

**Photo-  
electrochemical  
reduction of  
CO<sub>2</sub> with PDA  
catalyst**



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Bachelor of Science

in the Bachelor program

Biological Chemistry

## **Statement of Authorship**

I hereby declare this bachelor thesis was entirely written by me and without foreign help. No other person's work has been used without due acknowledgement in this thesis. All used references are cited in the bibliography in all conscience.

Linz,

.....

František Jířík

## **Task**

The conductive biopolymer polydopamine is utilized as a catalyst for CO<sub>2</sub> reduction in the field of electrochemistry. In this thesis I have focused on the photoelectrochemical reduction of CO<sub>2</sub> using polydopamine as photoelectro catalyst.

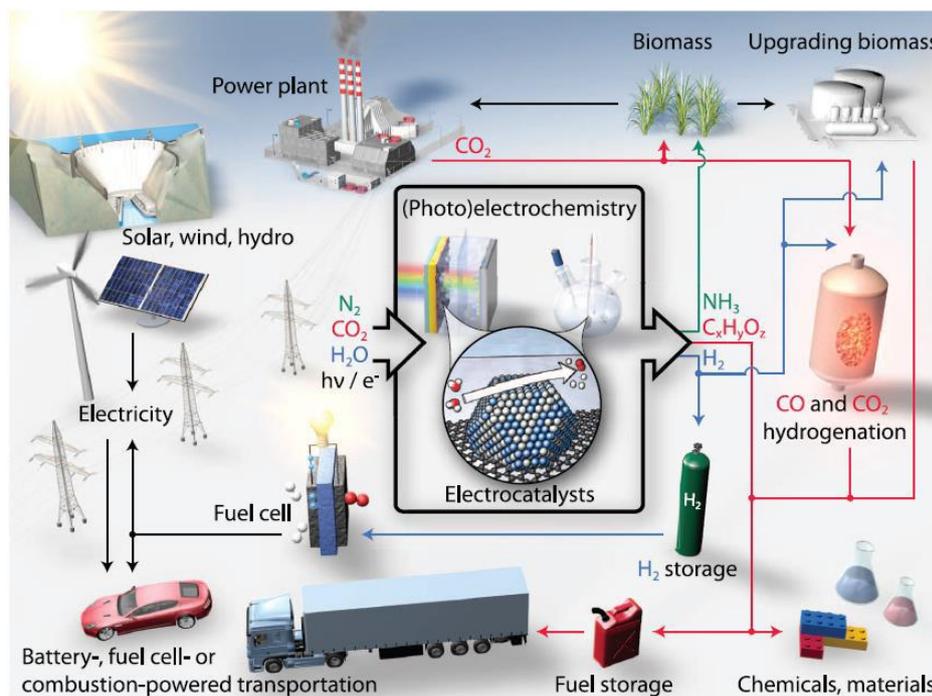
The polydopamine was synthesised by oxidative chemical vapour deposition on the fluorine doped tin oxide glass. Polydopamine was characterized by optical microscopy and fourier-transform infrared spectroscopy. The fluorine doped tin oxide glass was characterized by UV-Vis spectroscopy. The polydopamine catalysed CO<sub>2</sub> reduction was performed using cyclic voltammetry and chronoamperometry under the dark and light (AM 1.5). Ion chromatography was used to analyse the change of the products concentration in the electrolyte.

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# 1. Abstract

In the recent time there is a high demand for storage and conversion of renewable energy production, since this production is fluctuating all the time [1]. A possible way of storage is (photo) electrochemical energy conversion to fuels e.g. by splitting  $\text{CO}_2$  to hydrocarbons and  $\text{CO}$  as shown in Figure 1.



*Figure 1: Scheme of global electrochemical energy storage [2]*

The conversion of carbon dioxide to the reduced forms of carbon, which can be again utilized as fuels (e.g. conversion of  $\text{CO}_2$  to methanol), would lead to significant enhancement of the global environment and at least partial liberation from non-renewable source [1]. Although this idea seems promising for our future, the reduction of  $\text{CO}_2$  is energetically demanding process which requires a good catalyst and input of energy.

The idea behind the photoelectrochemistry is that the part of the energy required to reduce  $\text{CO}_2$  will be compensated by energy of the light. This process requires special p-type semiconductor which can both efficiently catalyse the  $\text{CO}_2$  reduction reaction and concomitantly absorb visible light. In this thesis we explored first time

polydopamine (PDA) as photoelectro catalyst. PDA was shown to possess catalytic activity to reduce CO<sub>2</sub> to formate [3].

**The tasks for the thesis are:**

Synthesis of PDA by o-CVD on FTO substrate

Cyclic voltammetry of PDA electrodes

Cyclic voltammetry of PDA electrodes under illumination

Ion chromatography of the products

## 2. Theoretical background

The electrochemical reduction is one of the most efficient methods of how to convert carbon dioxide to reduced C<sub>1</sub> compound such as methanol, carbon monoxide or formate, which can be again utilized as carbon feedstock and as such form an anthropogenic chemical carbon cycle [4]. The reduction of carbon dioxide is energetically intensive process and requires a proper catalyst that accelerates the kinetic losses in the energy conversion [4].

Table 1: Standard electrochemical potentials for CO<sub>2</sub> reduction [5]

Reduction potentials of CO <sub>2</sub>	$E^\circ$ [V] vs SHE at pH 7
$\text{CO}_2 + \text{e}^- \rightarrow \text{CO}_2^-$	-1.9
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	-0.61
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.52
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	-0.34
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.51
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.38
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-0.24
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	-0.42

There are many various ways of carbon dioxide reduction, which includes various kinds of catalysts. In this thesis I have decided to use a heterogeneous catalysis with catalyst-functionalized organic semiconductor electrodes.

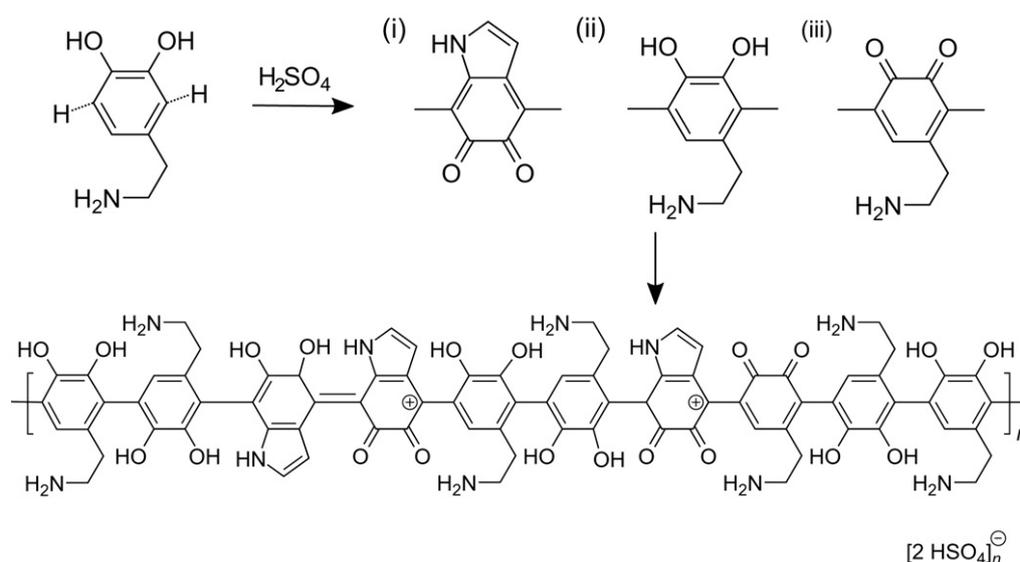
The heterogeneous catalysis provides its user several advantages in comparison to the homogeneous catalysis and it is more suitable for the photoelectrochemical experiments. In the case of heterogeneous catalysis the catalyst is in the different phase than the carbon dioxide that is going to be reduced [4]. As a certain type of catalysis for heterogeneous catalysis we have chosen an electrode functionalized with organic semiconductor. This type of catalysis is common and useful also for the photoelectrochemistry. The function of a semiconductor in these reactions is a transport of electrons between source, usually electrode, and the catalyst or directly carbon dioxide [4]. In this work I have used a polymerized dopamine as a catalyst for carbon dioxide reduction deposited on the FTO glass.

FTO (fluorine doped tin oxide) glass is a n-type semiconductor which is formed by deposition of mixture of  $\text{SnCl}_4$  and HF of the borosilicate glass at temperature of  $490^\circ\text{C}$ – $525^\circ\text{C}$ . The FTO is stable semiconductor of low resistance and high transparency. The transparency of FTO was determined to above 80% for the light in the wavelength range of 200 nm to -1300 nm [6]. The low resistance and high transparency of FTO makes this material useful for photoelectrochemical reactions such as those in my work.

The development of proper catalysts for carbon dioxide reduction is recently the most important task on the field of carbon dioxide reduction and back-utilization. There has been already many researches done in order to find an effective catalyst. As an effective group of catalysts the organometallic complexes are considered. The faraday efficiency (FE) is usually in a vicinity of 90% or even higher, and regularly shows a high turn-over number (TON) [4]. Although these compounds are effective on a laboratory scale, their industrial use in the future is unpredictable, since they are principally based on elements with a low natural abundance and high socioecological impact [3]. This fact was the main reason to start looking for an alternative catalysts created from an organic compounds that will have significantly smaller affect on the environment and could represent inexpensive alternatives for large-scale industrial processes in future.

The PDA is a polymer form of naturally abundant compound dopamine, which can be formed by an oxidative polymerization in a vapour state [7]. This compound was revealed to be an effective electro-catalyst for carbon dioxide reduction. Its

catalytic function is based on enzymatic principles which uses the hydrogen bonding system between amino and carboxyl functional groups (Figure 2) [3]. The electron pair that is utilized for the reduction is provided to carboxyl group by the backbone of PDA polymer, which is formed by conjugated-conductive chain of aromatic rings where the electron pair is transferred to the functional groups through a conjugated system of  $\pi$ -bonds [3]. The significance and suitability of PDA catalyst increases even more with the fact that the number of functional groups is equal to the number of molecules of dopamine present in the polymer structure [7]. Another advantage is the stability of PDA. Continuous measurements such as the CA scans show that PDA performs consistently as catalyst for 16 hours without noticeable degradation [3].



*Figure 2: Synthesis of PDA, intermediate monomers (i) diketoindole, (ii) dopamine, and (iii) oxidized dopamine [3]*

The principle of photo-electrochemistry is built up on the ability of semiconductor to transfer energy from light to electrical or chemical energy. The energy difference between valence and conductive band called a band gap is specific for each semiconductor [8]. On the photochemical charge transfer of photo excited carriers is activated to the heterogeneous reduction process occurring at the surface (at the interface with electrolyte) ( $h\nu > E_{bg}$ ) [9]. This causes the movement of either electrons or holes to the particles of the opposite charge. Once the hole or electron reaches this interface the photoelectrochemical reaction is occurs [10].

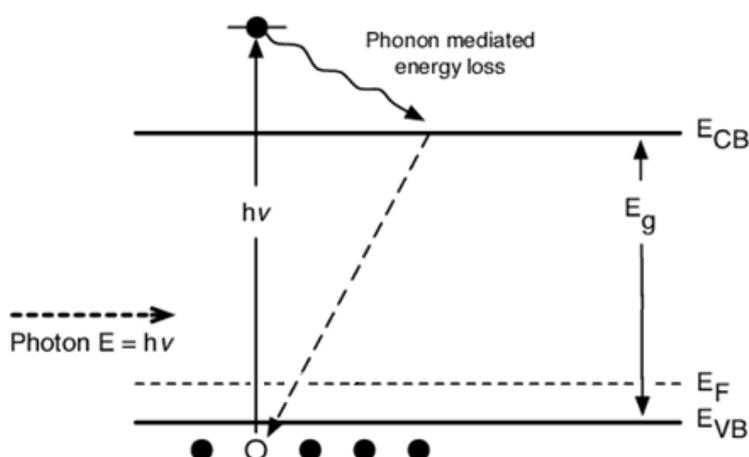


Figure 3: Photoexcitation of p-type semiconductor [11]

## 3. Materials and methods

### 3.1 PDA Synthesis

The PDA substrate is the essential component for all further experiments within this work. The synthesis of this polymer I have performed with o-CVD in the furnace at 335°C using 500 mg of dopamine and 0.5 ml of conc. sulphuric acid as an oxidation agent [7]. The dopamine had been deposited on FTO glass of two various sites (35 mm x 11 mm and 25 mm x 16 mm), which were used for cyclic voltammetry without light influence and cyclic voltammetry with light influence respectively. Subsequently after the synthesis the resistivity of PDA coated FTO glass substrates were measured and compared with the resistivity of pure FTO glass.



Figure 4: Tube furnace used for o-CVD PDA synthesis

### 3.2 Cyclic Voltammetry

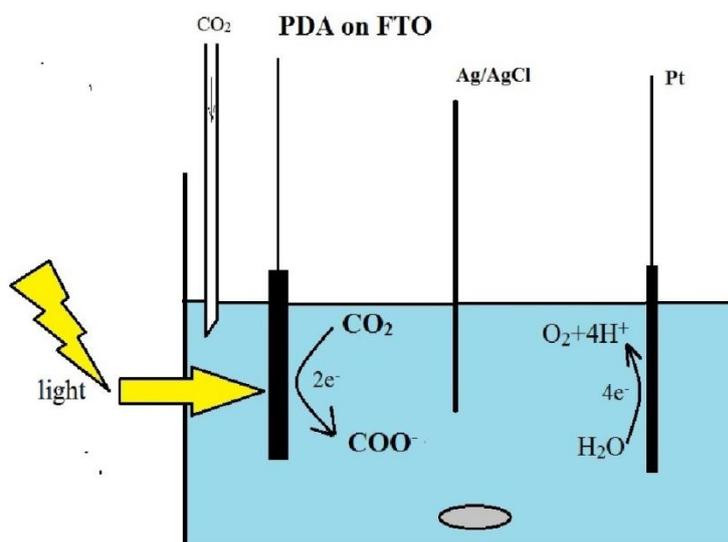
The cyclic voltammetry (CV) is the main task for my investigations. In the first row of CV I have focused only on the electrochemical catalysis of the CO<sub>2</sub> reduction with PDA. The PDA substrate on FTO glass was compared with a bare FTO glass for their catalytic functions. The CVs in the first row of measurements were performed at inert conditions in the glove box using a standard three electrode arrangement in one cell compartment. The electrodes were chosen in the following way. The PDA coated FTO glass or FTO glass was used as a working electrode. As a counter electrode the Ni-plate was used and Ag/AgCl was used as a QRE (calibrated at -210 mV vs. SHE) [3]. As an electrolyte for these experiments 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBA-PF<sub>6</sub>) in acetonitrile-water (1 % vol. H<sub>2</sub>O) solvent was chosen. CO<sub>2</sub> possesses a solubility of 0,5 mol/L in this solution during previous experiments [3]. In the first series of CVs the first measurements were done in the (N<sub>2</sub>) pure electrolyte without CO<sub>2</sub>. The aim of these measurements was to test the cell and electrolyte for any side reaction that might occur and also test the stability of PDA in the (TBA-PF<sub>6</sub>) in acetonitrile-water solution. The CVs were performed from an initial potential 0 mV to the maximum reduction potential, which was set to -1000 mV, -1200 mV and -1500 mV.

In the second part of these measurements the PDA catalysed electrochemical reduction of CO<sub>2</sub> in 0.1 M TBA-PF<sub>6</sub> acetonitrile-water electrolyte was performed in the same one cell compartment as was used for first measurements. The volume of the electrolyte which was used for this measurement was 40 ml. In order to provide sufficient concentration of CO<sub>2</sub> in the electrolyte, the electrolyte was constantly bubbled with CO<sub>2</sub> flow with a flow rate 2 L min<sup>-1</sup> 15 minutes before a measurement and also during the whole measurement. During this measurement the CO<sub>2</sub> reduction was performed by applying reduction potential of magnitude from 0mV to -1500 mV on the PDA working electrode with voltage change rate of 50 mV s<sup>-1</sup>. This cycle was repeated three times. This measurement was performed several times all the time upon the same conditions.

### **3.3 Cyclic Voltammetry with Illumination**

The main task for the thesis is testing of an effect of a light on the PDA catalysed CO<sub>2</sub> reduction. For these measurements again the one compartment cell was used. The arrangement of the cell was similar in comparison to the one used in first row

of CVs measurements. The exceptions are a material of the counter electrode which was changed from Ni to Pt and a higher volume of the cell. The recent arrangement is PDA substrate as a working electrode, Pt plate as a counter electrode and Ag/AgCl wire as a QRE (calibrated at -210 mV vs. SHE). The whole experiment was performed in the fume-hood because of the better spatial manipulation with (AM 1.5) lamp. The lamp provided a beam of light in the visible spectra with a constant intensity of  $192 \text{ mW cm}^{-2}$ . The cell was put on a magnetic stirrer and fixed in the fume-hood to a lab stand. Since the volume of the cell was increased and thus a bigger volume of electrolyte was used, the electrolyte was constantly stirred during along all measurements with rotation speed 160 rpm in order to provide a homogenous solution. Once the cell was assembled the light beam was pointed on the backside part of the PDA substrate from a distance of 10.5 cm in the angle of approximately  $75^\circ$ . The electrolyte was constantly bubbled with  $\text{CO}_2$  flow of flow rate  $3 \text{ L min}^{-1}$  .15 minute before a measurement and during all of the measurements in order to maintain an equal concentration of  $\text{CO}_2$ . At this point the set up was ready to use.



*Figure 5: Schematic drawing of photoelectro cell*

Each measurement was divided into two parts, dark and light. Within the dark CV the light source was covered by an Al-plate, which absorbed all of the light. In the light measurement the Al plate was taken off and the PDA substrate was exposed to the light beam. During the whole experiment the light in the room was switched off

in order to avoid any side effect of an ambient light. All the CVs were performed using reduction potential in range from 0 mV to -1500 mV at a scan rate 50mVs<sup>-1</sup> and 10mVs<sup>-1</sup>. The voltage change from 0 mV to -1500 mV was repeated three times for all CVs.

The experiment was performed twice, each time with different PDA substrate area. For the first measurement the area was 1.17 cm<sup>2</sup> the area of the second substrate was 1.45 cm<sup>2</sup>.

### **3.4 Chronoamperometry**

Additionally to the CVs a few chronoamperometry (CA) tests were done in order to examine the light effect on PDA within a longer time periods. For this experiment the cell was kept same as for the previous measurements. The area of PDA on substrate was again 1.45 cm<sup>2</sup>. The influence of light was tested for three various constant reduction potentials. The dark and light phases were altered periodically within a certain time intervals. At first the voltage applied on the working electrode was -1500 mV and the time interval between dark and light phase was 5 minutes. This measurement was hold for 30 minutes. The same measurement was performed subsequently with -1000 mV applied on the system. Within last test the voltage was set to -1200 mV. The time interval between dark and light phase was 10 minutes. The duration of this trial was 43 minutes. The used electrolyte from all of these CA measurements was collected and used for an analysis of products.

### **3.5 Analysis of reaction products**

After the CA measurements the used electrolyte was analyzed for the products. According to the previous investigations for PDA as a CO<sub>2</sub> reduction catalyst the formate (HCOO<sup>-</sup>) was expected to be a major product of the cyclic CV and CA [3]. For this reason I have decided to focus only on the formate concentration in the used electrolyte. The used electrolyte was analyzed with IC against a fresh electrolyte as a reference.

### **3.6 Chemicals**

The Table 2 provides a complete list of chemicals used for the PDA synthesis and preparation of electrolyte.

Table 2: Chemicals used within the work

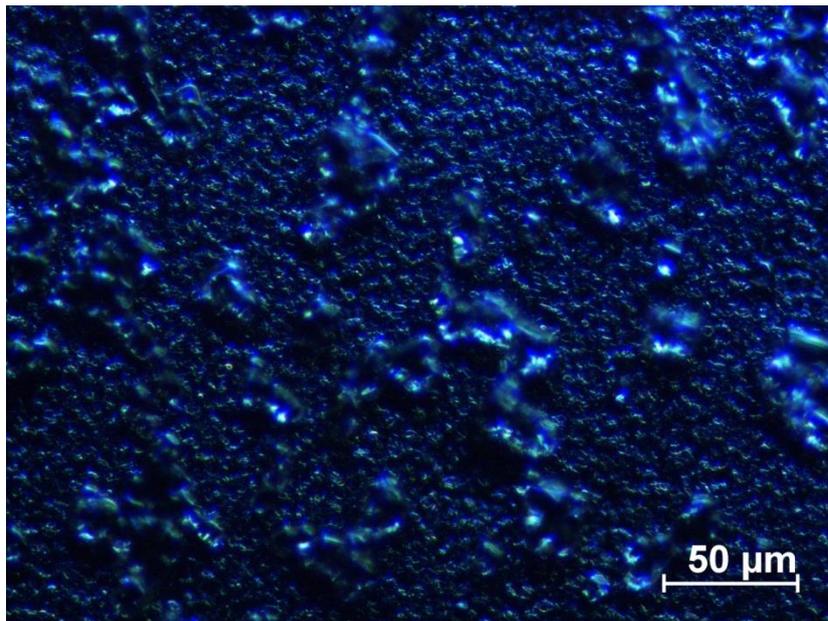
Substance	Purity	Company
Dopamine hydrochloride	98 %	Sigma Aldrich
Sulphuric acid	95 – 98 %	Sigma Aldrich
Sodium sulphate	≥ 99 %	J.T.Baker
TBA-PF <sub>6</sub>	≥ 99 %	Sigma Aldrich
acetonitrile	95 – 98 %	Sigma Aldrich

## 4. Characterization of PDA

Since the effect of light on PDA as a catalyst for CO<sub>2</sub> is the main point of investigation, as an additional task, the photochemical properties of PDA were characterized through several spectroscopic methods and microscopic method.

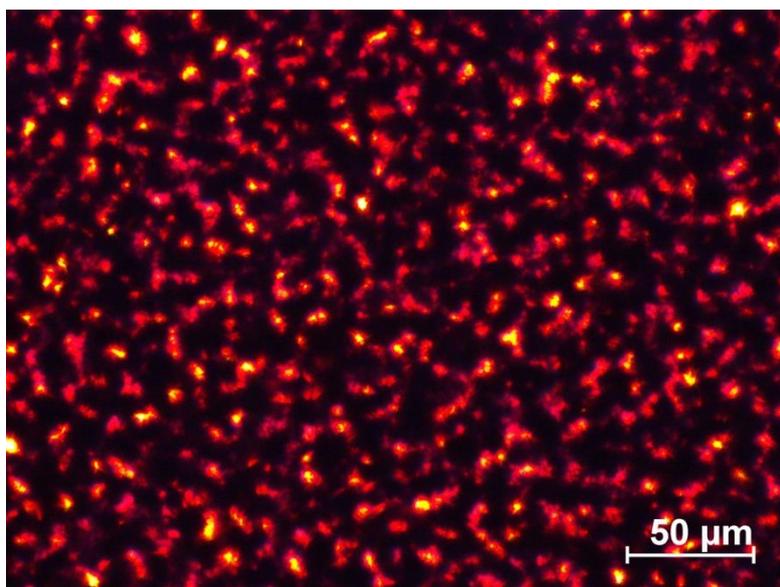
### 4.1 Optical microscopy

In this method the surface of the PDA on FTO glass was characterized with optical microscope. The magnification of eyepiece lens was 18x and was used for all measurements. In the case of the objective lens four various magnifications, 2.5x, 5x, 10x and 40x, were used to characterize the surface of PDA in detail. Additionally in some cases the light source was used to illuminate the PDA in to provide a better look on the surface. The specimen was illuminated with the light source coming either from below or above directions. The surface of PDA substrate on FTO glass was observed in detail under the optical microscope with general magnification of 45x, 90x, 180x, 720x. The pictures from the microscope have shown a quiet rough surface of the PDA. The best picture describing the surface only the PDA was taken under 720x magnifications with light source illuminating the substrate just from above.



*Figure 6: PDA substrate surface illuminated from above under magnification of 720x*

The substrate was also observed from the back side with the back side direction of light beam. The pictures that were taken under magnification of 720x. On this picture the FTO can be observed as a red spots on the back ground, which is caused by PDA substrate.



*Figure 7: The back side photo of PDA /FTO glass with illumination from underneath.*

## 4.2 FTIR spectroscopy

Among analyses done on the PDA substrate on FTO glass was FTIR spectroscopy. Within this analysis the transition of radiation waves through the blank (FTO glass) and sample (PDA) was measured on Bruker Vertex 80 in the range of 8000 to 600  $\text{cm}^{-1}$  with resolution of 4  $\text{cm}^{-1}$ . This analysis helps to identify the main components of PDA molecule, which presence approve the quality of PDA.

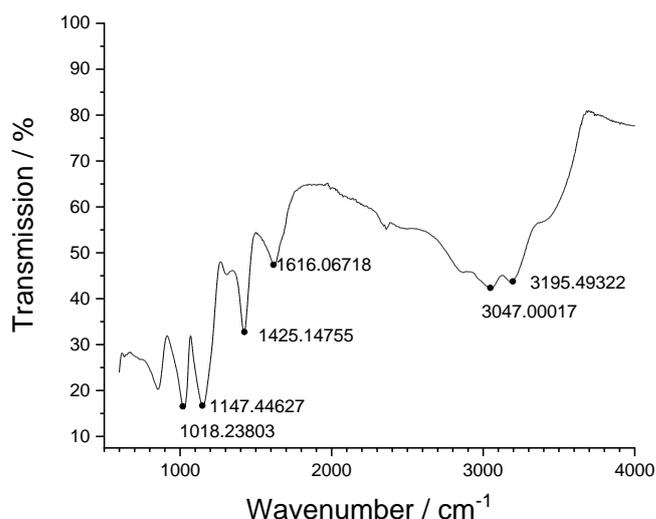
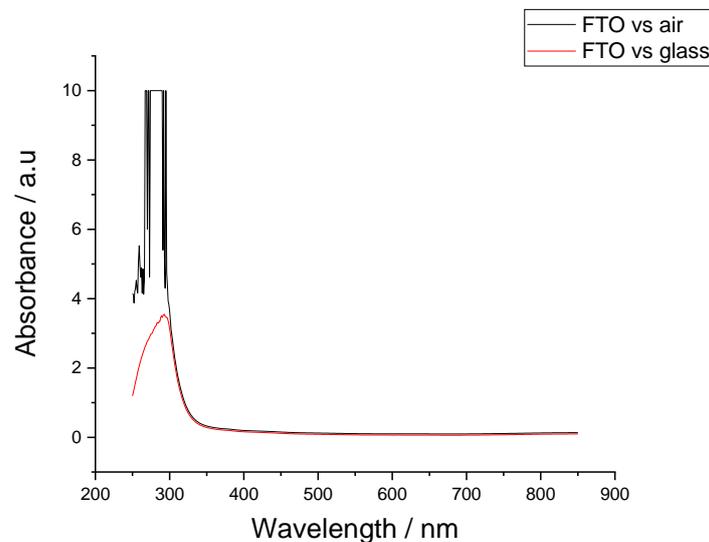


Figure 8: FTIR spectra of PDA coated FTO plate

The transition of pure FTO sample was measured to be in range between 90-100% for all of the wavelengths the sample was exposed. The FTIR of the PDA-FTO sample has shown significantly smaller transition. The points described on Figure show the peaks of vibration bands, which refer to the particular molecular interaction present in the polymer. Sharp bands below 1700  $\text{cm}^{-1}$  refer to the strong stretching of C=C and C-H bonds in aromatic components. In the spectra there was another broad band observed with two peaks at 3050  $\text{cm}^{-1}$  and 3190  $\text{cm}^{-1}$ . These peaks are typical either for O-H bond stretching or C-H bond bending within and aromatic system. The spectrum from my PDA substrate was compared with the spectra from previous research focused on o-CVD PDA synthesis, which had successful results, done by H. Coskun at all. The compared spectra were similar in all of the features [7].

### 4.3 Optical UV – Vis spectroscopy

I have analysed the absorbance of the light by PDA coated FTO glass and pure FTO glass using Lambda 1050 UV-Vis Spectrometer. I did the measurement in the range of light wavelength from 850 nm to 250 nm. I measured of the absorbance spectra using two various reference samples. The first measurement was done against the watch glass plate reference. For the second measurement I used the simple air as a reference sample.



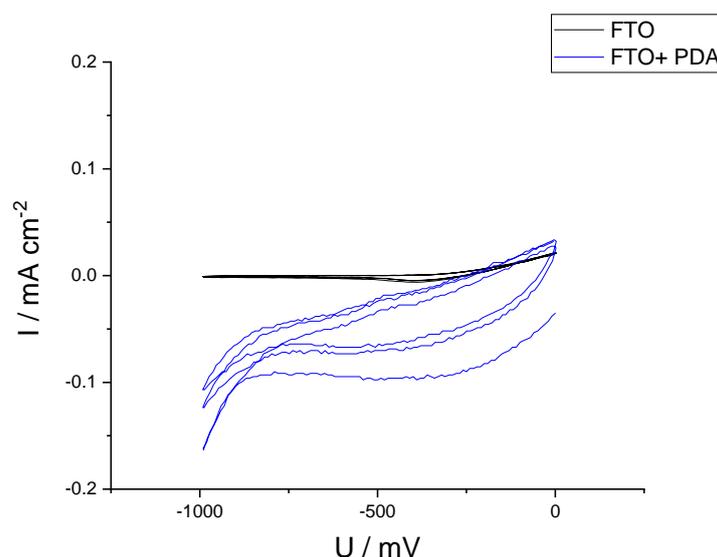
*Figure 9: The absorbance of FTO glass compared to the air and glass reference*

The light absorption ability of FTO glass is according to the data on the Figure 9 low. The highest absorption of the light by FTO was measured to be around 10% for the region of wavelengths between 250 nm and 300 nm with air as the reference sample. In the case of the glass reference the absorption of 4% was measured for the same region. In general can be said that the absorbance of FTO is low and takes place in ultraviolet region of light spectra. Since photo-electro chemical part of the work is done using a light in the visible spectrum (400-700 nm) the absorption of light by FTO will not cause any disturbances and thus it doesn't have to be taken in account.

## 5. Results

### 5.1 Cyclic voltammetry

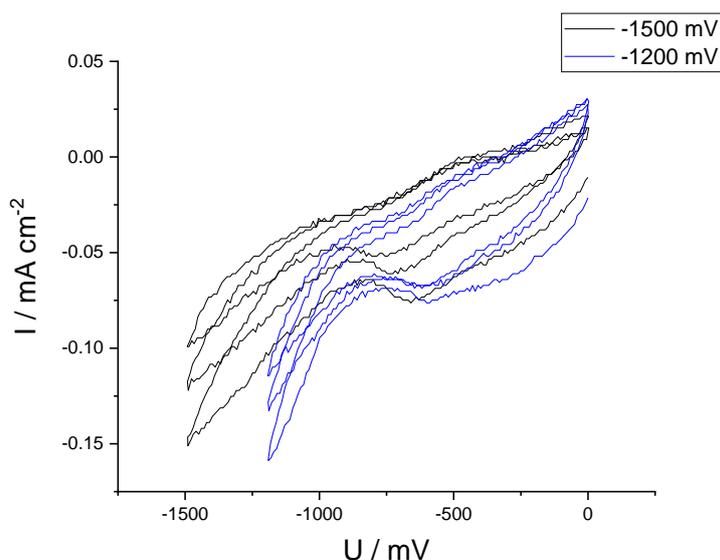
The first experiments of the main part of the work were focused on the reduction of  $\text{CO}_2$  without taking the light influence into account. For all experiments in this part of the work the plate with  $1.45 \text{ cm}^2$  of PDA coated FTO was used. All potentials were measured vs. Ag/AgCl QRE. First of all the pure FTO substrate was tested for its inertness in the  $0.1 \text{ M TBA-PF}_6$  acetonitrile-water electrolyte under the nitrogen atmosphere without  $\text{CO}_2$  enrichment and its behaviour was compared with PDA coated FTO plate. Both CVs were performed in three cycle regime with return potential set on  $-1000 \text{ mV}$ .



*Figure 10: CVs of FTO and PDA coated FTO in  $\text{N}_2$  atmosphere*

The results show that either the PDA or FTO plate is inert in the electrolyte. In the case of CV performed with the PDA coated FTO plate there was a current of magnitude  $-0.16 \text{ mA cm}^{-2}$  observed when the potential at the working electrode was in vicinity of  $-1000 \text{ mV}$ . This non-Faraday current however does not have any importance for next measurements and thus can be neglected.

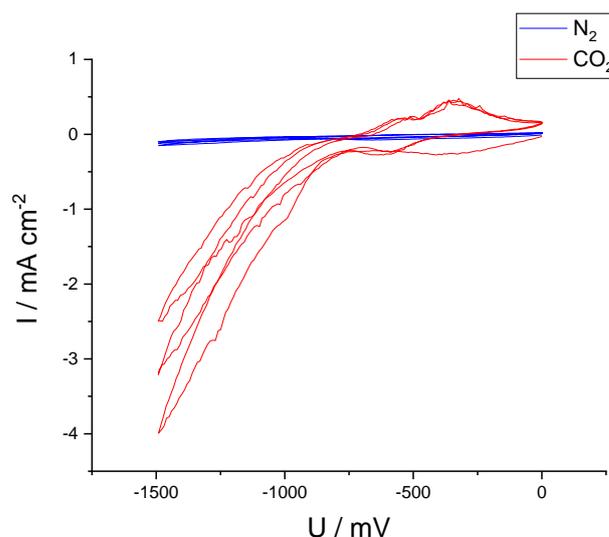
Consequently the stability and inertness of PDA substrate in the electrolyte was tested for CVs with returns potentials of  $-1200 \text{ mV}$  and  $-1500 \text{ mV}$ .



*Figure 11: CVs with PDA substrate in  $N_2$  atmosphere, return potential -1200 mV and -1500 mV*

These two CVs has proved that the PDA substrate is stable in the electrolyte upon nitrogen atmosphere and there are no side reactions happening, which would disturb following measurements. The measured current of  $-0.15 \text{ mA cm}^{-2}$  was probably caused by impurities left on the PDA and has no significance for the following experiments.

A after the PDA substrate was tested in nitrogen atmosphere the  $CO_2$  was incorporated in the experiment and the electrochemical reduction was performed. The return potential of  $-1500 \text{ mV}$  was chosen for the following measurements based on the previous tests. The rate of voltage change was  $50 \text{ mV s}^{-1}$ . At first the CV in electrolyte without  $CO_2$  was performed which was subsequently followed by CV using the same components , however in this case the electrolyte was saturated with  $CO_2$  by constant bubbling with  $CO_2$  gas at constant flow of  $3 \text{ L min}^{-1}$ .



*Figure 12: CV with PDA substrate in pure electrolyte and electrolyte saturated with CO<sub>2</sub>*

The difference between pure electrolyte and saturated is obvious. The measured current of the first cycle was 4 mA cm<sup>-2</sup>. The current had decreased in the second and third cycle to 2.5 mA cm<sup>-2</sup>.

The next measurement was focused again on the electrochemical reduction of CO<sub>2</sub> with PDA catalyst. A fresh substrate and electrolyte saturated with CO<sub>2</sub> were used and five CVs were performed with return potential -1500 mV rate voltage change rate of 50 mV s<sup>-1</sup>. The result of the first CV was similar to the previous experiment with measured current of 4,01 mA cm<sup>-2</sup>. In the following two CVs however the current decreased to value of 2.12 mA cm<sup>-2</sup> approximately a half of the magnitude of the first measurement. The current measured in the subsequent measurements were still decreasing however the decrease wasn't so intense.

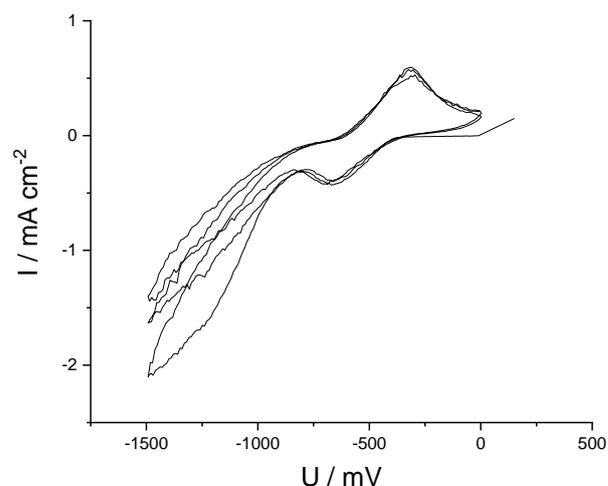


Figure 13:  $\text{CO}_2$  PDA reduction, three cycles

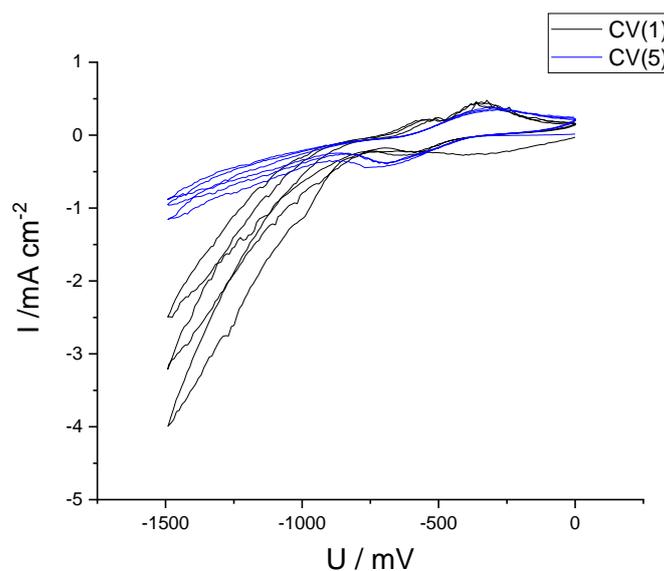
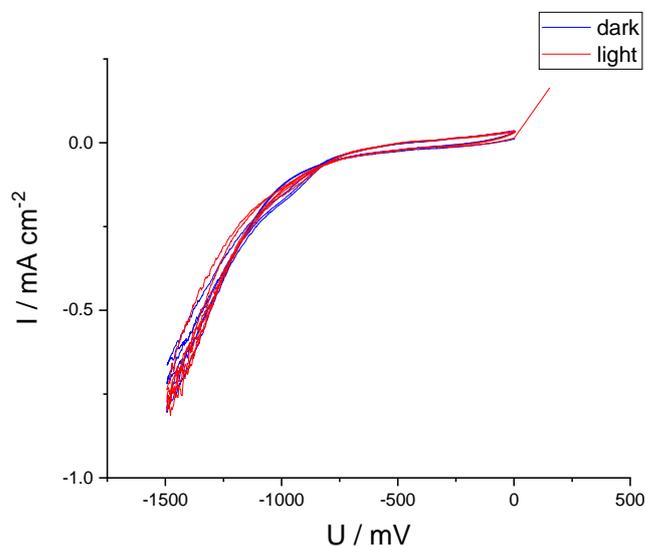


Figure 14: Comparison of first and five cycles

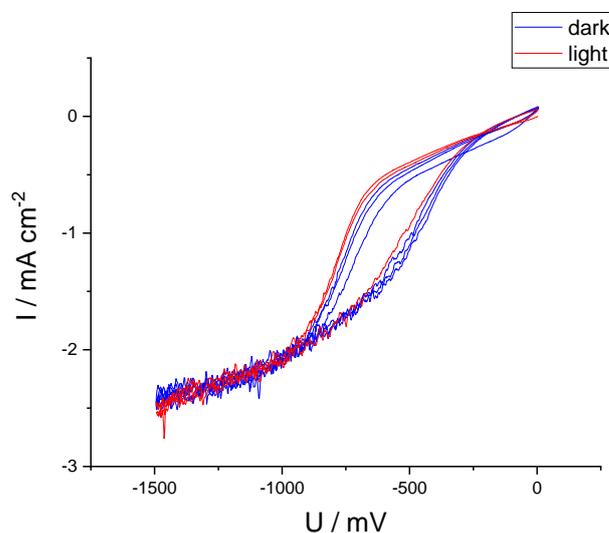
## 5.2 Cyclic voltammetry with illumination

The PDA substrate was exposed to the light of intensity  $192 \text{ mW cm}^{-2}$ . Under a constant flux of  $\text{CO}_2$  CVs were performed in the regime of alternating the dark and photo conditions after each measurement. All the potentials were measured vs QRE. There were two measurements performed within this experiment. Most of the conditions were the same expect the size of the PDA substrate. The measurements

were started with 0 mV starting potential and -1500 mV as a return potential in two various scan rates,  $10\text{mV s}^{-1}$  and  $50\text{mV s}^{-1}$ .



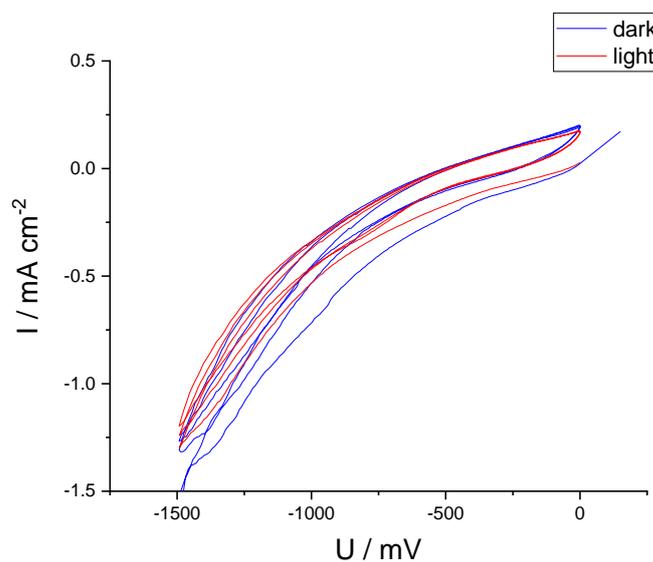
*Figure 15: CO<sub>2</sub> reduction with PDA, -1500 mV return potential and  $10\text{mV s}^{-1}$  rate, first measurement*



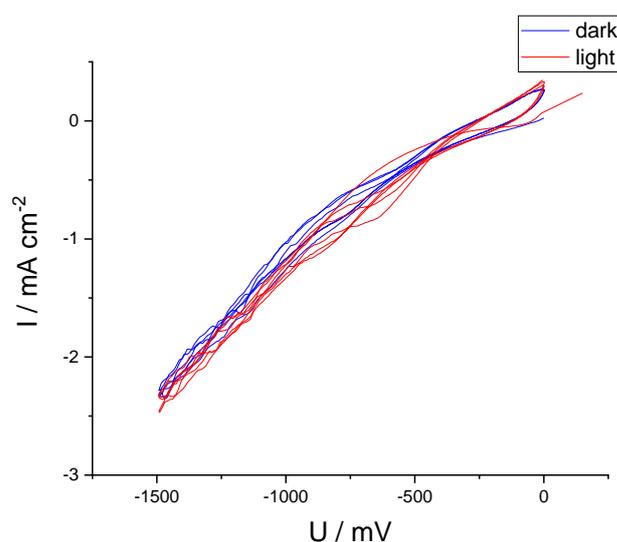
*Figure 16: CO<sub>2</sub> reduction with PDA, -1500 mV return potential and  $10\text{mV s}^{-1}$  rate, second measurement*

These graphs show the comparison between measurements upon illumination of the PDA and in the dark. In the both measurements the same result was observed. The current in the first measurement was measured  $0.69\text{ mA cm}^{-2}$  for both dark and

illuminated cyclic voltammetry. Similar situation is observed within a second measurement. In this case the current for dark CV was calculated to be  $2.42 \text{ mA cm}^{-2}$ . The current of light CV was determined to be  $2.51 \text{ mA cm}^{-2}$ . The difference between dark and light cyclic voltammetry in this case is  $0.09 \text{ mA cm}^{-2}$ .



*Figure 17:  $\text{CO}_2$  reduction with PDA,  $-1500 \text{ mV}$  return potential and  $50 \text{ mV s}^{-1}$  rate, first measurement*

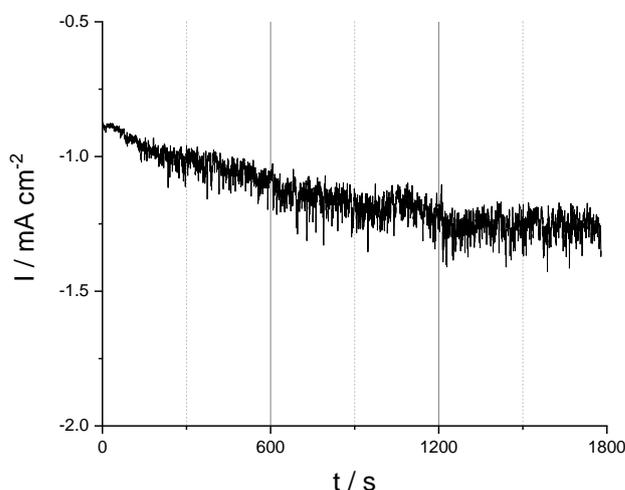


*Figure 18:  $\text{CO}_2$  reduction with PDA,  $-1500 \text{ mV}$  return potential and  $50 \text{ mV s}^{-1}$  rate, second measurement*

In the measurements, where the voltage change rate was set on  $50 \text{ mV s}^{-1}$  the current measured within first experiment has increased to approximately  $1.4 \text{ mA cm}^{-2}$  but this change was noticed to be same for both dark and light condition. In the case of second measurement there wasn't any change seen in comparison to the measurement with  $10 \text{ mV s}^{-1}$ . The currents of dark and light cyclic voltammetry in first measurement were calculated to be  $1.38 \text{ mA cm}^{-2}$  and  $1.28 \text{ mA cm}^{-2}$  respectively. In this case the difference is  $-0.1 \text{ mA cm}^{-2}$ . In the case of second measurement the currents for dark and light CV were determined to be  $2.41 \text{ mA cm}^{-2}$  and  $2.50 \text{ mA cm}^{-2}$ . The difference between these two values is  $0.09 \text{ mA cm}^{-2}$ .

### 5.3 Chronoamperometry

During the first test  $-1500 \text{ mV}$  were applied on the system homogenized by constant steering of  $160 \text{ rpm}$ . The light conditions were changed in the time interval of 5 minutes between dark and light. Within this measurement three cycles of dark and three cycles of light conditions were alternated.

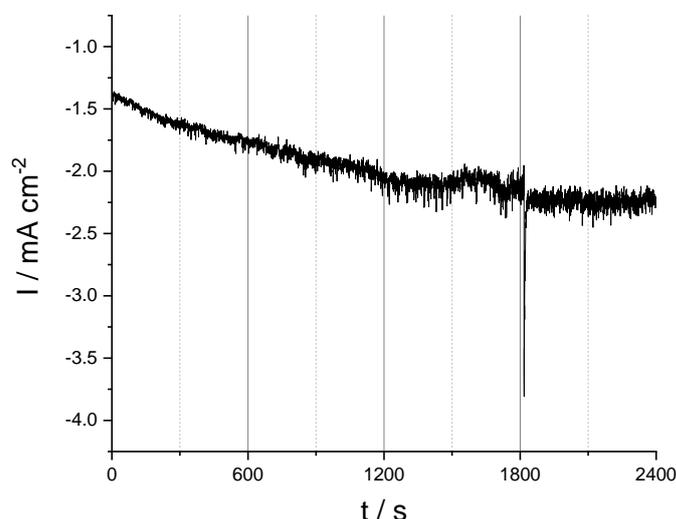


*Figure 19: PDA  $\text{CO}_2$  reduction at  $-1500 \text{ mV}$  constant potential, change  $d/l$  300 s*

The graph above shows the results of the first CA measurement. The time interval of 5 minutes (300 s) and the change from dark to the light is depicted on the graph by dashed line. The full line represents the change back from light to dark condition. According to these data there is no effect of light happening during the

reduction. At the beginning of the measurement the current was measured at  $-0.90 \text{ mA cm}^{-2}$ . Within first ten minutes of the measurement the current has increased by  $0.11 \text{ mA cm}^{-2}$  to the value of  $-1.1 \text{ mA cm}^{-2}$  however the increased was observed to be constant for the whole time without any major change when light was introduced. The same trend was observed for other two cycles except the increase of the current which had slowed down from  $0.11 \text{ mA cm}^{-2}$  to  $0.07 \text{ mA cm}^{-2}$  per 10 minutes.

In the measurement at  $-1200 \text{ mV}$  constant potential the time period between dark and light condition was prolonged to 10 minutes.

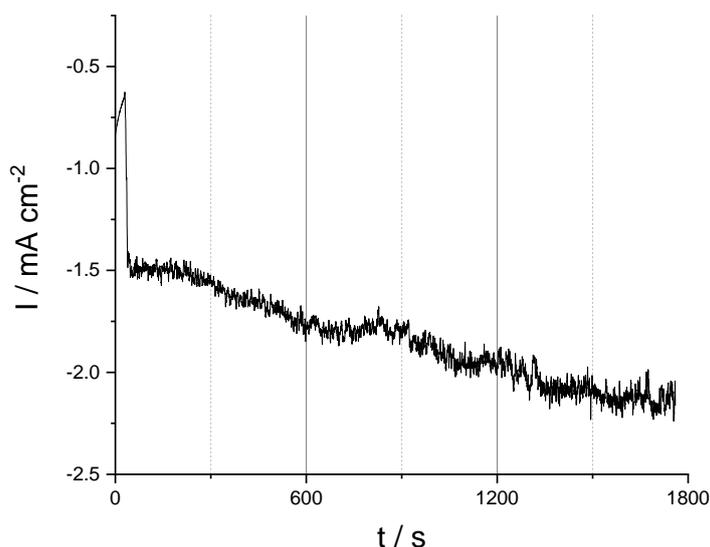


*Figure 20: PDA  $\text{CO}_2$  reduction at  $-1200 \text{ mV}$  constant potential, change  $d/l$  600 s*

The current at the beginning was measured to be approximately  $-1.5 \text{ mA cm}^{-2}$ . In the first twenty minutes of the measurement the current decreased to the expected value of  $-2.2 \text{ mA cm}^{-2}$  which had been observed before during the CV experiments. However the change of  $0.7 \text{ mA cm}^{-2}$  seems to be significant, it cannot be attributed to the light effect since the decrease was observed to be linear regardless on the illumination conditions. The decrease of the current about  $0.1 \text{ mA cm}^{-2}$  can be seen at second change from dark to light condition.

The electrolyte used for these two experiments was subsequently used for the analysis of the products by IC.

Within the last CA measurement the constant voltage of -1000 mV was applied on the system. The time interval for the change between dark and light was kept the same.

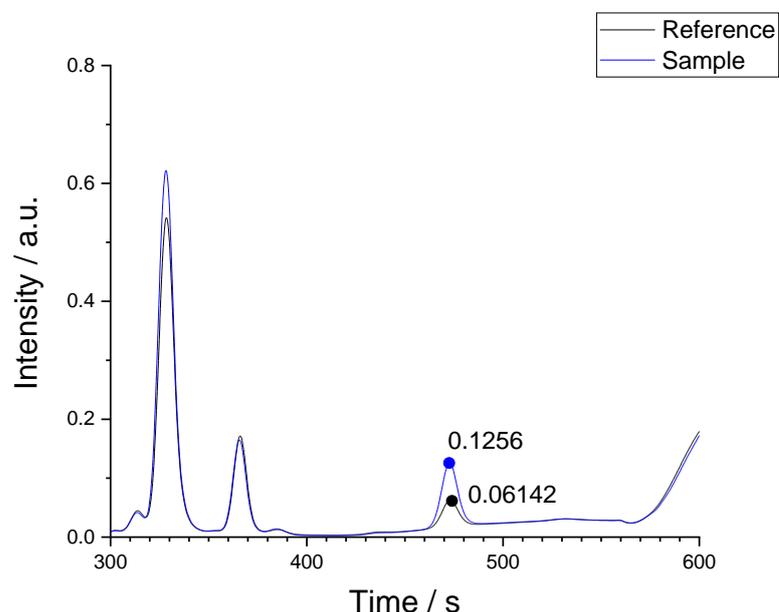


*Figure 21: PDA CO<sub>2</sub> reduction at -1000 mV constant potential, change d/l 300 s*

The resulting plot of relation between time and measured current was treated in the same way as the previous one in the Figure 21. The CA measurement with -1000 mV potential applied has shown a different result in the first two cycles that the rest of the graphs before. Similarly to the previous measurement the current at the beginning was measured at  $-1.5 \text{ mA cm}^{-2}$  and during the measurement has decreased to  $-2 \text{ mA cm}^{-2}$  but in this case the decrease of the current has in first two cycles a different slope for a dark and for illumination condition. In order to describe in more detail the rate of current increase in dark and upon illumination, I did the linear interpolation of dark and light part of both cycles. In the first cycle the increase of current was calculated to be  $0.2 \mu\text{A s}^{-1}$  for dark part and  $0.6 \mu\text{A s}^{-1}$  for light part. In the second cycle the results for dark and light were determined to be  $0.02 \mu\text{A s}^{-1}$  and  $0.5 \mu\text{A s}^{-1}$  respectively. The linear interpolation in the third cycles has shown an opposite result to those from first two cycles. The increase of current was determined to be  $0.5 \mu\text{A s}^{-1}$  for dark and  $0.08 \mu\text{A s}^{-1}$  for light.

## 5.4 Analysis of the reaction products

The result of IC chromatography of electrolyte used in chromatography has revealed an elevated concentration in electrolyte used for the chromatography.



*Figure 22: Chromatogram of IC*

On a Figure 22 the chromatogram of IC there is a peak depicted for the formate signal. The formate signal was observed in both sample and reference; however this foundation is due to the mistake in the procedure. By an accident the sample was measured first and the reference was measured afterwards. It is most probable that some formate stayed in the column and thus distorted a following measurement. Based on this prediction the peak for formate in reference sample is not taken into account for the following calculations.

The concentration of formate in the used electrolyte (with volume of 40 ml) the concentration of formate after 48 minutes of reduction of  $\text{CO}_2$  was measured to be 3,18 ppm. For the determination of FE for this reaction the amount of formate formed in this reaction has to be known. This number is than compared with theoretical yield at 100% FE. The amount of the formate produced in this reaction was calculated from the mass ration  $w$  (ppm), using a density of acetonitrile  $\rho=0,786 \text{ g cm}^{-3}$ , the molar mass of formate  $M(\text{formate}) = 45,03 \text{ g mol}^{-1}$  and the volume of electrolyte  $V= 40 \text{ cm}^3$ .

$$c = \frac{w(\text{ppm}) * \rho(\text{acetonitrile})}{M(\text{formate})}$$

$$c = \frac{3,18 * 10^{-3} \text{ g} * \text{kg}^{-1} * 0,786 \text{ kg} * \text{dm}^{-3}}{45,03 \text{ g} * \text{mol}^{-1}} = 0,0555 * 10^{-3} \text{ M} = 0,0555 \text{ mM}$$

$$n = c * V = 0,0555 \text{ mM} * 0,04 \text{ dm}^3 = 2,22 * 10^{-6} \text{ mol} = 2,22 \mu\text{mol}$$

The theoretical yield was calculated for 100% FE with electric charge C ( $\int I * dt$ ), Faraday constant  $F=96485.3 \text{ A s mol}^{-1}$  and number of electrons involved in reaction  $z=2$ .

$$n = \frac{\int I * dt}{z * F} = \frac{4,742 \text{ C}}{2 * 96485,3 \text{ A} * \text{s} * \text{mol}^{-1}} = 2,457 * 10^{-5} \text{ mol} = 24,57 \mu\text{mol}$$

Once both practical and theoretical yields were known, the Faraday efficiency for this reaction was determined, as ratio of these yields multiplied by hundred, to be 8,9 %.

$$FE = \frac{n(\text{produced})}{n(\text{theoretical})} * 100 = \frac{2,22}{24,57} * 100 = 9\%$$

## 6. Discussion

In this work I have tried to assess the photo electrochemical reduction of carbon dioxide with a PDA catalyst. The PDA was synthesised by oxidative vapour polymerization by sulphuric acid on the FTO glass.

The photoelectrochemical experiment I have performed in the one cell compartment using a 0.1M TBA-PF<sub>6</sub> acetonitrile-water electrolyte. The whole experiment was split into two parts. With the first part the several CVs were performed in order to analyse the behaviour of all components of the system. The results revealed that both FTO and PDA are stable in the electrolyte and don't do any side reactions with components of the electrolyte which would disturb the main part of the experiment.

The second part of the experiment was focused on the photoelectrochemical reduction of CO<sub>2</sub>. Within this part the sample was illuminated using a white light source at an intensity of 192 mW cm<sup>-2</sup>. The difference in current between dark and light CVs at scan rate of 50 mV s<sup>-1</sup> were only 0.09 mA cm<sup>-2</sup> for smaller

substrate(1.17 cm<sup>2</sup>) and -0.1 mA cm<sup>-2</sup> for the bigger substrate(1.45cm<sup>2</sup>). Similar results were obtained for scan rate of 10 mV s<sup>-1</sup>. The measured current density was identical from the smaller substrate and in the case of bigger substrate the difference between dark and light was only 0.09 mA cm<sup>-2</sup>. The results are summarized in Table 3.

Table 3: Summary of the CVs results from dark/ light measurements

Sample	Area PDA[cm <sup>2</sup> ]	Scan rate [mV s <sup>-1</sup> ]	Current dark [mA cm <sup>-2</sup> ]	Current light[mA cm <sup>-2</sup> ]	Current difference[mA cm <sup>-2</sup> ]
PDA-1	1.17	10	-0.69	-0.69	0
PDA-2	1.45	10	-2.42	-2.51	-0.09
PDA-1	1.17	50	-1.38	-1.28	0.1
PDA-2	1.45	50	-2.41	-2.50	-0.09

Additionally to CVs a series of CA scans were performed. The main aim of this additional experiment was to assess if there is no cumulative effect on energy coming from the light when the light is applied on the system for a longer periods of time. First two CA have shown no influence of the light at CO<sub>2</sub> reduction. Within the last CA the potential was again reduced to -1000 mV and the time period of illumination was set back to 5 minutes. In this case there was a change observed in rate of current increase between dark and light condition. However there was a change observed, this change was found to be 0.48 μA s<sup>-1</sup> between dark and light for the first cycle and 0.42 μA s<sup>-1</sup> in the case of second cycle.

The FE of the CA performed at -1200 mV constant potential was calculated to be around 9% which is smaller by factor of ten in comparison to previous experiments where the FE was above 90% [3]. However this problem is probably caused due to short time period at which the current was measured. In the experiment mentioned above the duration of CA was about 16 hours which is significant difference in comparison to CA performed within this thesis which last only for 43 minutes. Despite the low FE the production of formate during this reaction was proved to occur, which confirms the catalytic activity of PDA, but no significant photoelectro activity.

The results from CVs and CA measurements have revealed that there has been no significant photo effect on PDA catalysed CO<sub>2</sub> reduction recognized. The differences that were found during in CVs and CA have no significant values. Especially in the case of CVs the differences between dark and light conditions are in the range of hundredths of mA which is one order smaller than the differences between separate CVs performed with this work. The FE of 9% calculated for CA at -1200 mV comes from electrocatalysis and has no correlation with photo effect.

For further research on the field of photoelectrochemistry of PDA I would suggest to focus on the photo conditions of the reaction, in particular to obtain a more precise measurement of the intended photoelectrochemical process.

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## Abbreviations

PDA – polydopamine

FTO – fluorine doped tin oxide

o-CVD – oxidative chemical vapour deposition

CV – cyclic voltammetry

CA - CA

IC – ion chromatography

FTIR – fourier transform infrared spectroscopy

FE – Faraday efficiency

TON – turn over number

TBA-PF<sub>6</sub> – tetrabutylammonium hexafluorophosphate

QRE – quasi reference electrode

SHE – standard hydrogen electrode