Immobilization of Lehn's Catalyst on Metal Oxides for Heterogeneous Electrocatalysis

Submitted by
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STATUTORY DECLARATION

I hereby declare that the thesis submitted is my own unaided work, that I have not used other than the sources indicated, and that all direct and indirect sources are acknowledged as references.

This printed thesis is identical with the electronic version submitted.

Linz, 26.6.2018   Zoja Lakovič

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Abstract

This thesis focuses on heterogeneous electrocatalysis for CO_2 reduction, using [Re(bpy)(CO)$_3$Cl], also called Lehn catalyst, which is a well-known catalyst for electrochemical reduction of CO_2 to CO. Lehn catalyst was immobilized on TiO_2 nanotubes and nanoporous ZnO electrodes using –COOH moieties as anchoring groups. Immobilization was achieved by dissolving Lehn-COOH in acetonitrile and drop casting it onto electrodes. Cyclic voltammetry, scanning electron microscopy and Fourier-transform infrared spectroscopy measurements were performed for characterization of the electrodes. Electrochemical experiments were performed in one compartment cell and reduction of CO_2 to CO was confirmed with gas chromatography.

Table of contents

1. Introduction

1.1 CO_2 and global warming

Greenhouse gases are the ones that absorb and emit radiant energy within the thermal infrared range, the most prominent in the Earth atmosphere being water vapor, carbon dioxide, methane, nitrous oxide, and ozone[1]. Absorbing the solar radiation they keep the Earth surface warm (without them average temperature would be about -18°C [2]), however due to the human activity their atmospheric concentration has been increasing rapidly, consequently the average surface temperature of the Earth as well.
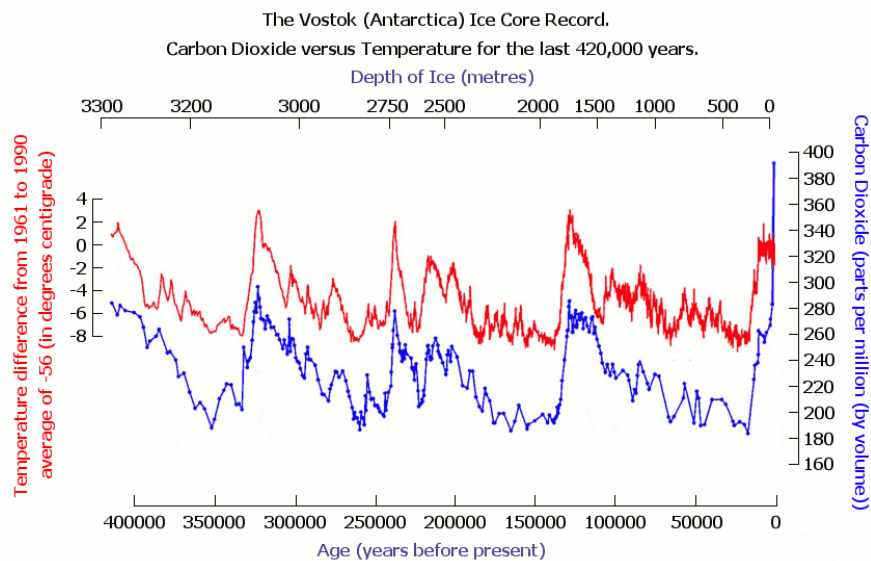

Figure 1: CO_2 and temperature changes over the last 420 000 years[3].

Since industrial revolution in 1750 the atmospheric concentration of CO_2 has increased for 40%. The main sources of emissions are fossil fuels combustion, industrial processes (cement manufacture) and land use (deforestation)[4].

1.2 Carbon capture, storage and utilization

Different technologies are used to reduce the emissions of CO_2. Carbon capture and storage (CCS) is a process of capturing CO_2 at the emission sources, such as fossil fuels power plants and industrial processes, liquefying it, and then transporting by pipeline or by ship and storing underground in deep geological formations, such as a depleted oil or gas field, or in the deep oceans. Carbon capture can

reduce the CO_2 emissions of the modern conventional power plan by approximately 80 – 90% [5]. However, there are drawbacks of using this method, such as high costs of capturing, transportation and injection. Safety is also an issue thus monitoring the sequestration areas after closing is needed to prevent any leakage.

Carbon capture and utilization is an alternative approach, looking into ways to utilize captured CO_2 rather than treating it as a waste product and store it away. CO_2 can be used in the food and drink industry (e.g. as carbonating agent, preservative…), for enhanced oil recovery (injecting the gas into oil reservoir to increase the extracted amount) for chemical synthesis (synthesis of urea, salicylic acid, polycarbonates) or converted into fuels[6].

IEA predicts that despite rapid deployment of clean energy technologies, the CO_2 emissions will continue to grow, especially from oil use in transport and industry (20% increase by 2040) [7].

If the renewable energy is used (such as solar, wind, hydro, geothermal energy) to power the conversion of CO_2 back into fuels, this results in carbon-neutral energy cycle, lowering the emissions and our dependency on the fossil fuels. Wind towers for example are often stopped, because the grid is saturated[8], and the electrochemical reduction of CO_2 could be used to store the excess electric energy.

1.3 CO_2 reduction

CO_2 is kinetically and thermodynamically stable, with a standard Gibbs free energy of formation of -394.4 kJ mol^{-1}[9]. *Table 1* shows standard reduction potentials for different electrochemical conversions of CO_2. It can be seen that the one electron reduction occurs at very negative potential of -1.9 V. This is due to the high energy needed to change the shape of the molecule from linear CO_2 a bent $CO_2^{\bullet-}$ radical anion. This change in structure is the reason for a very slow self-exchange rate for the $CO_2 - CO_2^{\bullet-}$ couple and high overpotentials in the reduction of CO_2[10].

Table 1: Formal electrochemical redox potentials for the reduction of CO_2 (at pH 7, in aqueous solution, vs. NHE)[11].

$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	$E_0 = - 0.53$ V
$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$	$E_0 = - 0.61$ V
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	$E_0 = - 0.48$ V
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	$E_0 = - 0.38$ V
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	$E_0 = - 0.24$ V
$CO_2 + e^- \rightarrow CO_2^{\bullet-}$	$E_0 = - 1.90$ V

Catalysts are used to stabilize the intermediate transition state in the reduction and therefore lower the overpotentials and increase the reaction rates.

Catalysis can be either homogeneous, meaning that the catalyst used is in the same phase as the reactants or heterogeneous, when the catalyst is in different phase as the reactant and the catalysis takes place in the interface of the two phases.

Different catalytic approaches, such as thermal, electrochemical, photochemical, photo-electrochemical, can be used to drive the conversion of CO_2 to higher energy molecules[8]. Most common catalysts used are transition metals and their complexes[12]. The most common CO_2 reduction products obtained by electrochemical catalysis are carbon monoxide, formic acid, oxalic acid, formaldehyde, methanol, methane, ethylene, and ethanol[12].

1.4 Lehn catalyst

[Re(bpy)(CO)$_3$Cl] (bpy = 2,2'-bipyridine) complex, as well called Lehn catalyst, was first reported by Hawecker, Lehn and Ziessel in 1983 to be an efficient homogeneous catalyst for photochemical reduction of CO_2 to CO[13]. In 1984 the same group showed that it can also be used successfully as electrocatalysit. They used [Re(bpy)(CO)$_3$Cl] in solution of DMF and water (9:1) and 0.1 M Et$_4$NCl, and performed 14 hours electrolysis at a potential of $-$ 1.4 V (vs. NHE), which is much less than $-$ 1.9 V required for one electron CO_2 reduction. CO was produced with 98% current efficiency. They also observed that if water content in electrolyte was increased over 10% yellow precipitate formed and H_2 was produced. With no water CO was produced at much lower rate [14].

Sullivan et al.[15] studied the electrochemical behavior of [Re(bpy)(CO)$_3$Cl] and related derivatives on order to understand the catalytic pathway for CO_2 reduction. Cyclic voltammetry in MeCN solution showed two reduction peaks, the reversible first one was independent on the variation of the ligand and thus attributed to bipyridine reduction. The second irreversible peak was assigned to be due to the metal reduction as its position changed with different ligands. When solution was saturated with CO_2 only the second peak showed the catalytic increase. *Figure 2* shows the two reduction pathways the authors proposed. First path is one electron reduction that involves [Re(bpy)(CO)$_3$] radical intermediate. They suggested that the reduction of bipyridine is followed by electron transfer to metal, loss of Cl$^-$, and in case of no CO_2 to green precipitate formation which was characterized as [Re(bpy)(CO)$_3$]$_2$ dimer. When CO_2 is present in solution the formation of dimer was suppressed completely. Second reduction pathway includes formation of [Re(bpy)(CO)$_3$]$^-$ anion and two electrons.
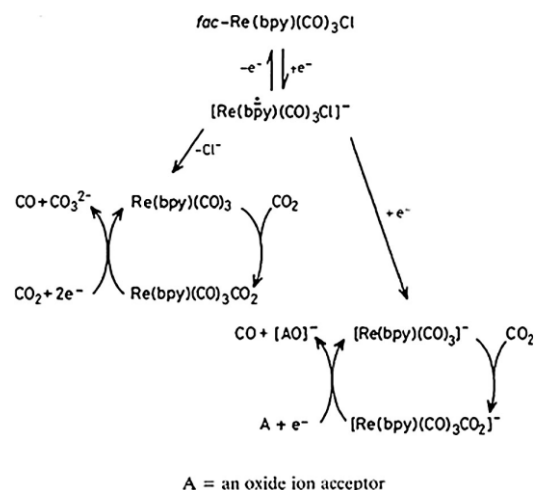
Figure 2: CO₂ reduction pathways[15].

Johnson, George, Hartl, and Turner[16] carried out a number of spectroelectrochemical experiments to further investigate the reduction mechanism. They found out that in strongly coordinating solvents such as MeCN stable radical $[Re(bpy)CO)_3(CH_3CN)]^{\bullet}$ is formed and reduction proceeds in two electron pathway. Anion $[Re(bpy)(CO)_3Cl]^{\bullet-}$ does not interact directly with CO_2 but only acts as catalyst precursor. However, in absence of CO_2 or in solvents like THF or DMF one electron path via $[Re(bpy)(CO)_3]^{\bullet}$ becomes prevalent.

Many attempts were made to improve original Lehn catalyst. In 2010 Smieja and Kubiak[17] studied Lehn catalyst complexes with modified bipyridine ligands and reported significant increase in catalytic activity and Faradaic efficiency of $Re(bpy-tBu)(CO)_3Cl$ (bpy-tBu = 4,4'-di-tert-butyl-2,2'-bipyridine) comparing to original $[Re(bpy)(CO)_3Cl]$.

Portenkirchner et al. compared $[Re(bpy)(CO)_3Cl]$ to $[(5,5'$-bisphenylethynyl-2,2'-bipyridyl)Re(CO)_3Cl]$[18] and $[(4,4'$-Bisphenyl-Ethynyl-2,2'-Bipyridyl)Re(CO)_3Cl]$[19] and saw 6.5-fold increase in current density in CO_2 saturated solution for the first compound and 11-fold for the second one, comparing to 4.5-fold for Lehn catalyst. However the second compound showed rather low efficiency of 12% for 5h electrolysis.

1.5 Heterogeneous catalysis

Issues such as dimer formation can be addressed by immobilizing the catalyst on the electrode. Other potential benefits of heterogeneous catalysis are that many different solvents can be used since the catalyst does not need to be soluble in the electrolyte and it is easy to recover it from the reaction mixture[20]. Electropolymerization or binding via anchoring groups can be used for immobilization. One

possibility is to modify the catalyst by attaching the carboxylic acid which can act as anchoring groups and bind to metal oxides electrodes. Possible modes of binding of –COOH groups on TiO_2 surfaces are by electrostatic attraction, hydrogen bonding, ester linkage, bridging, and chelating[21].
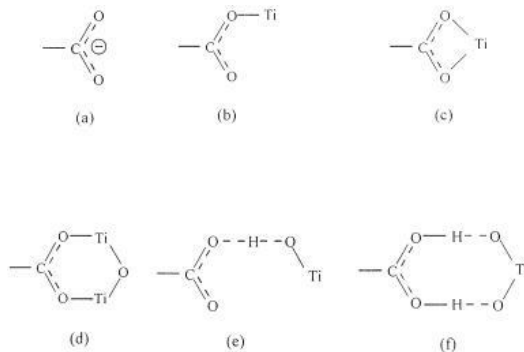

Figure 3: Possible modes of carboxylic acids binding to TiO_2 [22].

Anfuso et al. investigated binding of [Re(dcbpy)(CO)₃Cl] (dcbpy =4,4'-dicarboxy-2,2'-bipyridine) to rutile TiO_2 and observed that rhenium complex binds through the carboxylate groups with bidentate or tridentate linkages nearly perpendicular to the surface, exposing rhenium to the solution and making it easy for CO_2 to interact with it[23].

This thesis focuses on heterogeneous catalysis, using modified Lehn catalyst [Re(dcbpy)(CO)₃Cl] (Lehn-COOH) with –COOH moieties as binding anchor on ZnO and TiO_2 electrodes.
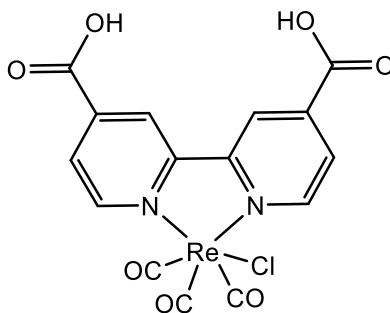

Figure 4: Molecular structure of Lehn-COOH.

2. Experimental part

2.1 Materials

Chemicals used during the thesis work are listed in *Table 2.*

Table 2: Used materials.

Material	Formula	Supplier	Purity	Abbreviation
Acetone	C_3H_6O	VWR Chemicals	technical	-
Acetonitrile	C_2H_3N	Roth	> 99.9%	MeCN
Carbon dioxide	CO_2	Linde	99.995%	-
N,N-dimethylformamide	C_3H_7NO	VWR Cemicals	100%	DMF
Eosin Y	$C_{20}H_8Br_4O_5$	Sigma Aldrich	99%	-
Glassy Carbon, 2 mm		Alfa Aesar	type 1	GC
Isopropanol	C_3H_8O	VWR Chemicals	AnalaR Normapur	IPA
Nitrogen	N_2	JKU		-
Potassium Hydroxide	KOH	Alfa Aesar	85%	-
Tetrabutylammonium hexafluorophosphate	$C_{16}H_{36}NPF_6$	Sigma Aldrich	> 99.0%	$TBAPF_6$
Zinc Nitrate	$Zn(NO_3)_2$	Sigma Aldrich	98%	-

2.2 Methods

2.2.1 Electrochemical measurements

Cyclic voltammetry (CV) was applied to study the electrochemical behavior of electrodes and the catalyst. All experiments were carried out in a one compartment cell set up with three electrodes.

As working electrode either glassy carbon, TiO_2 nanotubes (NTs) or nanoporous ZnO (on indium tin oxide (ITO) coated glass) were used. Platinum was used as counter electrode and as reference Ag/AgCl quasi reference electrode.

TiO_2 NTs electrodes were provided by Dr. Engelbert Portenkircher from University of Innsbruck.

TiO_2 NTs electrodes were cleaned between measurements TiO_2 NTs electrodes using Soxhlet apparatus with toluene as the solvent. Platinum electrodes were cleaned with flame.

10 ml of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) dissolved in acetonitrile was used as an electrolyte. Each time CV was first measured in solution that was purged with N_2 for 40 minutes before measurement to remove any dissolved oxygen. Afterwards the solution was purged with CO_2 for 15 minutes and CV was measured again. Measurements were performed on bare electrodes first and then repeated on the electrodes coated with Lehn-COOH catalyst.

Following the characterization of the electrodes with CV, constant potential electrolysis was conducted. After the electrolysis 2 ml sample was taken from the headspace of the cell using a gas-tight glass syringe and injected into a *Thermo Scientific Trace GC Ultra* to obtain the amount of product.

For further characterization of the electrodes, scanning electron microscopy (SEM) and attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy were measured. SEM images were taken with a JEOL JSM 6360-LV scanning electron microscope and to record FTIR spectra *Bruker Vertex 80 FTIR* spectrophotometer equipped with a Platinum Diamond-ATR accessory was used. Electrode coated with Lehn-COOH was placed downwards on the Platinum Diamond-ATR module and pressured down to remove any trapped air that could cause interference.

2.2.2 ZnO electrode preparation

ZnO was prepared by electrodeposition, following the procedure described by Yoshida et al.[24]

ZnO was deposited electrochemically onto indium tin oxide (ITO) glass substrate. First the ITO glass was cut into rectangular shapes in the desired size of electrodes. Afterwards it was cleaned ultrasonically in base piranha solution – first for 30 minutes at 70 °C in NH_4OH and water solution, then H_2O_2 was added. This step is necessary to make the glass substrate surface smooth.

One compartment cell was prepared with 10 mL of aqueous solution containing 0.1 M $Zn(NO_3)_2$ and 55 µM eosin Y. Platinum was used as counter electrode and Ag/AgCl as a quasi-reference electrode. Cell was placed in a water bath and temperature was adjusted to 70 °C. Then the potential of – 850 mV was applied for one hour and the solution was kept at 70 °C. After the deposition white coating with slightly pinkish color was observed on the ITO glass. The pinkish color is due to the eosin Y, which gets reoxidized on the air. For removing the eosin Y 0.1 M KOH solution was used. The electrode was dipped into the solution for half an hour, washed with MilliQ water and dried.

Figure 5: Set up for electrodeposition of ZnO/eosin Y.

3. Results and discussion

3.1 Electrochemistry of Lehn-COOH in solution

For comparison Lehn-COOH was first tested in solution. Glassy carbon was used as working electrode, Ag/AgCl as quasi reference, and 0.1 M $TBAPF_6$ in acetonitrile as electrolyte. 1 mM solution of Lehn-COOH was prepared by weighing 5.5 mg of catalyst powder and dissolving it in 10 mL of electrolyte. Cyclic voltammetry was measured, first in solution saturated with N_2 and afterwards with CO_2. The results of the measurements are shown in *Figure 6*. Characteristic reduction peak of bipyridine was observed at around – 1000 mV under N_2 saturated conditions while this peak shifted to more positive values under CO_2-saturated conditions. Upon introduction of CO_2 into the reaction atmosphere the current was increased 2.2-fold signaling the reduction of carbon dioxide by Lehn catalyst. This is a clear indication of catalytic activity towards carbon dioxide reduction which have been demonstrated many times in the literature.
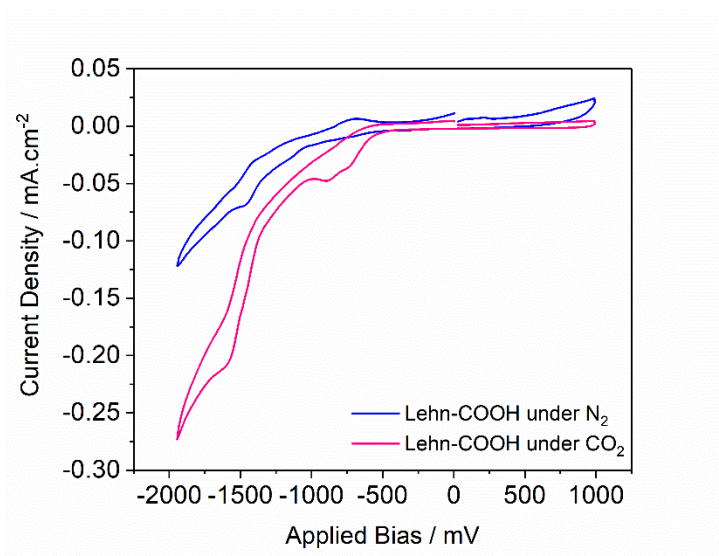

Figure 6: Cyclic voltammograms of Lehn-COOH in solution.

3.2 Immobilization of Lehn-COOH

3.2.1 Lehn-COOH on TiO₂ nanotubes electrode

In order to immobilize Lehn-COOH on TiO_2 NTs electrode, 1 mg of Lehn-COOH was dissolved in 2 mL of acetonitrile and drop-casted on the electrode. For insulation the electrode was covered with Teflon tape

in which holes with diameter of 11 mm were made, so only small area covered with catalyst was exposed to the electrolyte.
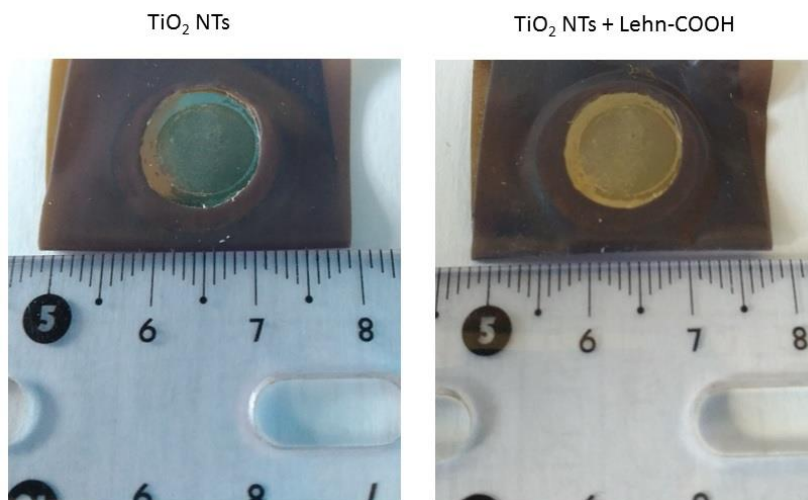
TiO$_2$ NTs   TiO$_2$ NTs + Lehn-COOH

Figure 7: TiO$_2$ NTs electrode before and after Lehn-COOH application.

SEM images of the electrode were taken before (*Figure 8)* and after coating with Lehn-COOH (*Figure 9)*, and also after electrolysis *(Figure 10).* It can be seen in *Figure 8* that nanotubes are around 0.1 µm wide. In *Figure 9* the nanotubes can no longer be observed due to the coverage of the surface with a film of Lehn catalyst. Although the surface coverage of the TiO$_2$ NTs is observed, filling of the individual tubes cannot be deduced from the SEM measurements.
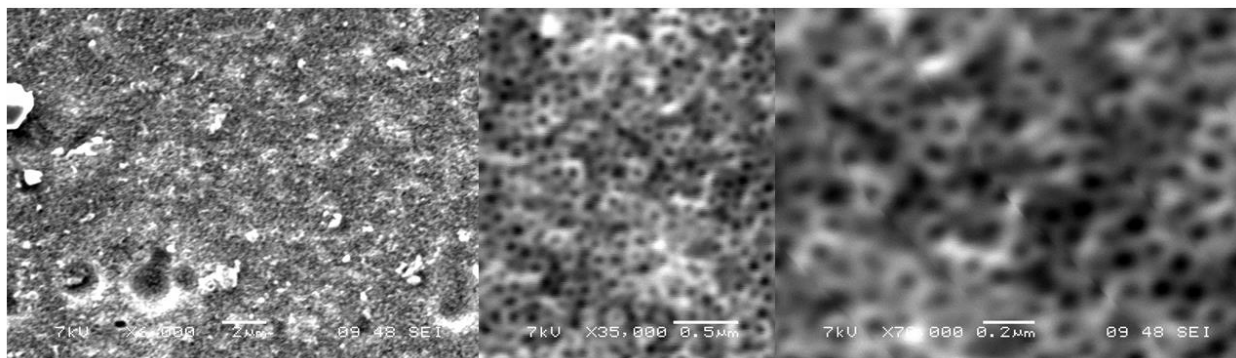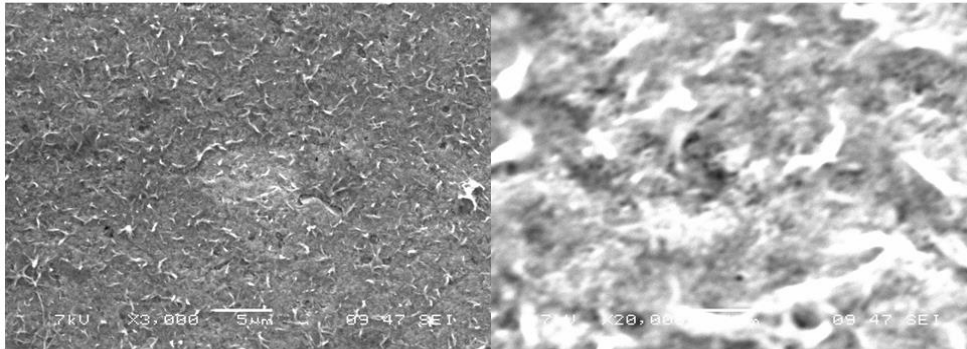

Figure 8: SEM images of bare TiO$_2$ NTs.

Figure 9: SEM images of TiO$_2$ NTs coated with Lehn-COOH.

Figure 10 shows the SEM images after extensive electrochemical measurements. It can be seen that the film on the electrode is partially removed exposing the TiO$_2$ NTs structures. However, the film is mostly intact which indicates the possible covalent bonding of the film on the oxide surface.
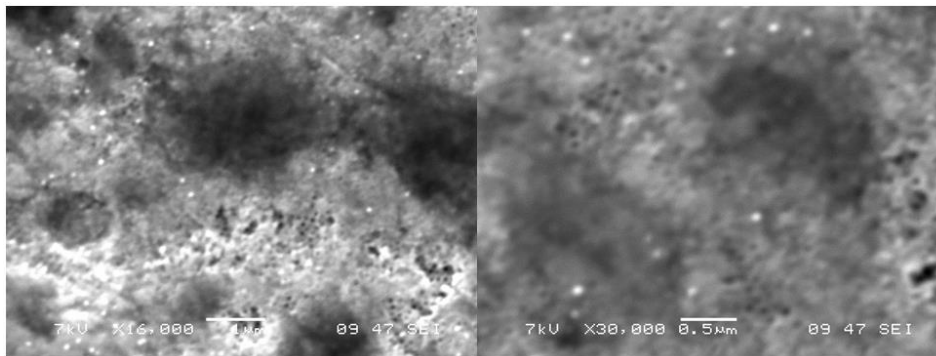

Figure 10: SEM images of TiO$_2$ NTs coated with Lehn-COOH after electrolysis.

As already mentioned in the introduction, the possible binding modes of carboxylic acid on metal oxides are hydrogen bonding, electrostatic attractions and covalent bonds[21]. To investigate the binding ATR-FTIR measurements were taken, first of bare TiO$_2$ NTs electrode and later of TiO$_2$ NTs coated with Lehn-COOH. *Figure 11* shows the difference in absorption of the two obtained spectra. Two peaks at wavenumber around 2000 cm^{-1} correspond to the CO vibrations from ketone that forms when carboxylic acid binds to the surface of the electrodes, indicating the covalent bonding of the catalyst to the surface. No characteristic peak for –OH vibrations (at around 3000 − 3500 cm^{-1}) was observed which further points to covalent bonds rather than hydrogen bonding.
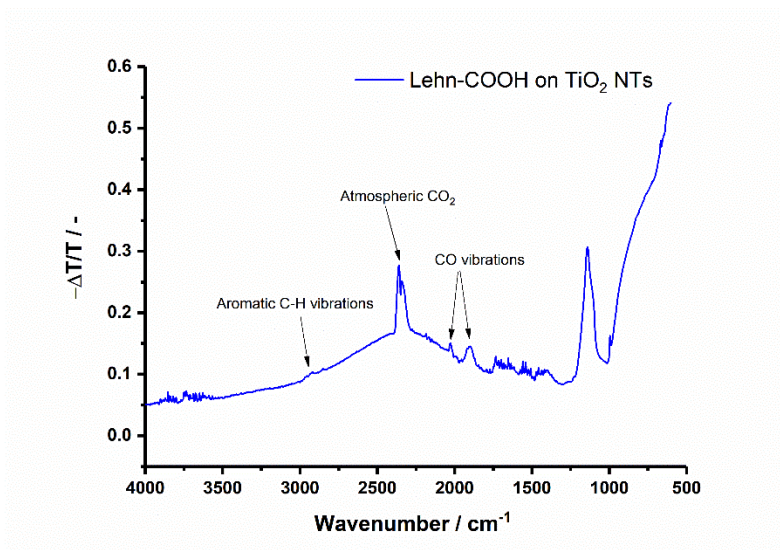
Figure 11: FTIR spectrum of Lehn-COOH coated TiO$_2$ NTs electrode.

CV measurements were carried out in 0.1M TBAPF$_6$ in MeCN, first on bare TiO$_2$ NTs electrode *(Figure 12)*. Little to no reductive current can be observed under nitrogen atmosphere, while the measurement after purging the solution with CO$_2$ shows increase in reductive current at around – 1900 mV.

To check if CO is produced by bare TiO$_2$ NTs, electrolysis was performed at potential held at – 1800 mV for two hours. Afterwards the headspace sample was checked with GC for CO and no product was observed.
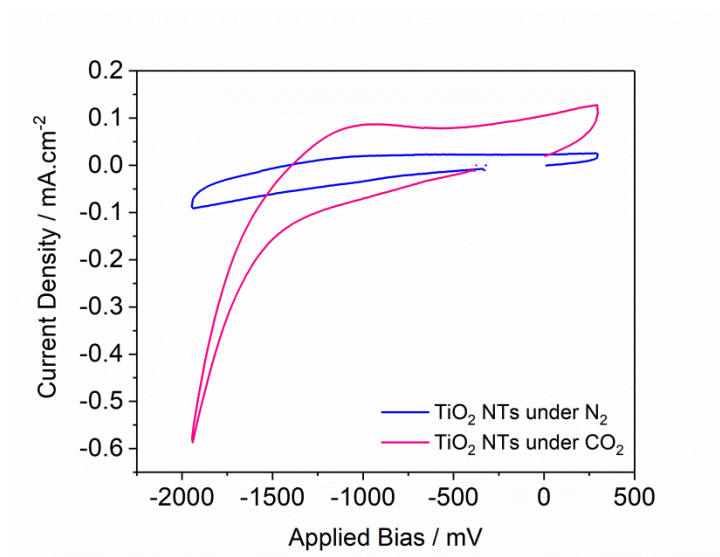

Figure 12: Cyclic voltammograms of TiO$_2$ NTs bare electrode in 0.1M TBAPF$_6$ in MeCN.

Electrode was then coated with Lehn-COOH and CV was measured (*Figure 13*). Voltammogram under N_2 shows similar behavior as Lehn-COOH in solution (*Figure 6*), with two peaks, first one with onset at around − 1000 mV and a second more negative one. Under CO_2 atmosphere the first reduction peak of bipyridine seems to disappear while the second shows catalytic increase and is shifted to more positive potential, starting to increase around − 1250 mV. Approximately 2.7-fold increase in current density can be observed, which indicates catalytic reduction of CO_2 to CO.
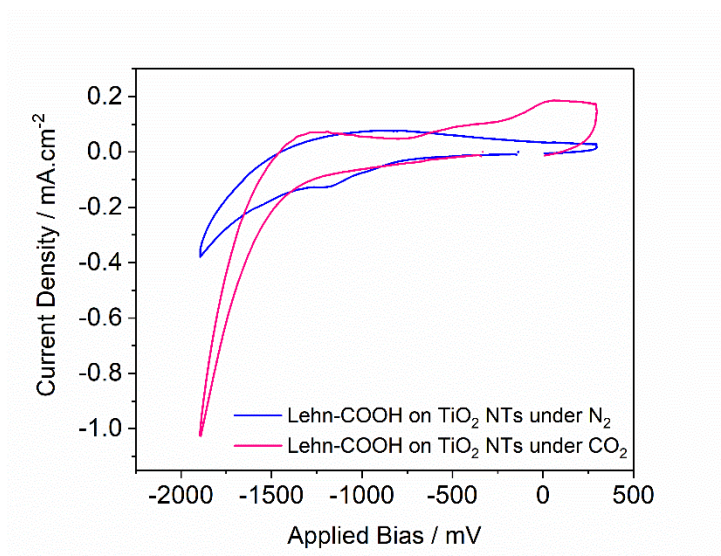

Figure 13: Cyclic voltammograms of Lehn-COOH coated TiO$_2$ NTs electrode in 0.1M TBAPF$_6$ in MeCN.

Electrolysis was performed with Lehn-COOH on TiO_2 NTs several times and afterwards obtained CO amount was checked via GC using 2mL of the headspace gas.

Faradaic efficiency is a measure of the selectivity of a catalyst towards a certain product and was calculated by dividing numbers of moles of product by moles of electrons transferred during electrolysis, and multiplying that by two, since it is a two electron reduction (Equation (1)).

$$Faradaic\ efficiency = \ 2 * \frac{n\ (CO)}{n\ (e^-)} \quad (1)$$

Amount of electrons transferred was obtained by dividing integral under the electrolysis curve with Faraday constant.

The obtained efficiency values were pretty low, ranging from 2.5 − 5.6%.

3.2.2 Lehn-COOH on ZnO electrode

Thin film of nanoporous ZnO was deposited electrochemically on ITO substrate from aqueous solution of $Zn(NO_3)_2$. Eosin Y was added to solution, acting as a template for obtaining the porous structure. *Figure 14* shows the current during 1 h of electrodeposition.

Potential was held at $-$ 850 mV against Ag/AgCl quasi reference electrode. At the cathode the NO_3^- is reduced to NO_2^- [25]:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$$
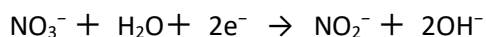
The OH^- then reacts with Zn2+ and precipitates as ZnO upon dehydration[25]:

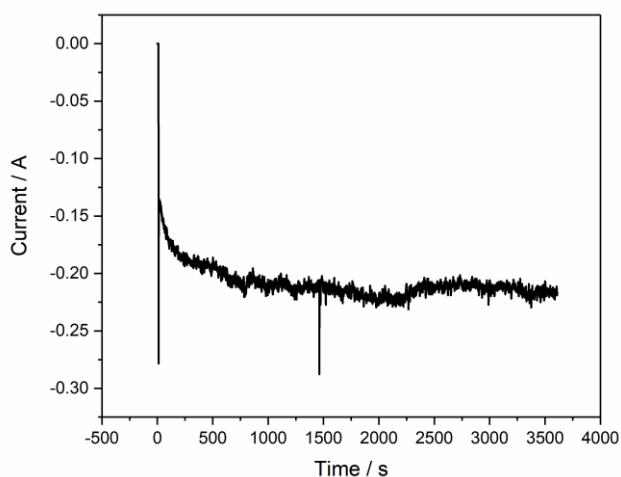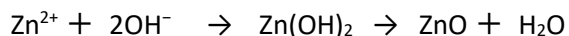$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O$$

Figure 14: ZnO growth.

Figure 15 shows the obtained ZnO film on ITO, covering the area of around 1 cm^2 of the substrate. As before 1 mg of Lehn-COOH was dissolved in 2 mL of MeCN and drop-casted on the electrode. In *Figure 16* on the left the coated electrode before the electrolysis and on the right after the electrolysis is shown. After electrolysis the color of the catalyst turned slightly darker.
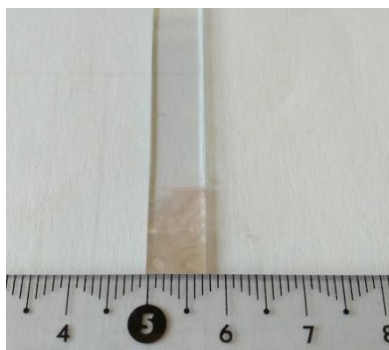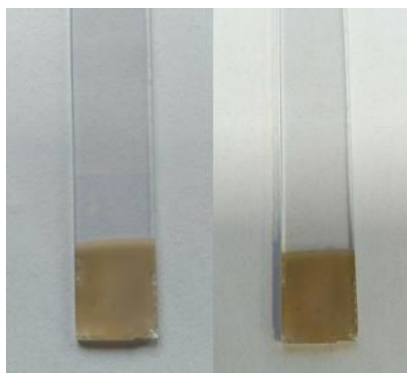
Figure 15: ZnO on ITO.

Figure 16: ZnO electrodes coated with Lehn-COOH before (left) and after (right) electrolysis.

Randomly shaped Lehn catalyst aggregates covering the surface can be observed on the SEM images of the coated electrode before the electrolysis (*Figure 17*). On the images recorded after the electrolysis (*Figure 18*) it appears that the coating stayed mostly intact, indicating the possible covalent bonding of the catalyst to the surface.
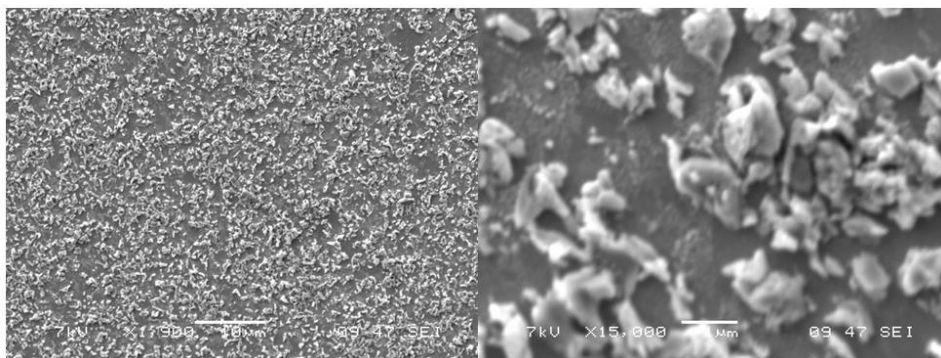

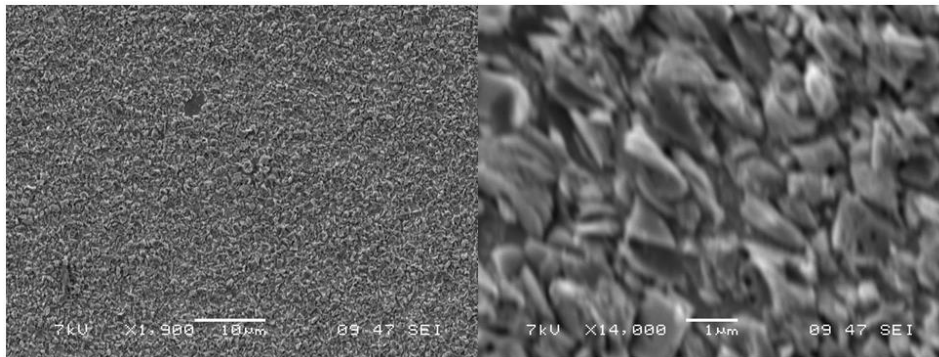*Figure 17: SEM images of Lehn-COOH on ZnO electrode.*

Figure 18: SEM images of Lehn-COOH on ZnO electrode after electrolysis.

As with the TiO$_2$ NTs electrode the ATR-FTIR measurements were taken to further investigate the binding of the catalyst to the surface. As before two peaks occur around 2000 cm^{-1} corresponding to the CO vibrations, which points towards covalent attachment of the carboxylic groups of catalyst to the surface of ZnO (*Figure 19*).
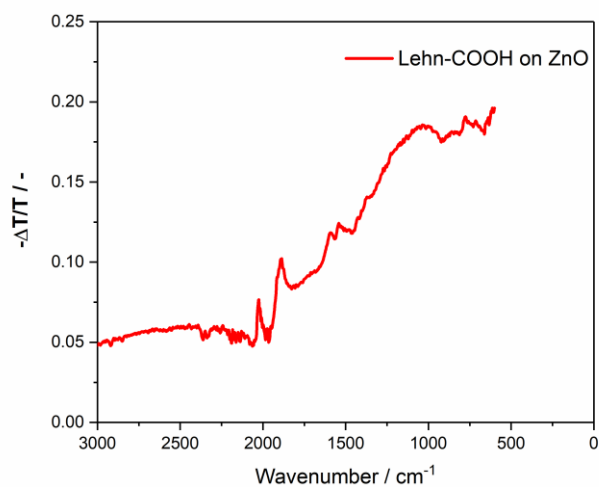
Figure 19: FTIR spectrum of Lehn-COOH coated ZnO electrode.

Cyclic voltammetry was measured first on bare ZnO electrode (*Figure 20*). CV scan under N$_2$ shows two reductive waves, first one with onset at around − 1000 mV and second one starting at − 1200 mV. CV under CO$_2$ shows more complex behavior, with another peak appearing at − 650 mV and the crossing of the cathodic and anodic currents can be observed at − 900 mV and − 1050 mV. Crossing of anodic and cathodic traces in cyclic voltammetry indicates a chemical reaction of a reduced species forming a product which is easier reduced than the initial compound.

16

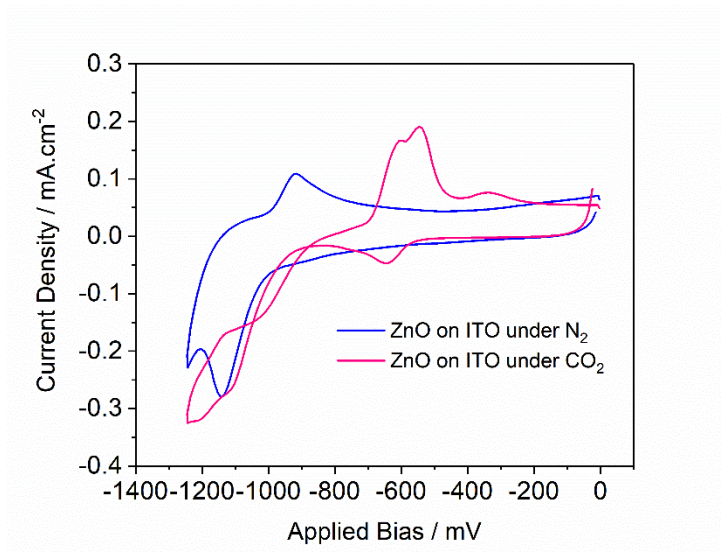*Figure 20: Cyclic voltammograms of ZnO electrode.*

After coating the electrode with Lehn-COOH similar behavior as with Lehn-COOH on TiO_2 NTs can be observed (*Figure 21*), reductive current seems to appear at the same potential. 3-fold increase in current density was observed after purging the electrolyte solution with CO_2.
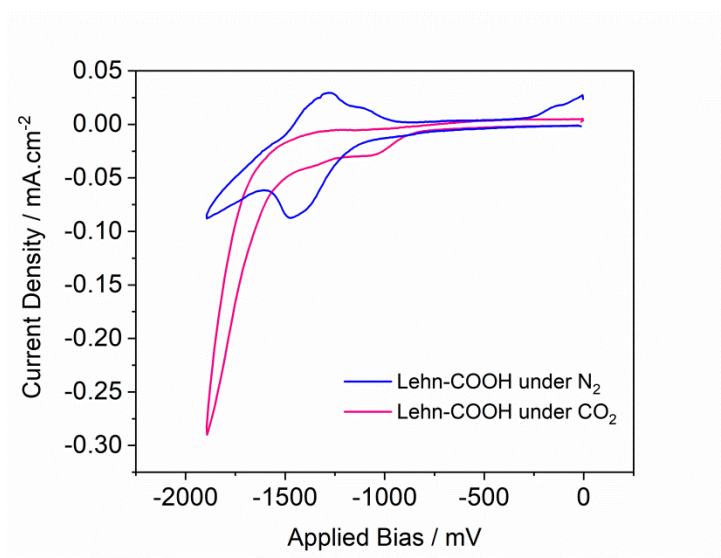

Figure 21: Cyclic voltammograms of Lehn-COOH coated ZnO electrode in DMF.

After electrochemical characterization of ZnO electrode coated with Lehn-COOH electrolysis was performed at potential – 1750 mV against Ag/AgCl for one hour in CO_2 saturated DMF. Afterwards the CO amount was checked with GC using the headspace gas and Faradaic efficiency was calculated to be 17.6%.

4. Conclusion

The aim of this thesis was to use the rhenium bipyridine complex known as Lehn catalyst for heterogeneous catalysis. Modified Lehn catalyst was used with carboxylic acid groups attached to bipyridine. Carboxylic acids act as anchoring moieties on the metal oxides. Lehn-COOH was successfully immobilized on TiO_2 and ZnO electrodes. Electrodes were characterized using SEM, FTIR and electrochemistry. SEM images showed that the catalyst covered the surface and stayed attached to even after extensive electrochemical measurements. Together with FTIR spectroscopy results indicate covalent attachments of Lehn-COOH to the surface of the electrodes. Nevertheless, to confirm the covalent bonding of the catalyst, further measurements are necessary.

Cyclic voltammetry measurements showed increase in the reduction current when the solution was saturated with CO_2, confirming the catalytic activity of immobilized Lehn-COOH. Reduction of CO_2 to CO was confirmed with gas chromatography measurements after the electrolysis experiments were conducted. Faradaic efficiencies were ranging between 2.5 and 5.5% for TiO_2 based electrodes. Faradaic efficiency for ZnO based electrode was 17.6%.

The obtained efficiencies seem low comparing to the originally reported efficiency for homogeneous catalysis using Lehn catalyst, which was 98% [14] and to the efficiencies obtained by immobilized Lehn catalyst, which were reported to be as high as 92% for electropolymerized [ReCl(CO)$_3$(4-vinyl-4'-methyl-2,2'-bipyridine)] [26].

The reasons for low efficiencies achieved in this work could be that the film is not fully covering the surface or that not all of the active sites of the catalyst are fully exposed to the solution and reachable.

5. References

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