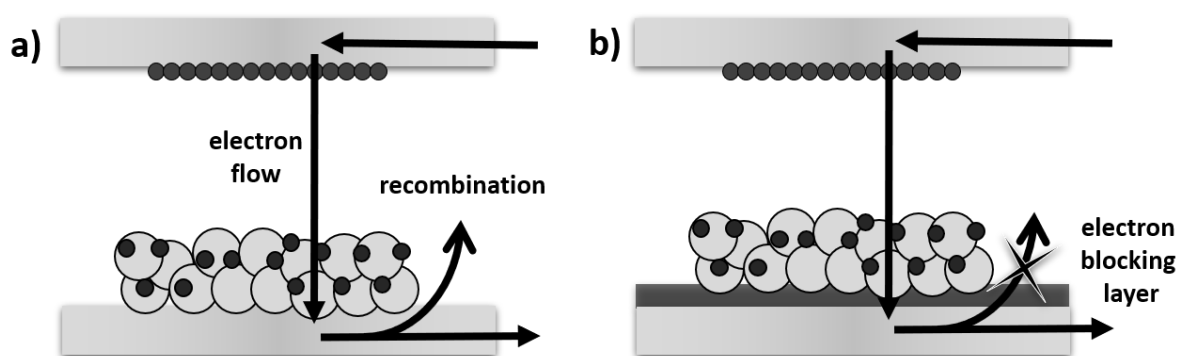


Figure 6.1. Schematic representation of a) the electron/electrolyte recombination pathway in the typical architecture of DSSC and b) the effect of electron blocking layer.

The electron blocking layer could be deposited directly on the titanium(IV) oxide surface^[148] or on the FTO glass before the screen printing of titania paste^[149]. According to the latest

knowledge, the dominant recombination occurs at the substrate/electrolyte rather than at the mesoporous TiO₂/electrolyte interface. That is a relevant information, because it is much more easier to cover the flat surface of FTO than a few micrometers thick layer of sintered nanoparticles. Two significant conditions have to be fulfilled by EBL to perform properly. Firstly, the coating should be continuous to avoid FTO contact with electrolyte. Secondly, it should be thin enough to prevent a high ohmic resistance through the layer, because the resistance is proportional to the thickness of the layer.

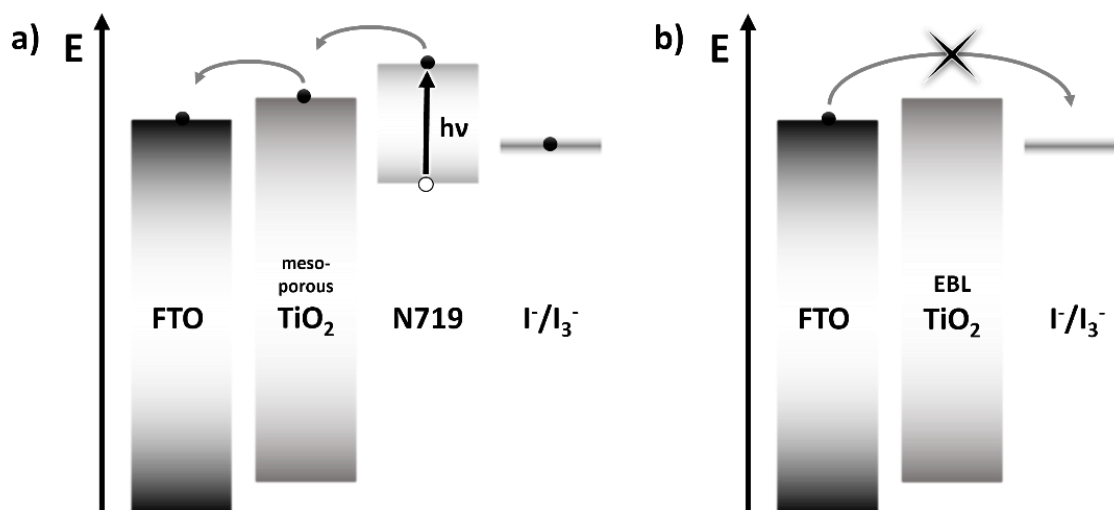


Figure 6.2. Energy diagrams presenting a) the electron injection to the FTO electrode and b) the effect of electron blocking layer, which prevents electrons from being injected back to the electrolyte.

Reported materials that were deposited directly on the mesoporous TiO₂ were often represented by metal oxides with wide band gaps, such as Al₂O₃, HfO₂^[150] or MgO^[151]. Because it is difficult to prepare a continuous coating on a mesoporous structure, CVD methods are required. The precursor gas is able to penetrate the layer, thus, a large part of the surface can be covered. However, CVD is complicated to use, because it requires a toxic and hazardous precursor that can be harmful to the people and the environment. Secondly, the process is carried out at high temperature, which can reach several hundred Celsius degrees, which may affect other layers. Thus, EBL are placed more often directly on the FTO glass. Various methods have already been reported, from which sol-gel^[152], electrodeposition^[153] or spray-coating^[154] are the most popular. That low-cost deposition techniques are typically considered as most promising. However, they are not able to provide a highly repeatable process, which is a great disadvantage of wet deposition methods. In case of EBL, the parameters, such as thickness, stoichiometry and layer purity are crucial for further DSSC performance. Hence, magnetron sputtering seems to be the best choice due to its simplicity and repeatability. Among many possible materials for electron blocking layer (SnO₂^[155], ZnO^[149], Nb₂O₅^[156]) TiO₂ is suggested to be the most suitable, because of its low-cost, high *n*-type conductivity, chemical inertness to electrolyte, availability and energy band structure matching to other layers.

6.2 Experimental

6.2.1 Magnetron sputtering

Magnetron sputtering is an example of physical vapour deposition (PVD) method^[157]. The process chamber must be pumped to reach a high vacuum, which minimizes the pressure of all background gases and potential contaminants. When the proper pressure is reached, argon is injected into the chamber with a specific flow rate to maintain the constant pressure. Plasma is then generated by applying a high voltage between the cathode and the anode. The cathode is located behind the sputtering target, which is the material to be deposited. The electrons presented in the sputtering gas are accelerated and ionise the gas through multiple collisions. Positively ionised argon atoms are then attracted by a high potential to the negatively charged target. As a result of such bombardment, the atoms are ejected into the vacuum with a high kinetic energy (see Figure 6.3). The substrate, which is located opposite the cathode, is then coated by atoms sputtered from the target material.

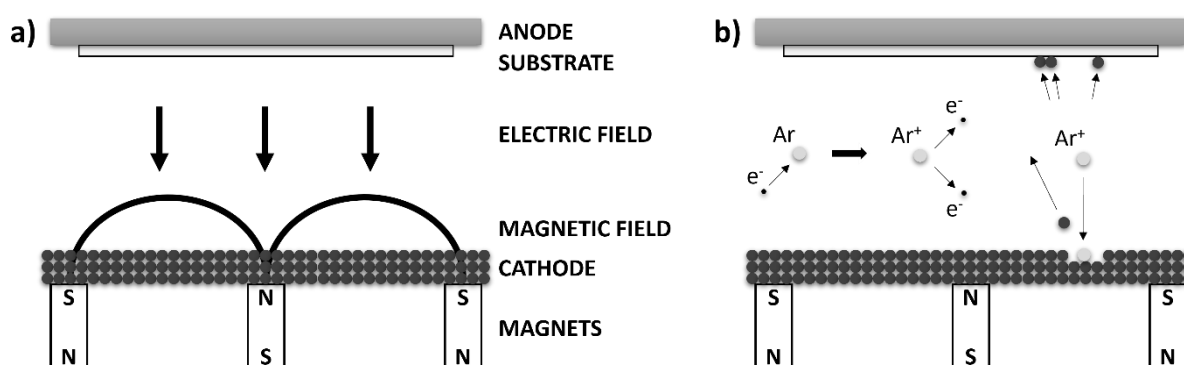


Figure 6.3. Schematic representation of a) the configuration of magnetron sputtering system and b) the process of plasma generation and layer deposition.

Additionally, modern magnetron guns are equipped with magnets. Their role is to generate the magnetic field, which changes the electron path from a straight line to a helix, which is caused by the Lorentz force. Because of the enhanced probability of collision with sputtering gas, the plasma density increases, leading to higher deposition rates. Secondly, the magnetic field prevents the damage, which could be caused by direct impact of the accelerated electrons with the substrate or the forming coating. Magnetron sputtering method is widely used to produce a conductive materials (DC sputtering) or insulators and semiconductors (RF sputtering)^[158]. It is also possible to strictly control the stoichiometry of growing film by applying the reactive sputtering^[159]. In such process, plasma gas is generated from a mixture of argon and additional gas, for example oxygen, which is able to build into the crystal structure of deposited material.

6.2.2 Preparation of dye-sensitised solar cells

The reference samples were prepared as previously described. To study the effect of EBL, an additional step was introduced into the preparation process. Before the screen printing of titania paste, the FTO substrates were cleaned by ultrasonication. Then, they were transferred to the MiniSpectros PVD process chamber provided by Kurt J. Lesker (Figure 6.4). When the pressure of about 10^{-5} mTorr was reached, the substrates were heated to the temperature of

300 °C. Increased temperature was applied to enhance the adhesion of the layers and, thus, electric contact between them. After a 10 minutes of stabilisation, the argon was injected with a plasma ignition pressure of 10 mTorr. At the same time, the power of RF gun was set to 100 W to induce the plasma ignition. When the plasma was already launched, the pressure was decreased to working value of 3 mTorr and keep at that level for the whole process. Five minutes of pre-sputtering was applied to clean the target surface from any contaminations before opening the substrate shutter. Then, the deposition time was tuned to receive a layer of approximately 30 nm, which was reported elsewhere as the most effective thickness for EBL in DSSC^[160]. When the process was already finished, the chamber was vented and TiO₂ coated substrates were transferred to the screen printer, where the titania paste was applied on their surface. In the following steps, the entire DSSC preparation process was completed and the devices were then ready for measurements. Herein, two sizes of active layers were tested to study the EBL effect. The first, laboratory-sized one with dimension of 7×7 mm² and up-scaled dimension of 7×80 mm².



Figure 6.4. The interior of PVD process chamber in ML System laboratory with two magnetron sputtering guns: RF (left) and DC (right).

6.3 Results and discussion

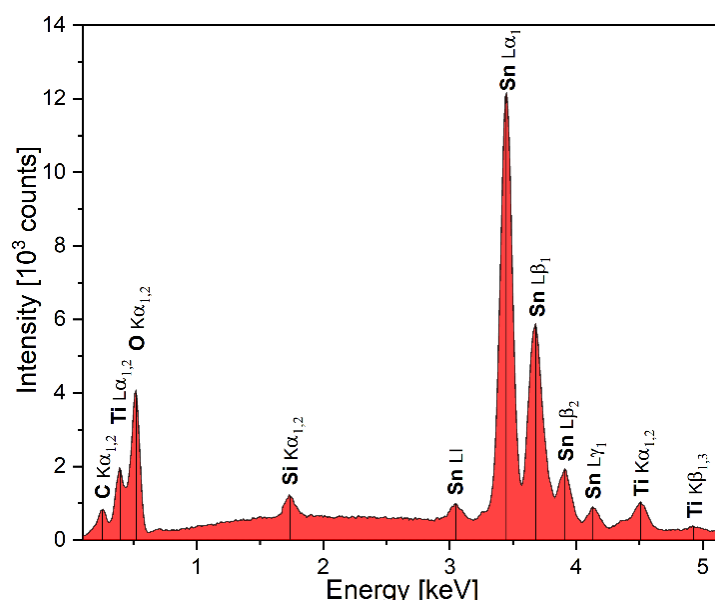
6.3.1 EDS analysis

To verify whether the TiO₂ coating was successfully deposited on the FTO substrate, the EDS measurements were carried out. For this purpose, the sample was transferred into the vacuum chamber with SwiftEDS 300 module (Oxford Instruments). The electron beam energy was set to 15 kV, which is a maximum analysis accelerating voltage for this apparatus. Characteristic X-ray emission lines were identified based on the database^[161] and tabulated in Table 6.1.

Table 6.1. Characteristic lines obtained from the EDS spectrum. The energy unit is keV.

Element	C	O	Si	Sn					Ti		
Line	K $\alpha_{1,2}$	K $\alpha_{1,2}$	K $\alpha_{1,2}$	Ll	L α_1	L β_1	L β_2	L γ_1	L $\alpha_{1,2}$	K $\alpha_{1,2}$	K $\beta_{1,3}$
Energy	0.27	0.52	1.74	3.05	3.44	3.67	3.91	4.13	0.39	4.51	4.93

One of the obtained spectra, presented in Figure 6.5, contains the signal for carbon (C), which is a result of atmospheric adsorption of carbon dioxide, because the sample was not heated prior to measurement. The weak signal from silicon (Si) was observed in the spectrum, because of the presence of glass substrate, which is a type of silica (SiO_x). The peak from oxygen (O) was a superposition of signals coming simultaneously from TiO₂, SnO₂:F and SiO_x layers. There was also a broad multipeak tin signal (Sn Ll, L α_1 , L β_1 , L β_2 , L γ_1), which came directly from the FTO substrate. According to the manufacturer's datasheet, the thickness of FTO is about 250 nm. The presence of three characteristic lines for titanium (Ti), identifies as L $\alpha_{1,2}$, K $\alpha_{1,2}$, K $\beta_{1,3}$, was a proof that the TiO₂ layer was successfully deposited on the substrate.

**Figure 6.5.** EDS spectrum obtained on the sample with the thin film of TiO₂.

6.3.2 Thickness of electron blocking layer

To determine the thickness of deposited coating, the Profilm3D optical profilometer (Filmetrics) in WLI mode was used. Before the deposition of TiO₂, the edge of the FTO glass was covered by the polyimide tape. After the process of material sputtering, the tape was removed and the edge was cleaned by isopropyl alcohol to remove the residues of glue that may affect the measurement. Then, the TiO₂ step was found under the profilometer's microscope objective and the profile data was acquired. To calculate the step height, the height histograms were prepared as presented in Figure 6.6. The area of bare FTO is represented by a cyan, whereas the titanium(IV) oxide coating is marked by olive colour. The visible grey area was probably the coating, which was ripped off during the tape detaching and it was not included in further calculations. The Gauss functions were fitted to the two

obtained peaks. To estimate the thickness of TiO₂, the difference between the centre of the two peaks was calculated. As shown in the histograms, the approximate thickness was 33 nm.

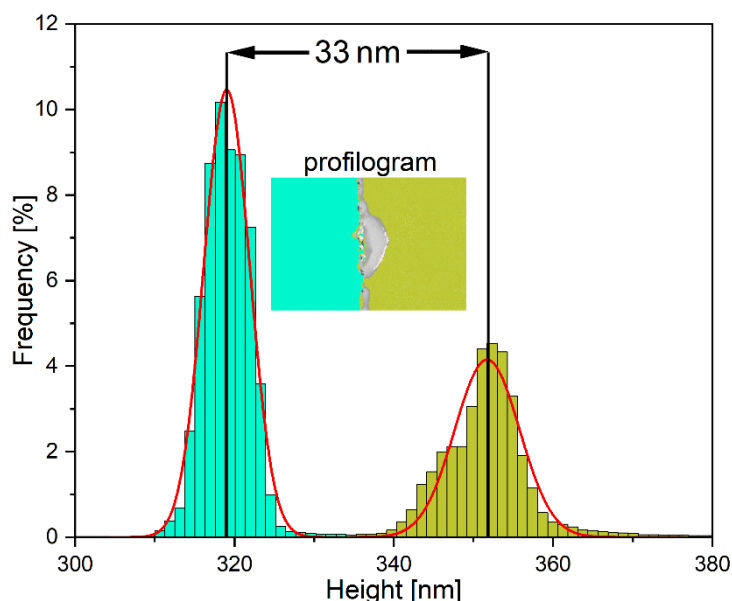


Figure 6.6. Results from the optical profilometer – the height histogram for TiO₂ step (olive) on bare FTO glass (cyan). The difference between the Gauss peaks determines the thickness of TiO₂.

6.3.3 SEM and AFM analysis

The deposited electron blocking layer was characterised by the Quanta 3D FEG SEM microscope (ThermoFisher) and the C3000 AFM (Nanosurf AG). The topography of the TiO₂ coated FTO (Figure 6.7b) was similar to the bare FTO. The same conclusion was made by Choi et al^[162]. In his work, he claimed that because of the high roughness of FTO the thin EBL layer was difficult to observe on the SEM image.

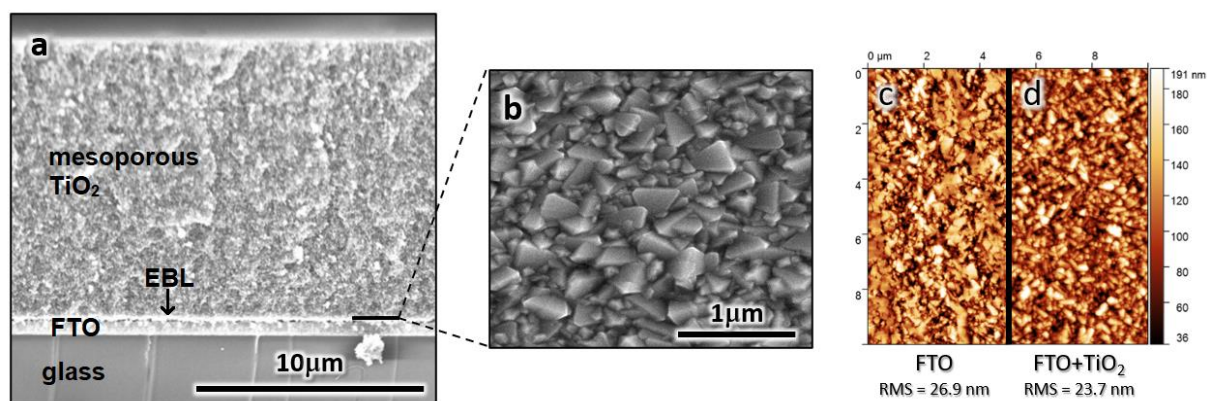


Figure 6.7. SEM images of a) photoanode intersection (from the bottom): glass, FTO, compact and mesoporous TiO₂ and b) top-view of the deposited TiO₂ EBL on FTO. AFM images of c) bare FTO surface and d) deposited TiO₂ electron blocking layer on FTO.

The AFM images are presented in Figures 6.7c and 6.7d. The RMS values were calculated in Gwyddion analysis software^[163] for the AFM data obtained in tapping mode. They were 26.9

and 23.7 nm for bare and coated substrate, respectively. For the same reason as described above, the thin film of TiO₂ did not significantly change the RMS parameter. Additionally, Figure 6.7a shows the intersection image containing all of the photoanode layers. From the bottom they were: glass substrate, FTO layer, TiO₂ compact layer and TiO₂ mesoporous layer. The thickness of the latter was obtained by the stylus profilometer and was approximately 11 μm what agreed with the thickness observed in the SEM image.

6.3.4 Crystal structure of electron blocking layer

The samples were analysed by Raman spectroscopy to obtain information about the polymorphism of the magnetron sputtered titanium(IV) oxide. The thin films were deposited on cleaned FTO substrates and then annealed with the same temperature programme as the TiO₂ paste. The thickness of deposited layers was higher (about 200 nm) than EBL used in DSSC to provide a good signal rate. Analysis was conducted with the He-Ne laser with the wavelength of 633 nm and the power of 17 mW. The system was equipped with a confocal microscope, two-dimensional multichannel CCD detector and automatic Czerny-Turner spectrograph with a slot width of 30 mm for a wide-flat field of view.

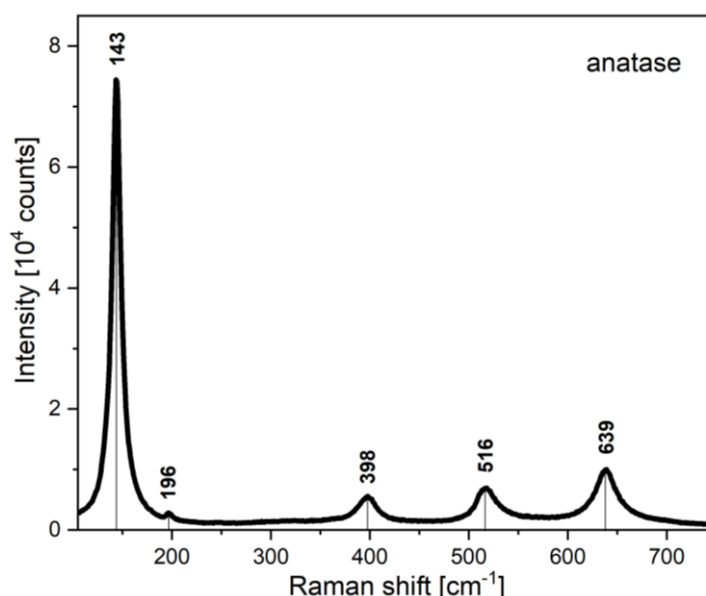


Figure 6.8. Raman spectrum of magnetron sputtered TiO₂. The data is characteristic for anatase^[137].

Acquired spectrum was similar to the spectrum for anatase TiO₂ reported in other studies^[137]. The signals for characteristic vibration modes are presented in Figure 6.8. We can distinguish a few characteristic vibrations that are located at 143 cm^{-1} (E_g), 196 cm^{-1} (E_g), 398 cm^{-1} (B_{1g}), 516 cm^{-1} (A_{1g}) and 639 cm^{-1} (E_g). The vibrational modes were described by the Mulliken symbols. They are associated with the point group and represent the symmetry of the molecule's vibrations. More detailed description could be found elsewhere^[164]. The data obtained confirmed that the 30 nm TiO₂ in EBL is in the form of anatase, the same as TiO₂ in mesoporous layer. It was a relevant information, because of the matching conduction band levels of both materials, it was possible to provide a good electrical flow of charge carriers to

the electrode. When two materials in contact have different energy levels, the potential barrier could occur and the electric flow may be disturbed.

6.3.5 UV-Vis-NIR spectroscopic analysis of photoanode

Typically, the DSSC is illuminated from the photoanode side. Thus, the UV-VIS-NIR spectrophotometry was used to analyse the transmittance of photoanode with additional EBL layer. Measurements were carried out by Jasco V-670 spectrophotometer with deuterium and halogen lamps. To average the signal from some area, the light spot size was set to maximum value of about 3×3 mm². Figure 6.9 presents the transmittance versus wavelength spectra for the different stages of photoanode preparation. The transmittance was the highest for the bare FTO. The deposited 30 nm layer of TiO₂ slightly changed the spectrum. The decrease was observed mainly in the range from 600 to 1100 nm. An additional layer of 11 µm mesoporous TiO₂ layer significantly changed the transmittance in the near UV region, because anatase energy band gap is about 3.2 eV, what corresponds to the photon's wavelength of approximately 387 nm.

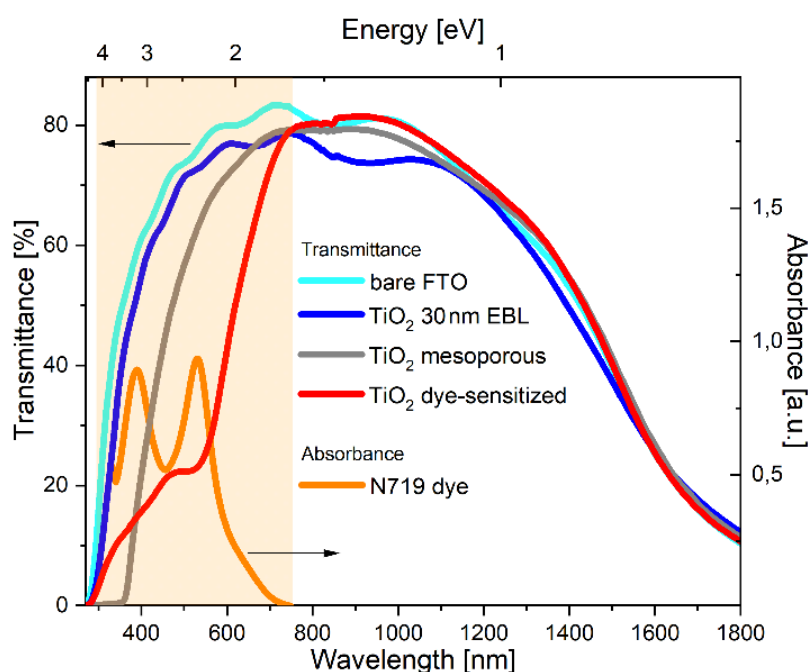


Figure 6.9. Spectroscopic spectra of individual components of DSSC photoanode. Transmittance spectra of bare FTO (light blue), 30 nm of TiO₂ EBL (navy blue), mesoporous TiO₂ (grey) dye-sensitized TiO₂ (red) and absorbance spectrum of N719 dye in ethanolic solution (orange).

After the dye-sensitisation, the relevant change in transmittance was observed in visible region (400-800 nm). It was caused by the fact, that the N719 dye has its absorbance in that range of wavelengths. In addition, the absorbance spectrum of pure N719 in ethanolic solution was presented in the spectrum. Measurement was performed for 10⁻⁴ M solution in quartz cuvette with an optical thickness of 1 cm. It is noteworthy that the dye molecule had two absorbance maxima (390 and 530 nm), but generally absorbs the light from 300 to almost 800 nm. As mentioned above, in comparison to bare FTO, the electron blocking layer changed

the transmittance spectrum just slightly. Thus, it could be assumed that it has no significant influence on the amount of light, which is reaching N719 dyes and should have no negative impact on the solar cell performance.

6.3.6 Performance of dye-sensitised solar cells

The performance of prepared DSSC devices was investigated by a CLASS-01 solar simulator (Test Solutions). The samples were illuminated with AM1.5 lamp with a light intensity of 100 mW/cm². The obtained current-voltage curves for laboratory-size (7×7 mm²) and up-scaled (7×80 mm²) devices are presented in Figure 6.10. In both cases there was a slight shift in open circuit voltage. The change was not significant, because the TiO₂ EBL and TiO₂ mesoporous layers had the same levels of the conduction band, providing good electrical contact and electrical stability between them. The same conclusion was also reported by other researches^[165]. Additionally, this effect could be explained by the fact that the U_{oc} value strictly depends on the difference between the level of TiO₂ conduction band and the electrolyte redox potential^[166]. Therefore, the thin film of the EBL should not relevantly affect this parameter.

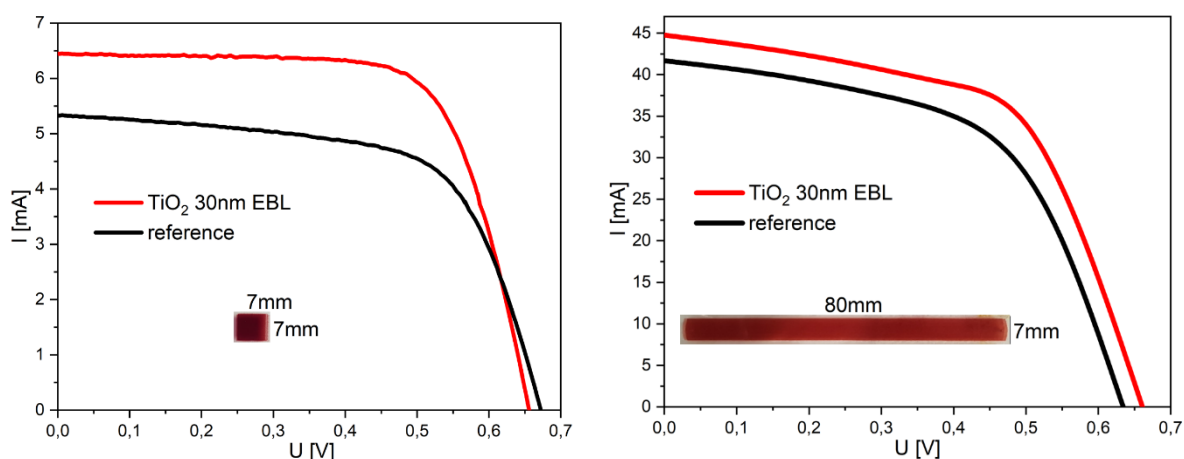


Figure 6.10. Current-voltage characteristics for 7×7 mm² and 7×80 mm² DSSCs with and without 30 nm electron blocking layer.

As shown elsewhere^[167], the onset of cathodic dark current could be increased by a thin film of electron blocking layer on the FTO electrode, which could be caused by the higher potential barrier for the electron transfer from the FTO to the electrolyte. In this research the same effect was observed. The presence of EBL led to the enhancement in the short circuit current and the fill factor. For small samples the I_{sc} increased from 5.33 mA to 6.44 mA and for large samples from 41.67 mA to 44.80 mA. Simultaneously, the FF was improved from 0.64 to 0.70 and from 0.55 to 0.58 for small and large samples, respectively. The increase in both parameters indicates that the recombination process was successfully mitigated. As a consequence, the DSSC devices with EBL exhibited 30% and 17% higher efficiency compared to the reference solar cells, depending on the sample's size. The PCE in 7×7 mm² devices increased from 4.67 to 6.07%, while for the 7×80 mm² devices from 2.62 to 3.06%. The lower efficiency for large samples could be explained by the recombination process. When the electron moves through the FTO layer, it can be scattered or recombined on the defects of crystal structure or crystal boundaries. Additionally, if the electron incidentally meets the hole in the structure

of FTO, it may undergo a relaxation process. In such situation, the longer is the electron path through the electrode, more often such effects occurs. To mitigate that problem in large samples, the silver electrodes were screen printed along the active layers, which were deposited about 2 mm from the mesoporous TiO₂ and had a dimension of 2×80 mm². These structures are visible as a silver strips in the photography shown in Figure 6.11. Their role was to collect the photogenerated charge carriers and ease their transport to the external electrodes, because the silver strip has lower resistance than FTO layer. The photovoltaic parameters were tabulated in Table 6.2, where the average values and errors (standard deviation) were calculated for 8 samples for each kind of DSSC.

Table 6.2. DSSC parameters obtained from U-I curves for 7×7 mm² and 7×80 mm² samples with and without 30 nm electron blocking layer.

Sample Size (mm ²)	U _{oc} (V)	I _{sc} (mA)	P _{max} (mW)	FF	PCE (%)
7×7 w/o EBL	0.67	5.33	2.29	0.64	4.67
	±0.03	±0.06	±0.05	±0.02	±0.12
7×7 w/ EBL	0.66	6.44	2.97	0.70	6.07
	±0.04	±0.09	±0.05	±0.02	±0.16
7×80 w/o EBL	0.63	41.67	14.75	0.55	2.62
	±0.04	±2.18	±0.93	±0.05	±0.34
7×80 w/ EBL	0.66	44.80	17.30	0.58	3.06
	±0.04	±2.28	±0.69	±0.04	±0.26

6.4 Conclusions

In the following chapter, the effect of thin titanium(IV) oxide film as an electron blocking layer in DSSC devices was studied. The RF magnetron sputtering method was chosen to prepare these layers on FTO substrates. This method was selected, because it has a great up-scaling ability and is characterised by high repeatability and simplicity in use. An approximately 30 nm thick layer of TiO₂ was deposited prior to screen printing of the mesoporous TiO₂ layer. Although the EBL layer was not visible in the SEM images, the RMS parameter, obtained by AFM measurements, decreased after the TiO₂ sputtering. Additionally, the characteristic titanium lines were observed on EDS spectrum, which confirmed the presence of EBL on the FTO surface. According to the measurements carried out by Raman spectroscopy, both EBL and mesoporous TiO₂ had the anatase polymorph, what suggested that the electrical contact between these two layers was good, because of the conductive band levels and crystal structure matching. Otherwise, a potential barrier could occur at the interface between them and negatively affect the flow of electrons to the external electrode. Data obtained by spectrophotometric measurements showed that the presence of EBL did not significantly change the amount of light that was passing by the photoanode in the range of the absorbance of N719 dye.

The performance was enhanced for both laboratory-sized (7×7 mm²) and up-scaled (7×80 mm²) DSSC devices. As a consequence of the increase in short circuit current and fill

factor, the power conversion efficiencies augmented from 4.67 to 6.07% and from 2.62 to 3.06% for small and up-scaled cells, respectively. The relevant difference between the PCEs was probably caused by the recombination process in FTO electrode, which is more significant for up-scaled substrates and could be a subject for further research on decreasing the recombination process in dye-sensitised solar cells.



Figure 6.11. Photography of up-scaled module with 8 individual dye-sensitised solar cells.

Chapter 7

Scalable Method for Horizontal-Dipping Electrodeposition of Platinum Nanoparticles

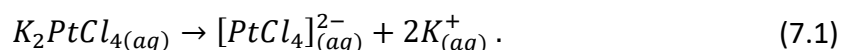
7.1 Introduction

A little over 30 years passed since M. Grätzel published his first article on dye-sensitized solar cells^[20]. However, there is still no information about the mass production of such devices for commercial use. DSSCs are getting more stable^[145] and efficient^[168], but certainly, one of the main remaining problems is the up-scaling^[169], which could lower the production costs^[170] and make them more favourable in production than silicon-based photovoltaics. The preparation process is still a great challenge. Making it more suitable for mass production will enhance the power-to-cost ratio. A full roll-to-roll process has not yet been reported for DSSCs, as it was for organic photovoltaic devices (OPV)^{[171]-[172]}. In this dissertation, a novel method to produce platinum nanoparticles will be presented. It is a combination of both sliding meniscus and electrodeposition techniques, which has a great opportunity to be up-scaled to large areas. In comparison to the traditional screen-printing method, where the platinum paste is deposited on the substrate and then annealed at high temperatures, it consumes less power and needs less time. Hence, we can assume that it is an eco-friendly and relatively cheap process. It does not need toxic substances, because the deposition process is carried out with the aqueous solution of platinum salt as a precursor. Additionally, the whole preparation process is done in one step, which is impossible in the traditional printing method with paste, where the samples have to be preheated, then annealed for several hours and finally cooled down to room temperature^[173]. Presented here results are demonstrated in application to DSSC devices. However, it could be used to prepare platinum-based antimicrobial^[174] or catalytic^{[175]-[176]} coatings, which have an opportunity to be applied in the field of medicine or chemistry.

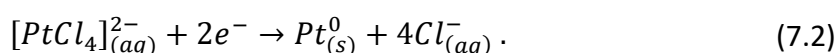
7.2 Experimental

7.2.1 Principle of platinum electrodeposition

The electrochemical reaction, which led to the formation of platinum nanoparticles is divided into a few steps. This process was described, for instance, by Zubimendi et al. in their article^[177]. Firstly, the platinum salt dissociates in water according to the following reaction



As presented in Figure 7.1, the platinum in $[PtCl_4]^{2-}$ ions undergoes a reduction on working electrode. Therefore, during the reduction process, the platinum particles are formed directly on the surface of conductive substrate. This electrochemical reaction is described as follows



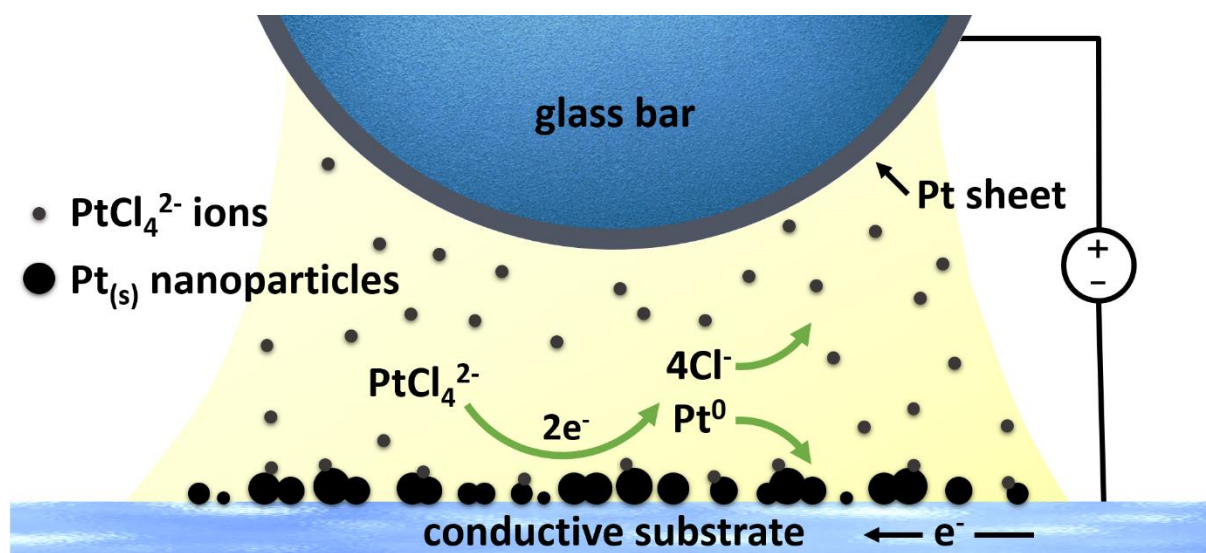


Figure 7.1. Schematic of the meniscus cross-section with the platinum electrodeposition process.

7.2.2 Novel electrodeposition method

The self-built apparatus was used to carry out the process of electrodeposition in the sliding meniscus. The device consists of a platinum-covered sheet glass bar and a moving stage, which moves horizontally. The distance between the bar and the substrate was set to 500 μm , which was controlled by a step motor. Then, the precursor solution with a volume of 100 μl was put between them, thus, as shown in Figure 7.2, the solution formed a meniscus. During the deposition, the meniscus was moving back and forward at the speed of 1 mm/s along the substrate to cover subsequent areas with nanoparticles. As mentioned above, this method was combined with electrodeposition. Hence, while the meniscus was moving, the constant current was applied between the bar and the conductive substrate.

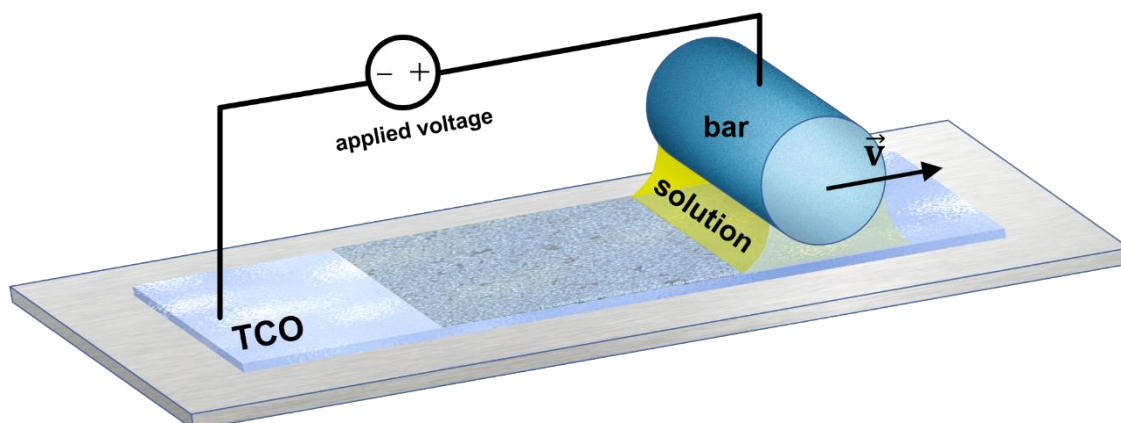


Figure 7.2. Self-built apparatus used to prepare electrodeposited platinum on TCO substrate.

The DSSCs' cathodes were prepared by the described above method for up-scaled electrodeposition in a two-electrode system. The working electrode was the FTO glass, which was subsequently coated, and the counter electrode was the platinum sheet covering the glass bar. The precursor solution of potassium tetrachloroplatinate(II) (K_2PtCl_4)^{[178]–[180]} with

a molar concentration of 0.1 M was applied to form a meniscus. This salt is highly soluble, so the solution is ready within a few minutes after adding deionised water to the precursor. It is a great advantage in case of potential mass production, because it does not need any further action, such as degassing, purification, etc. The platinum was applied as a counter electrode, because of its chemical inertness. Additionally, it served, in some extent, as an ion source to refill the lack of Pt ions in the solution. As a result of applied voltage during the horizontal movement of the meniscus, the whole substrate was covered by platinum nanoparticles. Thanks to that method, it is possible to cover large areas with a relatively small amount of precursor, especially when it is compared with the traditional electrodeposition process, where the substrate needs to be fully immersed into the solution. Thus, the volume of the solution needs to be hundreds to thousands bigger, depending on the deposition cell, than in the sliding meniscus method.

7.2.3 Preparation of DSSC devices

The platinum cathode was prepared with different currents to study various FTO coverages on dye-sensitized solar cells' efficiency. Platinum deposition efficiency depends on the applied voltage (in constant voltage mode) or current (in constant current mode). Here, the results of three different currents are presented. The samples were prepared with 1, 4 and 7 mA on the FTO substrates with a dimension of 20×75 mm², which were then cut to a dimension of 20×20 mm². Ready cathodes were then sealed with photoanodes. Their preparation was performed conventionally, as was described in the previous chapter. Filled with the commercial iodine-based electrolyte DSSCs were then characterised by current-voltage measurements under a solar simulator.

7.3 Results and discussion

7.3.1 Efficiency of electrodeposition process

To estimate the efficiency of electrodeposition process the absorbance measurements were performed. The initial solution of 0.1 M K₂PtCl₄ and pure water were measured by UV-VIS-NIR spectrophotometer in quartz cuvette. The water spectrum, presented in Figure 7.3, had two broad peaks between 900 and 1250 nm. These peaks were observed in other solutions and they were not taken into account in further calculations. In the case of precursor's spectrum, two additional peaks appeared. Their maxima were localised at the wavelength of 390 and 470 nm.

After each electrodeposition process, the precursor solution was picked up with a pipette and poured to sealed glass vial. Thereafter, their absorbance spectra were acquired by spectrophotometer to calculate the platinum ions loss. As expected, the smallest absorbance was recorded for the highest deposition currents, what agrees with SEM images, because the more platinum nanoparticles on the substrate, the less platinum ions remained in the precursor solution. According to Beer-Lamber law

$$A = \varepsilon \ell c \quad (7.3)$$

the absorbance linearly depends on molar absorptivity coefficient (ε), optical path length (ℓ) and solution concentration (c).

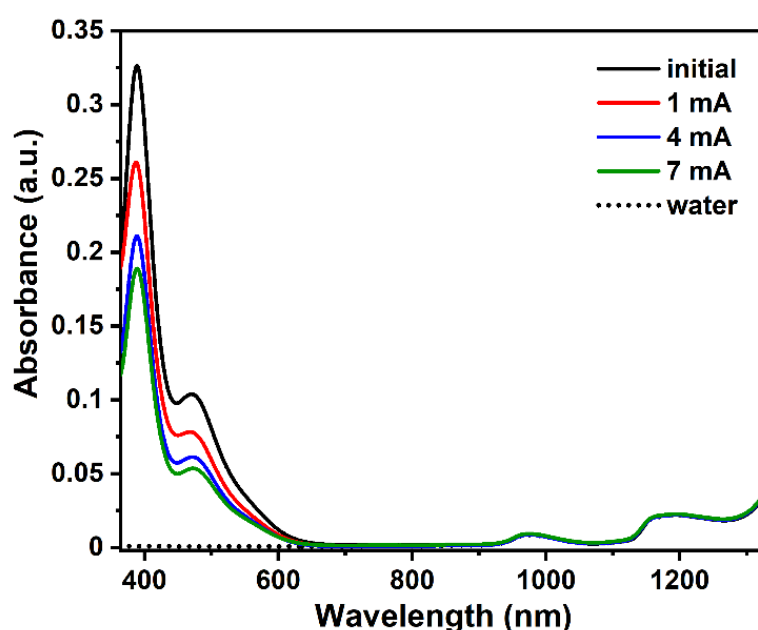


Figure 7.3. Absorbance spectra for pure water and K_2PtCl_4 solution before and after electrodeposition processes with different currents.

The values of absorbance in the peak maximum at 390 nm, shown in Figure 7.4, were known for pure water (0) and initial solution (normalised to 1). Recorded absorbances of solutions after electrodeposition were followingly put on the graph. Because the absorptivity coefficient and optical path length (2 mm) were constant for each measurement, it was possible to calculate the remaining concentrations. Based on that, the calculated molar concentrations were 0.080, 0.065 and 0.058 M for 1, 4 and 7 mA, respectively.

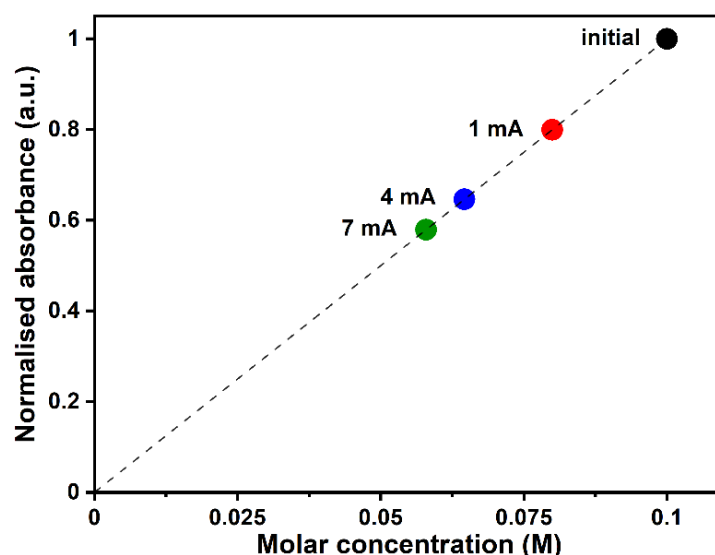


Figure 7.4. Normalised absorbance in a function of K_2PtCl_4 molar concentration. Absorbance for solutions after electrodeposition process were calculated from absorbance peaks.

The difference in concentration between 4 and 7 mA was lower than 1 and 4 mA. During the process, the increased deposition current resulted in higher deposition voltage. Hence, the effect could be explained by higher applied potential, which was able to transfer more platinum ions from counter electrode into the solution. As previously mentioned, the counter electrode plays an additional role of Pt reservoir, which is able to refill ions. Overall, the ions loss in the solution on $20 \times 75 \text{ mm}^2$ (1500 mm^2) substrate was calculated to 20, 35 and 42% relative to the initial solution. According to these results, it can be roughly approximated that the solution volume of $100 \text{ }\mu\text{l}$ is able to cover 7500 mm^2 for 1 mA, 4286 mm^2 for 4 mA and 3581 mm^2 for 7 mA deposition currents.

7.3.2 Nanoparticles morphology and surface coverage

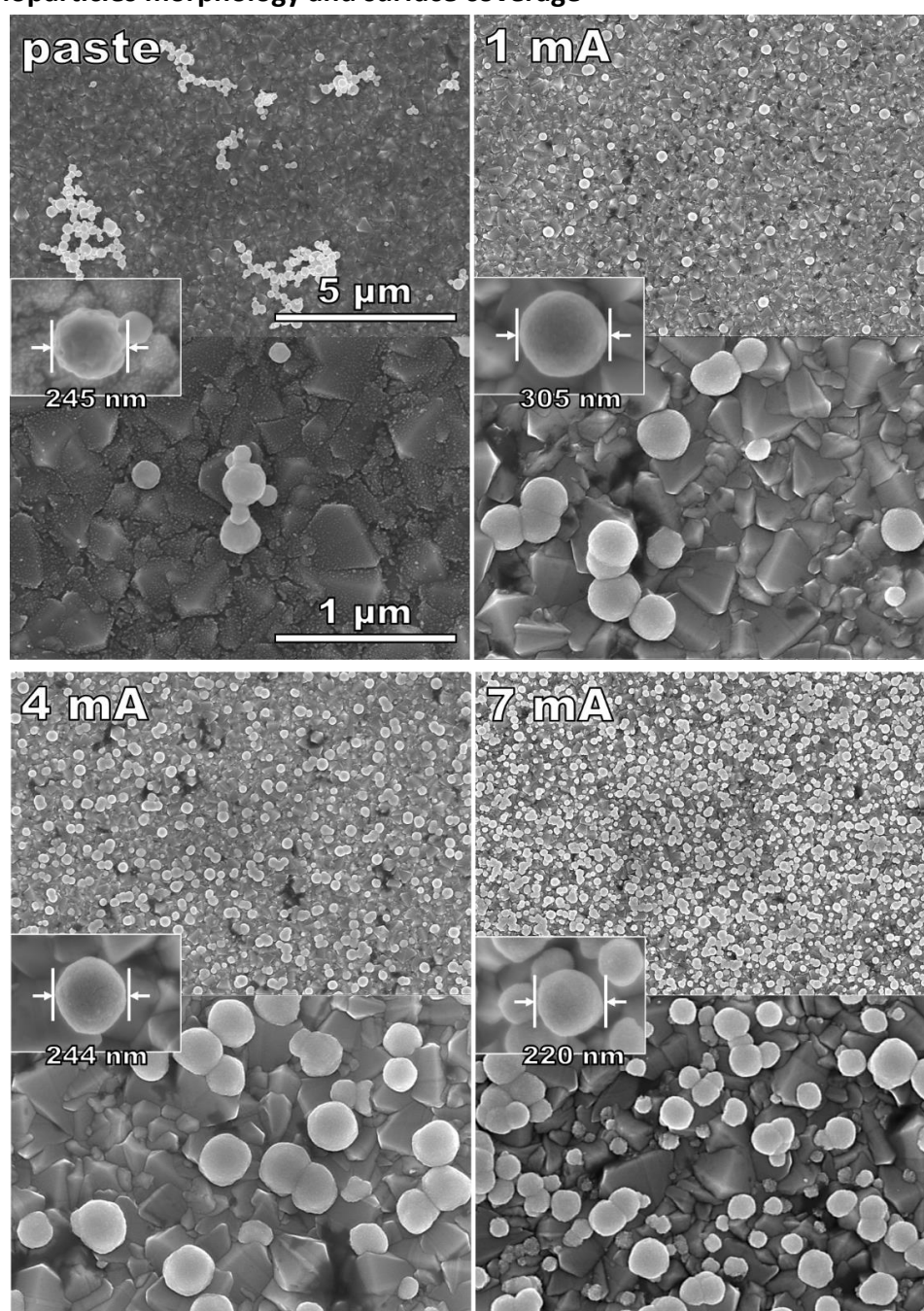


Figure 7.5. SEM images obtained from screen-printed and electrodeposited samples.

SEM method was used to observe the morphology of the nanoparticles. Obtained images are presented in Figure 7.5. They were acquired by BSE and SE detectors for general and detailed images, respectively. BSE was chosen in the first case to provide better contrast between the particles and the substrate. Large crystals visible in the background were the crystallites of the $\text{SnO}_2\text{:F}$ (FTO) substrate, which surface is rough in this scale. The reference sample, prepared by the screen-printing method, shows the aggregated platinum nanoparticles. Their spatial distribution was very inhomogeneous, especially when compared with electrodeposited samples. In this case, the nanoparticles were evenly distributed over the surface.

The deposition current was additionally correlated with the coverage of the substrates. That parameter was calculated in Gwyddion (ver. 2.58) software by the threshold method. Obtained SEM images were converted into binary images, where the background pixels were set to 0, while the bright nanoparticles to 1. The amount of 1-value pixels was divided by the number of all pixels (1280×960), what gave information about the percentage coverage of the substrates. Samples prepared with the current of 1 mA exhibited the lowest coverage of 7.8%, while the higher current led to higher coverage. It was equal to 23.0% and 48.6% for the samples prepared with 4 and 7 mA, respectively. Platinum nanoparticles prepared by screen-printing covered 8.6% of the substrate surface. Another interesting information obtained by SEM was the particles shape. These prepared by the electrodeposited method were spherical and their surface was relatively smooth. Nanoparticles received from the annealed paste were also spherical, but their surface was very rough.

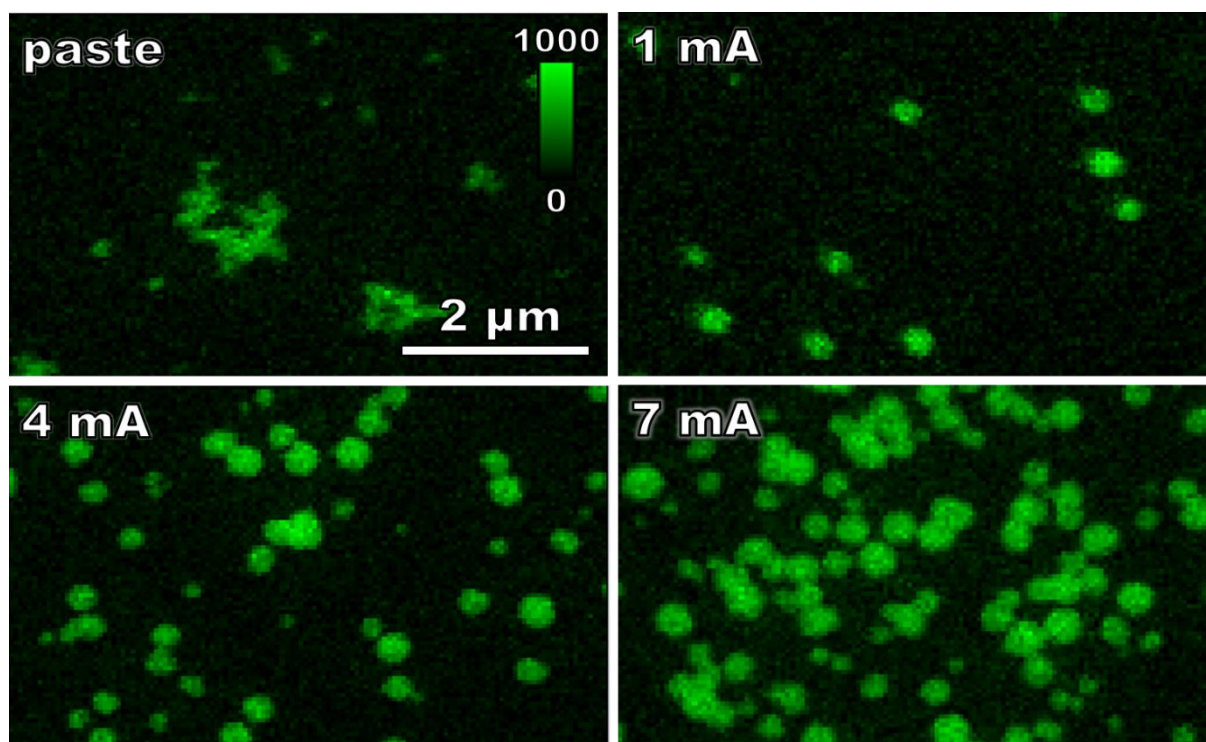


Figure 7.6. EDS maps obtained from screen-printed and electrodeposited samples. The signal from Pt L_α line was marked by green colour.

It is possible to produce rougher structures, which was reported by Hsieh et al.^[181] in their article. The addition of sulfuric acid (H_2SO_4) to the platinum precursor solution resulted in

more expanded and rough surface of deposited particles. As can be seen in the image corresponding to samples prepared with a current of 7 mA, the high concentration of particles on the substrate resulted in the formation of the nanoparticles agglomerates. Additionally, the diameter sizes of some nanoparticles were presented in the images. However, as presented in the wide view images, the size distribution of the spheres was very inhomogeneous. The diameter varied from tens to hundreds of nanometres in each sample, which was observed also in both SEM and EDS images. The results of EDS mapping is shown in Figure 7.6.

7.3.3 The electrochemically active surface of platinum nanoparticles

To calculate the electrochemically active surface (ECSA) of platinum nanoparticles, the cyclic voltammetry (CV) measurements were carried out in a 0.5 M solution of sulphuric acid (H_2SO_4). The scan rate was set to 20 mV/s. Recorded voltammograms are presented in Figure 7.7. The signal peak in the range of 0.4-0.9 V was a result formation/reduction of the platinum hydroxide (Pt-OH_{ad}). The formation of a double charged layer was observed for the potential region from 0.0 to 0.4 V.

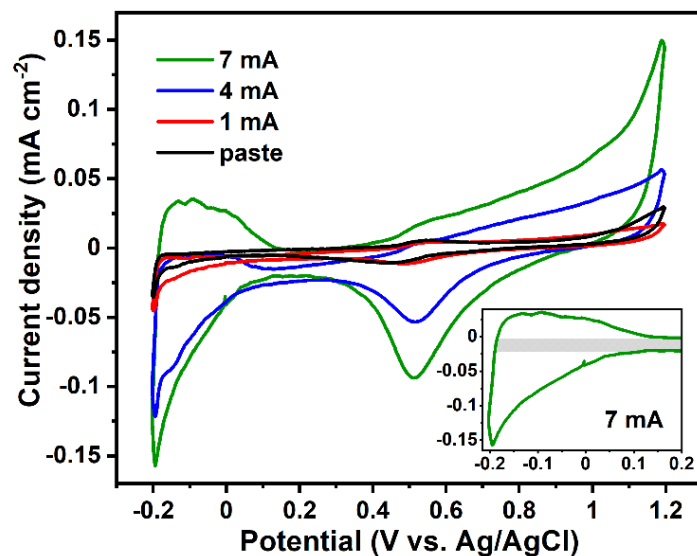


Figure 7.7. Cyclic voltammograms measured in 0.5 M sulphuric acid (H_2SO_4) at scan rate of 20 mV/s for the screen-printed and electrodeposited samples. The shaded area is an example of double hydrogen layer area, which was subtracted before the calculation of ECSA.

The values of ECSA were calculated from the hydrogen adsorption/desorption region, which was localised between the potential values from -0.2 to 0.2 V. The active surface of deposited platinum was estimated by integrating the current under the CV curves for forward and reverse scans within this range (Q_H^0). Followingly, the charge associated with the double layer was subtracted and divided by the scan rate. An example of the subtracted area is presented in Figure 7.7. It is a shaded area inside the CV curve. The calculations were done by using a simple equation:

$$ECSA = \frac{Q_H}{Q_H^0}. \quad (7.4)$$

The Q_H^0 is the theoretical quantity of charge that is required for a hydrogen monolayer adsorption on the assumption that one hydrogen atom bonds to one atom on the platinum surface (Pt-H_{ad}). Its value is equal to 0.21 mC/cm^2 . Such method was described in more detail by Li et al.^[182]

Calculated values of ECSA are presented in Figure 7.8. The platinum nanoparticles prepared by screen printing had the lowest active surface of 0.23 cm^2 . In the case of electrodeposited platinum, the ECSA was 0.50 cm^2 for 1 mA , 2.06 cm^2 for 4 mA and 3.90 cm^2 for 7 mA . The results are consistent with the SEM images, where it was clearly visible that higher deposition current led to higher substrate coverage.

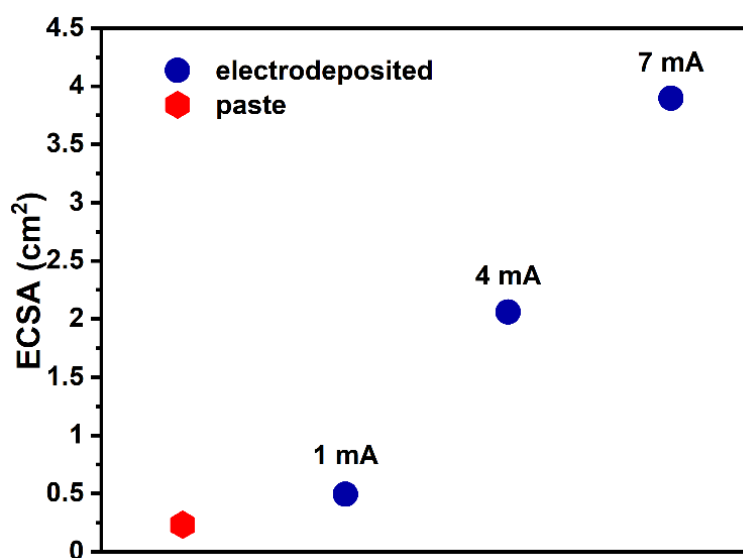


Figure 7.8. Electrochemically active surface area (ECSA) calculated from CV measurements in 0.5 M sulphuric acid (H_2SO_4) of platinum cathodes prepared by screen-printing and electrodeposition methods.

The electrocatalytic performance was also studied by the irreversible electro-oxidation reaction of ammonia. The solution contained 0.1 M of NH_3 and 1 M of KOH . The scan rate was set to 25 mV/s . As expected, the lowest peak current, which was observed in -0.3 V , was reported for the lowest ECSA in the case of nanoparticles prepared from platinum paste and the highest for the sample prepared by electrodeposition with the current of 7 mA . The mechanism of this irreversible electrochemical reaction was proposed in the article by Gerischer and Maurer^[183]. It includes the hydrogenation of NH_3 to N atom and recombination of two NH_x ($x = 1, 2, 3$), where partially dehydrogenated species of NH_2 and NH are active intermediates to give the final product of N_2 . Observed in Figure 7.9. anodic peak is characteristic for the oxidation in the proposed reaction. There is also an article showing that bare FTO or ITO do not participate in such electrochemical reaction^[184]. Hence, we can assume that the observed in the CV curves signal was generated only by the platinum presented in Pt/FTO cathode. High currents observed in CV experiments also indicate good electrical contacts between platinum nanoparticles and the FTO substrate, which provides a good charge transport between them. It also shows that nanoparticles are well connected to substrates, what prevents them from detaching.

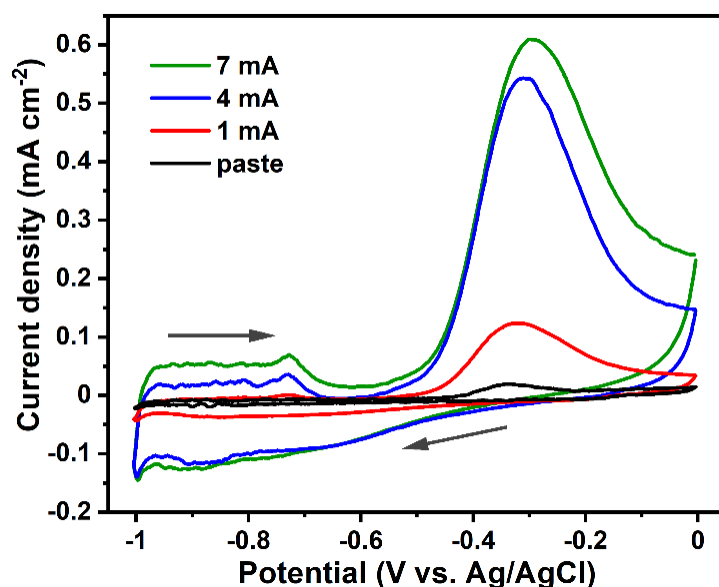


Figure 7.9. Cyclic voltammograms measured in 0.1 M NH_3 with 1 M KOH at 25 mV/s scan rate on platinum cathodes prepared by screen-printing and electrodeposition methods.

7.3.4 Performance of DSSCs

Prepared DSSCs were then characterised by U-I measurements under AM1.5 illumination. Based on the obtained curves, which are shown in Figure 7.10, the photovoltaic parameters were calculated and tabulated in Table 7.1. Presented values were averaged for three devices for each deposition method and the uncertainty of measurement was calculated by standard deviation. Additionally, some parameters were graphically presented in Figure 7.11.

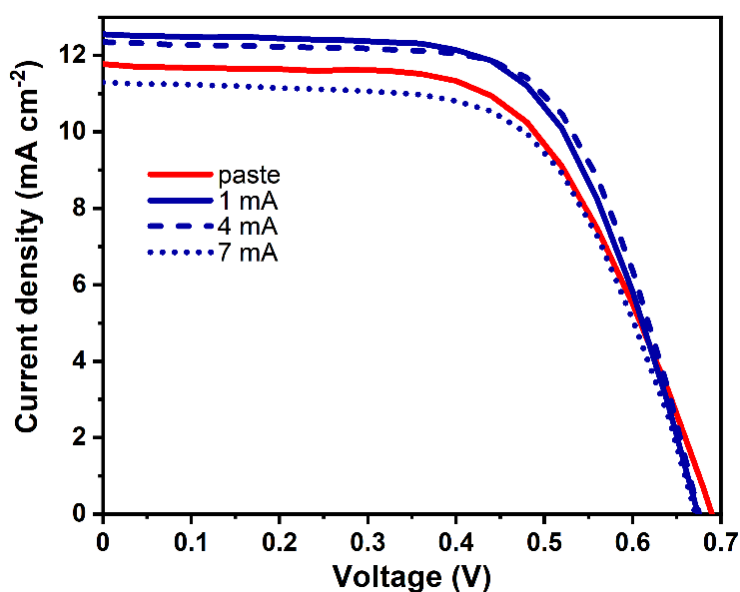


Figure 7.10. Current-voltage characteristics under AM1.5 illumination of prepared DSSCs with platinum cathodes prepared by screen-printing and electrodeposition methods.

The open circuit voltage was highest for the DSSC with the cathode prepared with platinum paste (0.687 V). It was lower for every device, which was prepared by electrodeposition. The

U_{oc} in these cases was 0.678, 0.671 and 0.668 V for 1, 4 and 7 mA, respectively. It is noteworthy that the difference between the lowest and the highest value was only 3%. Thus, this parameter had no significant impact on final power conversion efficiency. The short circuit current for screen-printed devices was located between the values for electrodeposited samples. It was 12.1 mA/cm² for the reference DSSC and 12.5, 11.9 and 11.4 mA/cm² for 1, 4 and 7 mA deposition currents, respectively.

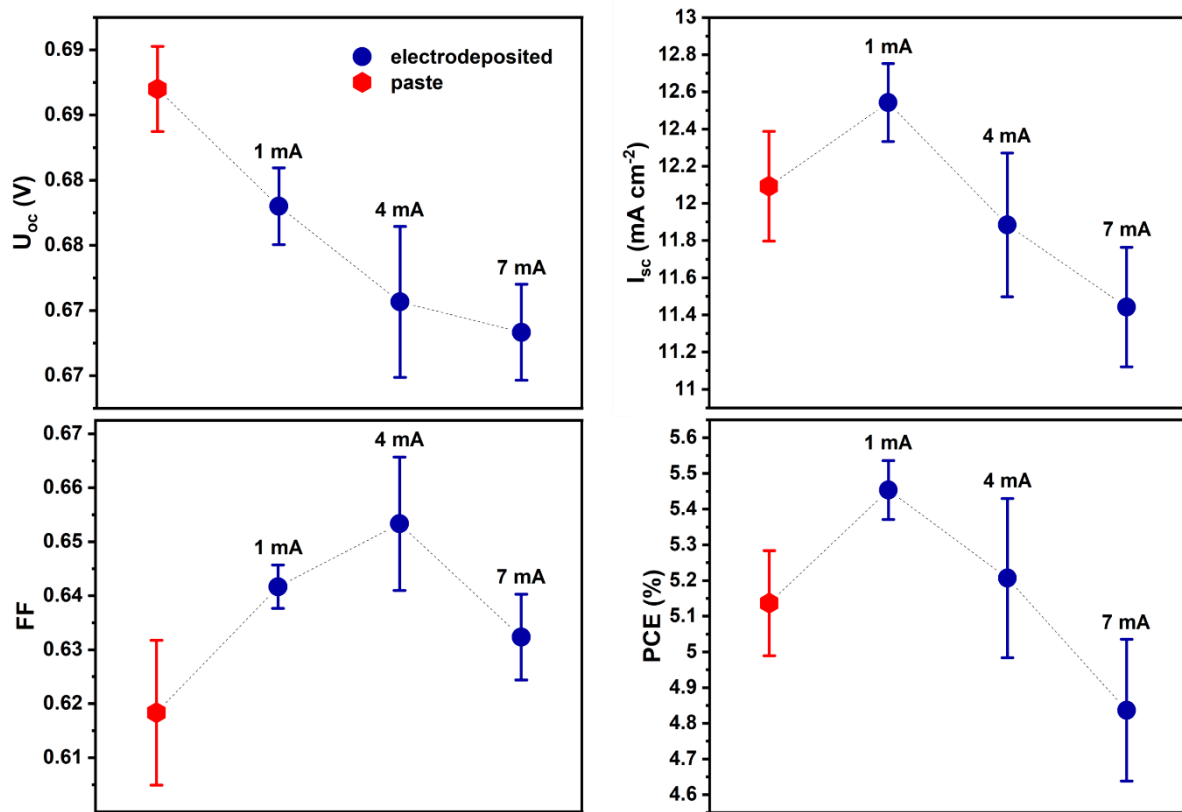


Figure 7.11. Photovoltaic parameters of dye-sensitized solar cells: open circuit voltage (U_{oc}), short circuit current density (I_{sc}), fill factor (FF) and power conversion efficiency (PCE).

Table 7.1. Photovoltaic parameters obtained by current-voltage measurements.

	U_{oc} (V)	I_{sc} (mA cm ⁻²)	FF	R_s (Ω)	PCE (%)
paste	0.687 ± 0.003	12.1 ± 0.3	0.62 ± 0.01	30.6 ± 1.8	5.14 ± 0.15
1 mA	0.678 ± 0.003	12.5 ± 0.2	0.64 ± 0.01	28.3 ± 1.8	5.45 ± 0.08
4 mA	0.671 ± 0.006	11.9 ± 0.4	0.65 ± 0.01	27.8 ± 2.9	5.21 ± 0.22
7 mA	0.668 ± 0.004	11.4 ± 0.3	0.63 ± 0.01	29.1 ± 2.0	4.84 ± 0.20

There were no noticeable trends for fill factor and series resistance parameters. However, each of the DSSCs with electrodeposited cathodes had a higher FF than the screen-printed one, what indicates that the current flow through the device was slightly enhanced. The power conversion efficiency, which is a combination of all mentioned parameters, was the highest for the sample prepared with the current of 1 mA. It was 5.45%, whereas the PCE for other currents was 5.21 and 4.84% for 4 and 7 mA, respectively. The efficiency of reference DSSC was localised between them, with the value of 5.14%. Considering all of that, we can assume that it is possible to prepare DSSC devices by the method of electrodeposition in sliding meniscus with the same or even greater PCE as traditionally DSSCs produced by screen-printing method with platinum paste.

7.3.5 Work function of FTO/Pt cathodes

To explain the effect of PCE decrease for higher electrocatalytic activity of cathode, the energy level diagram^[185] for each individual component of dye-sensitised solar cells was analysed. After a detailed analysis it could be noticed that change in work function of FTO/Pt cathode may affect the performance of DSSC device. Thus, the additional measurements were carried out by Kelvin probe method in air to obtain the WF of previously prepared cathodes. As shown in Figure 7.12, the WF of bare FTO was equal to 4.70 eV. This is a typical reported value, which may be slightly different depending on its preparation process or stoichiometry. Mostly, it ranges from 4.4^[186] to 4.9 eV^[187]. Measured FTO/Pt cathode prepared by screen-printing method had the WF of 5.05 eV, while the electrodeposited samples had 5.27, 5.53 and 5.77 eV for deposition currents of 1, 4 and 7 mA, respectively.

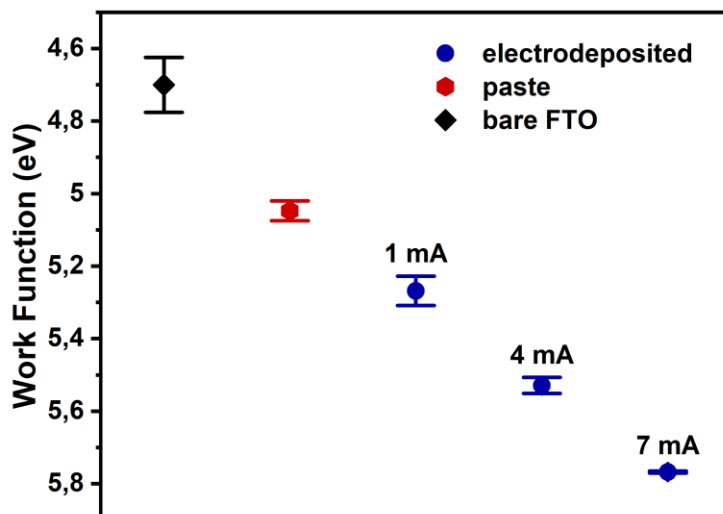


Figure 7.12. Work function measured by Kelvin probe for bare FTO and FTO/Pt cathodes prepared by screen-printing and electrodeposition methods. The reference probe was made of gold (Au).

Schematically presented energy levels for each DSSC materials is shown in Figure 7.13. As previously mentioned, lowering the cathode's level may affect the performance of the device. A significant difference between energies can cause an electron trapping in the Pt/electrolyte interface. The higher is the potential barrier, the higher voltage is needed to force the electron through this barrier. Thus, this result suggests that the lowering PCE effect

for higher electrodeposition currents was caused by increased loading of platinum on FTO substrate. The matching energy levels in an essential factor in photovoltaic device structure. This is also true for the cathode in DSSC, which is widely described in the article by Wu et al.^[188], where we can find an information that, apart from good catalytic activity and high conductivity, the counter electrode's energy level needs to match the potential of redox couple electrolyte to provide a good conditions for electrolyte to accept the electron from the electrode. Most of the scientific articles about DSSCs ignore the work function of the cathode and its function is limited to simply catalyse the redox reaction in redox electrolytes.

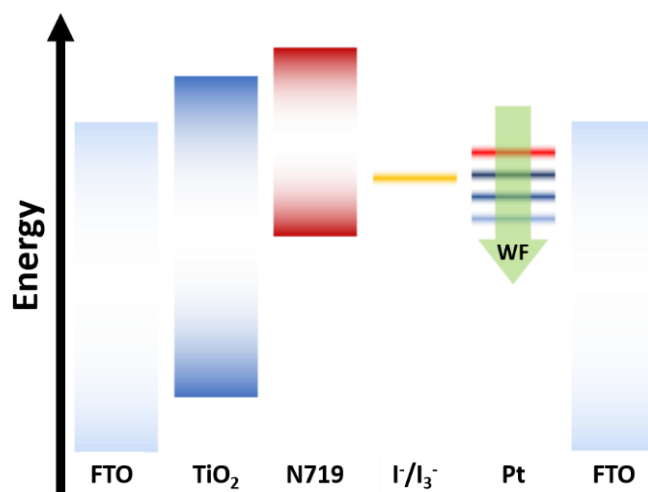


Figure 7.13. Schematic representation of energy level of each DSSC's component material. According to obtained results, the work function of FTO/Pt cathode decreases with higher deposition currents.

7.4 Conclusions

The novel functionalisation method of flat conductive substrates was presented. It is a modification of electrochemical deposition combined with sliding meniscus, which has an opportunity to be up-scaled for mass production. Such process could be easily conducted on flexible substrates, such as ITO-coated PET foils, because the method is compatible with roll-to-roll techniques. Here, the example of platinum nanoparticles deposition on FTO glass was presented. Obtained results showed that increased deposition current led to higher loading and coverage of platinum on the substrate. Observed by SEM structures were almost perfectly round, but their diameter distribution was significant. The CV measurements showed that prepared by electrodeposition platinum samples had a superior electrocatalytic performance than prepared by traditional screen-printing method. The electrochemically active area values were determined based on the cyclic voltammograms carried out in H₂SO₄ solution. As expected, the samples prepared with the highest current had the highest ECSA, while the lowest ECSA was for screen-printed sample. Prepared by the novel method platinum cathodes were also more electrocatalytically active, which was tested on irreversible electro-oxidation reaction of ammonia. Surprisingly, the power conversion efficiency of DSSCs was lower for higher deposition currents. This apparent discrepancy was explained by measuring work function of FTO/Pt cathodes. It was suggest that the decline in PCE was caused by the different loadings of Pt what led to the significant change in the WF values. Overall, prepared by

electrodeposition devices showed the PCE from 4.84 to 5.45%, for different deposition currents. The reference DSSC had an average PCE of 5.14%. Thus, it can be implied that the reported method of up-scaled electrodeposition is a promising alternative for screen-printing, which is commonly used in preparation of platinum cathode, but is very energy-consuming and difficult to up-scale. What is also important, presented here method could be applied to various materials, which can be prepared by electrodeposition, and be performed on any conductive substrate, including flexible ones. Additionally, presented here method of low-cost, scalable production of platinum nanoparticles could be further used in a production of catalytic or antibacterial coatings.

Chapter 8

Novel Polymer-Based Gel Electrolytes

8.1 Introduction

The typical dye-sensitized solar cell architecture contains a liquid redox electrolyte. Its role is to provide a charge flow between photoanode and cathode. The most popular are commercially available iodine-based mixtures, such as EL-HPE. Their wide use is mainly due to their low cost and good performance in short-term conditions. However, after being under solar illumination in ambient conditions, at least several problems could occur. First is the tightness problem. After long-lasting solar radiation the leakage or volatilisation problem may appear due to the electrolyte's high vapour pressure^[189]. Another problem, which is worth to mention, is the issue of corrosion. The iodine-based mixture contains some ingredients that could be corrosive to the elements in DSSC architecture. In the case of platinum nanoparticles, corrosion results in the formation of PtI_4 ^[190], which may cause that the counter electrode may not work properly and lower the solar cell efficiency. The third problem is most important in the countries in the middle latitudes, where the winters are cold. The liquid electrolyte is not thermally resistant and could cause physical damage to DSSC when it freezes^[191].

The exemplary solution for this problems could be the use of solid^[192] or quasi-solid state electrolytes^[193]. Unfortunately, the first one exhibits poor contact with mesoporous titanium(IV) oxide layer, because of its highly porosity, what causes low solar-to-electricity conversion rates. The quasi-solid state electrolytes provide better filling within the mesoporous structure of TiO_2 . This advantage makes it more suitable solution for DSSC^[194]. They are also known as gel electrolytes. This specific type of electrolytes are mainly composed of polymers, but contain some fraction of liquids as well, what provide a high ionic conductivity by trapping liquid electrolytes in cages formed by the polymer host matrix^[146].

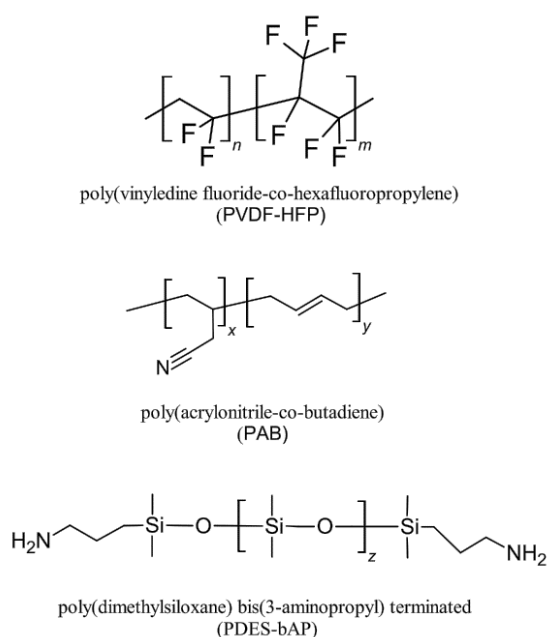


Figure 8.1. Chemical structure of polymers used to prepare the gel electrolytes^[195].

In this chapter, the results of novel polymer-based electrolyte for dye-sensitized solar cells are presented. The organic electrolyte was composed of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) doped with poly(acrylonitrile-co-butadiene) (PAB) or poly(dimethylsiloxane) bis(3-aminopropyl)-terminated (PDES-bAP) copolymers. Their structures are presented in Figure 8.1. Presented here gel electrolytes were designed and prepared by the group of prof. A. Iwan from the Military Institute of Engineering Technology (WITI, Wrocław, Poland). Gels with different concentrations were characterised at WITI, and their application in DSSC was tested in ML System S.A. (Zaczernie, Poland). The study was carried out to receive information about the electrical properties of fabricated DSSCs, its up-scaling capability to large area module and the time-dependent ageing process. Thus, two sizes of solar cells were tested – laboratory-size with dimension of $7 \times 7 \text{ mm}^2$ and up-scaled with dimension of $7 \times 80 \text{ mm}^2$.

8.2 Experimental

8.2.1 Preparation of gel electrolytes

The whole process of electrolytes preparation was held in the laboratory of Military Institute of Engineering Technology as follows. 10 wt.% of different polymers were dissolved in separate vials in 20 ml of acetonitrile. To obtain the homogenous mixture, the solutions were constantly stirred with a speed of 300 rpm and heated to 60 °C for 30 minutes and then to 80 °C. In order to optimise the properties and select the best-performing one, several electrolytes with different polymer ratios were prepared. Specific concentrations are shown in Table 8.1. Subsequently, crystalline iodine and lithium iodine were added to receive the concentrations of 0.08 mol/dm³ and 0.8 mol/dm³, respectively. A small amount of unbonded solvent was removed to receive a pure gel. The entire process was held in sealed flasks to avoid a significant loss of volatile compounds. After that, the temperature was decreased to 65 °C, what did not affect fluidity and homogeneity of the electrolytes. Further gelation process was performed in hermetically sealed glass bottles. The process lasted about ten days at room temperature and was additionally accelerated by freezing them down to -22 °C for 1 hour. The samples were then stored at stable room temperature prior to any measurements.

Table 8.1. Polymers content in electrolytes in relation to the weight of the solvent (acetonitrile).

Code	wt.% of PVDF-HPF	wt.% of PAB	wt.% of PDES-bAP
PVDF-HPF:PAB (9:1)	9	1	-
PVDF-HPF:PAB (8:2)	8	2	-
PVDF-HPF:PAB (7:3)	7	3	-
PVDF-HPF:PAB (6:4)	6	4	-
PVDF-HPF: PDES-bAP (9:1)	9	-	1
PVDF-HPF: PDES-bAP (8:2)	8	-	2
PVDF-HPF: PDES-bAP (7:3)	7	-	3
PVDF-HPF: PDES-bAP (6:4)	6	-	4

8.2.2 Preparation of dye-sensitized solar cells

The up-scaled device was prepared on 100×100 mm² FTO substrates. Before screen printing, the FTO was patterned to form electrically separated sections, each for a single DSSC. It was made by laser ablation (wavelength 1064 nm, DK Lasertechnik). Additionally, green laser (532 nm) was used to drill holes in the substrates (1 mm in diameter), which were used to fulfil the devices with electrolyte at the final step (Figure 8.2). The dye-sensitized solar cells were then prepared in a typical method described in Chapter 3, but devices were filled with the gel electrolyte instead of commercial, liquid electrolyte.

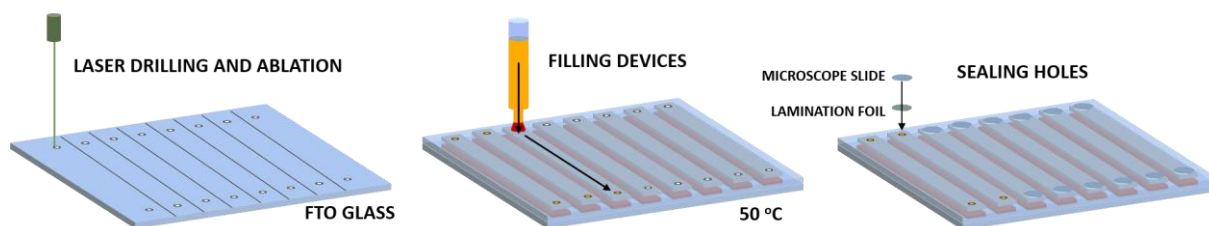


Figure 8.2. Preparation of DSSC module: drilling the holes and sections separation, filling the device, sealing the holes.

Before the filling, the vials with gels were heated in water bath at 80 °C. After approximately 2 hours, the solutions were homogenous, liquid and ready to use (see Figure 8.3). The main problem at this stage was the gelation of the electrolyte during the filling of the DSSC sections. Hot gel cooled down immediately after its injection and blocked the flow, preventing the entire volume of the cell from being filled. To avoid that, the DSSC modules were additionally placed on a hot plate at 50°C for 5 minutes, what solved that problem. Already filled DSSC modules were then protected from electrolyte leakage by sealing the holes with lamination foil and microscope slides. The laboratory-size devices were prepared in the same way on 20×20 mm² FTO substrates.

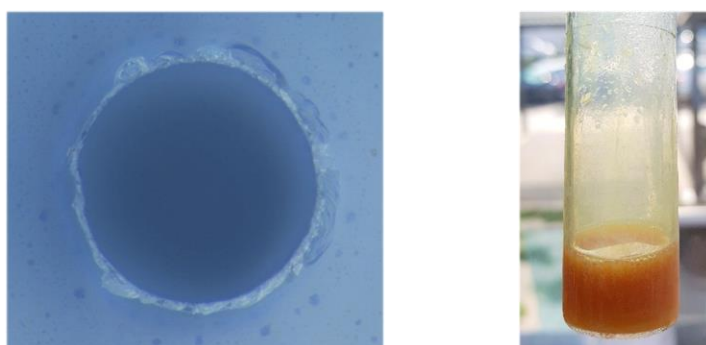


Figure 8.3. Laser drilled hole in FTO glass with a diameter of 1 mm and gel electrolyte after a water bath in 80 °C for 2 hours.

8.3 Results and discussion

8.3.1 Performance of gel electrolytes in dye-sensitized solar cells

To investigate the gel electrolytes performance in DSSCs, the current-voltage characteristics were measured under AM1.5 illumination with light intensity of 100 mW/cm². Calculated photovoltaic parameters are presented in Table 8.2. The results were averaged for three devices for each type of electrolyte. In case of laboratory-size devices, the highest efficiency

(5.07%) was obtained for PVDF-HPF:PAB (9:1) electrolyte. Other power conversion efficiencies were 4.72, 3.28 and 3.11% for 8:2, 7:3 and 6:4 PVDF-HPF:PAB ratios, respectively. As can be seen, as the concentration of PAB polymer increased, the performance of electrolytes worsened. The open circuit voltage for all that DSSC was in the range of 562-573 mV, so it was not the reason for lowering the efficiency. However, we can assume that this effect was caused by decreased conductivity in electrolytes, because the short circuit current decreased from 19.31 mA/cm² to 14.24 mA/cm² for 9:1 to 6:4 polymer ratios. That assumption could also be explained by the fill factor and series resistance. In the first case, its value decreased with higher PAB concentration from 0.47 to 0.39 for 9:1 to 6:4 ratios, respectively. But, after the analyse of R_s parameter, it was clear that the decreased efficiency was caused by increasing resistance. The R_s parameters, calculated from the U-I curves, were 24.7, 56.6, 73.6 and 90.3 Ω for subsequent PVDF-HPF:PAB ratios of 9:1, 8:2, 7:3 and 6:4.

DSSCs filled with gel electrolyte based on PVDF-HFP and PDES-bAP polymers, showed significantly lower power conversion efficiencies. For successive ratios of 9:1, 8:2, 7:3, 6:4 of PVDF-HFP to PDES-bAP, the PCE values were 0.73, 0.61, 0.20 and 0.01%. Despite the higher U_{oc} , which ranged from 685-848 mV, significantly lower values of I_{sc} were observed than in PVDF-HPF:PAB based gels. They ranged from 2.71 to 0.02 mA/cm². The same as previously conclusion could be drawn. The high electric resistance led to high R_s parameters, which negatively affected the performance of DSSC devices. In comparison to the based on PVDF-HPF:PAB polymers gel electrolyte the R_s values were significantly higher. They were 116.2, 160.5, 209.0 and 338.4 Ω for 9:1, 8:2, 7:3 and 6:4 PVDF-HFP:PDES-bAP ratios.

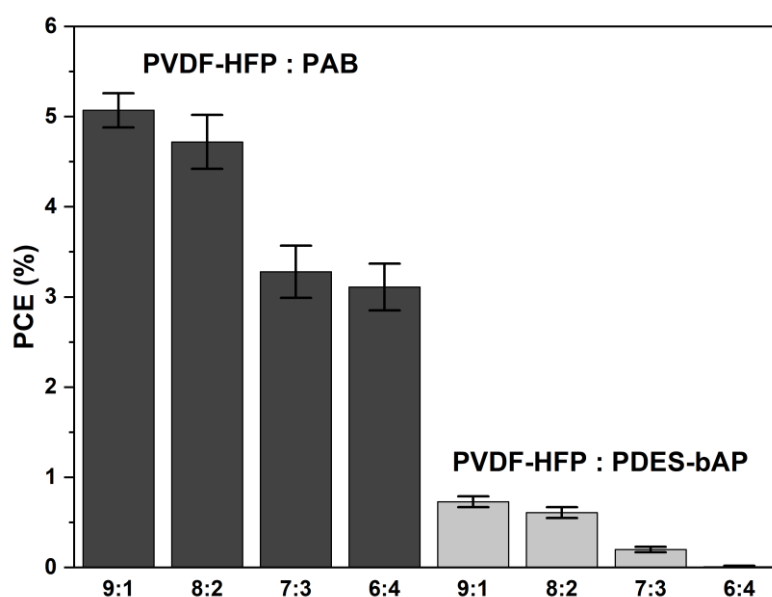


Figure 8.4. Power conversion efficiency for different polymer ratios of PVDF-HFP:PAB and PVDF-HFP:PDES-bAP based electrolytes.

The PVDF-HFP:PAB based gel with the ratio of 9:1 was chosen as best performing electrolyte for use in the scaled-up DSSC module, which contained six independent cells. When the DSSC module was already filled and sealed with a microscope slide, each individual solar cell was separately characterised. The exemplary current-voltage characteristics for PVDF-HFP:PAB

(9:1) gel electrolyte for laboratory and up-scaled DSSCs are shown in Figure 8.5. The averaged photovoltaic parameters are presented in Table 8.2. As expected, the scaled-up solar cell performance was inferior, which is a typical problem, when the solar cell's area is increased. In this case, the open circuit was 528 mV, which was similar to laboratory-sized devices, while the short circuit current dropped down to 6.4 mA/cm². The reason is the higher recombination and increased electrode resistance, because of the longer way that photogenerated charge carriers had to travel to external electrodes. It is noteworthy that the FF, equal to 0.46, was similar to the fill factor measured for the small device. Considering all that factors, the average efficiency calculated from six individual solar cells in the module, was 1.57%.

Table 8.2. Photovoltaic parameters for different gel electrolytes in DSSC. The best electrolyte was used to prepare the up-scaled DSSC device.

Code	U _{oc} (mV)	J _{sc} (mA/cm ²)	P _{max} (mW)	R _s (Ω)	R _{sh} (kΩ)	FF	PCE (%)
DSSC size 7×7 mm ²							
PVDF-HFP:PAB (9:1)	567 ± 6	19.31 ± 0.61	2.48 ± 0.18	24.7 ± 2.0	1.21 ± 0.34	0.47 ± 0.01	5.07 ± 0.19
PVDF-HFP:PAB (8:2)	567 ± 9	18.53 ± 0.69	2.32 ± 0.14	56.6 ± 6.3	1.31 ± 0.63	0.45 ± 0.04	4.72 ± 0.30
PVDF-HFP:PAB (7:3)	573 ± 4	16.12 ± 0.85	1.77 ± 0.13	73.6 ± 6.8	2.95 ± 0.27	0.39 ± 0.03	3.28 ± 0.29
PVDF-HFP:PAB (6:4)	562 ± 9	14.24 ± 0.40	1.53 ± 0.11	90.3 ± 8.7	3.28 ± 0.53	0.39 ± 0.03	3.11 ± 0.26
PVDF-HFP:PDES-bAP (9:1)	685 ± 8	2.71 ± 0.08	0.36 ± 0.02	116.2 ± 5.2	3.69 ± 0.64	0.39 ± 0.05	0.73 ± 0.06
PVDF-HFP:PDES-bAP (8:2)	848 ± 12	2.34 ± 0.16	0.30 ± 0.02	160.5 ± 3.4	4.17 ± 0.87	0.38 ± 0.03	0.61 ± 0.06
PVDF-HFP:PDES-bAP (7:3)	703 ± 10	0.73 ± 0.09	0.09 ± 0.01	209.0 ± 7.3	5.37 ± 0.79	0.31 ± 0.02	0.20 ± 0.03
PVDF-HFP:PDES-bAP (6:4)	798 ± 4	0.02 ± 0.01	0.01 ± 0.01	338.4 ± 25.7	25.66 ± 1.26	0.28 ± 0.03	0.01 ± 0.01
DSSC size 7×80 mm ²							
PVDF-HFP:PAB (9:1)	528 ± 17	6.40 ± 0.51	8.78 ± 0.44	5.49 ± 0.57	0.11 ± 0.06	0.46 ± 0.02	1.57 ± 0.08

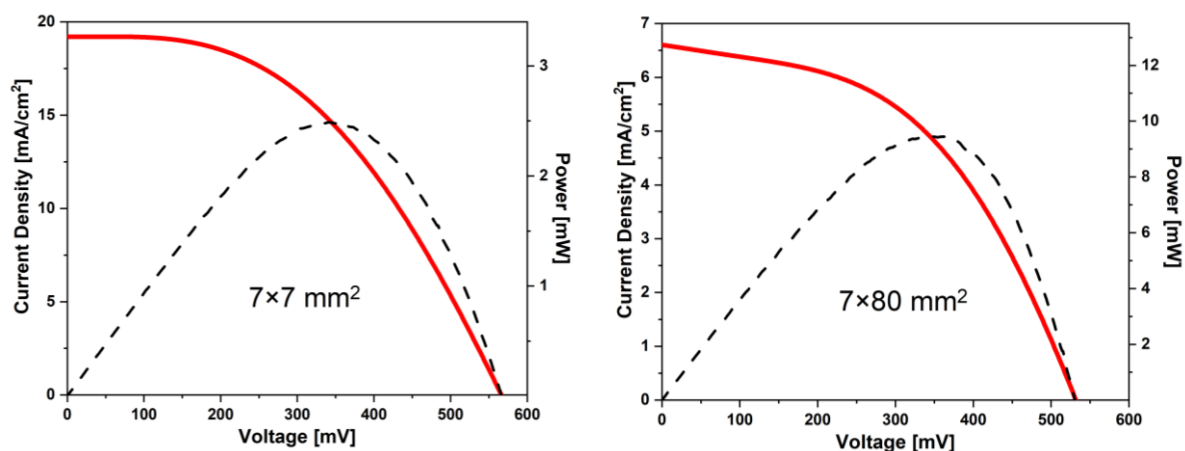


Figure 8.5. Current-voltage characteristics (solid red) and power curves (dashed black) of 7×7 mm² and 7×80 mm² DSSC with PVDF-HFP:PAB (9:1) gel electrolyte.

8.3.2 Time-dependent stability of gel electrolytes

To investigate the long-term stability of gel electrolytes, the power conversion efficiency was measured over a six weeks with a one-week interval. The DSSCs were stored in conditions that mimic the daily cycle of illumination with stable temperature of 22 ± 1 °C. Obtained data was normalised to the initial value and is presented in Figure 8.6. Each point is averaged value of efficiency calculated for six individual 7×80 mm² solar cells in the DSSC module. After a week, the PCE decreased slightly to 99% from initial efficiency. Then, after approximately 10 days, the efficiency dropped down to about 95%. In following weeks the DSSC performance stabilised and in sixth week reached a plateau. Overall, during 42 days the PCE decreased from 1.57% to the average value of 1.47%, so the loss was at the level of approximately 7%.

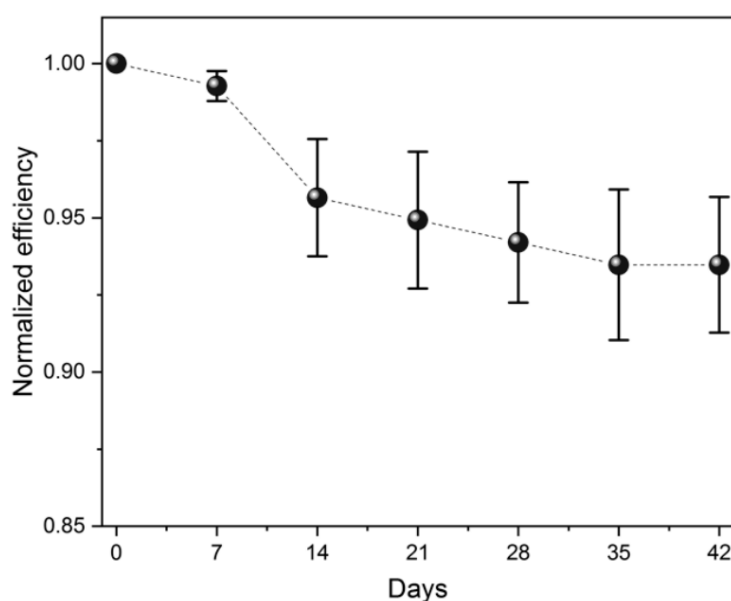


Figure 8.6. Ageing test of gel electrolyte in DSSC module. The normalised efficiency as a function of storage time at ambient conditions.

8.4 Prototype of solar charger

In co-operation with Military Institute of Engineering Technology the prototype of DSSC solar charger was created. The device was composed of DSSC module, supercapacitors, voltage control system and camouflaged case. To ensure appropriate charging parameters for supercapacitors the solar cells' architecture had to be modified. Thus, eight, instead of six, separate solar cells were prepared on 100×100 mm² FTO glasses, because there was a need to increase the open circuit voltage. Fabricated DSSC module was filled with the best gel electrolyte selected from the previous studies. The separate solar cells were connected in series and then characterised by measuring the U-I curves under solar illumination according to AM1.5 standard. The measured open circuit voltage and the short circuit current were $U_{oc} = 5.0$ V and $I_{sc} = 44$ mA, and was enough to charge the supercapacitor proposed by the Military Institute of Engineering Technology. Completed DSSC module was then delivered to the co-partners and then set up into the prototype. The device presented in Figure 8,7, called IMŁS0-2-W, was presented in the 30th International Defence Industry Exhibition MSPO in Kielce^[196] as prototype made in co-operation of ML System and Military Institute of Engineering Technology.



Figure 8.7. DSSC module, which was a part of solar charger prototype IMŁS0-2-W.

8.5 Conclusions

Eight novel gel electrolytes were prepared from poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) doped with poly(acrylonitrile-co-butadiene) (PAB) or poly(dimethylsiloxane) bis(3-aminopropyl)-terminated (PDES-bAP) copolymers. Their performance was tested in laboratory-size DSSC devices to select the best one, which was then used to prepare DSSC module. In case of electrolytes based on PVDF-HFP and PDES-bAP, the power conversion efficiency was lower than 1%. The highest efficiency of 5.07% was obtained for PVDF-HFP:PAB mixture with a copolymers ratio of 9:1. This gel electrolyte was then selected to prepare DSSC module with six separate solar cells. Their average PCE was 1.57%, a significantly smaller than for $7 \times 7 \text{ mm}^2$ devices. The up-scaling increases the recombination process in solar cells and generally leads to decrease in solar-to-electricity conversion efficiency. Followingly, the DSSC architecture was modified to accommodate eight solar cell with the same dimension as previously ($7 \times 80 \text{ mm}^2$) to increase the open circuit voltage, which was needed to obtain proper charging parameters for built-in supercapacitors. The new module with eight cells was then assembled into the DSSC solar charger prototype (IMŁS0-2-W) and presented in the 30th International Defence Industry Exhibition MSPO in Kielce.

Chapter 9

Implementation Potential

Presented in this dissertation results were focused on increasing the efficiency and up-scaling the production methods of photovoltaic devices. The applicative nature of the research was one of the aims of a PhD program, which was realised in cooperation of two institutions: Jagiellonian University and ML System company. The research was carried out in two units simultaneously: the Department of Advanced Materials Engineering in the Faculty of Physics, Astronomy and Applied Computer Science in Cracow and the Research & Development Centre for Photovoltaics in Zaczernie.

The dye-sensitised solar cells were chosen as the most prospective in terms of further commercialisation. They have great advantages, such as up-scalability, low-cost production and, what was very important for the company, the possibility of implementing in building integrating photovoltaic (BIPV), which made them selected as the most profitable from the group of third generation solar cells. This is a new technology that, despite its availability on the market, requires a number of improvements. The main challenges described in this dissertation were: increasing the solar-to-electricity power conversion efficiency, reducing of unfavourable recombination process, finding a replacement for a liquid electrolyte and developing a scalable method of platinum catalyst deposition.

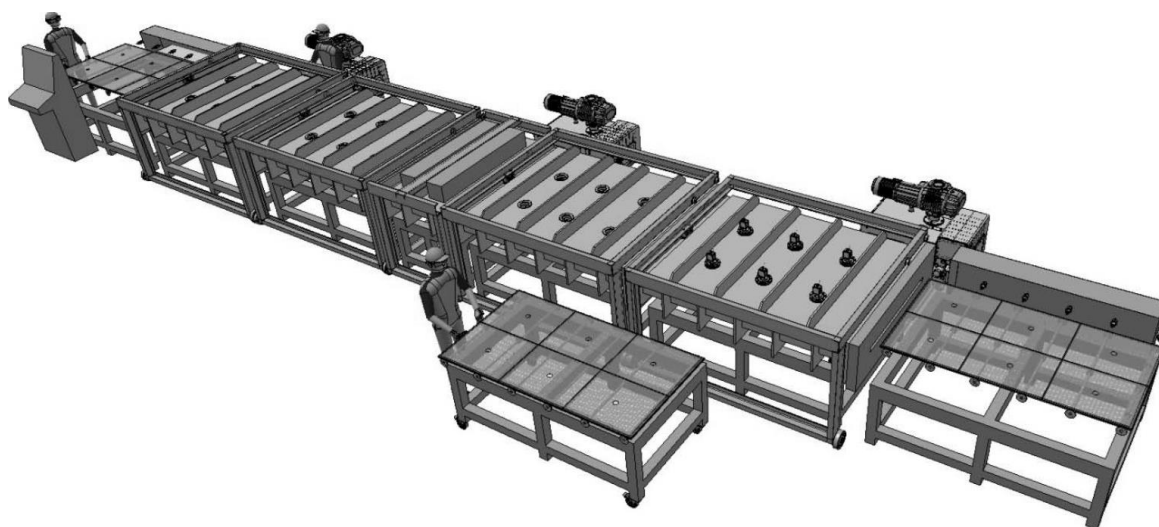


Figure 9.1. Scheme of magnetron sputtering PVD system, which is used by ML System.

In the first instance, the effect of ozonisation was presented as an effective method to clear the surface of the mesoporous TiO_2 layer from organic residues. Such process increased the dye-sensitised solar cell efficiency by 28%. The method of ozone generation by ultraviolet irradiation is widely used in production to degrease many types of inorganic materials. For example, it is widely used by semiconductor companies, where the ozone is implemented to clean the semiconductor surface from any organic contaminants that could disrupt the operation of produced by them devices. Here, it can be applied in the production line of DSSCs to clean the mesoporous TiO_2 before the dye-sensitising process, to provide photovoltaic

devices with enhanced performance. The same conclusion can be drawn for electron blocking layers. Prepared by the magnetron sputtering PVD method layer increases the efficiency of DSSC, which is due to the reduction of the recombination process at the FTO/electrolyte interface. The problem is very noticeable with large format solar cells, where the electron has a long path to the external electrode. The longer the path, the higher probability of recombination and higher photocurrent loss in the device. The main advantages of the magnetron sputtering method are e.g. simplicity in use, high process repeatability and ability to be up-scaled. The company of ML System is already equipped with a production line PVD system (Figure 9.1), which is able to produce coatings on flat substrates with a dimension up to $2250 \times 1300 \text{ mm}^2$. Thus, it is possible to implement the EBL coating on large-scale DSSC devices.

The novel method of platinum deposition was another challenge presented in this dissertation. Electrodeposition in sliding meniscus was successfully patented at the Patent Office of the Republic of Poland. Contrary to the commonly used screen-printing method with a platinum paste, the presented here method has at least several important advantages. Firstly, the whole procedure is relatively cheap, because the precursor is easily soluble in water and needs no purification. The deposition is also eco-friendly due to the fact that there are no toxic chemicals or by-products of the reaction. Additionally, the process is relatively fast, because it does not need long-lasting, energy-consuming annealing and can be done within a minutes. Presented here results were obtained for the substrate dimensions of $20 \times 75 \text{ mm}^2$, but there is no restriction to scale it up to larger formats. Such attempts have already been made by a novel device, which is presented in Figure 9.2, where the width of the substrate may be even 300 mm.

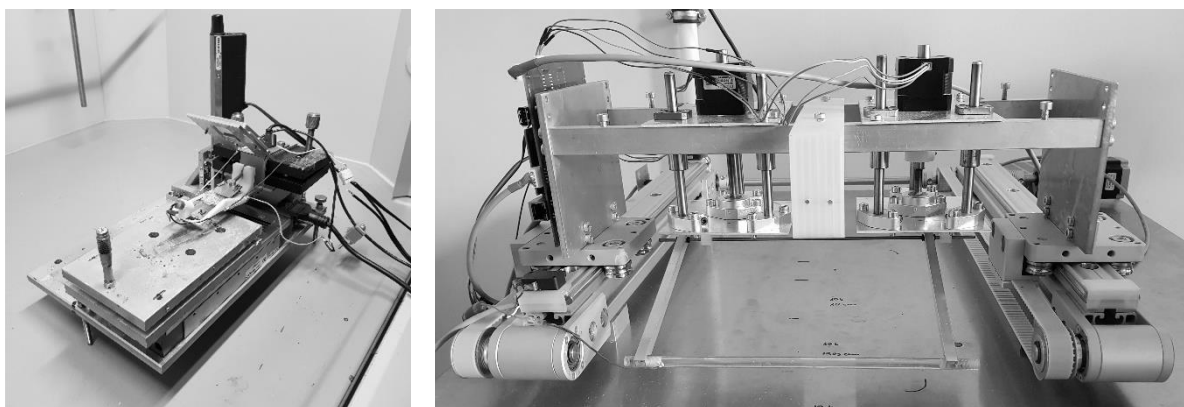


Figure 9.2. Apparatus for electrodeposition in sliding meniscus for small (left) and large (right) formats of substrates, which was home-built at the Department of Advanced Materials Engineering.

In cooperation with the Military Institute of Engineering Technology, the new type of gel electrolytes were tested in DSSC devices. Commonly used and commercially available liquid electrolytes, which are based on iodine and acetonitrile, have a high vapour pressure. For this reason, when the solar cell is irradiated by the sunlight, the device frequently unseals, which led to the leakage of the electrolyte. To solve that problem, novel gel electrolytes were developed. Their performance and stability were tested. The results showed that they may be

successfully implemented in DSSC. Thus, one up-scaled module was integrated with the supercapacitor and presented at the 30th International Defence Industry Exhibition MSPO in Kielce as a prototype made in co-operation of ML System and Military Institute of Engineering Technology.

Summary

The results presented in this dissertation were obtained within the framework of the Implementation Doctorate programme of The Ministry of Science and Higher Education and realised in cooperation with Jagiellonian University and ML System S.A. The research was focused on dye-sensitised solar cells. In particular, processes to increase their solar-to-power conversion efficiency, facilitate the production by novel methods of deposition and new materials that improve their durability. All these issues have been addressed to enhance the implementation capabilities of DSSC devices, which are a product offered by ML System, but the obtained results can be also applied to other generations of solar cells.

The first thesis was focused on the cleaning effect of the mesoporous layer of titanium(IV) oxide, thus, the DSSCs were prepared with an additional step. In order to clean its expanded surface, low-power UV light was applied to generate ozone. Before the dye-sensitising bath, the layer of sintered TiO_2 nanoparticles was transferred to the UV-ozone process chamber, where it was exposed to O_3 molecules. As a result, the organic residuals were removed from the surface of the TiO_2 , what improved the dye absorption. The cleaning effect was proved by several methods. Firstly, the decline of contamination was observed by SEM imaging, then the samples were analysed by Raman and FTIR spectroscopies, where it was shown that the signals from organic residues were significantly reduced after the UV-ozone treatment. To verify, if the bulk properties were changed, the UV-VIS spectroscopic measurements were performed. According to the Tauc plot for TiO_2 before and after UV-ozonisation, the E_g has not changed (3.22 eV), but the work function, obtained by the Kelvin probe, decreased. Therefore, it could be assumed that the modification affected only the surface of the material. After the bath in the dye solution, the absorbance and photoluminescence spectra were acquired. It was shown that the amount of adsorbed dyes significantly increased. As seen in the depth profiles obtained by SIMS, the enhancement of dye adsorption was the highest in the subsurface layers. Overall, the power conversion efficiency was augmented from 4.59 to 5.89%, mainly by increasing the short circuit current.

Secondly, the effect of magnetron sputtered electron blocking layer was presented. Its role was to decline the recombination process on FTO/electrolyte interface, which decreases the efficiency in DSSCs with traditional architecture. The magnetron sputtering was chosen, because of its high repeatability and scalability. Before the deposition of titania paste, the FTO substrates were coated by a 30 nm layer of TiO_2 . It was not visible in SEM images, because of the high roughness of FTO, but its presence was proven by the presence of Ti characteristic emission lines observed in the EDS spectrum. The thickness of the TiO_2 layer was measured by an optical profilometer. The data obtained by Raman spectroscopy gave information about its crystal structure. The spectrum was characteristic for anatase, so it was the same as mesoporous TiO_2 , which guaranteed good electrical contact between the layers. Additionally, it was proved by the transmittance measurements that the EBL layer did not affect the light, which passes through the photoanode, in the wavelength range of N719 dye absorption. Photovoltaic parameters obtained by current-voltage measurements showed that the efficiency of DSSC devices was increased from 4.67 to 6.07% in the case of $7 \times 7 \text{ mm}^2$ and from 2.62 to 3.06% in the case of $7 \times 80 \text{ mm}^2$ samples.

Another challenge raised in this dissertation was the up-scaled, eco-friendly and cheap deposition of platinum on conductive substrates. Using a combination of self-built apparatus for coating by a sliding meniscus and an electrodeposition process, the FTO cathodes were covered by platinum nanoparticles with various coverage rates. According to SEM images, the particles were nearly perfectly round and their size distribution was very wide. The coverage was the highest for the highest deposition current. The electrochemically active area was calculated based on cyclic voltammetry curves measured in the solution of 0.5 M H_2SO_4 on the assumption that one hydrogen atom bonds to one atom on the platinum surface. That area was the lowest for screen-printed platinum and the highest for the deposition current of 7 mA. The electrocatalytic properties of prepared cathodes were also studied by electro-oxidation reaction of ammonia (NH_3). Presented CV curves showed that the electrodeposited platinum performed better than platinum received from the commonly used platinum paste. Completed DSSC devices were electrically characterised under the illumination of solar simulator. According to obtained results, it can be assumed that solar cells fabricated with the electrodeposited cathodes had a comparable and even higher efficiency to reference DSSCs. In the case of cathodes prepared by screen-printing, the PCE was 5.14%, while the samples prepared with deposition current of 1, 4 and 7 mA had the PCE of 5.45, 5.21 and 4.84%, respectively. The decrease in efficiency for higher platinum loadings was explained by the different WF values. The higher work function may generate the potential barrier in the FTO/Pt cathode and electrolyte interface, which reduces the solar cells' PCE. To estimate the electrodeposition process efficiency, absorbance measurements were carried out for the initial precursor solution and solutions after deposition for each condition. As shown, the drop in absorbance peaks' intensity was related to the decrease in the molar concentration of PtCl_4 ions. According to that, it was roughly approximated that the solution volume of 100 μl was able to cover 7500 mm^2 , 4286 mm^2 and 3581 mm^2 in the case of 1, 4 and 7 mA deposition currents, respectively.

The fourth thesis posed in this dissertation is that gel polymers can replace commonly used and commercially available liquid electrolytes. Thus, in cooperation with Military Institute of Engineering Technology, eight gel electrolytes were prepared from poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) doped with poly(acrylonitrile-co-butadiene) (PAB) or poly(dimethylsiloxane) bis(3-aminopropyl)-terminated (PDES-bAP) copolymers. Their performance was studied in laboratory-size DSSCs to select the best one, which was further used to prepare an up-scaled DSSC module. In electrolytes based on PVDF-HFP and PDES-bAP, the power conversion efficiency was lower than 1%. The best performing was the one prepared by PVDF-HFP:PAB mixture with a ratio of 9:1. It gained the highest PCE of 5.07%, so it was chosen to be implemented in the DSSC module with a dimension of 100×100 mm^2 . The module was composed of eight separate solar cells with the dimension of 7×80 mm^2 , which were electrically connected in series to reach proper charging voltage for the supercapacitor fabricated at the Military Institute of Engineering Technology. Based on that components, the new prototype of the solar charger, called IMŁS0-2-W, was built and presented at the 30th International Defence Industry Exhibition MSPO. According to the ageing tests, the efficiency of such electrolyte in DSSC drops down only by 7% in the time of 42 days.

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List of Figures

Figure 1.1. Net renewable capacity additions by technology ^[15]	2
Figure 2.1. Working principle of DSSC shown on the energy level diagram.	5
Figure 2.2. Solar cell equivalent circuit model.	6
Figure 3.1. SEM images of FTO and ITO coatings in different magnifications.	8
Figure 3.2. The photography of a) titania paste and b) SEM image of mesoporous TiO ₂ morphology.	9
Figure 3.3. Schematic representation of N719 molecule.	10
Figure 3.4. The height profiles of annealed TiO ₂ mesoporous layer obtained by stylus and optical profilometers. The average thickness was approximately 7 µm.	11
Figure 3.5. Schematic representation of a) photoanode and cathode, b) architecture of completed dye-sensitised solar cell.	12
Figure 4.1. Schematic diagram of the stylus profilometer instrumentation.	14
Figure 4.2. The working principle of optical profilometer.	15
Figure 4.3. Schematic representation the cantilever deflection measurement using a photodetector with four independent segments.	16
Figure 4.4. Three basic AFM modes: a) contact mode (C-AFM), b) non-contact mode (NC-AFM) and c) tapping mode (TM-AFM).	17
Figure 4.5. Schematic diagram of electron beam formation in SEM.	18
Figure 4.6. The teardrop interaction volume of electrons with a sample. The secondary electrons (SE), backscattered electrons (BSE), characteristic X-ray (CHAR) and continuous X-ray (CONT) are released in different depths. The volume shape varies depending on e.g. primary electrons acceleration voltage or the atomic number of the sample elements.	19
Figure 4.7. The mechanism of creating X-rays in the sample as a result of electrons bombardment.	19
Figure 4.8. Schematic representation of the description of the characteristic lines in EDS method. First letter represents the shell with electron vacancy, while second describes at which shell was the vacancy-filling electron.	20
Figure 4.9. Three possible mechanism of light interaction with a material: transmission, reflection, absorption and three spectrophotometric modes: transmittance, reflectance and absorbance.	21
Figure 4.10. Three methods of reflectance measurements: a) zero angle with a optic fibre, b) specific angle and c) absolute reflectance with integration sphere.	21
Figure 4.11. Schematic representation of a) Jabłoński diagram and b) spetrofluorometer instrumentation.	23
Figure 4.12. Schematic representation of the FTIR instrumentation. The sample could be analysed by different methods, such as (6A) transmission spectroscopy, (6B) IRRAS – infrared reflection absorption spectroscopy or (6C) ATR – attenuated total reflectance ^[93]	24
Figure 4.13. Energy level diagram presenting the principle of IR absorption, Rayleigh, Stokes and anti-Stokes scattering.	26
Figure 4.14. Schematic representation of the Raman spectrometer instrumentation.	27

Figure 4.15. Schematic diagrams of a) the four quadrants, where the power is generated ($P < 0$) or consumed ($P > 0$) by the device, b) the exemplary solar cell curve with characteristic points and c) the localization of maximal power point.....	29
Figure 4.16. Spectral irradiance of the AM1.5 spectrum.....	30
Figure 4.17. Energy level diagram presenting the principle of CPD between the gold probe and the sample. The E_{VAC} , $E_{F,S}$, $E_{F,Au}$ are the vacuum level, the Fermi level of the sample and the Fermi level of the gold probe.	31
Figure 4.18. Schematic representation of a) Kelvin probe circuit and b) exemplary current-voltage characteristic for three different heights.	32
Figure 4.19. The example of voltammogram for a simple reversible redox reaction.	33
Figure 5.1. Ozone generation process: UV light splits the diatomic oxygen into two single molecules that attach to other diatomic oxygens and form triatomic ozone.	36
Figure 5.2. Schematic representation of the UV-ozone cleaning process of TiO_2 particles. ...	37
Figure 5.3. Tabletop specimen cleaner (ZoneSEM II ^[135]) used in ML System laboratory.	37
Figure 5.4. SEM images of a) reference and b) UV-ozone treated TiO_2 mesoporous layer. Marked areas presents the surface area, which was exposed to electron beam for two minutes.....	38
Figure 5.5. FTIR spectra of titania paste (dotted black), mesoporous TiO_2 before (dashed blue) and after (solid red) UV-ozone treatment. The C-H stretching region disappeared as a result of ozone cleaning.	39
Figure 5.6. Raman spectra of titania paste (dotted black), mesoporous TiO_2 before (dashed blue) and after (solid red) UV-ozone treatment. The peaks corresponding to $\nu(CC)$ disappeared after ozone cleaning.....	40
Figure 5.7. Tauc plot of mesoporous TiO_2 before (dashed blue) and after (solid red) UV-ozone treatment. The linear extrapolation (dotted black) presents the optical band gap.....	41
Figure 5.8. Work function for mesoporous TiO_2 before (blue) and after (red) UV-ozone treatment obtained by Kelvin probe measurements in air.	41
Figure 5.9. Spectra of a) absorbance and b) photoluminescence of N719-sensitized TiO_2 , which were treated (solid red) and untreated (dashed blue) by UV-ozone.	42
Figure 5.10. Depth profiles of N719-sensitized TiO_2 , which were treated (solid red) and untreated (dashed blue) by UV-ozone. The analysed ions: NCS^- for N719 molecule and TiO_2^- for TiO_2 layer.	43
Figure 5.11. Current-voltage characteristics of treated (solid red) and untreated (dashed blue) by UV-ozone DSSCs.	44
Figure 6.1. Schematic representation of a) the electron/electrolyte recombination pathway in the typical architecture of DSSC and b) the effect of electron blocking layer.....	46
Figure 6.2. Energy diagrams presenting a) the electron injection to the FTO electrode and b) the effect of electron blocking layer, which prevents electrons from being injected back to the electrolyte.	47
Figure 6.3. Schematic representation of a) the configuration of magnetron sputtering system and b) the process of plasma generation and layer deposition.	48
Figure 6.4. The interior of PVD process chamber in ML System laboratory with two magnetron sputtering guns: RF (left) and DC (right).	49
Figure 6.5. EDS spectrum obtained on the sample with the thin film of TiO_2	50

Figure 6.6. Results from the optical profilometer – the height histogram for TiO ₂ step (olive) on bare FTO glass (cyan). The difference between the Gauss peaks determines the thickness of TiO ₂ .	51
Figure 6.7. SEM images of a) photoanode intersection (from the bottom): glass, FTO, compact and mesoporous TiO ₂ and b) top-view of the deposited TiO ₂ EBL on FTO. AFM images of c) bare FTO surface and d) deposited TiO ₂ electron blocking layer on FTO.	51
Figure 6.8. Raman spectrum of magnetron sputtered TiO ₂ . The data is characteristic for anatase ^[137] .	52
Figure 6.9. Spectroscopic spectra of individual components of DSSC photoanode. Transmittance spectra of bare FTO (light blue), 30 nm of TiO ₂ EBL (navy blue), mesoporous TiO ₂ (grey) dye-sensitised TiO ₂ (red) and absorbance spectrum of N719 dye in ethanolic solution (orange).	53
Figure 6.10. Current-voltage characteristics for 7×7 mm ² and 7×80 mm ² DSSCs with and without 30 nm electron blocking layer.	54
Figure 6.11. Photography of up-scaled module with 8 individual dye-sensitised solar cells.	56
Figure 7.1. Schematic of the meniscus cross-section with the platinum electrodeposition process.	58
Figure 7.2. Self-built apparatus used to prepare electrodeposited platinum on TCO substrate.	58
Figure 7.3. Absorbance spectra for pure water and K ₂ PtCl ₄ solution before and after electrodeposition processes with different currents.	60
Figure 7.4. Normalised absorbance in a function of K ₂ PtCl ₄ molar concentration. Absorbance for solutions after electrodeposition process were calculated from absorbance peaks.	60
Figure 7.5. SEM images obtained from screen-printed and electrodeposited samples.	61
Figure 7.6. EDS maps obtained from screen-printed and electrodeposited samples. The signal from Pt L _α line was marked by green colour.	62
Figure 7.7. Cyclic voltammograms measured in 0.5 M sulphuric acid (H ₂ SO ₄) at scan rate of 20 mV/s for the screen-printed and electrodeposited samples. The shaded area is an example of double hydrogen layer area, which was subtracted before the calculation of ECSA.	63
Figure 7.8. Electrochemically active surface area (ECSA) calculated from CV measurements in 0.5 M sulphuric acid (H ₂ SO ₄) of platinum cathodes prepared by screen-printing and electrodeposition methods.	64
Figure 7.9. Cyclic voltammograms measured in 0.1 M NH ₃ with 1 M KOH at 25 mV/s scan rate on platinum cathodes prepared by screen-printing and electrodeposition methods.	65
Figure 7.10. Current-voltage characteristics under AM1.5 illumination of prepared DSSCs with platinum cathodes prepared by screen-printing and electrodeposition methods.	65
Figure 7.11. Photovoltaic parameters of dye-sensitized solar cells: open circuit voltage (U _{oc}), short circuit current density (I _{sc}), fill factor (FF) and power conversion efficiency (PCE).	66
Figure 7.12. Work function measured by Kelvin probe for bare FTO and FTO/Pt cathodes prepared by screen-printing and electrodeposition methods. The reference probe was made of gold (Au).	67
Figure 7.13. Schematic representation of energy level of each DSSC's component material. According to obtained results, the work function of FTO/Pt cathode decreases with higher deposition currents.	68

Figure 8.1. Chemical structure of polymers used to prepare the gel electrolytes ^[195]	70
Figure 8.2. Preparation of DSSC module: drilling the holes and sections separation, filling the device, sealing the holes.	72
Figure 8.3. Laser drilled hole in FTO glass with a diameter of 1 mm and gel electrolyte after a water bath in 80 °C for 2 hours.	72
Figure 8.4. Power conversion efficiency for different polymer ratios of PVDF-HFP:PAB and PVDF-HFP:PDES-bAP based electrolytes.	73
Figure 8.5. Current-voltage characteristics (solid red) and power curves (dashed black) of 7×7 mm ² and 7×80 mm ² DSSC with PVDF-HFP:PAB (9:1) gel electrolyte.	74
Figure 8.6. Ageing test of gel electrolyte in DSSC module. The normalised efficiency as a function of storage time at ambient conditions.	75
Figure 8.7. DSSC module, which was a part of solar charger prototype IMŁS0-2-W.	76
Figure 9.1. Scheme of magnetron sputtering PVD system, which is used by ML System.	77
Figure 9.2. Apparatus for electrodeposition in sliding meniscus for small (left) and large (right) formats of substrates, which was home-built at the Department of Advanced Materials Engineering.	78

Table of Contents

Acknowledgements	I
Podziękowania.....	II
Academic Achievements	III
Symbols	IV
Abbreviations	V
Theses.....	VI
Abstract	VII
Streszczenie	IX
Chapter 1 Introduction.....	1
Chapter 2 Theoretical Background.....	4
2.1 Dye-sensitised solar cell – working principle	4
2.2 Equivalent electrical circuit of photovoltaic device	6
Chapter 3 Experimental.....	8
3.1 Materials.....	8
3.1.1 TCO glass	8
3.1.2 Mesoporous TiO ₂	9
3.1.3 N719 dye	9
3.1.4 Iodine-based electrolyte	10
3.1.5 Platinum nanoparticles	10
3.2 Dye-sensitized solar cell preparation	10
3.2.1 Deposition of TiO ₂ layer	10
3.2.2 Dye-sensitising of TiO ₂ layer.....	12
3.2.3 Deposition of platinum nanoparticles.....	12
3.2.4 Electrodes sealing and electrolyte filling	12
Chapter 4 Measurement Methods.....	14
4.1 Stylus profilometer	14
4.2 Optical profilometer	14
4.3 Atomic Force Microscopy	15
4.4 Scanning Electron Microscopy	17
4.5 Energy Dispersive X-Ray Spectroscopy	19
4.6 UV-VIS-NIR Spectrophotometry	20
4.7 Spectrofluorometry	22

4.8 Fourier Transform Infrared Spectroscopy	24
4.9 Raman Spectroscopy	25
4.10 Secondary Ion Mass Spectrometry	27
4.11 Current-Voltage Characteristics	29
4.12 Kelvin Probe.....	31
4.13 Cyclic Voltammetry	32
Chapter 5 Effect of Post-Annealing UV-Ozone Treatment of TiO ₂ Mesoporous Layer	35
5.1 Introduction.....	35
5.2 Experimental	36
5.2.1 UV-ozone generation	36
5.2.2 Preparation of dye-sensitized solar cells.....	37
5.3 Results and discussion.....	38
5.3.1 Contamination effect	38
5.3.2 Spectroscopic determination of organic residuals.....	39
5.3.3 Influence of UV-ozone treatment on TiO ₂ properties	40
5.3.4 Enhanced dye-sensitising efficiency.....	42
5.3.5 Performance of dye-sensitized solar cells.....	43
5.4 Conclusions.....	44
Chapter 6 Effect of Magnetron Sputtered TiO ₂ Electron Blocking Layer	46
6.1 Introduction.....	46
6.2 Experimental	48
6.2.1 Magnetron sputtering	48
6.2.2 Preparation of dye-sensitised solar cells.....	48
6.3 Results and discussion.....	49
6.3.1 EDS analysis	49
6.3.2 Thickness of electron blocking layer	50
6.3.3 SEM and AFM analysis.....	51
6.3.4 Crystal structure of electron blocking layer	52
6.3.5 UV-Vis-NIR spectroscopic analysis of photoanode	53
6.3.6 Performance of dye-sensitised solar cells.....	54
6.4 Conclusions.....	55
Chapter 7 Scalable Method for Horizontal-Dipping Electrodeposition of Platinum Nanoparticles	57
7.1 Introduction.....	57

7.2 Experimental	57
7.2.1 Principle of platinum electrodeposition	57
7.2.2 Novel electrodeposition method	58
7.2.3 Preparation of DSSC devices	59
7.3 Results and discussion	59
7.3.1 Efficiency of electrodeposition process	59
7.3.2 Nanoparticles morphology and surface coverage	61
7.3.3 The electrochemically active surface of platinum nanoparticles	63
7.3.4 Performance of DSSCs	65
7.3.5 Work function of FTO/Pt cathodes	67
7.4 Conclusions.....	68
Chapter 8 Novel Polymer-Based Gel Electrolytes	70
8.1 Introduction.....	70
8.2 Experimental	71
8.2.1 Preparation of gel electrolytes.....	71
8.2.2 Preparation of dye-sensitized solar cells.....	72
8.3 Results and discussion.....	72
8.3.1 Performance of gel electrolytes in dye-sensitized solar cells	72
8.3.2 Time-dependent stability of gel electrolytes	75
8.4 Prototype of solar charger	75
8.5 Conclusions.....	76
Chapter 9 Implementation Potential	77
Summary	80
Bibliography.....	82
Financial Support.....	94
List of Figures.....	95
Table of Contents	99