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Preparation of multicomponent photoelectrodes for
photo-electrocatalytic reduction of carbon dioxide

Příprava multikomponentní fotoelektrody pro foto-elektrokatalytickou
redukci CO₂

Bachelor's thesis

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Prague, 2025

Declaration of authorship

I declare that this thesis was elaborated solely by myself with the guidance from my supervisor and that I cited all the sources used for research of the topics discussed in this thesis. This thesis was not used for obtaining another academic degree.

In Prague 16.5.2025

Hana Štrkolcová

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Abstract

The increasing concentration of carbon dioxide (CO₂) in the atmosphere, caused mainly by fossil fuels combustion, is one of the key environmental issues nowadays. Therefore, its capture and further utilization are highly relevant topics in the current research. One of the ways of CO₂ conversions is photo-electrochemical (PEC) approach. PEC process and design of multicomponent photoelectrodes for PEC CO₂ reduction reaction (CO₂RR) are investigated by this bachelor's thesis. Copper(I) oxide (Cu₂O) is our primary photoresponsive material, due to low band gap allowing the photoexcitation by visible light and its suitable redox potential for CO₂RR. However, Cu₂O suffers from a high rate of charge recombination and significant photocorrosion. Hence, we investigated the protective overlayer of various microporous (*BEA, FAU-Y, Zn-FAU-Y) and mesoporous (MCM-41, KIT-6) materials to improve the overall photocathode stability.

The porous materials were synthesized through hydrothermal methods and thoroughly characterized. Cu₂O layers were prepared via electrodeposition onto FTO glass and subsequently coated with the synthesized porous materials using spray-coating technique. The resulting multicomponent electrodes were evaluated using linear sweep voltammetry (LSV) and chronoamperometric measurements under constant illumination. Chronoamperometric tests were combined with the product analysis of gas and liquid phase contained in the reactor after the tests. Product analysis was performed by both gas chromatography (GC) and proton nuclear magnetic resonance (¹H NMR) spectroscopy.

The results show that the usage of porous materials as protective overlayers, particularly zeolites *BEA and Zn-FAU-Y, can improve the photostability and affect the catalytic performance of Cu₂O-based photoelectrodes in terms of product distribution in CO₂RR. These multicomponent photoelectrodes demonstrate decrease in the photocorrosion process when compared with the bare FTO/Cu₂O electrodes. This work highlights the potential of multicomponent photoelectrodes including porous materials for efficient CO₂RR PEC.

Key words

Photo-electrochemical (PEC) catalysis, CO₂ reduction reaction (CO₂RR), semiconductors, multicomponent photoelectrodes, Cu₂O, zeolites, mesoporous silica materials

Abstrakt

Spalování fosilních paliv způsobující zvyšování koncentrace oxidu uhličitého (CO_2) v atmosféře je jedním z klíčových environmentálních problémů současnosti. Proto je zachycování a další využití CO_2 velmi aktuálním tématem současného výzkumu. Jednou z možností přeměny CO_2 je fotoelektrochemický (PEC) přístup. V rámci této bakalářské práce byl zkoumán PEC proces a byly navrženy a připraveny multikomponentní fotoelektrody pro PEC redukci CO_2 (CO_2RR). Jako primární fotoaktivní materiál byl zvolen oxid měďný (Cu_2O) především díky jeho malému zakázanému pásu, který umožňuje jeho fotoexcitaci viditelným světlem a kvůli vhodnému redoxnímu potenciálu pro CO_2RR . Cu_2O ovšem má značnou nevýhodu z důvodu rychlé rekombinace náboje a fotokoroze. Proto jsme zkoumali ochranné vrstvy z různých mikroporézních (*BEA, FAU-Y, Zn-FAU-Y) a mezoporézních (MCM-41, KIT-6) materiálů s cílem zvýšit celkovou stabilitu fotokatody.

Porézní materiály byly syntetizovány hydrotermálními metodami a důkladně charakterizovány. Vrstva Cu_2O byla připravena elektrodpozicí na FTO sklo a následně na ni byla nanášena vrstva syntetizovaného porézního materiálu pomocí techniky nástřiku. Výsledné multikomponentní elektrody byly hodnoceny pomocí lineární voltametrie (LSV) a chronoamperometrických měření za stálého osvětlení. Chronoamperometrické testy byly doplněny analýzou produktů v plynné a kapalně fázi obsažených v reaktoru po testech. Analýza produktů byla provedena plynovou chromatografií (GC) a nukleární magnetickou rezonanční (^1H NMR) spektroskopií.

Výsledky ukazují, že použití porézních materiálů jako ochranných vrstev pro Cu_2O , zejména zeolitů *BEA a Zn-FAU-Y, může zlepšit celkovou fotostabilitu a ovlivnit katalytické chování fotoelektrod na bázi Cu_2O z hlediska distribuce produktů CO_2RR . Tyto multikomponentní fotoelektrody vykazují zmírnění procesu fotokoroze ve srovnání s nepokrytým FTO/ Cu_2O . Tato práce zdůrazňuje potenciál multikomponentních fotoelektrod obsahujících porézní materiály pro efektivní PEC redukci CO_2 .

Klíčová slova

Foto-elektrochemická (PEC) katalýza, redukční reakce CO_2 (CO_2RR), polovodiče, multikomponentní fotoelektrody, Cu_2O , zeolity, mezoporézní materiály na bázi oxidu křemičitého

Abbreviations

*BEA	Zeolite Beta
^1H NMR	Proton nuclear magnetic resonance
ABF	Annular bright-field detector
ADF	Annular dark-field detector
AR	After reaction
BED	Backscattered electrons detector
BET	Brunauer, Emmett and Teller
BG	Band gap
BJH	Barrett-Joyner-Halenda
BR	Before reaction
CB	Conduction band
CE	Counter electrode
CMC	Critical micellization concentration
CO ₂ RR	Carbon dioxide reduction reaction
D	Sacrificial electron donor
DFT	Density functional theory
EC	Electrochemical
EDX	Energy dispersive X-ray
ETD	Everhart–Thornley secondary electrons detector
FAU-Y	Zeolite faujasite type Y
FIB	Focused ion beam
FID	Flame ionization detector
FTO	Fluorine doped tin oxide
GC	Gas chromatography
HER	Hydrogen evolution reaction
HOMO	Highest occupied molecular orbital
HRTEM	High-resolution transmission electron microscopy
ICP-MS	Inductively coupled plasma with mass spectrometry
IUPAC	International Union of Pure and Applied Chemistry
IZA	International Zeolite Association

LCT	Liquid crystal templating
LSV	Linear sweep voltammetry
LUMO	Lowest unoccupied molecular orbital
MSE	Mercurous sulphate electrode Hg/Hg ₂ SO ₄
OER	Oxygen evolution reaction
OSDA	Organic structure directing agent
P	Photosensitizer
PC	Photochemical
PCET	Proton-coupled electron transfers
PEC	Photo-electrochemical
PXRD	Powder X-ray diffraction
RE	Reference electrode
RHE	Reversible hydrogen electrode
SBU	Secondary building unit
SED	Secondary electrons detector
SEM	Scanning electron microscopy
SHE	Standard hydrogen electrode
SSCE	Silver/silver chloride electrode Ag/AgCl
STEM	Scanning transmission electron microscopy
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
USY	Ultra-stable faujasite Y
UV-VIS	Ultraviolet-Visible
VB	Valence band
WE	Working electrode
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
Zn-FAU-Y	Aluminozincosilicate faujasite

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1. Introduction

Future sustainable development plays a truly crucial role in recent research across many scientific fields. The increasing human population and economic development are the factors that are increasing the global energy demand. As nowadays about 85 % of the global energy supply comes from fossil fuel combustion,¹ the supply of these fuels cannot meet ever-growing demands for energy linked with growing population, and therefore it is imminent to find alternative sources of carbon. Besides the obvious scarcity of the fossil fuels their combustion releases large number of air-pollutants, including the greenhouse gases, which are directly responsible for the global warming and climate change. These ecological risks have an immense impact on the environment and human civilization. Even presently the consequences of the climate change and global warming can be seen, and the weather extremes will become even more frequent. One of the primary subjects that needs to be addressed is the level of various greenhouse gases in the atmosphere, most importantly the level of carbon dioxide, which constitutes to approximately 80 % of all greenhouse gas emissions.¹ Therefore, its capture, utilization and storage are very important topics for research. Besides lowering the greenhouse gas emissions the CO₂ can be used as an alternative carbon source since it is readily available. One way of utilization of carbon dioxide is its conversion (via CO₂ reduction reaction, CO₂RR) into value-added products, e.g. methane, formic acid or methanol,² by photocatalytic, electrocatalytic and photo-electrocatalytic processes. The photo-electrocatalytic conversion stands out because it combines the advantages of the photocatalytic and electrocatalytic processes. CO₂ conversions face many challenges since the CO₂ is a very stable molecule and its conversion therefore needs a large amount of energy. These processes involve catalysts, which should be ideally cheap, abundant, non-toxic, less corrosive and chemically stable^{1,2}

To tackle this issue, this thesis employs Cu₂O based photoelectrodes for photo-electrocatalytic CO₂RR. Cu₂O possesses many advantages, but main limiting factor of its efficiency is the photocorrosion of the material, which significantly lowers its photo-activity. Multiple strategies are employed to deal with this issue, among them also preparation of heterostructure photoelectrodes. This thesis focuses on the assessment of photo-activity of heterostructure photoelectrodes consisting of Cu₂O and the protective overlayer using various porous materials.

2. Goals

This thesis aims to enhance the photo-electrocatalytic properties and stability of copper(I) oxide (Cu_2O) for reduction of carbon dioxide via preparation of multicomponent photoelectrodes. The photoelectrodes compose of copper(I) oxide layer with a cover layer of porous materials. This thesis has following partial objectives:

- The synthesis of the various porous materials (microporous – zeolites and mesoporous silica-based materials):
 - Hydrothermal synthesis of zeolites *BEA, FAU-Y and Zn-FAU-Y.
 - Hydrothermal synthesis of mesoporous amorphous silica MCM-41 and KIT-6.
 - Characterization of their crystallinity, textural properties, morphology and elemental composition.
- Preparation of composite photocathodes:
 - Electrodeposition of copper(I) oxide on FTO glass.
 - Spray-coating of the porous materials over the layer of copper(I) oxide.
- Photo-electrochemical characterization of photocathodes:
 - Linear sweep voltammetry (LSV).
 - Chronoamperometric measurements under illumination – assessment of long-term photostability and CO_2RR product analysis.

3. Theoretical part

3.1. Conversion of carbon dioxide

Carbon dioxide has been denoted as a major greenhouse gas, with its emissions constituting to approximately 80 % of all greenhouse gas emissions.¹ This together with increasing global energy demand are the main reasons for development of new strategies and technologies. The main goals are at least partial replacement of fossil fuel energy and also the moderation of CO₂ emissions through its capture, storage and mainly the utilization. These strategies should ideally use abundant, non-toxic, low-cost and efficient materials. Since the storage of carbon dioxide comes with many limitations and possible dangers (such as accidental leakage back to the atmosphere), the direct utilization of CO₂ through conversion into value-added products (fuels and chemicals) has been gaining a huge attention. This approach can turn waste into a new carbon source, contribute to slowing down the growth of CO₂ emissions and help to moderate the energy crisis all at once. CO₂ is nowadays definitely a cheap, safe and most importantly abundant source of carbon, therefore it is an ideal candidate as carbon source thus also contributing to circular carbon economy.^{1–}

3

CO₂ conversions and utilization can be divided into three main categories: chemical/catalytic conversions (chemical processes), enzymatic conversions (biological/biochemical processes) and technological utilization (physical processes). The technological utilization holds many practical and real application such as additive to beverages, food preservation, dry cleaning, fire extinguishers, etc. Enzymatic conversions are processes occurring in the living organisms (animals, plant and microorganisms). Biological processes mainly include the photosynthesis and CO₂ mineralization. The restriction of the potential of biochemical processes is the slow conversion rate. The chemical/catalytic processes use CO₂ as a raw material but in many cases, they have shown low conversion rate and poor selectivity.^{1–4}

Chemical conversion of CO₂ can be divided into two categories: low-energy (non-reductive) exchange and high-energy (reductive) exchange (see Figure 1). Low-energy exchange uses less energy to convert CO₂ into organic high-carbon chemicals, with its carbon in oxidation state +4 or +3. The high-energy exchange uses greater energy to reduce

CO₂ to chemicals or fuels with carbon in oxidation states of +2 or lower.⁴ In current economy where the demand for the fuels (e.g. CH₄, CH₃OH, etc.) is higher than that of chemicals the second approach is more attractive.^{1,2,4}

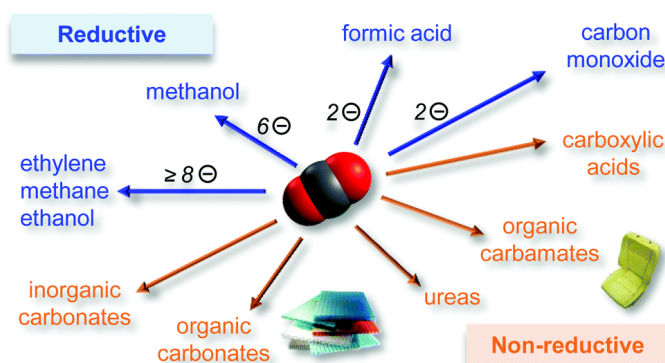


Figure 1: The chemical CO₂ conversions with different products can be divided into two categories: reductive (high-energy) conversions and non-reductive (low-energy) conversions.⁵

From the chemical CO₂ conversions the mainly explored ones are based on thermochemical, photochemical (PC), electrochemical (EC) and photo-electrochemical (PEC) processes.³ Apart from the PC and PEC conversions, the processes face many disadvantages, such as high-energy demanding conditions (high temperature and pressure). The PC and PEC processes stand out for a few reasons: they require lower energy, that can be obtained from sustainable source (they use natural solar light as the main energy input). They are performed under mild conditions compared to other methods and they are highly controllable through reaction temperatures and electrode potential. Moreover, the systems used for these conversions are modular, scalable and compact.¹⁻⁴

3.1.1. Molecular structure and thermodynamic stability of CO₂

Linear molecule of CO₂ is held together by strong covalent bonds, where the atoms have strong electrical affinities towards each other. Oxygen atoms are better at pulling electron pairs from the carbon atom; therefore, the C atom is at relatively low energy state. The bond length is 116 pm, which is interestingly shorter than that of a typical C=O double bond (124 pm in acetaldehyde) and closer to the length of the C≡O triple bond (112.8 pm in carbon monoxide).⁴ The energy of C=O bond in CO₂ molecule (803 kJ/mol) is much higher when compared with H–O bond in H₂O molecule (463 kJ/mol).⁴ These properties are attributes of the sp-hybridized orbitals of C. Each hybridized orbital forms a σ bond with O atom and

the two left p orbitals form a π bond with O atom. Combination of low polarity, high energy and high symmetry of the molecules leads to very high stability of this molecule.^{1,4}

CO_2 is one of the main products of any combustion. Main problem encountered by any form of CO_2RR is that CO_2 is very thermodynamically stable molecule. Therefore, the CO_2RR is thermodynamically uphill process (endergonic reaction), and will not occur spontaneously. Energy must be supplied into the system in order to overcome negative potentials and give value-added products.^{3,4,6}

3.1.2. Electrochemical (EC), Photochemical (PC) and photo-electrochemical (PEC) reduction of CO_2

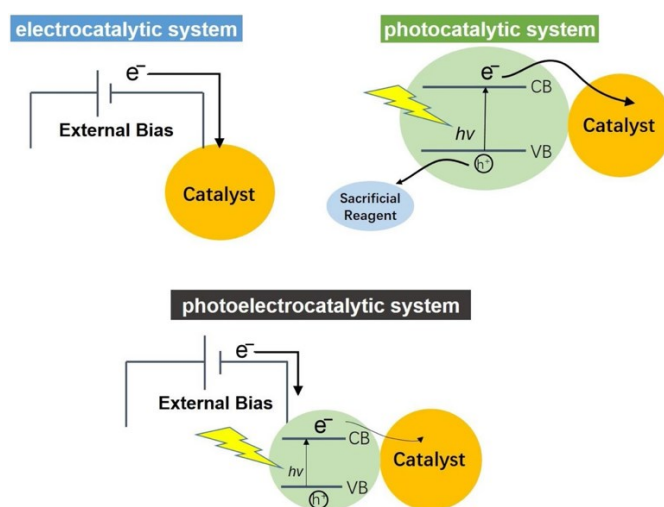


Figure 2: Scheme of electrocatalytic, photocatalytic and photo-electrocatalytic system.¹

Electrocatalysis

The renewable electrical energy is readily available via large-scale solar and wind facilities nowadays, therefore the electrocatalytic CO_2RR is considered as a promising, clean and sustainable way of turning industrial CO_2 into value-added chemicals and fuels. The process starts with the activation of adsorbed CO_2 molecule on a catalyst surface via electric energy to form CO_2^- (see Figure 2). Further transfer of electrons and/or protons leads to formation of other intermediates.^{1,7}

The most commonly used electrocatalysts are metallic, organo-metallic and carbon-based materials. For the purpose of EC CO_2RR , the transition metals, such as Au, Ag and Pd are commonly used as catalysts. The great disadvantage of this process when using the

noble metal catalysts is poisoning effect by CO molecule, which is one of the most common products of CO₂RR. CO molecule exhibits strong affinity towards coordination with transition metals. If this interaction is too strong it can create difficulties for the desorption of molecule, therefore lowering the catalytic activity. Additional downsides are toxicity of some metals (e.g. Co, Pb are rarely used because of their toxicity), their cost inefficiency and environmental unfriendliness (e.g. Pd, Ag, Pt). Further development of electrocatalytic CO₂RR is limited because of low Faradaic efficiency, low selectivity, limited current density, large overpotentials and unstable intermediates.^{1,7}

Photocatalysis

PC conversions of CO₂ are based on the solid photocatalysts absorbing the light energy through photoexcitation of electrons from the valence band into the conduction band and further usage of this energy for CO₂RR (see Figure 2). They harvest the energy from solar light and converts it into electron-hole pairs needed for driving the reduction and oxidation reactions. It involves three basic steps: light absorption, charge separation and transfer to the surface to perform the catalytic reaction.^{1,3,4}

Photocatalytic conversions of CO₂ can be done in both homogenous and heterogenous systems. Homogenous systems usually consist of a catalyst, a photosensitizer, a sacrificial electron donor and/or electron relay.³ The mechanism of CO₂RR in homogenous PC systems uses of photosensitizer, which is able to absorb the radiation and becoming excited (P*). This excited state is reduced by a sacrificial electron donor (D), creating reduced photosensitizer (P⁻) and oxidised sacrificial agent (D⁺). Photosensitizer then transfers the electrons to the catalyst, which is able to perform CO₂RR. In some cases, the photosensitizer and catalyst are the same species. This approach usually requires expensive metals, sacrificial agent and it is afflicted by poor performance and stability issues.^{3,8}

In heterogenous system, which is also core of this thesis, the three main types of photocatalysts used for CO₂RR are: semiconductor materials, graphene-based nano-catalysts and organometallic complexes. Mostly, the large number of semiconductors has been explored. The appropriate semiconductor must satisfy certain conditions: I) it must have a suitable band gap (ideally to enable the excitation of electrons by absorption of visible light), II) the redox potential of conduction band must be more negative than the redox potential of

CO₂ reduction, and III) the redox potential of valence band must be more positive than redox potential for oxidation of H₂O. The presented requirements therefore narrow the number of semiconductors, which can be used for PC processes. Crucial properties of these semiconductors are also high photostability and efficient charge separation to avoid its recombination, ergo photodegradation of the material. The type of photocatalysts also affects the kinetics, selectivity, efficiency and yield of the process. Because photocatalyst is the core of the PC and PEC systems, various semiconductors have been studied (see Figure 3). Among them, TiO₂ is widely researched material, which is cheap, highly stable, non-toxic and abundant. The disadvantages of TiO₂ include a large band gap and therefore requiring ultraviolet light for the photoexcitation and low efficiency. In contrast, Cu₂O has a suitable band gap energy for absorption of visible light, but it suffers from photocorrosion.¹⁻⁴

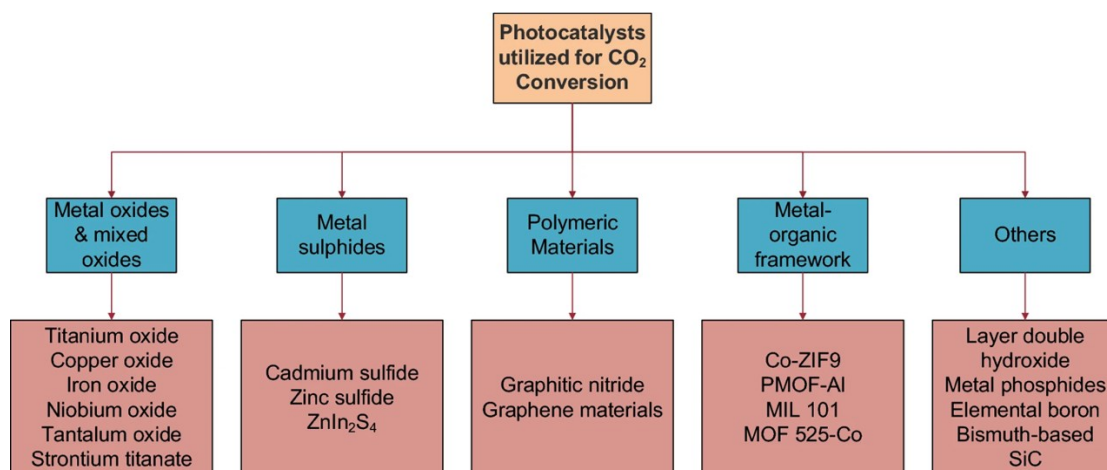


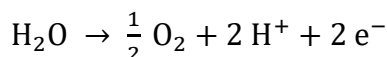
Figure 3: Used photocatalysts for PC and PEC CO₂RR.¹

Photo-electrocatalysis

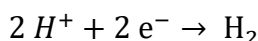
Photo-electrocatalytic processes stand out since they combine the advantages of both photocatalytic and electrocatalytic processes. Higher product yields and selectivity, cost-effectiveness since it requires less energy compared to EC systems and more catalyst options are the main advantages. PEC system (similarly to PC and EC systems) is based on combining the photoelectrode in direct contact with liquid electrolyte, which provides efficient and straight way of converting light into chemical energy, with applied external bias (see Figure 2).³ When the light interacts with photoelectrode, the electron-hole pairs are generated and are capable of driving oxidation/reduction reactions. The application of external electric field results in band bending and therefore, it is directly responsible for the

prolonging of the excited state of electron/hole pairs and thus lowering the recombination rate. The amount of applied external bias can also have an impact on the product selectivity. Moreover, it broadens the options of catalysts suitable for PEC CO₂RR, even to those with not suitable band gap energies.^{1,3,4}

Besides CO₂RR, PEC has been widely used for water splitting. In PEC water splitting there are two reactions taking place: anodic and cathodic reaction. Anodic reaction (oxidation reaction) produces oxygen gas via oxygen evolution reaction (OER):²



However, the more interesting part of water splitting is cathodic reaction (reduction reaction) since it produces hydrogen gas via hydrogen evolution reaction (HER). Hydrogen has high energy density when compressed to its liquid state, thus being important part of the future energetics development.²



PEC water splitting is one of the most promising ways to generate sustainable and renewable energy source. However, in CO₂RR process, the HER is competitive process and hydrogen production is undesired.²

Photo-electrochemical (PEC) cell consists of semiconductive photo-active electrode (photoelectrode – electrode coated with light-sensitive semiconductor), electrolyte, counter electrode (might also be a photoelectrode) and generally a separation membrane. The presence of a separation membrane is crucial since it acts as a molecular barrier, only allowing the migration of protons from the anodic compartment to the cathodic compartment to react with CO₂. The proton exchange membrane therefore protects the system from back reactions (like oxidation of CO₂RR products by oxygen) and thus prevents decrease in the efficiency. Currently, there are 3 different types of PEC systems used for CO₂RR: photocathode-driven (see Figure 4a), photoanode-driven (see Figure 4b), and photoanode-photocathode-driven PEC cell (see Figure 4c). Unfortunately, since the PEC conversion into fuels is a very complex process, most systems suffer from low selectivity and/or low efficiency.³

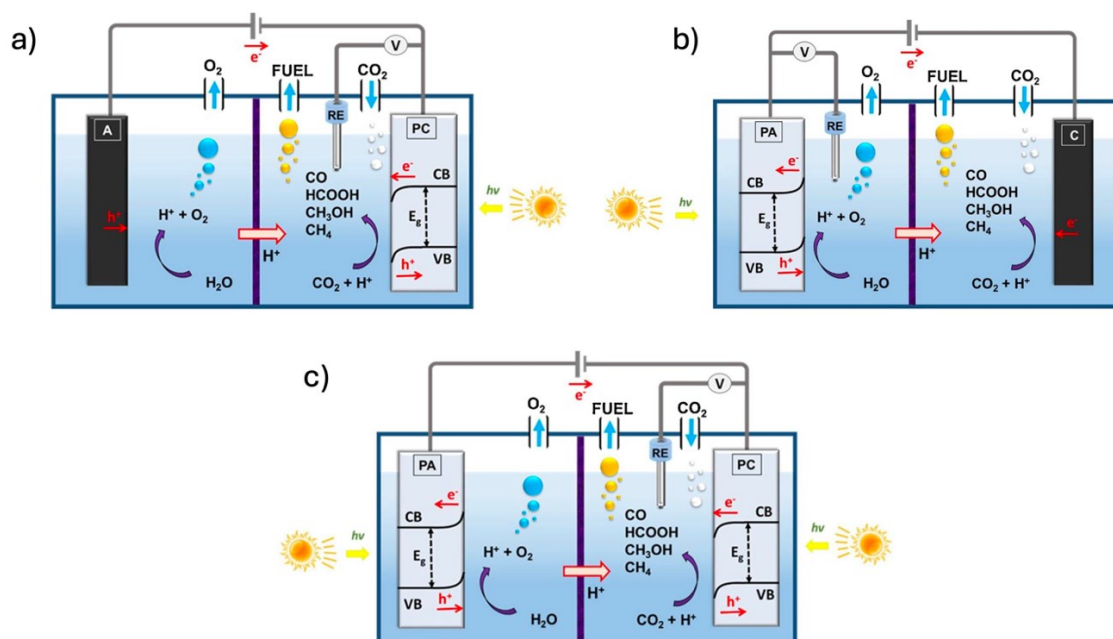


Figure 4: Scheme for three types of PEC systems: a) photocathode-driven system (using p-type semiconductor), b) photocathode-driven system (using n-type semiconductor), c) photoanode-photocathode-driven system.³

3.1.3. Kinetics of photo-electrochemical (PEC) reduction of CO₂

As already mentioned, the CO₂ molecule is thermodynamically very stable and therefore, its reduction is not favourable process. There has been extensive research conducted on the PEC CO₂RR mechanism. The first mechanism was proposed by Halmann⁹ and it suggested that the initial and rate-determining step is the formation of intermediate carbon dioxide anion radical (CO₂^{•-}). The initial step is followed by another electron and proton addition provided by anodic half reaction, thus forming HCOO⁻. Alternative pathway for this step is formation of carbon monoxide, in which electron transfer and another CO₂ molecule are involved. However, more recent study by Li et al.¹⁰ suggests that the CO₂^{•-} intermediate is converted into methanol through a series of consecutive electron reductions and protonations. Another mechanism proposed by Inoue et al. involves the multiple proton-coupled electron transfers (PCET), which prevents large activation barriers and also reduces the production of unstable intermediates. Although the PEC CO₂RR has been explored thoroughly, the mechanistic pathways and kinetics was not extensively researched. The situation is even more complicated because the research has been done on a large variety of different PEC systems. Furthermore, the adsorptive and catalytic processes on the surface of semiconductor are still not fully clear. Adsorption of CO₂ is the initial step of CO₂RR,

therefore it is crucial to understand the adsorption processes as it has direct impact on the overall efficiency of the system.³

The CO₂ conversions can be divided into two main afore-mentioned categories according to the oxidation state of the C in final product: non-reductive and reductive conversions. In non-reductive conversions the oxidation state of C either stays +IV (e.g. urea) or it is lowered to +III (e.g. salicylic acid). In reductive conversions the oxidation state of C is decreased to +II and lower (e.g. carbon monoxide, formic acid, methane, methanol, ethanol).⁴

3.2. Semiconductors

Semiconductors can be excited into the state, in which they conduct electricity. They have properties between conductors and insulators, depending on the external conditions such as temperature, light or applied voltage. In the case of solid semiconductors, their properties can be explained by band theory. It is based on the existence of bands formed by overlapping of molecular orbitals.¹¹ This can be assumed since the energy levels of orbitals are so densely packed that they do not form discrete molecular orbitals, but rather broad bands.¹² A valence band (VB) of a material is formed by closely packed filled energy levels (molecular orbitals). A conduction band (CB), on the other hand, is formed by closely packed vacant energy levels.¹¹ A VB can be seen as analogous to the highest occupied molecular orbitals (HOMO) in a molecular metal complex and a CB as the parallel to the lowest unoccupied molecular orbitals (LUMO).¹³ Electrical conductivity is directly dependant on the energy levels of these two bands. The VB and the CB can be separated by energy gap called band gap (BG). It creates a certain energy barrier for electrons, when moved from the VB to the CB (see Figure 5).¹¹

Conductors are characterised by overlapping VB and CB (BG is non-existent, $E_g = 0$ eV)¹⁴, therefore the electrons can freely move from VB to CB. On the other hand, insulators have a large band gap ($E_g > 3.0$ eV)¹⁴ that cannot be crossed by electrons no matter the amount of excitation energy provided to the material. Semiconductors are characterised by a low enough band gap ($E_g = 0.1 - 3.0$ eV)¹⁴ between the VB and the CB that can be crossed easily once sufficient amount of energy is provided to the material. Semiconductors

are a huge part of the modern-day electronics, since their properties can be well controlled. There is a huge variety of commonly used semiconductors, e.g. Si, Ge, SiC, ZnO, CdTe, PbTe, GaN, GaAs, Cu₂S, TiO₂, Cu₂O, CuO etc.¹⁵

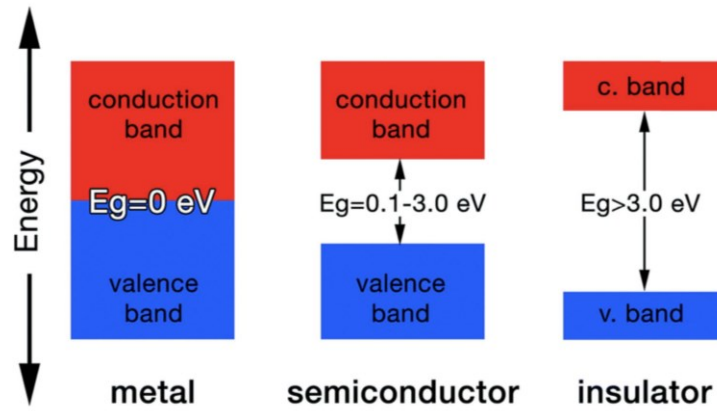


Figure 5: Comparison of the energy gaps between the VB and the CB in a conductor, a semiconductor and an insulator.¹³

Semiconductors can be divided into intrinsic and extrinsic semiconductors. Intrinsic semiconductors are semiconductors made up of very pure semiconductive material, and therefore the number of holes equals the number of excited electrons in the CB. In the case of intrinsic semiconductor, the Fermi level, describing the energy state in which the electron is located with 50 % chance at absolute zero, is located roughly halfway between the valence and conduction band. On the other hand, in the case of extrinsic semiconductors, the tiny amount of impurities (dopants or doping agents) is deliberately introduced into pure material. The type of dopant gives rise to two types of semiconductors: p-type and n-type semiconductors. The Fermi level shifts from intrinsic position according to the type of semiconductor and the amount of impurity present.^{15,16}

3.2.1. p-type and n-type semiconductors

Semiconductive properties can be changed by introduction of defects or impurities into the structure. This defect can either lead to increasing the overall number of electrons in the material creating the n-type semiconductor (n as negative), or it can cause the decrease in the number of electrons in the structure creating the p-type semiconductor (p as positive) (see Figure 6). In both cases, the band gap energy is effectively reduced.

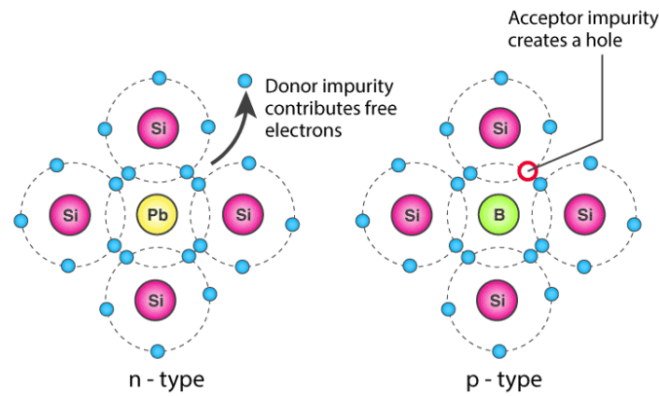


Figure 6: Introduction of dopant into material, giving rise to n-type and p-type semiconductors.¹⁷

N-type semiconductors are produced by exchanging one atom in the structure with the atom with a higher number of electrons (see Figure 6). Since the excess electrons are not used for covalent bonds, they can be removed from dopant atom and can be shifted to the CB. These free electrons then function as conduction electrons. These electrons do not create the corresponding holes in the VB, since they are already in excess. Therefore, the majority charge carriers become electrons over holes. Impurities of this type are known as donor impurities. Since the dopant introduces excess electrons, the Fermi level of n-type semiconductor is shifted upwards just below the CB (see Figure 7).^{11,15,16}

P-type semiconductors are produced in the opposite way compared to the n-type semiconductors. One atom is removed from the lattice or exchanged for the atom with a lower number of electrons thus creating holes in the bonding orbitals (see Figure 6). This vacancy can be filled by excited electron from nearby atom. Vacancy created by this can be filled by another neighbouring atom, and so on. Accordingly, electrons move through the material in one direction, while the positively charged holes move in the opposite direction. The holes are majority charge carriers over electrons. Electron deficient impurities are known as acceptor impurities. Introduction of them into material creates excess holes and therefore the Fermi level of p-type semiconductor is shifted downwards, just above the edge of VB of material (see Figure 7).^{11,16}

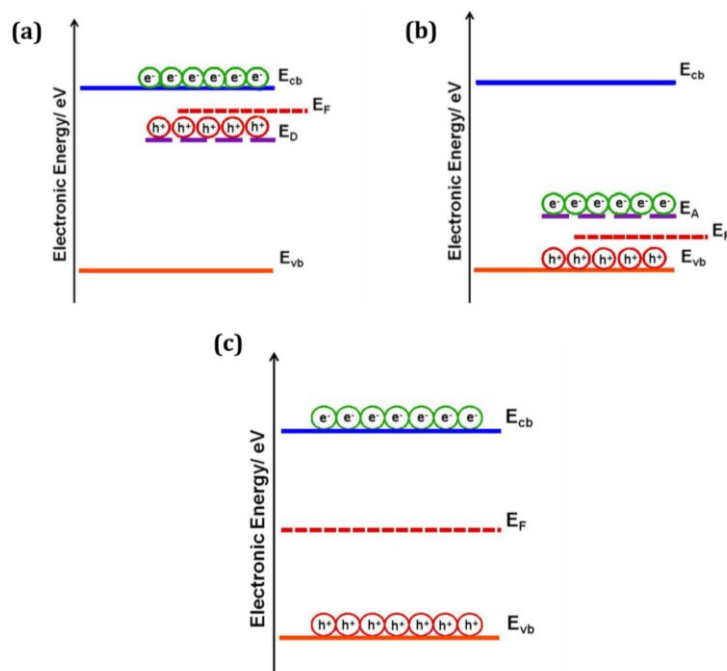


Figure 7: Schematic diagram of energy levels of (a) n-type semiconductor, (b) p-type semiconductor and (c) an intrinsic semiconductor.¹⁶

3.2.2. p-type semiconductor used for CO₂RR

The use of semiconductors for PEC processes is one of the most promising approaches when it comes to scaling up the technology. When the light is absorbed by a semiconductor, the electron-hole pairs are generated. P-type semiconductor is used to drive cathodic reaction (reduction reaction). When p-type semiconductor is placed into contact with agents in the electrolyte with energetically suitable redox potential – the redox potential of the electrolyte should align with the CB of the semiconductor (for reduction reactions). Thus, the electrons from electrolyte will move to fill the photogenerated holes in the semiconductor. Consequently, the Fermi level energy will shift until electronic equilibrium is reached between the semiconductor and the electrolyte (see Figure 8 right).^{2–4,18}

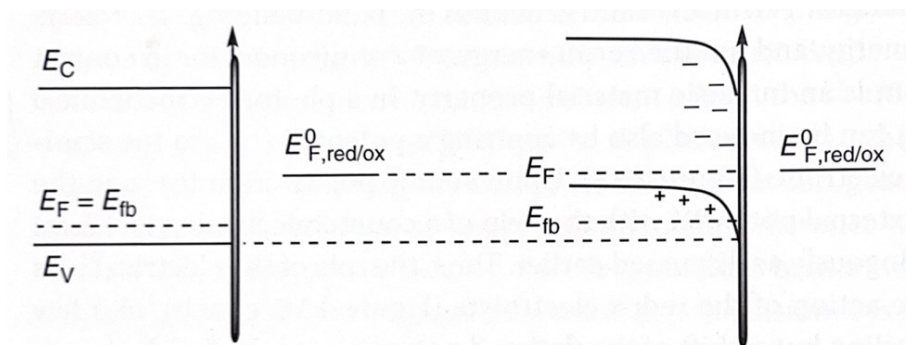


Figure 8: The scheme of band bending of p-type semiconductor before and after establishing the equilibrium between the semiconductor and the electrolyte.¹⁹

The internal electric field created at the semiconductor-electrolyte interface drives the electrons toward the interface and the holes toward the bulk of the semiconductor. In the semiconductor, this region is known as a depletion layer, while on the electrolyte side it creates the Helmholtz layer consisting of positively charged ions adsorbed onto the semiconductor surface. This results in a band bending – the valence and conduction bands bend downwards due to the different electrochemical potential. The band bending creates internal electric field inside the semiconductor, which is strong enough to break the electron/hole pairs, pushing holes towards the bulk of semiconductor and electrons towards the interface. The photogenerated charge carriers can drive the half reactions thanks to the electrical field at the semiconductor/liquid junction. Additionally, the application of external potential can further drive the charge separation, by increasing the band bending effect.^{2-4,18}

3.3. Copper(I) oxide

Cuprite mineral is a major ore for copper and is still mined in many places around the world. Of all copper ores the cuprite gives the greatest yield of copper per molecule. It is red to deep red colour that can appear almost black. Copper(I) oxide is one of the oldest materials of semiconductor electronics, therefore its electronic and atomic properties have been widely researched. Copper(I) oxide and other Cu-based semiconductors are very promising materials for the usage in the PEC water splitting and other PEC processes, since unlike other extensively researched semiconductors its band gap (BG) is approximately 2.17 eV (e.g. TiO₂ has a band gap of 3.2 eV).² This BG energy is low enough to drive the desired half reaction in PEC systems just by absorption of visible light. Cu₂O can be prepared via

several different methods (e.g. thermal oxidation of metals, reduction of copper-amine complex solution with glucose under microwave radiation, sputtering). The most attractive one for industrial scale up is electrodeposition. This method has various advantages, among them it is cheap, it can easily work on different substrates and it is highly tuneable through parameters like applied potential, the current, the temperature and pH of the bath.^{2,20}

3.3.1. Structure

Cu₂O crystals possess the simple cubic cuprite structure with Pn3m symmetry space group (see Figure 9). It can be described as two sublattices: a face-centered cubic (fcc) sublattice of copper cations and a body-centered cubic (bcc) sublattice of oxygen anions. Copper ions are bound linearly to two oxygen atoms and each oxygen atom is tetrahedrally coordinated to four copper ions, having the copper ions on the vertices of the oxygen tetrahedron (see Figure 9). This unusual structure and low coordination numbers is limited to a few other compounds, such as Ag₂O, Pb₂O, Cd(CN)₂ and Zn(CN)₂. Another rarity of Cu₂O is its short copper-oxygen bond length (1.85 Å),² when compared with the sum of the ionic radii of Cu⁺ and O²⁻ seen in literature. The spontaneous copper vacancies in the lattice create holes in the VB and are the source of conductive properties.^{2,20}

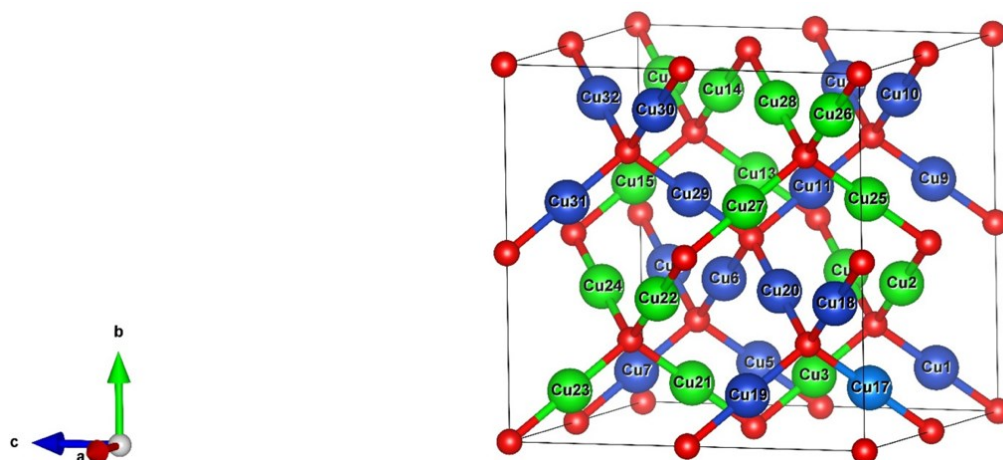


Figure 9: Scheme of copper(I) oxide cell. Oxygen atoms are shown in red and copper atoms in blue and green.²

3.3.2. Application of Cu₂O in photo-electrocatalysis for CO₂RR

Advantages

As already mentioned, Cu₂O has properties which make it suitable for PEC CO₂RR. Most importantly it has a direct band gap of 2.17 eV, which is low enough to allow the

sunlight absorption. The BG position is suitable for both the OER and HER, what means that the edge of CB is more negative than redox potential for H^+/H_2 and the edge of VB is more positive than the O_2/H_2O redox potential. It is one of a few materials with a narrow band gap that can still perform both of these reactions (see Figure 10). It is a low-cost material, which is prepared from abundant precursors. It is also a non-toxic material and more environmentally friendly than other materials. It can be prepared via cheap and fast synthetic methods (e.g. precipitation, electrodeposition).²

Disadvantages

Since the BG of Cu_2O is narrow, it is associated with a relatively high probability of a recombination of electron/hole pairs. Besides that, the most prominent disadvantage of the material is the position of redox potentials for reduction/oxidation of the material itself lying within the BG (see Figure 10). Therefore, both the photogenerated holes and electrons may interact with the material itself causing its oxidation and reduction, respectively. The material is prone to photodegradation process, which is the competing reaction for CO_2RR .²

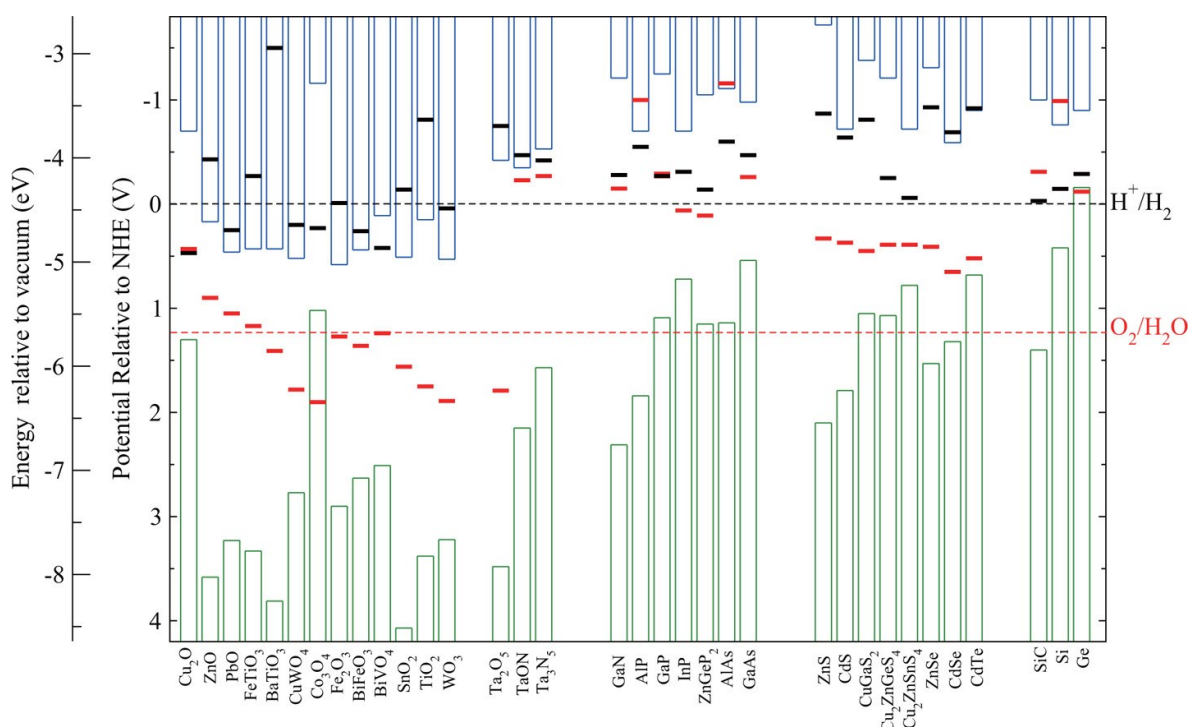


Figure 10: The comparison of band gap energies of multiple researched semiconductors, the red bars represent the calculated oxidation potentials of materials, the black bars represent the calculated reduction potentials of materials.²¹

Improving the properties

Two main approaches to extend the lifetime and efficiency of a material have been explored: doping and protection with an overlayer. Doping of a material means an introduction of impurities into the lattice. It changes the BG of a semiconductor, since the dopants introduce another energy levels (donor or acceptor levels) into the BG. This approach improves the photocatalytic properties. The second approach, using the protective overlayer, is usually used with another semiconductor. The second semiconductor can transport the photogenerated charge carriers away and thus lower the recombination rates. The composite electrode then forms a type of semiconductor heterojunction.^{2,22}

A non-conducting material can be also used as a protective overlayer. Materials used for suppression of photocorrosion process of Cu_2O electrode should be electronically and chemically stable. They should be able to rapidly extract the photogenerated electrons from the surface before they can accumulate and cause undesirable recombination or even photocorrosion of the Cu_2O itself. Thus, various electron scavengers (e.g. TEMPOL)²² or materials causing preconcentration of the reactant close to the surface of electrode (e.g. porous materials) can be used.

3.4. Zeolites

Zeolites are highly crystalline, microporous silica-based materials. Microporous materials are according to International Union of Pure and Applied Chemistry (IUPAC) classified by their pore sizes being up to 2 nm. They were originally discovered as naturally occurring aluminosilicate minerals, but it did not take long for them to be extensively researched and synthesized in a large scale. Zeolites were first studied in 1756 by Swedish mineralogist Axel F. Cronstedt, who noticed that when these minerals are heated up in the blow-pipe flame they seemed to boil (they produced large amount of steam). Production of steam is caused by a loss of water from the structure. Because of this property, which is not present in other minerals they were named zeolites (from the Greek ζέω (zéō), meaning "to boil" and λίθος (lithos), meaning "stone").²³ During the 19th century many scientists reported new materials classified as zeolites, and successfully described their general properties. The term molecular sieve was first described in 1932 by McBain who discovered

that chabazite mineral had the property of selectively adsorbing the molecules of the certain size.^{23–26}

Nowadays there are known many types of natural (around 50 different types) and synthetic zeolites (254 different types).^{27,28} When the zeolitic framework is officially recognized by International Zeolite Association (IZA) it gets the 3 letter code. Their porous character exceptionally increases their surface area, increasing their surface to volume ratio. Other useful zeolitic properties include their thermal stability, adsorption capacities, ion exchange, acidity, molecular sieving and shape selectivity. Zeolites in their typical form as aluminosilicates or silicates are insulators. Thanks to the pores and their various diameters, zeolites have found widespread application in many industrial processes. They are hugely employed in petrochemical and oil refinery industry as the components of fluid catalytic cracking catalysts, hydrocracking catalysts and the isomerization and alkylation catalysts. Their cation exchange properties make them useful as industrial water-softeners, for removal of heavy metal cations from groundwaters and for removal of radioactive cations from liquid nuclear waste. They are well known for their usage as commercial heterogeneous solid acid catalysts where they replaced dangerous acids (HF, H₂SO₄) in many processes. Other applications are support for catalysts (catalysts for biomass conversion combining both the acid and metal active sites), adsorbents (components of vehicle catalysts for emission control, where zeolites adsorb harmful gases until they are converted) and separators (selective gas separators). Since their crystal structure has direct impact on their physical properties, their structural chemistry is widely investigated. Zeolitic structures are also interesting for research since numerous possible chemical substitutions and structural defects make them highly adaptive and responsive to modification.^{23,24,27,29}

3.4.1. Structure

Zeolites are composed of primary tetrahedra units TO₄ (T is tetrahedral cation located in the centre). T atoms are mostly presented by Si atom, but can be substituted by other atoms, typically Al. The O atoms are located on the vertices of the tetrahedron (see Figure 11). Typical Al–O and Si–O bond lengths are 1.73 and 1.61 Å respectively. The OTO bond angle is close to the tetrahedral angle with 109.4°. ^{23,24,30}

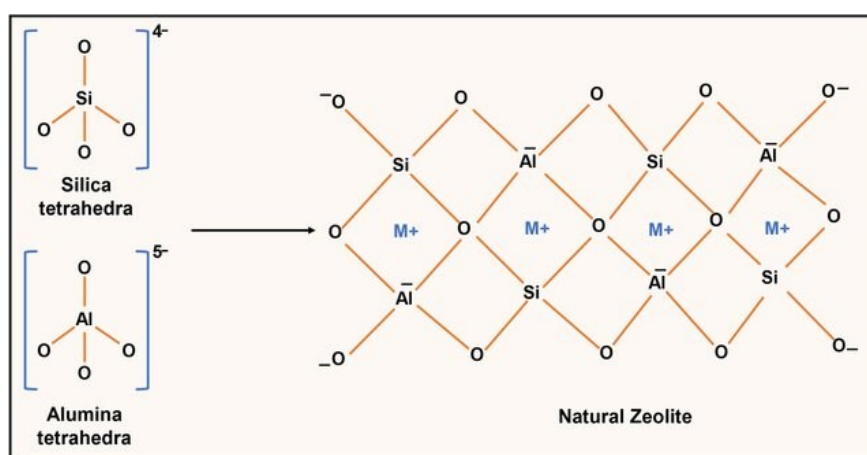


Figure 11: Primary building blocks of zeolitic structure.³¹

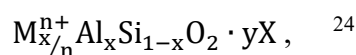
Individual tetrahedrons are connected through O atoms in the corners into three dimensional frameworks, creating pores and channels of variable sizes (see Figure 11). The arrangement of primary tetrahedra gives rise to secondary building units (SBUs). Subsequently the SBUs alone or more frequently in combination with other types of SBUs form three-dimensional frameworks. The arrangement of SBUs into framework is theoretically limitless.^{23,24}

Zeolites are commonly described by the size, geometry and connectivity of the pores. Pore diameter can alter in the size usually up to 1 nm but could be even more. Zeolite pore sizes are defined by the number of tetrahedral cations in the ring opening (e.g. 8-membered, 10-membered or 12-membered rings). Zeolites are characterized by their pore size into following main groups: small pore (with 8-membered rings and pore size around 4 Å), medium pore (with 10-membered rings and pore size of 5.5 Å), large pore zeolites (with 12-membered rings and pore size of 7.5 Å), and extra-large pore zeolites (with 14-membered, 18-membered or even more membered). The size and shape of pore opening and channels is a very important structural property, since it controls the access of molecules into the pores. This property makes them shape selective, which is particularly important for their use as catalysts, since it makes them efficient and highly specific and thus improving the overall economics of the processes. There are three types of shape selectivity based on which molecule during the reaction is the limiting factor: reactant, product or transition state shape selectivity.^{23,24,30}

The pore space geometry can be uniform and non-uniform in the cross section, creating channels which may intersect with each other, thus generating the cages. The linkage of the

channels can be dimensional: 1D (unconnected channels), 2D (the channels go through material in 2 perpendicular directions) or 3D (channels intersect in 3 directions). In aluminosilicate zeolites with high aluminium contents (Si/Al approaching 1) the material requires ordering. In the case of Si/Al = 1, the strict Si–O–Al–O–Si alternation in adjacent tetrahedra is observed (in the case of zeolite A).^{23,24,30}

A simplified empirical formula for an aluminosilicate zeolite is:²⁴



where x can vary from 0 – 0.5 and M^{n+} represents the inorganic or organic charge balancing cation. X represents the neutral guest molecule or included species (e.g. H₂O molecule).²⁴

The substitution $Si^{4+} \rightarrow Al^{3+}$ creates a negative charge in the framework, which has to be balanced by exchangeable extra-framework cations (usually alkali or earth-alkali metals). When the extra-framework cation is H^+ , it creates Brønsted acid centres. When the exchanged trivalent atoms are not coordinated tetrahedrally, but only trivalently, it creates the Lewis acid centres.^{23,24,30}

The Si and Al atoms can be replaced or partially replaced in the lattice with titanium, boron, gallium, germanium, indium, zirconium, iron and other elements, creating the heteroatomic zeolites. Introduction of various heteroatoms into zeolite structure is very convenient since it can improve the properties of the parent molecular sieve (such as acidity, thermal stability, catalytic activity and selectivity, hydrophobicity, conductivity, etc.) for its target application. Heteroatomic zeolites can be prepared either via direct synthesis or through post-synthetic treatment method. Direct synthesis consists of introduction of heteroatom into the synthetic gel. Since direct synthesis method produces a low metal content and can be applied only to certain heteroatoms, the post-synthetic treatment method is an alternative option (also often more suitable in the large-scale preparation in industry). In post-synthetic treatment the heteroatoms are introduced to the lattice by isomorphous substitution.^{7,23,24,30,32}

3.4.2. Synthesis

Zeolites can be synthesized in aqueous media or ionic liquids under hydrothermal conditions (under high temperature and high pressure) in the presence of organic and/or inorganic cations and a mobilizing (mineralizing) agent.²⁴

In nature, zeolites crystallize from saline water and volcanic glass by a volcanic force. This reaction occurs at temperatures between 27 °C and 55 °C with typical pH being between 9 and 10. Unfortunately with these conditions the crystallization takes approximately 50 to 50,000 years. Naturally synthesized zeolites often contain many impurities, such as quartz, amorphous glass and other zeolites and thus they cannot be efficiently used in the catalytic commercial processes. They can be, however, used as adsorbents (e.g. odour absorbents, dehumidifiers).²⁷

Since the first description of laboratory hydrothermal synthesis of zeolites by Barrer in 1940s,²⁴ the scientific and industrial interests in these materials have been continuously increasing. Regardless the extensive efforts to understand the preparation of zeolites, the relationship between the formed structure and initial synthesis variables is not yet fully understood. There has been a number of proposed synthesis mechanisms of zeolites, which provide very important information; however, the large number of chemical reactions, solubility and equilibria variations make it a very complex process. Moreover, following the initial states of crystallization is very difficult experimentally. Therefore the mechanism remains the main challenge in zeolite synthesis.²⁴

Hydrothermal synthesis is not only dependent on the temperature and pressure, but also on other factors, such as reactant sources, silica to alkali ratio, aging time, composition, stirring conditions, alkalinity, inorganic cations, seeding time and the type of organic structure directing agent (OSDA). Accordingly, adjustment of these parameters offers precise control over the final product.³³

3.4.3. Zeolite Beta (*BEA)

Beta zeolite (*BEA) is the first highly silicious, purely synthetic zeolite (usually it crystallizes with Si/Al ratio from 10 to 30).³⁴ It exhibits improved thermal and acid stability when compared to previously synthesized zeolites. Usually, it is synthesized with usage of OSDAs. It is highly silicious material with large pores (12-membered ring openings). Beta

zeolite has industrial and scientific importance, since it plays crucial role in several hydrocarbon conversion reactions, including cracking, hydrocracking, biomass conversions and etc.^{32,35,36}

Beta zeolite is one of the most complex materials and it is also one of the most important materials from the zeolitic family. It is an intergrowth hybrid of two structures with stacking sequence disorder (see Figure 12). This structural disorder is reflected by the combination of broad and sharp reflections in the powder X-ray diffraction (PXRD). The sharp reflections are the result of a normal Bragg's interference maxima, and the broad reflections arise from non-Bragg scattering which is related to the disorder in the structure. Beta zeolite does not contain cages (unlike faujasite) but three-dimensional mutually intersecting channels.^{24,35–37}

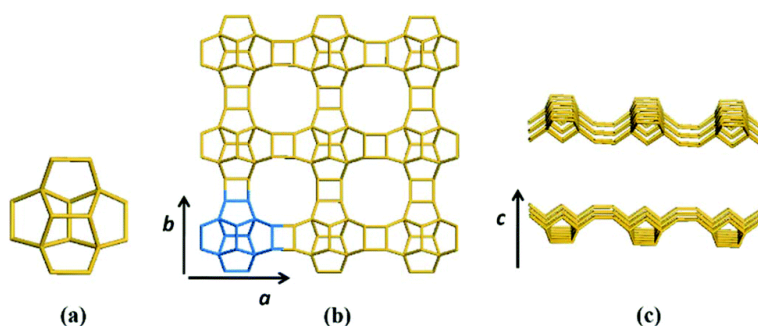


Figure 12: Scheme of the structure of (a) secondary building unit, (b) centrosymmetric layer from top view and (c) from side view of zeolite Beta.³⁶

3.4.4. Zeolite Faujasite – Linde type Y (FAU-Y)

Faujasite Y is industrially widely used large-pore zeolite. It was first synthetically prepared by Breck in 1964.³⁸ Faujasite has a three letter code FAU and two topological analogues – zeolite X and zeolite Y. The difference between the zeolite X and Y stems from their different silicon to aluminium molar ratio. Faujasite with Si/Al lower than 1.5 is categorized as zeolite X (it has higher Al content) and faujasite with Si/Al higher than 1.5 is classified as zeolite Y (it has lower Al content). Since the high alumina content of the zeolites destabilizes them, zeolite Y found very important role in the industrial processes. It became one of the most important catalytic zeolites, especially for petroleum refining and petrochemical processes. It has a very significant role in acid catalysis. Zeolite Y can be also post-synthetically dealuminated without the collapse of its framework to produce ultra-stable faujasite Y abbreviated as USY.^{30,32,39}

FAU is composed of sodalite cages connected through hexagonal prisms (also known as double 6-rings) (see Figure 13). It has 192 primary tetrahedra located in the cubic unit cell. FAU has large pores composed of 12-membered rings of about 8 Å in diameter, therefore it can fit quite large molecules. FAU has a three-dimensional channel structure. The pores are connected into so-called supercages, which have approximately 12 Å in diameter (see Figure 13). These characteristics are directly responsible for large adsorption capacity.^{30,39}

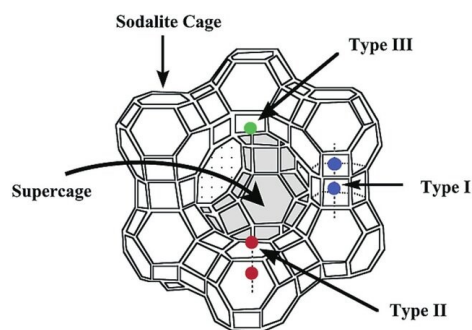


Figure 13: Structure of faujasite showing the central supercage surrounded by sodalite cages.²⁷

3.4.4.1. Aluminosilicate faujasite (Zn-FAU-Y)

Since zeolites (including FAU) are electrically insulating, their usage for electrochemical processes is very limited and has not been researched widely. Their use for electrocatalytic CO₂RR is restricted not only because they are insulators but also because of competing hydrogen evolution reaction (HER). The presence of Al species makes zeolites catalytically active for the competing HER, therefore, incorporating conductive Zn moieties into zeolite Y structure, as a substitution of Al atoms (see Figure 14) might improve zeolite conductivity. Such material could be attractive for use in the electrochemical CO₂RR.⁷

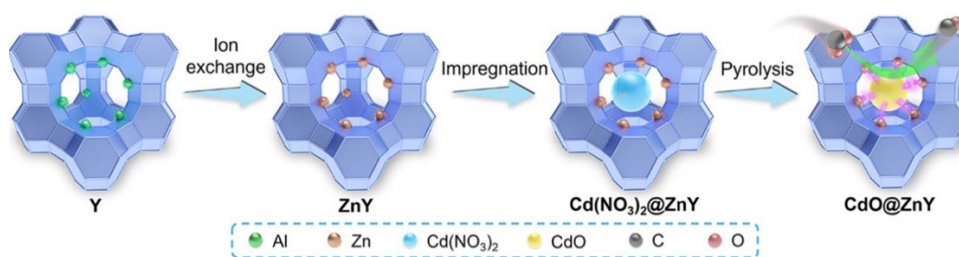


Figure 14: Schematic catalysts design, depiction of route to obtaining the Zn FAU-Y with incorporated CdO nanoclusters as guest species.⁷

Zn-FAU-Y was prepared and published by Zhang et al.⁷ Synthesis was performed without the use of OSDA and the incorporation of heteroatom was done by direct synthesis (addition of zinc nitrate into the reaction gel).⁷

Zhang et al.⁷ reported the incorporation of Zn atoms instead of Al into aluminium-oxygen tetrahedra while preserving the structure of zeolite Y. The synthesized Zn-FAU-Y showed characteristic features of faujasite Y, such as presence of supercages and 12-membered pore openings. The substitution of Al atoms for Zn causes a little lattice expansion since the Zn atom has a larger atomic radius compared to Al atom. Consequently, this can lead to the shift of the diffraction peaks to the smaller angles. The most important outcome of this study was the decrease in the band gap energy from 5.09 eV determined for aluminosilicate form FAU-Y down to 4.56 eV for Zn-FAU-Y (see Figure 15).⁷

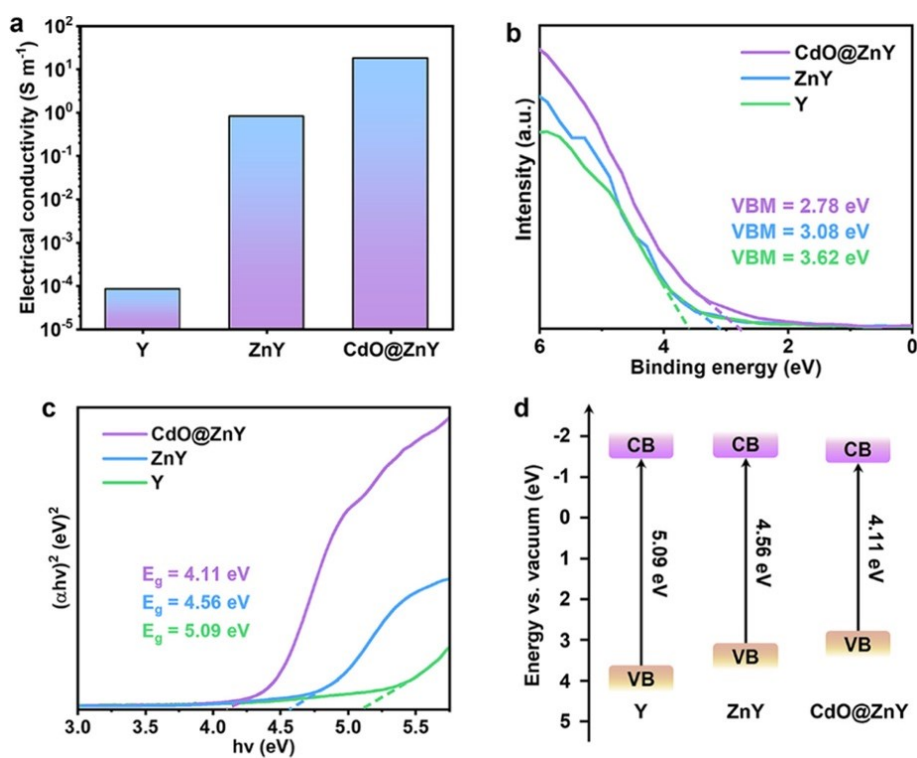


Figure 15: Study of electronic conduction of individual materials, a) electronic conductivities at a room temperature, b) VB XPS spectra, c) Tauc plots acquired from UV-VIS spectroscopy, d) band gap energies diagram.⁷

3.5. Mesoporous silica materials

Mesoporous silica are inorganic porous materials, with the pore size ranging from 2 nm to 50 nm according to IUPAC. Along with microporous zeolites they have gained interest of research because of their potential widespread usage. Mesoporous materials are a result of the demand for the well-defined and large-pored structures. They have been studied particularly as a catalyst support and adsorbents, mainly in the reactions involving large molecules. In the early 1990s, Yanagisawa et al. introduced the synthesis of the material with similar structure that is nowadays known as MCM-41.⁴⁰ Unfortunately, the lack of further characterization (besides the XRD) caused the disregard of this discovery. In 1992, the Mobil Corporation discovered the M41S family of silicate/aluminosilicate mesoporous molecular sieves with large uniform pore structures. The discovery lead to worldwide revival of the interest in these materials.^{25,26,41–43}

The walls of mesoporous silicate materials are created by amorphous silica phase. The presence of mesopores promotes rapid diffusion of macromolecules (e.g. polymers, proteins, nucleic acids, pharmaceuticals and dyes) towards internal active sites. Mesoporous materials also exhibit large specific surface area, which is easily modifiable by various organic and inorganic moieties. Functionalization of mesoporous materials can be achieved by post-synthetic modifications or by direct synthesis. Other advantages of these materials are tuneable pore sizes and pore channels, narrow pore size distribution, stability and biocompatibility. Mesoporous materials can be used in catalysis, adsorption, separation, optical devices, controlled polymerization etc. Unfortunately, their industrial-scale application is not widespread as it had been believed in the beginning. Industrially, there is only used a few materials for very specific processes. When modified they could be applied in liquid pollution control (together with zeolites, activated carbons and aluminas). They are used due to their ability to uptake even trace amounts of transition and heavy metals (e.g. from textile dyes) and radioactive compounds. Modified silicate mesoporous materials are more advantageous when compared with other adsorbents and conventional methods such as precipitation.^{25,26,43–45}

3.5.1. Synthesis

Mesoporous silica materials are produced via hydrothermal synthesis with the organic molecules present in the synthesis gel. The organic molecules, also called surfactants, are

usually long chained molecules. Mesoporous silica materials can be synthesized using the anionic, cationic and neutral surfactant or non-surfactant molecules. The types of organic molecules have direct impact on the structure of the resulting product. The concentration of organic molecules is a very important factor influencing the structure. At low concentrations the surfactant molecules exist usually as sole molecules. With increasing concentration, they combine together to form micelles and thus decrease the entropy of the system. This aggregation of the molecules is characterized by the threshold of the initial concentration called critical micellization concentration (CMC). Aside from the surfactant concentration, the nature of the surfactant itself, such as the length of the hydrocarbon chain or hydrophilicity of the head group, plays also crucial role. Changing the various factors during the synthesis can lead to the production of different products. Besides the type of the template molecule, the source of silica, presence of auxiliary compounds (other gel components serving as pore expanders, co-templates or stabilizers) or reaction condition (such as the type of solvent, temperature, aging time, pH and mole ratio of the reactants) have also direct impact on the product.^{25,26}

3.5.1. Mobile crystalline material 41 (MCM-41)

MCM materials are obtained by hydrothermal synthesis and liquid crystal templating (LCT) mechanism. They are widely researched since they report excellent hydrothermal and hydrolytic stability. They possess remarkably high surface area of around 1000 m²/g, and their porosity can reach up to 80 % of their total volume. MCM-41 is investigated extensively since the other members in the family are either difficult to obtain or thermally unstable.²⁶

MCM-41 has hexagonal arrangement of non-intersecting cylindrical pores of diameter in the range of 15 – 100 Å (see Figure 16). Pore diameter depends on the used template molecule and reaction parameters. The walls of the channels are composed of amorphous SiO₂, and since MCM-41 is purely silicate material it does not possess the Brønsted acid sites, and its overall acidity is similar to other silicate materials. They tend to possess weak overall acidity connected with the presence of silanol groups on the surface.²⁶



Figure 16: Schematic diagram of the structure of M41S family materials, MCM-50 (layered), MCM-41 (hexagonal) and MCM-48 (cubic).²⁶

However, the absence of active sites limits the application in the field of catalysis. Consequently, the doping of various elements into the MCM-41 walls has been extensively researched.²⁶

3.5.2. KIT-6

KIT-6 has been first synthesized by Korean Institute of Science and Technology, which gave it its name.⁴⁶ Due to its unique structure, it has been studied for various applications, including catalyst support material, nano-containers and nano-casting template for other non-silica mesoporous materials. As a consequence of its widespread potential application, the synthesis of KIT-6 has been extensively studied. The use of copolymers as a large structure directing surfactant molecules has been noted before, but Kleitz et al. reported the use of Pluronic P123, which is commercially available triblock copolymer, making the synthesis more attractive for commercial use in large quantities.^{44,46,47}

KIT-6 has two three-dimensional continuous interpenetrating networks of channels and uniform pores (see Figure 17). Thanks to this unique channel network it provides a highly opened porous support for guest species and active sites, possibly mitigating the commonly occurring pore blockage. It has a large average pore diameter of about 4 – 12 nm and wall thickness of 4 – 6 nm.⁴⁷ The pore sizes are direct result of gel compositions and synthetic conditions. Usually the pores vary between 7 – 9 nm, with larger pores being achieved by hydrothermal synthesis with temperatures as high as 130 °C.⁴⁴ It possesses cylindrical pore system similar to those of MCM-48 (see Figure 16), but with larger mesopores. The material exhibits an ordered mesostructure with cubic symmetry (space group Ia3d) (see Figure 17).^{44,46,47}

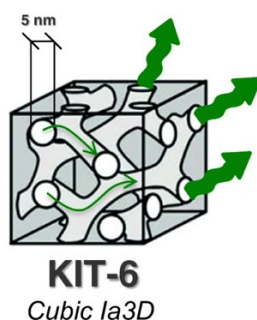


Figure 17: Cubic structure of interconnected mesopore channels of KIT-6.⁴³

3.6. Photo-electrochemical characterization

3.6.1. Linear sweep voltammetry (LSV)

Linear sweep voltammetry (LSV) is a basic potentiostatic method, where the potential is swept across the certain range and the current flowing through the system is measured as a function of applied potential. The output of LSV is usually a voltammogram, the curve of current vs the applied potential. This method uses three-electrode system, which consists of working electrode, counter electrode and a reference electrode. In the characterization of prepared photoelectrodes the LSV is used to determine the photocurrent density. It is usually performed in three modes: under dark, light and chopped illumination. Comparison of three modes shows direct response of photoelectrode to light illumination.^{48–50}

3.6.2. Chronoamperometric tests

The chronoamperometry is an analytical method in which the current is measured as a function of time. It is typically done under fixed applied potential. It also uses the three-electrode system. It is one of the most important PEC characterization methods for assessment of photostability of prepared photoelectrodes in long term range (in hours). This type of test is usually combined with the product analysis after its termination (from the electrolyte and gas phase).^{51–53}

3.7. Product analysis of CO₂RR

The analysis of the products after chronoamperometric tests uses various methods, mainly gas chromatography (usually with TCD and FID detectors) and proton nuclear magnetic resonance. The combination of both methods has been used in this study.

3.7.1. Gas chromatography (GC)

Gas chromatography is a separation analytical method employed for analysing volatile substances in the gas phase. The sample is dissolved in the solvent and vaporized. The individual components of the sample are distributed between two phases: a stationary and a mobile phase. The mobile phase (carrier gas) is an inert gas (usually nitrogen or helium) which carries the vaporized sample through the heated chromatographic column. The stationary phase is either a solid adsorbent or a non-volatile liquid coated on an inert solid support. The retention time, time which a component spends in a chromatographic column until it is detected, is an important parameter characteristic for sample and a certain chromatographic column.^{54,55}

GC can be used with various detectors but, in this thesis two detectors were used: thermal conductivity detector (TCD) and flame ionization detector (FID). The TCDs are the most widely and the oldest used universal detectors with GC. It is based on a heated metal filament spiral (see Figure 18a) which senses the small changes in the thermal conductivity of pure carrier gas compared to carrier gas containing sample. Advantages of the TCDs are mostly that it is universal, and it has a linear and broad detection of basically all compounds. On the other hand, it is less sensitive and specific than the other detectors. It is usually used for analysis of light hydrocarbons, permanent gases and compounds that cannot be analysed on the FID detector.^{56–58}

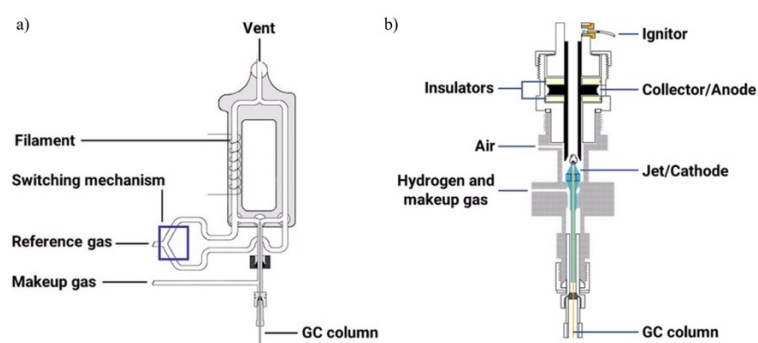


Figure 18: Scheme of a) TCD and b) FID.⁵⁹

FIDs are most widely used detectors nowadays. It consists of miniature flame, in which the mixture of hydrogen and gas is burnt. The outlet of chromatographic column is also placed into this flame. On the other side of the source of the flame, there is metal electrode

with applied potential (see Figure 18b). When the sample coming out of chromatographic column is burnt, the amount of ions and electrons increases and the amount of electrical current flowing through the system increases as well, which is recorded as a signal. Among the advantages of FIDs are their universality, reliability and versatility. When compared with TCD they are significantly more sensitive while still being able to detect broad amount of compounds.^{56,57,60}

3.7.2. Proton nuclear magnetic resonance (¹H NMR)

Nuclear magnetic resonance (NMR) is a spectroscopic method using the magnetic properties of the nuclei of certain isotopes. For a nucleus to be easily measured by NMR it must have spin quantum number of $I = \frac{1}{2}$ (e.g. ¹H, ¹³C, ¹⁹F, ³¹P). When the external magnetic field is applied on the nucleus with non-zero spin quantum number, it creates new energy levels. If the energy difference between newly created energy levels meets the frequency of transition, it meets resonance condition, the signal is detected. It is one of the most important analysis methods for determination of the structure of mainly organic substances. It is considered rapid, non-destructive and reliable method for qualitative method. It provides many advantages: simple sample preparation and development of method and relatively shorter analysis time.^{61,62}

3.8. Characterization methods of materials

3.8.1. X-ray diffraction (XRD)

X-ray diffraction (XRD) has become one of the most important techniques since the discovery of X-ray radiation. Nowadays, the powder X-ray diffraction (PXRD) is one of the most valuable analysis methods for polycrystalline samples. PXRD is effective and non-destructive method for analysis of the crystalline material. The ability of X-rays to provide the structural information is a direct result of its wavelength. Wavelength of the X-rays is typically about 0.5 – 2.5 Å,⁶³ which coincides with the size of atoms and molecules. The crystalline material causes the incident beam of X-ray to diffract into many directions and by measuring the angles and the intensities of diffracted X-rays, the three-dimensional electron density map can be produced. As multiple X-rays are diffracted by multiple planes within the crystalline material into various angles, they can interfere together constructively

or destructively. In the case of constructive interference, the consequent intensity is higher. In the case of destructive interference, the resulting intensity is lower, often negligible. The interference only happens under certain conditions described by Bragg's law:

$$n\lambda = 2d \sin \theta \quad (1)$$

where n is an integer, λ is the wavelength of the incident X-rays, θ is the angle of the incidence and d is the spacing in between the planes of the crystal. When the Bragg's law is satisfied the peak occurs on the diffractogram. Position of peaks serve for an identification of a crystalline structure when compared to known database. Ideally the peaks should be sharp narrow lines, but in practice the peaks are often broad, which is caused by various factors. This is the first indicator of material's crystallinity, since the sharp peaks mean well-defined cell unit parameters. The presence of an amorphous phase is usually revealed by a broad band around $25^\circ 2\theta$, that is not true Bragg diffraction. It is a result of the short-range ordering in the amorphous materials. Thus, the phase identification is the most widespread use of PXRD analysis.^{32,63}

3.8.2. Adsorption of gases

Adsorption of gases is an important property of materials, and particularly significant for porous materials since they possess large surface areas and pore volumes. Adsorption occurs when the gas molecules interact with the material surface and/or enter pore system and temporarily bind to the sites in internal surface. Adsorption is divided into I) physical adsorption (physisorption), when the gas molecule is bound weakly due to induced or permanent dipoles (Van der Waals forces); and II) chemical adsorption (chemisorption), when the exchange of electrons and thus formation of the chemical bond is involved. Physisorption is usually observed at low temperatures while the chemisorption can be limited at higher temperatures. Physisorption is also completely reversible with lowering the partial pressure, while chemisorption might need extra driving force (e.g. heat) or is irreversible.³²

The adsorption is quantitatively described by adsorption isotherm, the amount of adsorbed gas as the function of relative pressure at a fixed temperature. Adsorption isotherms are therefore plotted as the adsorbed amount of the gas against the relative pressure of the gas (see Figure 19). Isotherms can be measured using two types of analysis: volumetric and

gravimetric. According to IUPAC the pore sizes of porous materials are characterized mostly by the gas adsorption data. IUPAC specifies six types of the isotherms (see Figure 19).^{26,32}

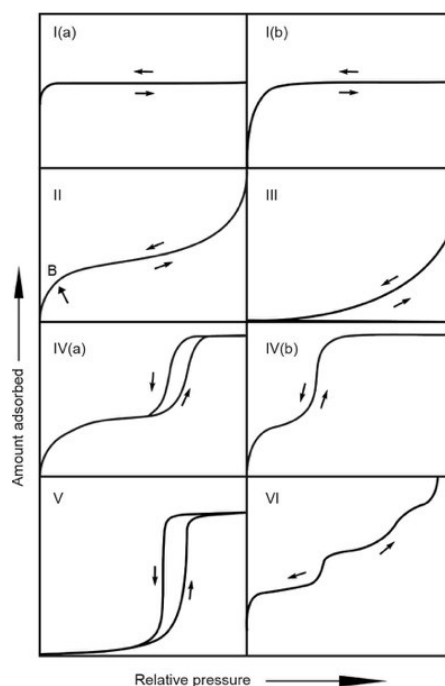


Figure 19: The IUPAC classification of adsorption isotherms, denoting both the adsorption and desorption curves, adsorption isotherm for microporous materials (type I), non-porous or macroporous materials (type II), materials with no identifiable multilayer formation (type III and V), mesoporous materials (type IV) and smooth non-porous surfaces (type VI).⁶⁴

The most common way of characterizing the surface area and pore volume of the material is through two theories: Langmuir and BET. Langmuir theory assumes that all binding sites on the surface of the material are energetically equivalent, and it does not consider the interactions between gas molecules. It also assumes that the collision between gas molecule and the surface is inelastic and that this is the adsorption process itself. BET (Brunauer, Emmett and Teller) theory follows up the Langmuir theory incorporating the effect of multilayer gas adsorption. While these theories are not strictly applicable to all porous materials they can be useful for comparison between the structures.³²

3.8.3. Electron microscopy

Usage of electron microscopy for structural determination as well as morphology of porous materials has a long history. Unlike the X-rays the electron beam has a very strong interaction with a solid sample. The electrons can be absorbed by the sample; however, a large portion of incident electrons are backscattered electrons, secondary electrons,

transmitted electrons, scattered electrons and energy loss electrons. Moreover, another energy forms can be created from incident electron beam, such as Auger electrons, X-rays, etc. All of these different energy manifestations carry various information on the morphology, structure or chemical composition of the sample.³²

Scanning electron microscopy (SEM)

SEM can be helpful in identification of the different phases (both amorphous and crystalline), their spatial relationship and sizes of individual aggregates, their morphology, texture and uniformity. Overall, SEM assesses the structural features and homogeneity of materials. When the focused beam of electrons is scanned onto the sample, some of the electrons can pass their energy to the electrons in the sample and later be ejected from the sample as secondary electrons with low energy. The secondary electrons are then collected by the detector, and they contribute to the brightness of the image. Electrons from incident beam can be also elastically scattered in backwards direction (backscattered electrons) with little or no energy loss. Presence and amount of backscattered electrons is directly proportional to the distribution of larger atoms (atoms with larger atomic number), since they have higher probability of causing elastic scattering. Considering that SEM uses the secondary and backscattered electrons ejected from the surface of the sample it naturally produces only images of the surface.^{32,63}

Transmission electron microscopy (TEM)

TEM is a widespread method for analysing the crystallographic structure at atomic level. In TEM the incident electron beam is transmitted through an ultra-thin sample while interacting with the sample and producing the reciprocal space images. Unlike SEM, TEM is not limited to the surface morphology of the sample and produce bulk structural information. TEM usage for zeolitic structures also has a long history. After emerging of high-resolution TEM (HRTEM) it was soon used for observing the microporous systems in zeolites. Considering that zeolitic materials very often contain distinct microstructures such as intergrowths, twin structures and other defects, HRTEM became very powerful method for their characterization. The main problem with TEM imaging of the zeolitic samples is that most of these structures are beam sensitive and thus they start to decompose within a few seconds to a few minutes under direct electron irradiation.^{32,63}

Energy dispersive X-ray (EDX) spectroscopy

EDX spectrometers are usually attached to the SEM and TEM (it is additional analysis method). They allow determination of local chemical composition of individual particles; therefore, it cannot be considered a fully quantitative method. Analysis through EDX spectrometers is based on the ejection of electrons from various shells of atoms of the sample via the incident electron beam. When this vacancy is formed the electrons from the energetically higher shells migrate to fill it. This movement of the electrons from energetically higher states into states with lower energy releases distinct X-ray energy, corresponding to the difference between energy of these two levels. This process leads to a series of characteristic emitted X-rays, which are directly dependant on the atomic number of the elements.³²

3.8.4. Inductively coupled plasma with mass spectrometry (ICP-MS)

ICP-MS is highly sensitive method for detection and determination of elemental composition of the sample. It combines the ICP as an ion source with MS for the separation of prepared ions and their detection. The solid samples must be converted into liquid phase first. In the case of zeolitic materials, they are usually dissolved in the solution of strong acids (HF, HCl, HNO₃). Liquid sample is then nebulised (creating a fine aerosol) and afterwards it is transferred into plasma (ionised gas, consisting of positively charged ions and free electrons), which completely atomises and ionises the sample. Created ions are subsequently transferred into the set of electrostatic lenses, which focuses and guides the ion beam into the MS analyser. In the MS analyser the ions are then separated according to their mass to charge ratio and they are measured by detector.⁶⁵

4. Experimental part

4.1. Chemical list

Table 1: List of used chemicals.

Chemical:	Formula/Abbreviation:	Purity:	Dealer:
Aluminium nitrate nonahydrate	$\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$	98%	Thermo Scientific
Ammonia solution	NH_4OH	28%	VWR Chemicals
Butan-1-ol	BuOH	99.8%	VWR Chemicals
Copper(II) sulphate pentahydrate	$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$	$\geq 98.5\%$	VWR Chemicals
Ethanol	EtOH	100%	VWR Chemicals
Ethyl acetate	EtOAc	99.9%	VWR Chemicals
Hexadecyltrimethylammonium bromide	$\text{C}_{16}\text{TMABr}$	$\geq 99\%$	VWR Chemicals
Hydrochloric acid	HCl	37%	VWR Chemicals
Hydrogen peroxide	H_2O_2	30%	Sigma Aldrich
Lactic acid	$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$	90%	VWR Chemicals
Ludox HS	SiO_2	40%	Sigma Aldrich
Nafion solution in propanol	—	5%	Sigma Aldrich
Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol): Pluronic P123	P123	—	Sigma Aldrich
Potassium chloride	KCl	$\geq 99\%$	Sigma Aldrich
Potassium hydrogen carbonate	KHCO_3	100%	VWR Chemicals
Potassium sulphate	K_2SO_4	100%	VWR Chemicals
Silicon dioxide	SiO_2	99.5%	Sigma Aldrich
Sodium aluminate	Na_2AlO_3	50-56% Al_2O_3 , 40-45% Na_2O	Sigma Aldrich
Sodium chloride	NaCl	PA	LACHNER
Sodium hydroxide	NaOH	PA	LACHNER
Sodium metasilicate	$\text{Na}_2\text{SiO}_3 \cdot 5 \text{H}_2\text{O}$	—	Fluka
Sodium sulphate anhydrous	Na_2SO_4	100%	VWR Chemicals
Tetraethylammonium hydroxide	TEAOH	35%	Thermo Scientific
Tetraethylorthosilicate	TEOS	98%	Thermo Scientific
Zinc nitrate hexahydrate	$\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$	$\geq 99\%$	Sigma Aldrich

4.2. Synthesis of zeolites and mesoporous materials

4.2.1. Synthesis of Beta zeolite (*BEA)

The synthesis was performed according to the literature.⁶⁶ 11.64 g of deionized water was added into the 100ml plastic beaker. 25.6 g of 35% TEAOH was added to the beaker with a magnetic stirring bar. Next, 0.1325 g of NaCl and 0.36 g of KCl was added to the solution and stirred until dissolved. 7.385 g of SiO₂ was loaded into a Teflon insert of the 90ml steel autoclave. The solution mixture was poured into the Teflon insert with silica and left vigorously stirring for another 10 minutes. Separately, 5 g of deionized water was added into 25ml plastic beaker and 0.0222 g of NaOH was added to it while stirring. 0.4968 g of Na₂AlO₃ was added to the mixture in the beaker and the mixture was left vigorously stirring for another 10 minutes. Both mixtures were subsequently combined in the Teflon insert and left stirring for approximately 10 minutes. The Teflon insert was put into 90ml steel autoclave, and the autoclave was placed into oven.

Crystallization proceeded in the rotary oven set for 135 °C while autoclave was rotated at 60 rpm for 65 hours. The mixture was filtered using the Büchner funnel with filter paper, washed with deionized water and the product was dried out overnight at 60 °C. The crystallinity of the product was checked by PXRD.

The as-synthesized material was calcined in the calcination oven under air atmosphere at 620 °C for 8 hours with temperature ramp of 1 °C/min.

4.2.2. Synthesis of zeolite faujasite (FAU-Y)

The experiment was performed according to the literature.⁷ First, 117 g of deionized water was added into 250ml PP bottle with a magnetic stirring bar. 19.9985 g of NaOH was then slowly added while stirring. Afterwards 18.7567 g of Al(NO₃)₃ · 9 H₂O was added to the reaction mixture. Lastly, 45.06 g of Ludox HS was slowly added to the bottle with the reaction mixture while stirring. The reaction mixture was then left to age at room temperature for 30 hours.

The crystallization proceeded in the oven at 100 °C for 8 hours. The crystallinity was checked by PXRD pattern and based on the results, half of the batch of synthesis was then filtered using the Büchner funnel with filter paper, washed with deionized water and dried

out at 60 °C. The crystallization of the second half was restarted for another 4.5 hours (overall 12.5 hours). Afterwards the reaction mixture was filtered using the Büchner funnel with the filter paper and was dried out overnight at 60 °C. The crystallinity of the product was checked by PXRD.

The as-synthesized zeolite was calcined in the calcination oven under air atmosphere at 620 °C for 8 hours with temperature ramp of 1 °C/min.

4.2.3. Synthesis of zeolite Zn-faujasite (Zn-FAU-Y)

The experiment was repeated according to the literature.⁷ First, 117 g of deionized water was added into 250ml PP bottle with the magnetic stirring bar. 19.9985 g of NaOH was added slowly to the bottle while stirring. Afterwards 18.7567 g of $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ was added to the reaction mixture. 2.9747 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ was added slowly to the reaction mixture. Lastly, 45.06 g of Ludox HS was added slowly to the bottle while stirring. The reaction mixture was then left to age at room temperature for 30 hours.

The crystallization took place in the oven at 100 °C for 30 hours. The crystallinity was checked by PXRD pattern and based on the results, the half of the batch was filtered using the Büchner funnel with the filter paper, thoroughly washed with deionized water and dried out overnight at 60 °C. The crystallization of the second half was restarted in the oven at 100 °C for another 26 hours (overall 56 hours). The reaction mixture was filtered using the Büchner funnel with the filter paper and dried out at 60 °C. The crystallinity of the product was checked by PXRD.

The as-synthesized zeolite was calcined under air atmosphere at 620 °C for 8 hours with temperature ramp of 1 °C/min. The certain part of synthesized amount was calcined under same conditions second time.

Synthesis of zeolite Zn-faujasite using seeding

The preparation of the reaction mixture was the same as the synthesis without seeding. After the aging at room temperature 0.5214 g of already synthesised Zn-FAU-Y zeolite was added to the mixture and left stirring for another 10 minutes.

The crystallization took place in the oven at 100 °C for 29 hours. After this period, half of the reaction mixture was filtered using the Büchner funnel with the filter paper and dried out at 60 °C. The crystallinity of the product was checked by PXRD.

The crystallization of the second half of the reaction mixture was restarted for another 26.5 hours (overall 55.5 hours). Afterwards the mixture was filtered using the Büchner funnel with the filter paper and dried out at 60 °C. The crystallinity of the product was checked by PXRD.

The as-synthesized zeolite was then calcined under air atmosphere at 620 °C for 8 hours with temperature ramp of 1 °C/min.

4.2.4. Synthesis of MCM-41 mesoporous material

Synthesis was performed according to the literature.⁶⁷ 900 g of deionized water was added into the 1000ml Nalgene bottle with magnetic stirring bar. 4.0056 g of C₁₆TMABr was added to the bottle while stirring at 35 °C. Next, 6.955 g of Na₂SiO₃ · 5 H₂O was added while stirring, until complete dissolution. Subsequently, 5.0 ml of the ethyl acetate was added to the reaction mixture. The reaction mixture was left aging at 35 °C for 20 hours.

The synthesis proceeded in the oven at 95 °C for 4.5 hours and then the temperature was risen up to 100 °C for another 23.5 hours. After this period, the reaction mixture was filtered using the Büchner funnel with the filter paper and it was thoroughly washed with deionized water. The product was dried out at 60 °C.

The as-synthesized mesoporous material was calcined under air atmosphere at 540 °C for 8 hours with the temperature ramp of 1 °C/min.

4.2.5. Synthesis of KIT-6 mesoporous material

Synthesis was performed according to the reference synthesis from the literature.⁴⁷ 44 g of deionized water was added into the 250ml Nalgene bottle with magnetic stirring bar. 1.916 ml of HCl was added into the bottle. Next, 1.2360 g of P123 was added to the reaction mixture while stirring. The mixture was left stirring at 35 °C for 20 hours. Subsequently, 0.9951 g of butanol was added to the reaction mixture. Stirring at 35 °C was continued for

another 3 hours. 2.6648 g of TEOS was added to the reaction mixture. The mixture was left aging at 35 °C for 24 hours.

Afterwards the reaction mixture was transferred into a 60ml steel autoclave with a Teflon insert. The synthesis proceeded in the oven at 100 °C for 24 hours. Then the reaction mixture was filtered using the Büchner funnel with the filter paper and washed with 2% HCl/EtOH solution. The product was dried out at the room temperature.

The as-synthesized mesoporous material was calcined at 650 °C for 6 hours under air atmosphere with the temperature ramp of 1 °C/min.

4.3. Characterization of materials and prepared electrodes

4.3.1. Powder X-ray diffraction (PXRD)

PXRD was done on a Bruker AXS D8 Advance diffractometer equipped with a DLYNXYE XE-T detector in Bragg–Brentano geometry using Cu K α (λ = 1.54056 Å) radiation operated at 30 mA and 40 kV. Data were collected in continuous mode over a 2θ range of 3 – 40° in case of zeolites, in the range of 1 – 10° in the case of mesoporous materials and in the range of 3 – 70° in case of prepared electrodes. With exception of electrodes, the samples were prepared for measurement by grounding the materials into fine powder and then transferred into the plastic XRD holder.

4.3.1. Adsorption of gases

Porosity and textural properties of prepared materials were assessed via N₂ adsorption and desorption isotherms at –196 °C by using a 3-FLEX static volumetric Surface Area Analyzer from Micrometrics. Prior to sorption measurement, the materials were degassed by the turbomolecular vacuum pump (Smart Vac Prep instrument) from Micromeritics.

The surface area (S_{BET}) was calculated by BET method using the adsorption data in the range of relative pressures p/p_0 = 0.05 – 0.20. The adsorbed amount at relative pressure p/p_0 = 0.95 reflects the total adsorption capacity (V_{total}). The t -plot method was applied to determine the micropore volume (V_{micro}). The volume and pore-size distribution of mesopores was calculated from the desorption branch of the isotherm using density functional theory (DFT) method. The mesopore size distributions in the range 5 – 20 nm

were calculated using the Barrett-Joyner-Halenda (BJH) method from the desorption branch of the isotherms.

4.3.2. Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS was used for determination of chemical composition of samples, using Agilent 7900 ICP-MS. Process of sample preparation consisted of mixing approximately 50 mg of the sample with 1.8 ml of HNO₃ (67-69%, ANALPURE®), 5.4 ml of HCl (34-37%, ANALPURE®), and 1.8 ml of HF (47-51%, ANALPURE®) in a Teflon vessel, which was left open for 20 minutes. The vessel was then closed and placed into microwave (Speedwave® XPERT, Berghof) for 25 minutes, while being heated at 250 °C with a temperature ramp of 5 °C/min. Mixture was then left to cool down and excess of HF was captured into complex by addition of 12 ml of concentrated H₃BO₃ solution. Mixture was subsequently heated in the microwave at 190 °C with the same temperature ramp of 5 °C/min for 10 minutes. The resulting solution was left to cool down and was diluted to a total volume of 50 ml by distilled water.

4.3.3. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy

SEM images were obtained using multiple electron microscopes:

1. Thermo Fisher Scientific Scios 2 DualBeam FIB-SEM equipped with a Schottky-type field emission gun.
2. JEOL JSM-IT800 microscope (Viničná Microscopy Core Facility, VMCF of the Faculty of Science, Charles University) equipped with field-emission gun.

Sample morphology was analysed using multiple detectors: Everhart–Thornley secondary electrons detector (ETD), retractable backscattered electrons (BSE) detector, in-lens backscattered electrons (BSE) Trinity Detector T1, in-lens secondary electrons (SE) Trinity Detector T2. Images were collected at an accelerating voltage of 1.0 kV, 3.0 kV, 5.0 kV and 10.0 kV.

Ion-beam preparation was performed using the gallium Focused Ion Beam (FIB). Samples were covered with tungsten prior to milling. All samples were loaded onto conductive carbon tape (or copper tape) attached to the SEM aluminium stub holder.

Elemental composition analysis was performed using energy-dispersive X-ray spectroscopy (EDX) using the Thermo Fisher Scientific UltraDry X-ray detector integrated into the SEM system. Data collection was performed at an accelerating voltage of 10.0 kV.

4.3.4. Scanning transmission electron microscopy (STEM)

STEM images were acquired using a JEOL NEOARM 200 F microscope with Schottky-type field emission gun in the STEM mode. The emission gun was used with an accelerating voltage of 200 kV. Images were collected using the annular dark-field detector (ADF) or annular bright-field detector (ABF). EDX was collected using the EX-37001 energy dispersive X-ray analyser. All the samples were finely grinded and placed onto carbon-coated copper grids.

4.4. Electrodeposition of copper(I) oxide on FTO glasses

4.4.1. Cleaning of the FTO glasses by RCA-1 cleaning protocol

The FTO (fluorine doped tin oxide) glasses of size 3x1.5 cm were first thoroughly washed with deionized water and then placed individually into small 25ml beakers. The cleaning mixture was prepared by combining 195 ml of deionized water with 39 ml of 28% ammonia solution in a large beaker. This solution was heated up to 70 °C on the heating plate while stirring. When the solution reached 70 °C, it was removed from the heating plate and the stirring bar was removed. 39 ml of 30% hydrogen peroxide was added slowly to the solution. When the solution started bubbling vigorously it was poured over prepared FTO glasses, and they were left to soak in it for at least 15 minutes. Subsequently, the solution was poured out of the beakers and the FTO glasses were repeatedly washed with deionized water. Finally, the cleaned FTO glasses were dried out on the heating plate set for 150 °C.

4.4.2. Electrodeposition of copper(I) oxide on FTO glasses

The electrodeposition took place in a three-electrode system. 40 ml of 0.5M solution of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ was added into 100ml beaker with stirring bar. 10.08 ml of 90% $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ (lactic acid) was added into the solution. The beaker with solution was then submerged into preheated water bath placed on the heating plate set for 67 °C. The pH of the solution was adjusted to the value of 10.5 by slowly adding solid NaOH. The pH was checked by calibrated pH meter. After fine tuning of the pH, the stirring bar was replaced

with the smaller one. The solution was kept stirring also during the electrodeposition. The heating of the solution was ensured via water bath set to 67 °C.

FTO glass was heated at 150 °C on a heating plate prior to electrodeposition. Then, it was weighed, and the top was covered with a copper tape. Prepared FTO glass was then placed and screwed into the metal holder. The metal holder was placed into a beaker lid (with three ports) as a working electrode (WE). The platinum electrode was used as a counter electrode (CE) and the mercurous sulphate electrode (MSE), Hg/Hg₂SO₄, or silver/silver chloride electrode (SSCE), Ag/AgCl, was used as reference electrode (RE). The prepared three-electrode system was submerged into the prepared solution by placing the lid over the beaker.

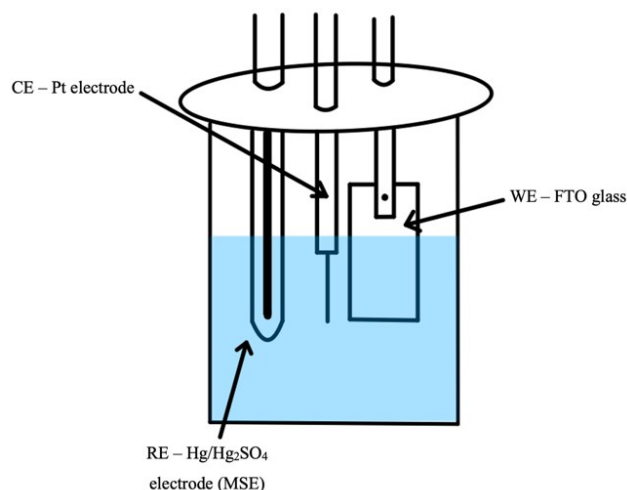


Figure 20: Scheme of three-electrode system used in the electrodeposition of Cu₂O.

The programme for potentiostatic electrodeposition was started. Settings of the programme was as followed: potential applied: 0.36 V vs RHE; duration of the procedure: 30 min.

After the electrodeposition, the electrode covered with Cu₂O was washed with deionized water and dried out on the heating plate set for 150 °C. It was weighed, and the area of the deposited Cu₂O was measured. The amount of deposited Cu₂O was calculated per unit of the area (usually in the range from 3.4 mg/cm² up to 5.0 mg/cm²).

4.5. Spray-coating of porous materials over FTO/Cu₂O

10.0 mg of particular material was added into small vial, 23.00 μ l of the Nafion in 2-propanol solution was pipetted into the vial and 2.00 ml of deionized water was added. The suspension was ultrasonicated for 15 min (using the ultrasonic cleaner – model: 613HT with parameters: ultrasonic frequency: 40 kHz; ultrasonic power: 360 W; heating power: 400 W). Subsequently it was mechanically shaken for another 15 min (using the mechanic shaker Unimax 1010 from Heidolph with speed 359 rpm). Prior to spray-coating the FTO/Cu₂O electrode was heated up on a heating plate at 150 °C for 30 min. The suspension was then spray-coated over FTO/Cu₂O using the air-brush gun FENGDA BD-207K, while heating up the electrodes at 150 °C on the hot plate ensuring the evaporation of the water. Afterwards the electrodes were dried for another 30 min at 150 °C. From the weights of the electrodes before and after spray-coating the amount of material per unit of area was calculated (usually in the range 0.2 – 0.8 mg/cm²).

4.6. Photo-electrochemical characterization tests

All photo-electrochemical (PEC) experiments were done in the two-compartment cell reactor equipped with a proton-exchange membrane (Nafion 117, thickness: 0.007 inches) (see Figure 21). The solar simulator LS0306 with 300W Xe-lamp from Optixs was used as the light source. This solar simulator is producing the broad spectrum (200 – 2500 nm), therefore similar to daylight. Light source was equipped with the AM 1.5-Global Filter (2x2 inch), for correcting the Xe-lamp to better match the total spectrum of incident rays when the sun is at the zenith angle at 37.0°. Light source was also corrected by using the UV filter. The light intensity was adjusted to 100 mW/cm², using the calibrated reference cell – portable radiometer (International Light Technologies Model 2400 with SEL623 and the thermopile detector with NIST Traceable Calibration). During the PEC experiments potentiostat CH Instruments (Austin, TX, USA) 660D Workstation was used.

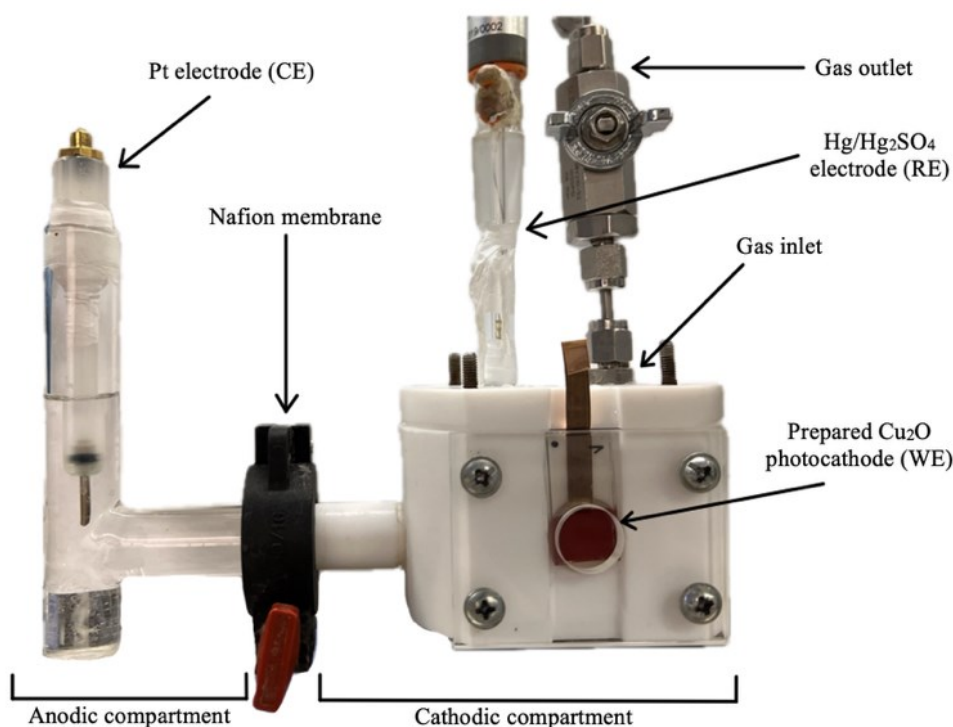


Figure 21: Photo of the two-compartment reactor used during the photo-electrochemical characterization tests.

4.6.1. Linear sweep voltammetry (LSV)

Prior to any tests, the prepared electrodes were heated up at 150 °C for 30 min on a heating plate. The cathodic part of the reactor (see Figure 21) was disassembled and thoroughly washed with deionized water to wash all the residues of the H_2SO_4 to ensure that it does not affect pH during experiments. When not used, the reactor is stored filled with 1M H_2SO_4 to prevent damaging the Nafion membrane. The reactor was then assembled back with the prepared working electrode. Electrolyte consisting of 0.5M KHCO_3 and 0.5M K_2SO_4 was carefully poured into the reactor to prevent bubbles of air staying on the Nafion membrane in the connection of two compartments (see Figure 21). After assembling the reactor, argon was bubbled through solution for 20 min (flow 70 ml/min) to remove all the gases (particularly oxygen) dissolved in the electrolyte. Subsequently, the argon flow was decreased to 20 ml/min. pH of the prepared solution was measured (usually in the range 8.1 – 8.4), and boundaries of the applied potential were calculated against RHE to be from 0.64 to 0 V. Series of voltametric experiments were done in three modes: under dark, under light irradiation and under chopped mode (regulated by shutter: opened and closed every three seconds). These three modes were repeated twice.

Afterwards the electrolyte was saturated with gaseous carbon dioxide. Carbon dioxide was bubbled through the solution for 20 min (flow 70 ml/min), subsequently, the flow was decreased to 20 ml/min. pH of the solution was measured again (usually in the range 7.0 – 7.3) and the boundaries of the applied potential were calculated to be 0.64 – 0 V against RHE. The series of voltametric experiments were done with three above-described modes and repeated twice as in the case of argon experiment.

4.6.2. Chronoamperometric stability tests with the product analysis

The sample and the reactor were prepared for the measurements in the same way as for LSV experiment, except the tine stirring bar was added to the cathodic compartment of the reactor. Afterwards, CO₂ was bubbled through the solution for 20 min with the flow of 100 ml/min. Subsequently, the closed gas circuit was established in the reactor. Chronoamperometric stability test was then performed under constant illumination for 2 hours, and with constant applied potential of 0.24 V vs RHE. When the experiment was finished both the electrolyte and the gas phase above it were analysed using the GC method with TCD and FID detectors. Additionally, the electrolyte was also analysed by ¹H NMR (1.0 ml of electrolyte with 0.1 ml of D₂O).

4.7. Analysis of CO₂RR products

4.7.1. Gas chromatography (GC)

GC product analysis was performed on the 7890B GC system from Agilent Technologies (with model number: G3440B). The GC system contains two inlets (front and back) each equipped with different detector. The back line is equipped with two columns connected in series: HP-molesieve (part number: 19095P-MS0, length: 30 m, diameter: 0.53 mm, film 50.0 µm) and PoraBOND Q (part number: CP7354, length: 25 m, diameter: 0.53 mm, film 10.0 µm). The column outlet leads to TCD detector. The front line is equipped with VF-WAXms column (part number: CP9206, length: 30 m, diameter: 0.25 mm, film 1.00 µm) and the outlet leads to FID detector. All columns are from Agilent Technologies.

Gas phase analysis

The gas phase analysis after performance of chronoamperometric 2-hour test was done online (the gas outlet of the reactor was directly connected to the GC). After the end of the

test the gas phase was done into GC using dosing loop (0.25ml) and analysed on the back line equipped with the TCD detector.

Liquid sample preparation

10 ml of electrolyte was taken into a 20ml vial enclosed with septum top. Then, it was heated up to 90 °C in the preheated water bath for 30 minutes. Next, 1 ml of headspace was injected in the GC using Hamilton syringe. The sample was analysed on the front line equipped with FID detector.

4.7.2. Proton nuclear magnetic resonance (^1H NMR)

^1H NMR spectra were measured by using Bruker Avance III spectrometer operating at ^1H Larmor frequency of 600 MHz equipped with room-temperature BBO probe. In all experiments, water signal was suppressed by excitation sculpting method (zgpg30 pulse program) with 2ms long water-selective pulse (sinc shape). 800 scans were accumulated with 6.5 s repetition delay resulting in a total time of 1.5 hour per spectrum. Vendor standard chemical shift referencing was used, based on chemical shift of the solvent peak used for locking (90% H_2O , 10% D_2O). Due to high salt content in all samples, excitation pulses were calibrated for every sample using the 'pulsecal' feature of the spectrometer software.

5. Results and discussion

5.1. Electrodeposited FTO/Cu₂O photoelectrodes

Multiple sets of electrodes were prepared using the electrodeposition from Cu²⁺ solution. The amount of deposited Cu₂O per area was calculated for each electrode (usually in the range 3.5 – 5.0 mg/cm²). The procedure was done under constant applied potential of 0.36 V vs RHE for 30 minutes (see Figure 22).

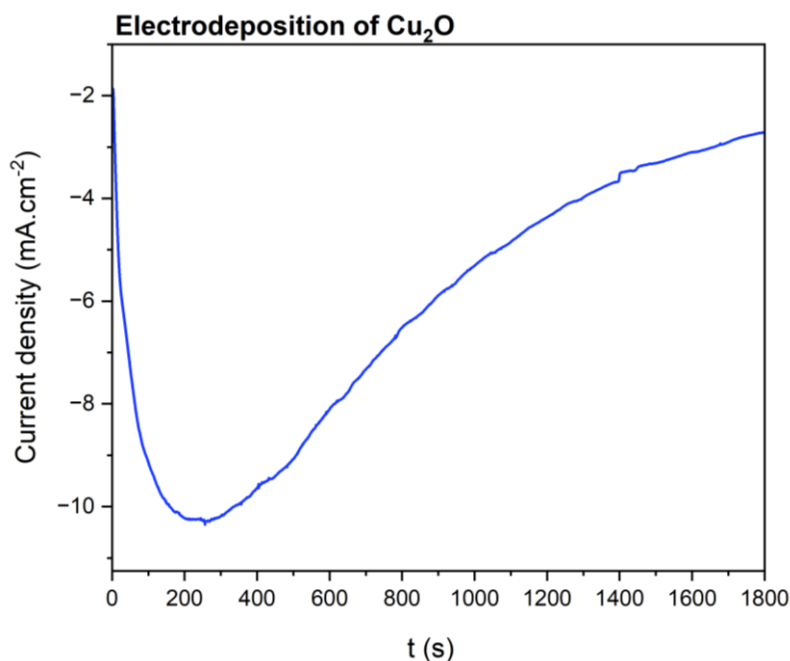


Figure 22: Electrodeposition of Cu₂O on FTO from Cu²⁺ solution.

5.2. Synthesized porous materials

Various microporous materials (*BEA, FAU-Y and Zn-FAU-Y) and mesoporous materials (MCM-41 and KIT-6) were synthesized. The duration of syntheses was optimized (in the case of FAU-Y and Zn-FAU-Y materials), and the materials were characterized by multiple characterization methods.

5.2.1. Powder X-ray diffraction (PXRD)

First characterization method used for determination of the crystallinity of the prepared materials was PXRD. For the mesoporous materials KIT-6 and MCM-41 the PXRD was performed in the 2θ range of 1 – 10 ° (see Figure 23), since they are amorphous materials

and therefore lack true Bragg's diffraction. Both patterns were compared with the patterns from the reference literature,^{47,67} confirming the presence of desired mesoporous materials.

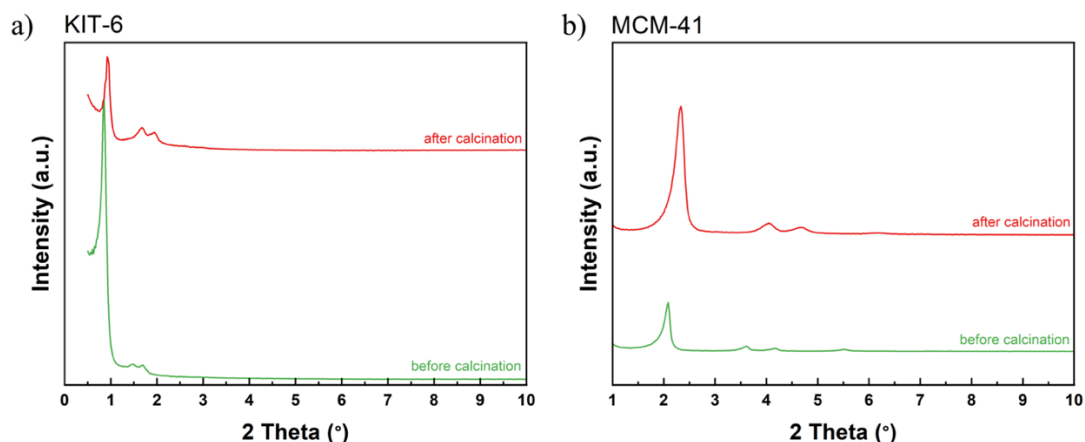


Figure 23: PXRD patterns of synthesized mesoporous materials a) KIT-6 and b) MCM-41.

PXRD analysis was also used in the case of microporous zeolites. The analysis was performed in the 2θ range of $3 - 40^\circ$ (see Figure 24 and Figure 25).

In the case of *BEA zeolite the PXRD pattern of commercial *BEA previously measured in our research group was used as a reference material. The presence of characteristic band and peaks confirmed the successful synthesis of *BEA structure (see Figure 24a).

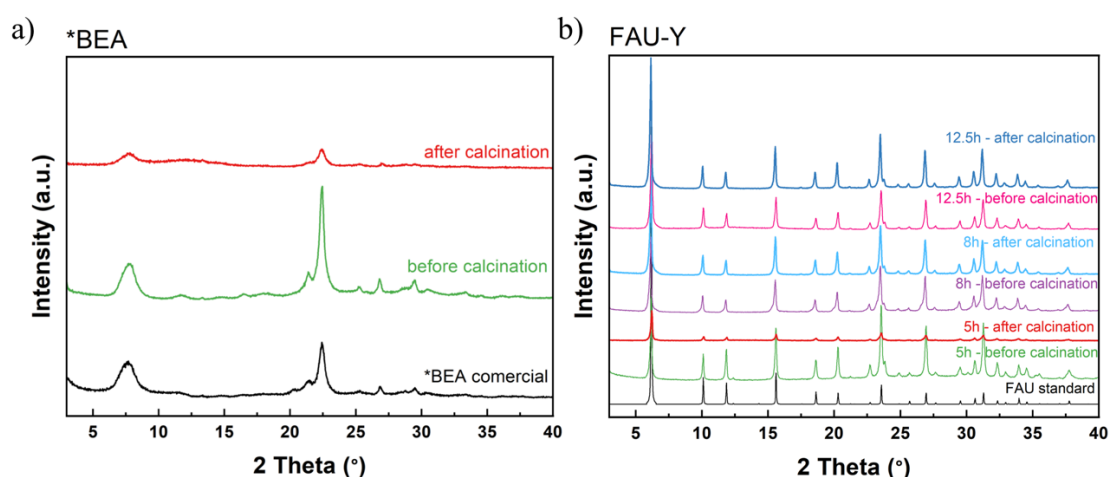


Figure 24: PXRD patterns of synthesized zeolitic materials a) *BEA and b) FAU-Y.

In the case of FAU-Y and Zn-FAU-Y, the theoretical XRD pattern obtained from IZA was used as a reference pattern.²⁸ Based on the PXRD analysis the crystallization time in

various syntheses was optimized to reach well crystalline material. FAU-Y was successfully synthesized with very similar results of PXRD analysis after 8 hours and 12.5 hours crystallization time (see Figure 24b). The material synthesized with the crystallization time of 12.5 hours was used for further analysis and experiments.

Synthesis of Zn-FAU-Y was performed both without the seeding and with the seeding method (already synthesized Zn-FAU-Y was used for seeding). In the case of non-seeded method, the successful synthesis was obtained after 56 hours as evident by the presence of characteristic peaks for FAU structure (see Figure 25a). The material synthesized with the crystallization time of 56 hours was used for further analysis and experiments.

In the case of seeded method, we observed typical peaks of FAU after shorter crystallization time (29 hours) compared to the non-seeded synthesis (see Figure 25). Half of the reaction mixture was allowed further crystallization reaching total time of 55.5 hours.

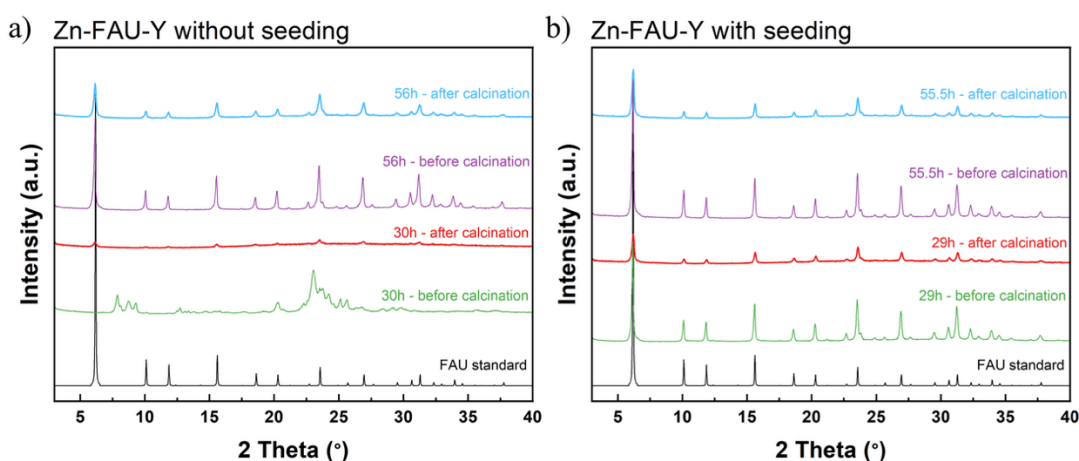


Figure 25: PXRD patterns of synthesized Zn-FAU-Y with different synthesis method a) synthesis without seeding and b) synthesis with seeding.

As seen on Figure 26, the highest intensity peaks are observed for aluminosilicate FAU-Y while both zincoaluminosilicate counterparts revealed significantly lower intensities (both seeded and non-seeded).

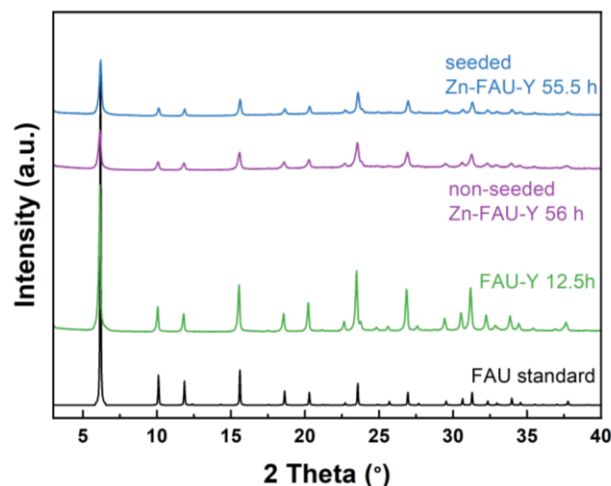


Figure 26: PXRD pattern of synthesized FAU type materials (FAU-Y, non-seeded Zn-FAU-Y and seeded Zn-FAU-Y) after calcination compared to FAU theoretical pattern.

5.2.2. Adsorption of N₂

Analysis of nitrogen adsorption-desorption isotherms is important method for characterization of porous materials. Textural properties, including BET surface area, total pore volume and micropore volume were analysed by sorption of nitrogen at 77 K.

Both mesoporous silica – MCM-41 and KIT-6 materials show type IV adsorption isotherms according to IUPAC (see Figure 27a), which is characteristic for mesoporous materials. For KIT-6 the type IV(a) isotherm was obtained with a narrow hysteresis loop. The capillary condensation in larger mesopores (> 4 nm) results in this shape of the hysteresis loop, which is characteristic for ordered mesoporous materials with ordered 3D pore networks. MCM-41 exhibited the type IV(b) isotherm. Since the MCM-41 lacks 3D pore network and exhibits uniform pores, we do not see any hysteresis in the adsorption isotherm. The average pore size in the materials was calculated via density functional theory (DFT) method: for MCM-41 it was estimated as 3.6 nm and for KIT-6 it was centred around 8.4 nm, which is a little bit larger than usually reported (7.0 – 7.6 nm) (see Figure 27b).

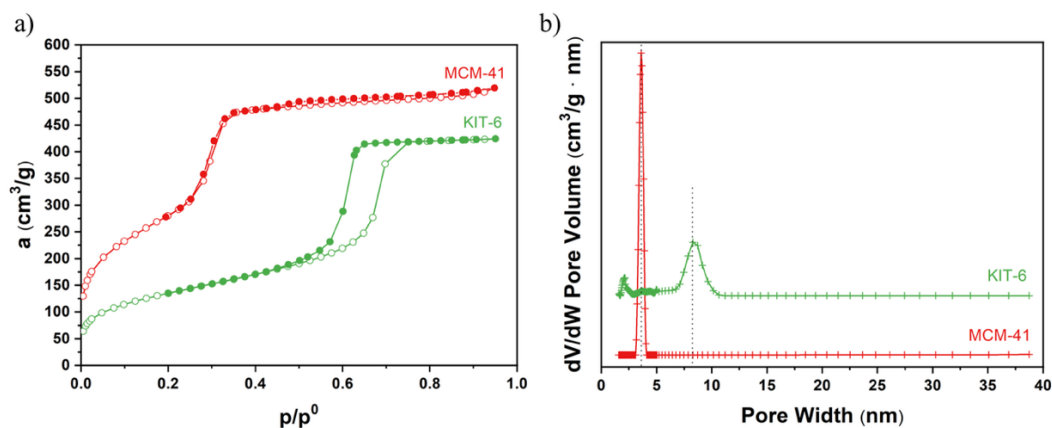


Figure 27: a) Adsorption (empty circles) and desorption (full circles) isotherms of synthesized mesoporous materials (MCM-41 and KIT-6) b) distribution of mesopores in materials: MCM-41 and KIT-6.

The data obtained for mesoporous materials are summarized in the Table 2. BET surface area obtained for KIT-6 of 491 m²/g is consistent with the literature. In the case of MCM-41, the BET surface area of 1026 m²/g is even larger than usually reported.

Table 2: Textural properties of mesoporous materials determined by N₂ adsorption and desorption.

Material	S _{BET} (m ² /g)	V _{total} (cm ³ /g)	V _{micro} (cm ³ /g)
MCM-41	1026	0.81	—
KIT-6	491	0.66	—

All zeolitic samples exhibited the type I isotherm (see Figure 28), which is typical for microporous materials.

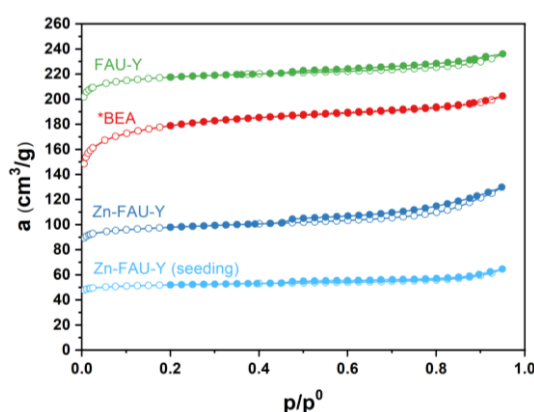


Figure 28: Adsorption (empty circles) and desorption (full circles) isotherms of synthesized zeolites (*BEA, FAU-Y and Zn-FAU-Y). In the case of Zn-FAU-Y both the synthesis with seeding (after 56 hours of crystallization) and without the seeding (after 55.5 hours of crystallization).

The textural properties of all zeolites are summarized in the Table 3. The values obtained for *BEA and of FAU-Y correspond with the typically reported values for these materials. The interesting case is the zincoaluminosilicate Zn-FAU-Y. It exhibits nearly half the BET surface area and pore volumes compared to FAU-Y and the values reported in the reference literature.⁶⁸ It may suggest the pore blockage. It opens the question whether Zn is truly incorporated in the zeolitic framework (as reported in the reference literature)⁷, or is present in some small clusters blocking the pores. In attempt to improve the textural properties of Zn-FAU-Y, the synthesis was performed with seeding. Nevertheless, the textural properties of seeded Zn-FAU-Y were even worse.

Table 3: Textural properties of zeolitic materials determined by N_2 adsorption and desorption.

Material	S_{BET} (m ² /g)	V_{total} (cm ³ /g)	V_{micro} (cm ³ /g)
*BEA	609	0.31	0.26
FAU-Y	731	0.37	0.32
Zn-FAU-Y	330	0.20	0.14
Zn-FAU-Y (seeding)	211	0.10	0.07

5.2.3. Inductively coupled plasma with mass spectroscopy (ICP-MS)

ICP-MS analysis was performed for the zeolitic materials to assess the elemental composition of the prepared materials. The results (as well as molar ratios of Si/Al and Si/Zn) are summarized in the Table 4.

Table 4: The results of ICP-MC analysis of synthesized zeolites.

Material	Si (mg/g)	Al (mg/g)	Na (mg/g)	Zn (mg/g)	Si/Al molar ratio	Si/Zn molar ratio
*BEA	269	22.0	—	—	11.8	—
FAU-Y	172	90.6	—	—	1.82	—
Zn-FAU-Y	197	90.1	8.34	35.1	2.10	13.1
Zn-FAU-Y (seeding)	276	123	16.1	66.9	2.16	9.60

The molar ratio of Si/Al for *BEA shows high silica content, which was expected in this case. Also, the molar ratio of all synthesized materials of FAU type can be categorised as type Y since their Si/Al molar ratio is higher than 1.5. Type Y of FAU zeolite is characterized by lower Al content when compared with the X type. As expected the Zn-FAU-Y materials contain lower amount of Al when compared with the FAU-Y as it was

reported that zinc atoms should replace aluminium atoms in the framework positions.⁷ Lower value of Si/Zn molar ratio in the seeded synthesis of Zn-FAU-Y suggests the higher content of Zn in the material.

5.2.4. Electron microscopy

The SEM images of *BEA (see Figure 29) show purely crystalline phase. The oval/spherical particles are typical for *BEA material. The individual crystals have about 0.5 μm in diameter.

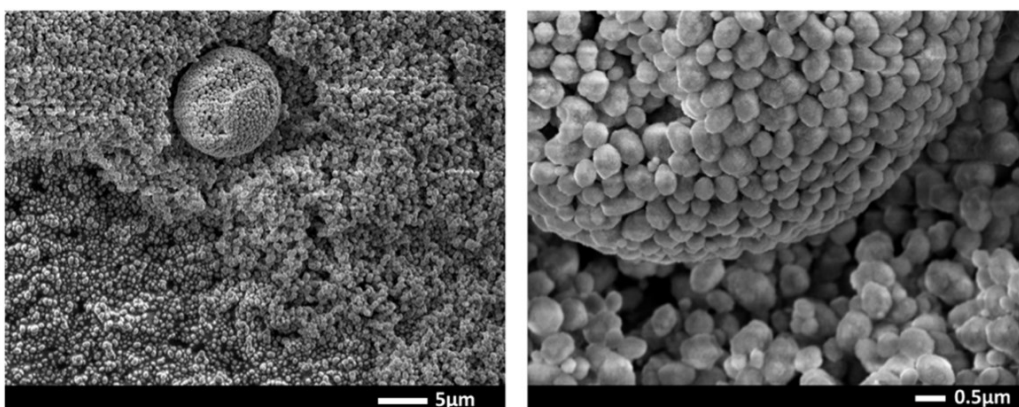


*Figure 29: SEM images of synthesized *BEA at different scales.*

The SEM images of FAU-Y (see Figure 30) show crystalline phase. The individual particles are uniform in the size, usually up to 0.5 μm . The particles show spherical crystal habit similar to *BEA particles.

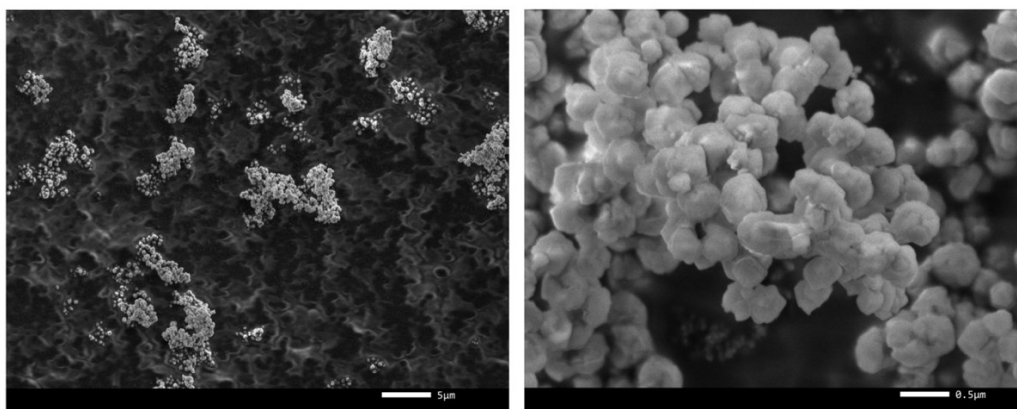


Figure 30: SEM images of synthesized FAU-Y at different scales.

The SEM images of non-seeded Zn-FAU-Y (see Figure 31) revealed aggregated crystalline particles with a morphology comparable to that of FAU-Y. However, the

individual crystals appear more fused together showing less defined boundaries and a slightly rougher surface texture.

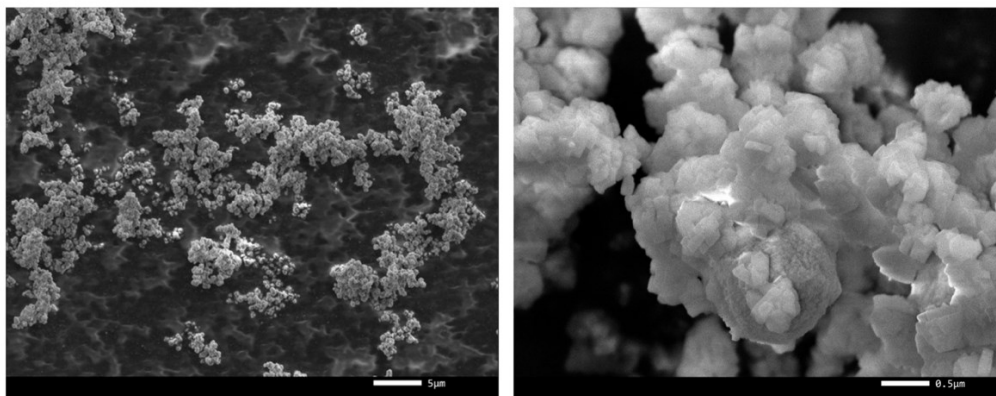


Figure 31: SEM images of non-seeded Zn-FAU-Y at different scales.

The non-seeded Zn-FAU-Y was also analysed using the backscattered electrons detector (BED) of the SEM (see Figure 32), showing more backscattered electrons due to presence of Zn in the structure. The Zn atoms does not seem to be aggregated into one place and therefore, we could assume that Zn atoms are uniformly distributed throughout the crystals.

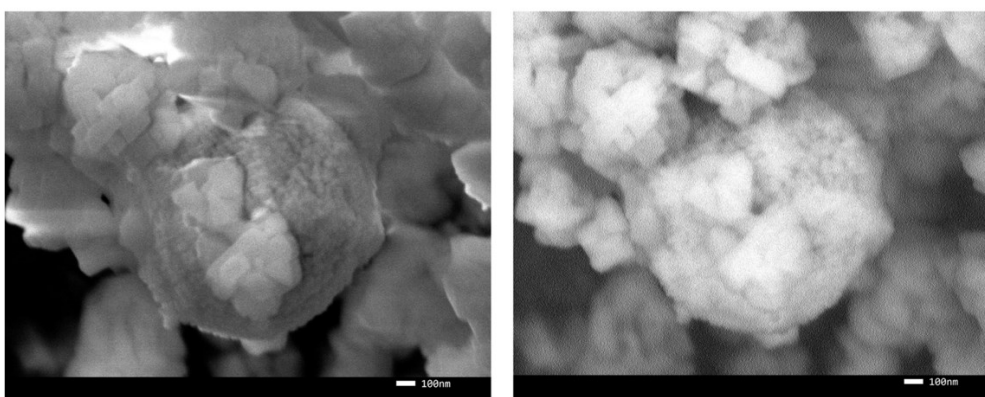


Figure 32: SEM images of non-seeded Zn-FAU-Y in the same scale collected from different detectors: secondary electrons detector (SED) on the left and backscattered electrons detector (BED) on the right.

The non-seeded Zn-FAU-Y was further characterized by TEM microscopy and EDX to investigate the possible distribution of Zn atoms through the sample (see Figure 33 and Figure 34). In both figures, the uniform distribution of Zn through the material can be observed. In the Figure 33, the Zn atoms can be observed shining in the structure, under the longer exposure of the sample to electron beam (the silicate structure is becoming amorphous

and heavier atoms become more visible). Also, through the elemental EDX mapping (see Figure 34) we can confirm that the Zn atoms seem to be uniformly distributed over the analysed area (as well as Si and Al atoms).

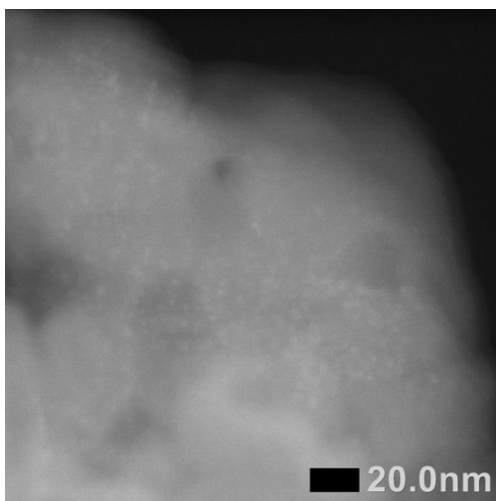


Figure 33: TEM image of non-seeded Zn-FAU-Y.

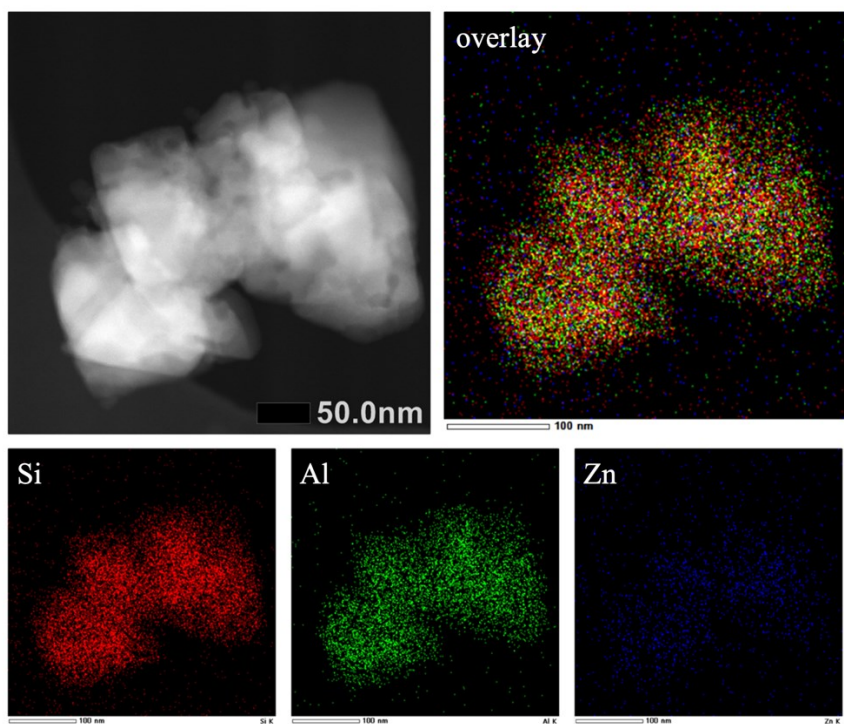


Figure 34: Elemental composition of the non-seeded Zn-FAU-Y obtained from EDX measurement.

The SEM images of MCM-41 (see Figure 35) do not show any kind of uniformity, confirming the amorphous nature of the material.

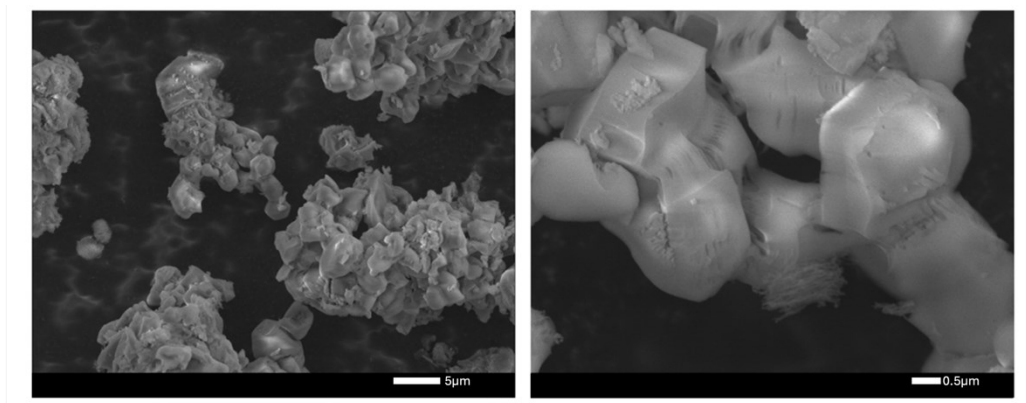


Figure 35: SEM images of synthesized MCM-41 at different scales.

The SEM images of KIT-6 (see Figure 36) also show the amorphous phase without any large-scale uniformity. However, some parts of the amorphous phase reveal a rod-like interconnected structures, which is well visible in Figure 36 on the right.

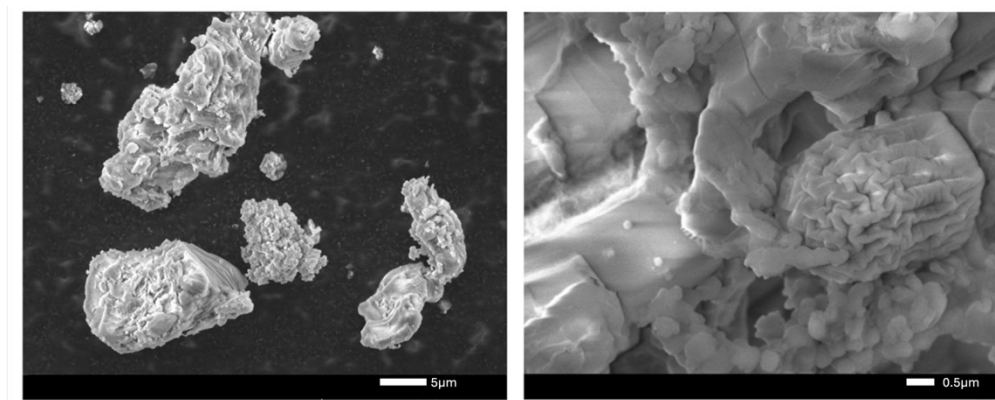


Figure 36: SEM images of synthesized KIT-6 at different scales.

5.3. Spray-coating of porous materials over FTO/Cu₂O

All spray-coated electrodes were characterized on SEM both from the top-view and the cross-section view. Cross-section view allowed us to see individual layers of FTO glass, deposited Cu₂O and porous material. The top-view images were collected using secondary electrons detector (SED) and backscattered electrons detector (BED). The cross-section images were collected by Everhart-Thornley detector (ETD) collecting secondary electrons and also by backscattered electrons detector (BED).

5.3.1. FTO/Cu₂O/*BEA

From SEM top-view of the electrode (see Figure 37), we can observe that the Cu₂O layer is uniformly covered with the particles of *BEA zeolite. The layer of Cu₂O can be seen on the bottom right picture (from BED detector) shining brighter than the layer of *BEA. It shows a little inconsistency in otherwise uniform layer of *BEA. The cross-section view of the electrode (see Figure 38) clearly shows individual layers. The Cu₂O and *BEA layers have a width of approximately 5 μ m and below 5 μ m, respectively.

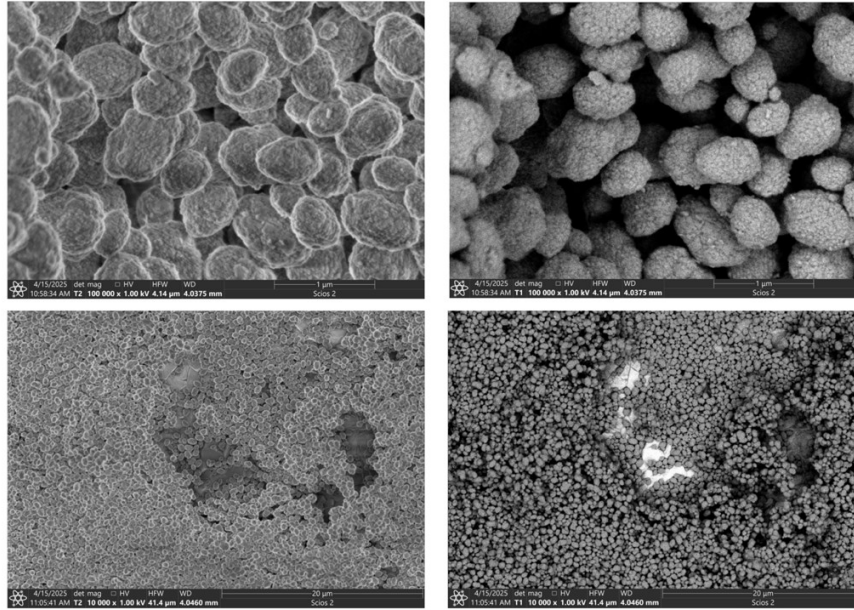


Figure 37: SEM images FTO/Cu₂O/*BEA electrode (top-view) collected via secondary electrons detector (SED) on the left and via backscattered electrons detector (BED) on the right.

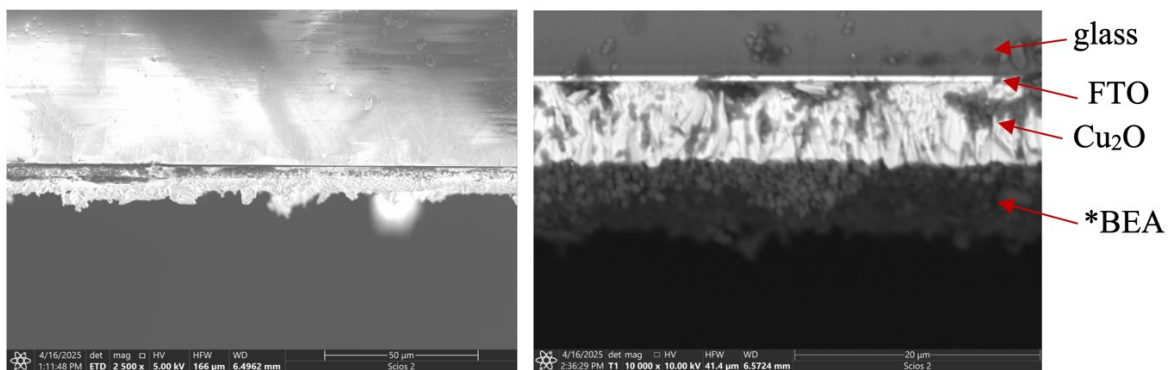


Figure 38: SEM images of the cross-section of the prepared electrode FTO/Cu₂O/*BEA collected via Everhart-Thornley detector (ETD) on the left and via backscattering detector (BED) on the right.

5.3.2. FTO/Cu₂O/FAU-Y

The SEM images from the top-view (see Figure 39) revealed some flaws in the coverage of the Cu₂O layer as the underlying crystals of deposited Cu₂O are visible in some parts. The cross-section view (see Figure 40) clearly shows individual layers. The Cu₂O layer is of approximately 6 μ m width, while the FAU-Y layer is of approximately 5 μ m. Nevertheless, it is very hard to assess the average width of the FAU-Y layer since the image shows also the particles in the space behind the cut (the angle of viewing is not perfectly perpendicular, and it also depends on the focus).

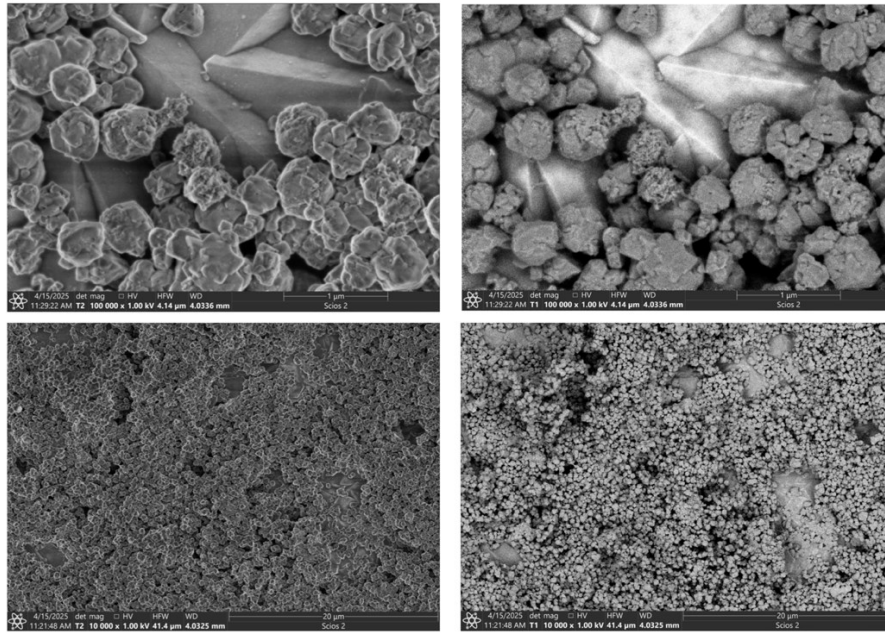


Figure 39: SEM images of FTO/Cu₂O/FAU-Y electrode (top view) collected via secondary electrons detector (SED) on the left and via backscattered electrons detector (BED) on the right.

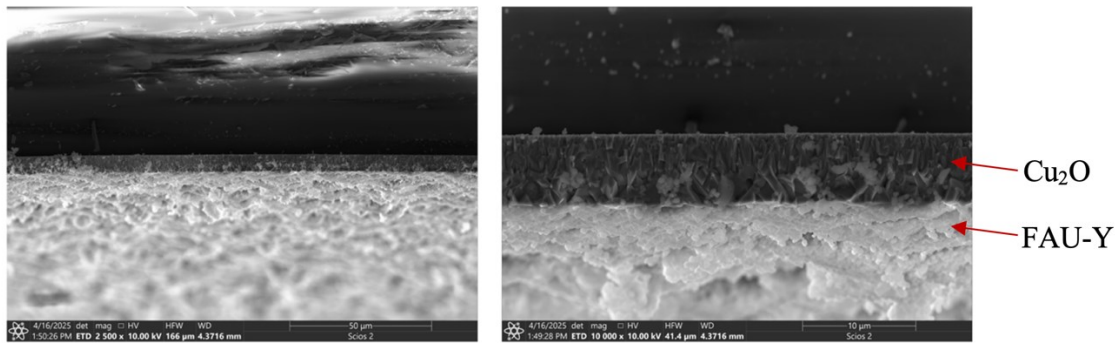


Figure 40: SEM images of the cross-section of the prepared electrode FTO/Cu₂O/FAU-Y collected via Everhart-Thornley detector (ETD).

5.3.3. FTO/Cu₂O/Zn-FAU-Y

The SEM images from top-view (see Figure 41) showed that the coverage of the Cu₂O layer is sufficient, but still with some imperfections. They can be most prominently seen in the image collected via backscattering electrons detector (BED) (see Figure 41, right down image). The cross-section view (see Figure 42) clearly shows the individual layers. The width of Cu₂O layer is approximately 6 μ m, while the width of Zn-FAU-Y is problematic to determine as in the case of FTO/Cu₂O/FAU-Y.

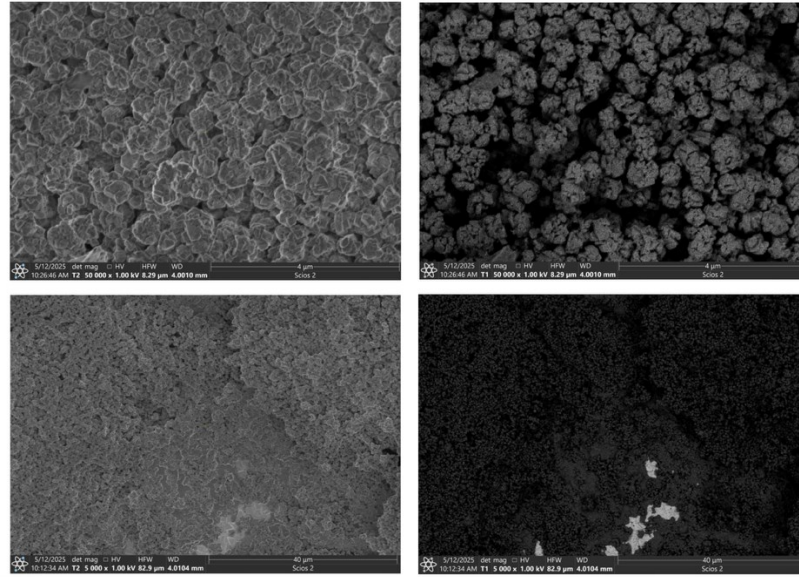


Figure 41: SEM images of FTO/Cu₂O/Zn-FAU-Y electrode (top view) collected via secondary electrons detector (SED) on the left and via backscattered electrons detector (BED) on the right.

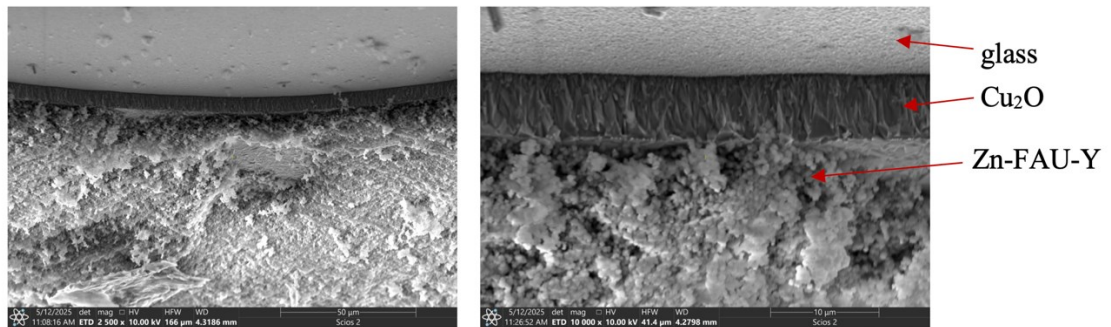


Figure 42: SEM images of the cross-section of the prepared electrode FTO/Cu₂O/Zn-FAU-Y collected via Everhart-Thornley detector (ETD).

5.3.4. FTO/Cu₂O/MCM-41

In the SEM images from top-view of the electrode (see Figure 43), the amorphous particles of the MCM-41 can be observed. The coverage in this case is not as uniform as in the case of zeolites. The SEM images show an electrode with the amount of MCM-41 of approximately 0.35 mg/cm². Therefore, from the top-view, the underlying crystals of the Cu₂O layer can be recognized coming out of the overlayer of MCM-41. These crystals of Cu₂O can be seen prominently on the image obtained from BED (bottom right). Even the cross-section view (see Figure 44) shows that the overlayer of MCM-41 is not as thick and uniform as in the case of zeolites. To improve the coverage, we suggest adjusting the ratio between MCM-41, Nafion solution and water used for spray-coating.

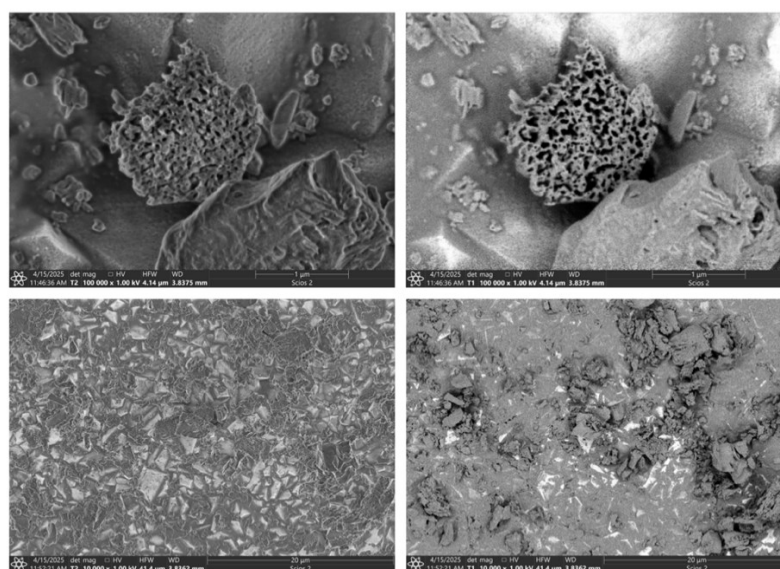


Figure 43: SEM images of FTO/Cu₂O/MCM-41 electrode (top-view) collected via secondary electrons detector (SED) on the left and via backscattered electrons detector (BED) on the right.

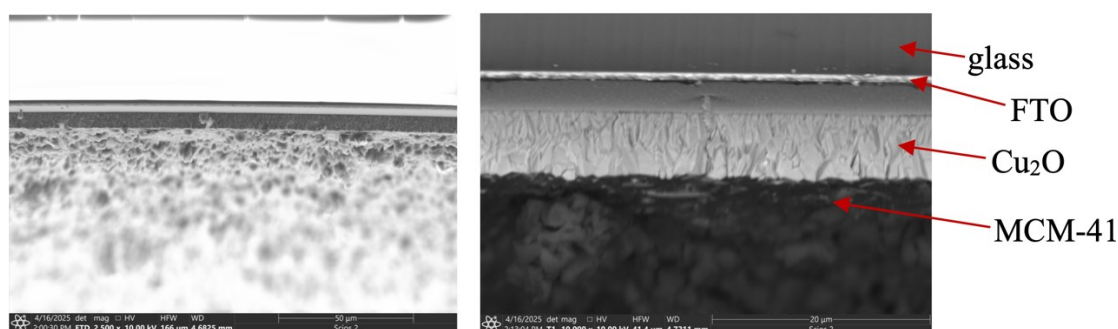


Figure 44: SEM images of the cross-section of the prepared electrode FTO/Cu₂O/MCM-41 collected via Everhart-Thornley detector (ETD).

5.3.5. FTO/Cu₂O/KIT-6

In the SEM images from the top-view (see Figure 45), the amorphous KIT-6 particles can be observed. Similarly, as in the case of MCM-41, the overlayer is not as uniform as in the case of zeolites. The SEM images show the electrode with the amount of KIT-6 of approximately 0.20 mg/cm². The crystals of Cu₂O are clearly visible peaking from the overlayer of KIT-6. From the cross-section view of the electrode (see Figure 45) the individual layers can be observed. Also, during the spray-coating, it was noted that the material did not stick to the surface of the Cu₂O layer as in the case of zeolites. Therefore, as in the case of MCM-41, we suggest adjusting the ratio between KIT-6, Nafion solution and water used for spray-coating.

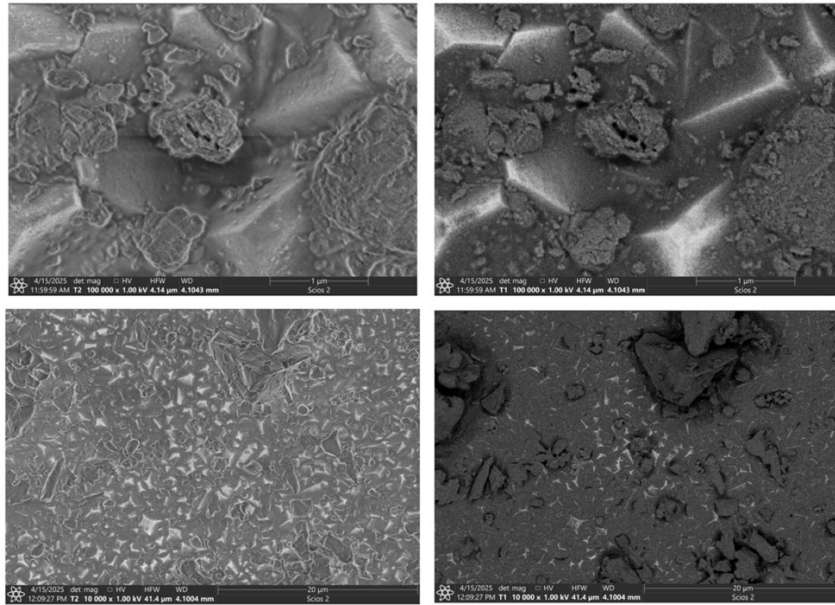


Figure 45: SEM images of FTO/Cu₂O/KIT-6 electrode (top-view) collected via secondary electrons detector (SED) on the left and via backscattered electrons detector (BED) on the right.

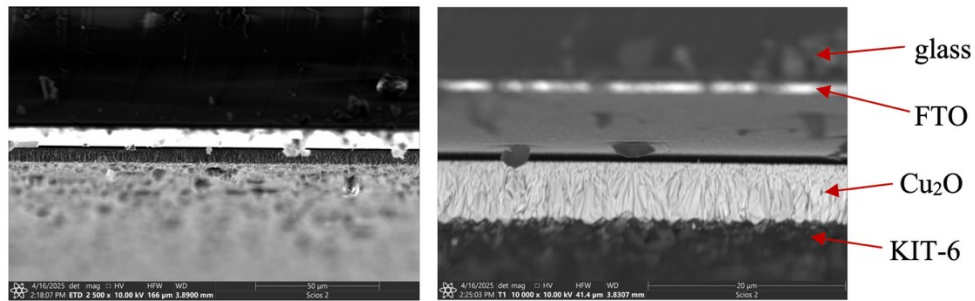


Figure 46: SEM images of the cross-section of the prepared electrode FTO/Cu₂O/KIT-6 collected via Everhart-Thornley detector (ETD) on the left and via backscattering detector (BED) on the right.

5.4. Photo-electrochemical characterization

5.4.1. Linear sweep voltammetry (LSV)

The LSV tests were performed on the FTO/Cu₂O electrode and on all prepared FTO/Cu₂O/porous material electrodes. The tests were executed in three modes: under dark, light and chopped illumination. The tests were carried out first in the Ar saturated solution and then in the CO₂ saturated solution to see the difference when the reactant is present in the electrolyte. The course of LSV achieved on FTO/Cu₂O electrode can be seen in the Figure 47. In evaluating the results, we focused mainly on three aspects:

1. How the electrode holds the dark current (ideally as close to zero as possible, which suggests good stability under applied potential).
2. The photocurrent density in the light mode of Ar saturated and CO₂ saturated electrolyte. More negative values of photocurrent densities when the CO₂ is present in the solution suggest the reduction reaction happening on the surface of the electrode.
3. The presence of the spikes in the chopped mode of measurement indicating the fast charge recombination in the electrode.

In the Figure 47, for bare FTO/Cu₂O electrode, the presence of charge recombination spikes can be clearly seen mainly under light illumination. Also, the bare FTO/Cu₂O does not hold the dark current very well, which can be observed especially in the chopped mode under CO₂ saturation of the electrolyte, suggesting weak photostability of the material.

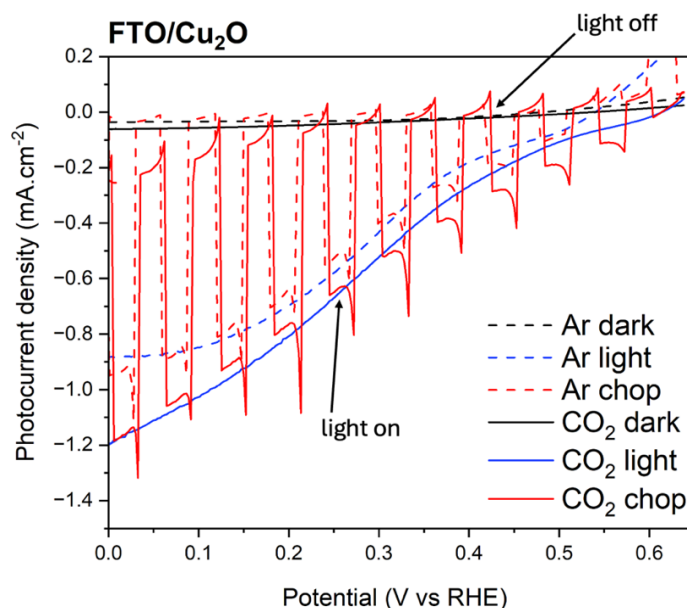


Figure 47: The measured photocurrent density in FTO/Cu₂O generated in the range of applied potentials in Ar saturated electrolyte (dashed curves) and in CO₂ saturated electrolyte (solid curves) in three modes of illumination: dark (black), light (blue) and chopped (red).

The prepared FTO/Cu₂O/porous materials were tested and compared with the bare FTO/Cu₂O by overlaying the results of chopped mode of LSV measurements under CO₂ saturation. It is essential for the sake of comparison that the prepared electrodes have the similar amount of individual layers, which unfortunately was not always achieved. It is, therefore, important to take into consideration that the amount of individual layers (meaning milligrams per area covered with Cu₂O) can have direct impact on the results of measurements. Thus, the amounts of deposited Cu₂O per surface area and spray-coated porous material per surface area for each prepared electrode are listed in Table 5.

Table 5: The amount of the individual layers of the composite electrodes used for LSV tests.

Electrode	m(Cu ₂ O) (mg/cm ²)	m(porous material) (mg/cm ²)
FTO/Cu ₂ O	3.88	—
FTO/Cu ₂ O/*BEA	4.10	0.59
FTO/Cu ₂ O/FAU-Y	3.59	0.57
FTO/Cu ₂ O/Zn-FAU-Y	5.07	0.46
FTO/Cu ₂ O/MCM-41	3.40	0.43
FTO/Cu ₂ O/KIT-6	3.62	0.44

In the case of FTO/Cu₂O covered with a zeolitic overlayer (see Figure 48), all prepared electrodes showed less negative photocurrent densities compared to bare FTO/Cu₂O.

Nevertheless, in the case of the electrodes covered with zeolite *BEA and Zn-FAU-Y, we perceived significant reduction of the recombination spikes both in dark and light parts of the curves.

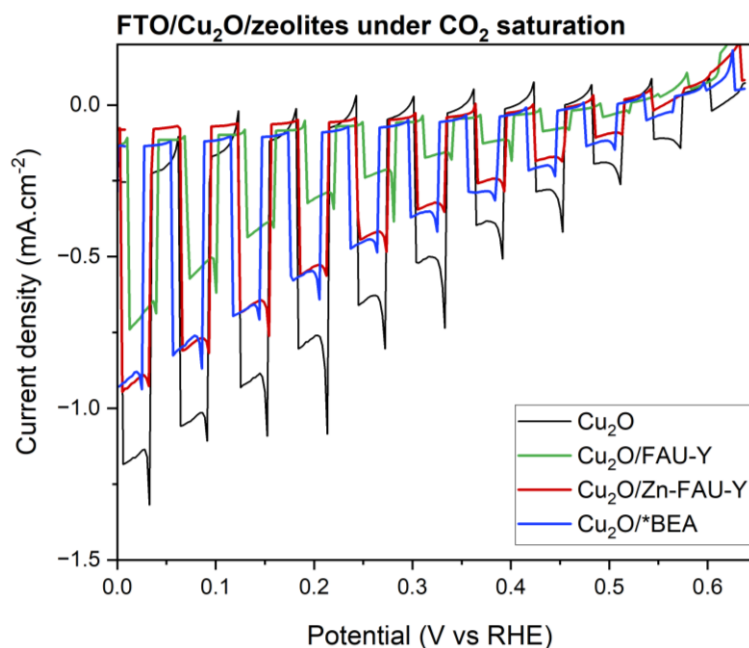


Figure 48: Comparison of results of chopped mode of LSV measurements for electrodes FTO/Cu₂O/zeolites under CO₂ saturation.

The results from protective overlayer of mesoporous materials are depicted in the Figure 49. The overlayer of mesoporous materials in both cases, results in less negative photocurrent density compared to bare FTO/Cu₂O. Still, the most promising results were obtained for FTO/Cu₂O/MCM-41 electrode, since I) it produced more negative photocurrent density when compared to KIT-6; II) the presence of recombination spikes was noticeably reduced, especially in the dark current part of the diagram.

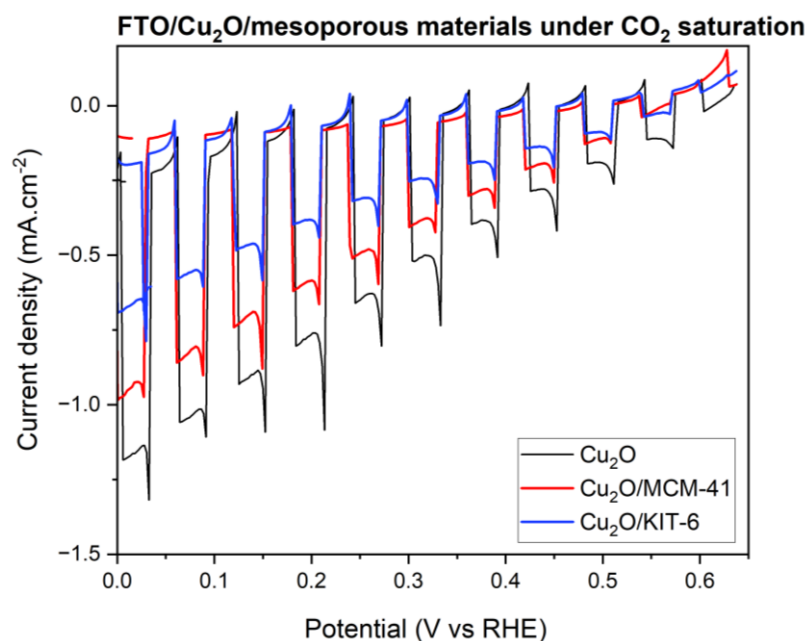


Figure 49: Comparison of results of chopped mode of LSV measurements for electrodes FTO/Cu₂O/mesoporous materials under CO₂ saturation.

5.4.2. Chronoamperometric tests

Chronoamperometric tests were performed in the standard setup of a two-compartment reactor (see Figure 21). The tests were performed under constant illumination and under applied potential of 0.24 V vs RHE for 2 hours. Afterwards the GC analysis of the gas phase from the reactor was performed. The electrolyte was carefully stored in the glass vial and used for the liquid phase GC analysis and ¹H NMR analysis.

The amounts of Cu₂O deposited per surface area and the amounts of spray-coated porous material per surface area for all electrodes used for chronoamperometric measurements are denoted in the Table 6.

Table 6: The amount of the individual layers of the composite electrodes used for chronoamperometric tests.

Electrode	m(Cu ₂ O) (mg/cm ²)	m(porous material) (mg/cm ²)
FTO/Cu ₂ O	3.75	—
FTO/Cu ₂ O/*BEA	4.17	0.34
FTO/Cu ₂ O/FAU-Y	3.86	0.74
FTO/Cu ₂ O/Zn-FAU-Y	3.70	0.85
FTO/Cu ₂ O/MCM-41	3.65	0.35
FTO/Cu ₂ O/KIT-6	4.19	0.24

The measured photocurrent density of individual electrodes was plotted against the time (see Figure 50 and Figure 51). The photocurrent density of electrodes covered with the protective overlayer of porous materials were compared with the bare FTO/Cu₂O electrode. In all measurements large amount of noise was observed (mainly in the case of FTO/Cu₂O/MCM-41 electrode). These experiments need to be repeated to confirm that it is just a result of an error in the measurement (or current lab conditions, vibrations, etc.) and not the result of decreased photostability of the electrodes themselves. The results of chronoamperometric measurement of electrode with bare FTO/Cu₂O, indicate poor photocurrent stability. Since after approximately 30 minutes of the measurement, the photocurrent density was almost zero. In the case of electrodes covered with zeolitic overlayer, we can perceive more negative photocurrent densities than in the case of bare FTO/Cu₂O electrode. The photocurrent density is in all case of FTO/Cu₂O/zeolites electrodes more negative than -0.35 mA/cm^2 , even after the 2 hour measurement. For FTO/Cu₂O/*BEA we can notice the least amount of noise when compared with other electrodes. In the case of overlayer of mesoporous materials the photocurrent density is not as negative as in the case of electrodes covered with zeolitic materials. Both of the electrodes covered with mesoporous materials produced almost zero photocurrent density after the 2 hours of the measurement, similar to bare FTO/Cu₂O electrode. Overall, the electrodes covered with mesoporous materials do not produce as negative photocurrent densities as the electrodes with zeolitic overlayer do.

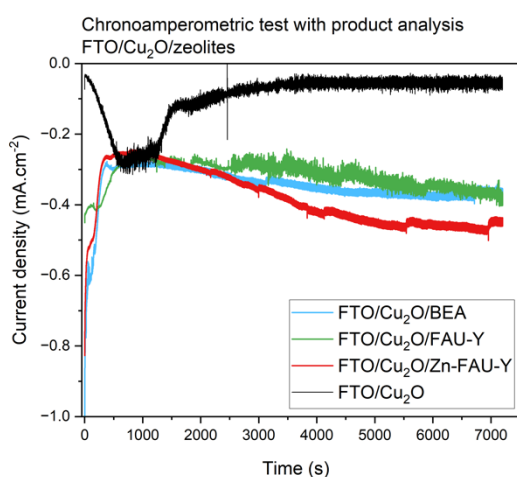


Figure 50: Comparison of chronoamperometric tests for electrodes covered with zeolites.

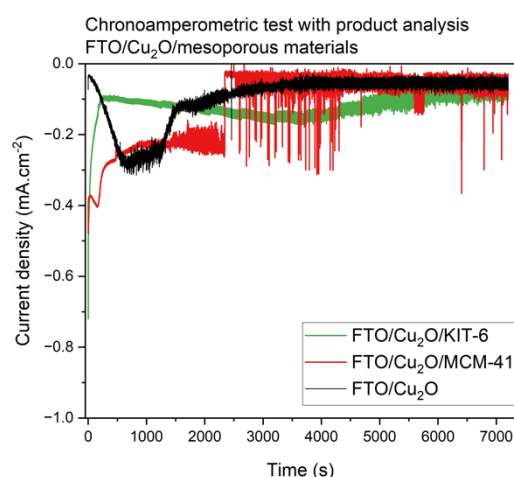


Figure 51: Comparison of chronoamperometric tests for electrodes covered with mesoporous materials.

XRD analysis was performed on all the prepared electrodes (denoted BR – before reaction) and also after the chronoamperometric test (denoted AR – after reaction). The diffraction pattern was in all cases compared with the patterns of the clean FTO glass, the bare FTO/Cu₂O and theoretical patterns of CuO, Cu₂O and Cu.

After the chronoamperometric test of the bare FTO/Cu₂O electrode (see Figure 52), a characteristic peak for metallic Cu can be observed (see Figure 52 highlighted with the dashed line). It suggests the reduction of the Cu₂O to Cu, meaning the photodegradation of the material.

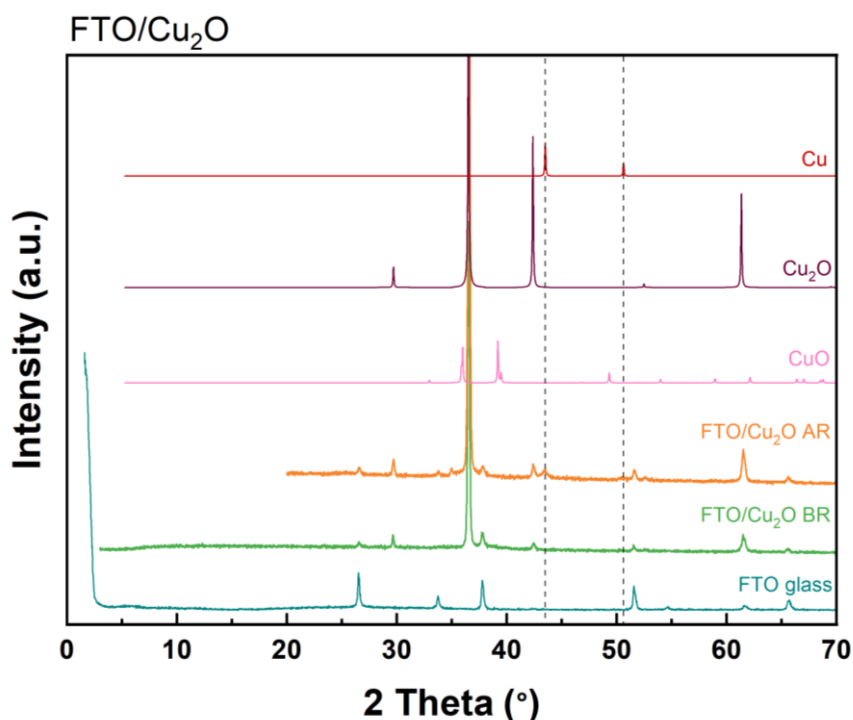


Figure 52: XRD analysis of FTO/Cu₂O electrode before (BR) and after (AR) the chronoamperometric tests compared with FTO glass, CuO, Cu₂O and Cu theoretical patterns.

The bare FTO/Cu₂O electrode was characterized via SEM before and after the chronoamperometric measurement to observe the photocorrosion process (see Figure 53). Before the measurement (on the left) the individual crystals appear polyhedral well-defined shape. After the measurement (on the right), the presence of reduced Cu is prominent. Cu can be perceived as the cubes sitting on top of pattern observed for pure Cu₂O layer.

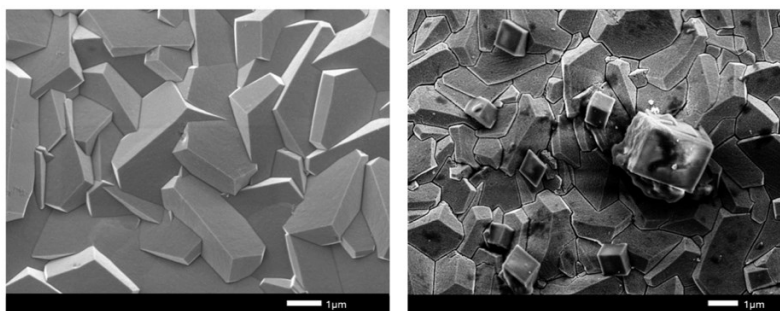


Figure 53: SEM images of deposited Cu_2O layer from top-view before (on the left) and after (on the right) the chronoamperometric measurement.

The FTO/ Cu_2O /porous materials electrodes were photographed before and after the measurement to visually assess the level of photodegradation.

In the XRD pattern of the FTO/ Cu_2O /*BEA electrode before the measurement, the characteristic peaks for Cu_2O and also the diffraction pattern for *BEA can be noted (see Figure 54, left). The XRD pattern after the measurement, shows the same characteristic diffraction peak for metallic Cu. It suggests the reduction of the Cu_2O to Cu, which was visually confirmed when the parent orange colour of Cu_2O turned into dark grey/black colour (see Figure 54, right). Interestingly, in the XRD pattern for electrode after the measurement, the presence of additional unidentified peaks can be noted. These peaks might be a result of crystallized particles from electrolyte (for instance K_2SO_4), since the photo of the electrode after the measurement, shows the light whitish layer on the surface of the electrode, which was in direct contact with the electrolyte.

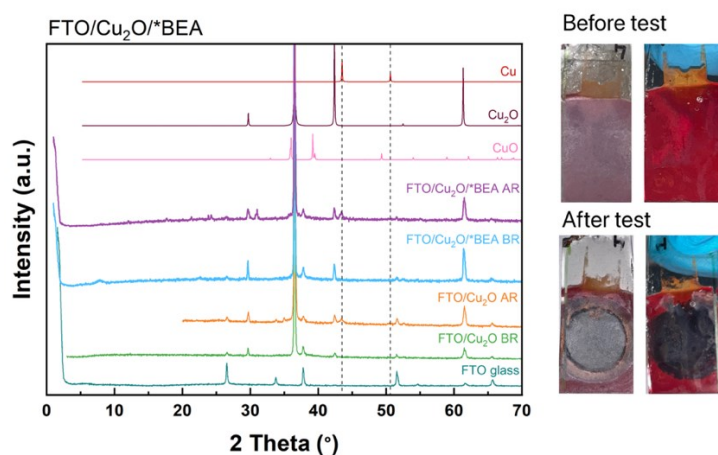


Figure 54: XRD analysis of FTO/ Cu_2O /*BEA electrode before (BR) and after (AR) the chronoamperometric measurement compared with FTO glass, CuO, Cu_2O and Cu theoretical patterns. On the right, the photos of the electrode from the front and back side before and after the measurement.

In the XRD pattern of the FTO/Cu₂O/FAU-Y electrode before the measurement, characteristic peaks for Cu₂O can be perceived (see Figure 55, left). Besides that, the diffraction pattern for FAU-Y can be also observed in both XRD pattern before and after the measurement. The XRD analysis after the measurement revealed the characteristic peaks for metallic Cu, which confirmed the photodegradation of the material. Photodegradation can be also visually corroborated in the Figure 55 on the right by the change of colour of parent Cu₂O from orange to shiny metallic copper red/brown colour after the measurement.

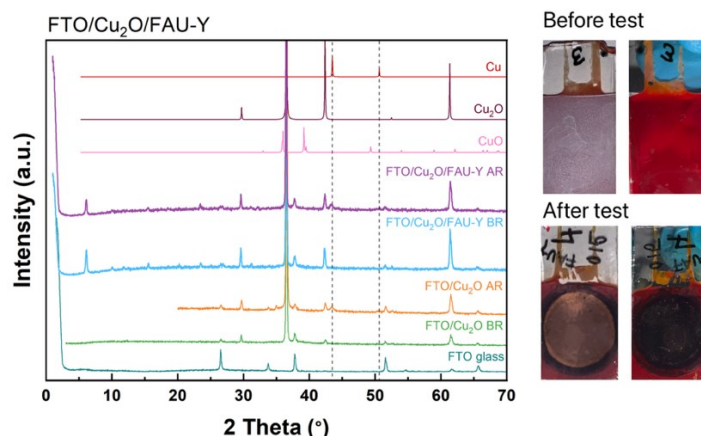


Figure 55: XRD analysis of FTO/Cu₂O/FAU-Y electrode before (BR) and after (AR) the chronoamperometric measurement compared with FTO glass, CuO, Cu₂O and Cu theoretical patterns. On the right, the photos of the electrode from the front and back side before and after the measurement.

In the XRD pattern of FTO/Cu₂O/Zn-FAU-Y electrode before the measurement both the XRD patterns for Cu₂O and Zn-FAU-Y material can be noted (see Figure 56, left). The XRD pattern after the measurement revealed the same characteristic diffraction peak for metallic Cu, which is confirming the photodegradation process happening in the material. Photodegradation can be also seen visually in the Figure 56, right, when the parent Cu₂O changed the colour from orange to dark grey/black. The layer of metallic Cu is not obvious from the top because the layer of Zn-FAU-Y is relatively thick.

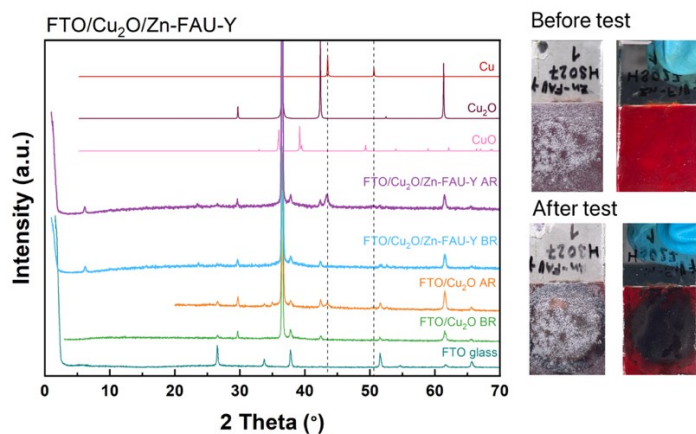


Figure 56: XRD analysis of FTO/Cu₂O/Zn-FAU-Y electrode before (BR) and after (AR) the chronoamperometric measurement compared with FTO glass, CuO, Cu₂O and Cu theoretical patterns. On the right, the photos of the electrode from the front and back side before and after the measurement.

In the XRD pattern of FTO/Cu₂O/MCM-41 electrode before the measurement, the prominent peaks for Cu₂O can be noted (see Figure 57, left). The XRD pattern for MCM-41 cannot be observed as in the case of zeolitic overlayer, because the amount of spray-coated MCM-41 was generally lower than in the case of zeolites. This fact can be also visually validated via photos of the electrodes before the measurement (see Figure 57, right), where the spray-coated layer of MCM-41 cannot be seen like in the case of zeolites. Therefore, the width of the MCM-41 layer might be under the detection limit of used XRD. From the XRD pattern of electrode after the measurement, the same characteristic diffraction peak for metallic Cu can be observed, proving the photodegradation of the Cu₂O. Photodegradation can also be seen visually in the Figure 57, right.

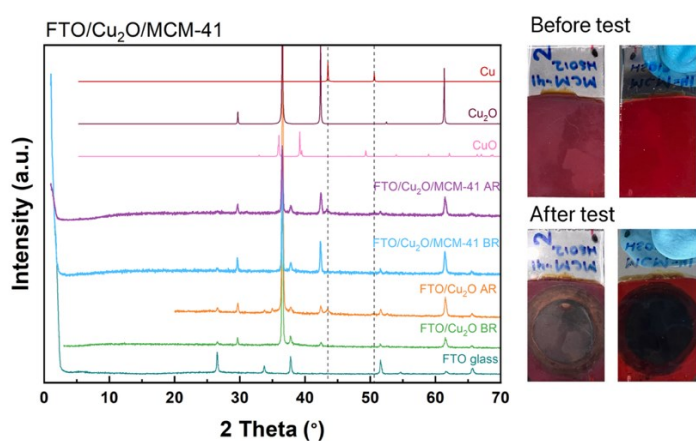


Figure 57: XRD analysis of FTO/Cu₂O/MCM-41 electrode before (BR) and after (AR) the chronoamperometric measurement compared with FTO glass, CuO, Cu₂O and Cu theoretical patterns. On the right, the photos of the electrode from the front and back side before and after the measurement.

In the XRD pattern of the FTO/Cu₂O/KIT-6 electrode (see Figure 58) before the measurement the pattern for Cu₂O can be clearly perceived. However, the XRD pattern for KIT-6 cannot be seen in the samples. It is caused by the thin layer of KIT-6 spray-coated on the electrode, which was the standard problem in case of both mesoporous materials. The absence of XRD pattern might be caused by the width of the KIT-6 being under the detection limit of used XRD. The XRD analysis after the measurement revealed the same characteristic diffraction peak for metallic Cu, which proves the photodegradation. Photodegradation can be also visually verified in the Figure 58, right. The colour change from the parent orange Cu₂O changed after the measurement to shiny metallic copper red/brown colour.

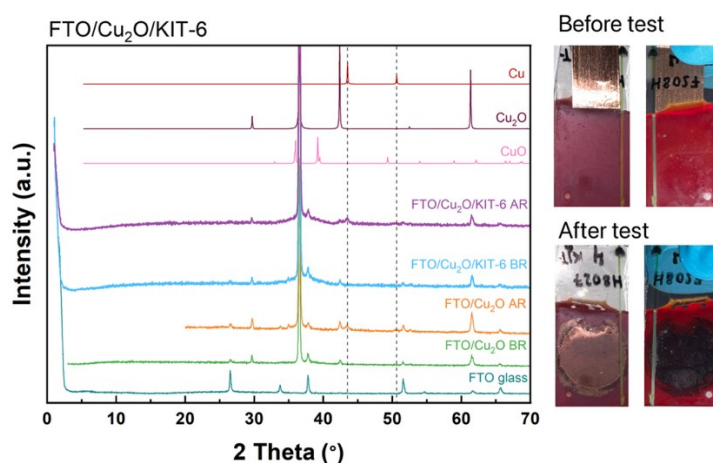


Figure 58: XRD analysis of FTO/Cu₂O/KIT-6 electrode before (BR) and after (AR) the chronoamperometric measurement compared with FTO glass, CuO, Cu₂O and Cu theoretical patterns. On the right, the photos of the electrode from the front and back side before and after the measurement.

5.4.3. Product analysis

5.4.3.1. Gas Chromatography (GC)

The GC analysis was performed in two ways: I) the analysis of gas phase present in the reactor (HP-molesieve and PoraBOND Q columns connected in series with TCD detector) and II) the analysis of the liquid phase (electrolyte) by heating the electrolyte up to 90 °C and injecting the gas headspace (VF-WAXms column with FID detector). The liquid electrolyte cannot be directly injected into the GC due to the possible damage of the column.

For the analysis of the liquid phase (electrolyte) four compounds were chosen for calibration. Two common products of PEC CO₂RR are methanol and ethanol. Acetone as a common air-contaminant and isopropanol as a possible residue of the Nafion solution used

during spray-coating, have been considered as well (see Figure 59). The compounds were calibrated by determination of their retention times and establishing calibration curves at various concentrations for quantitative analysis.

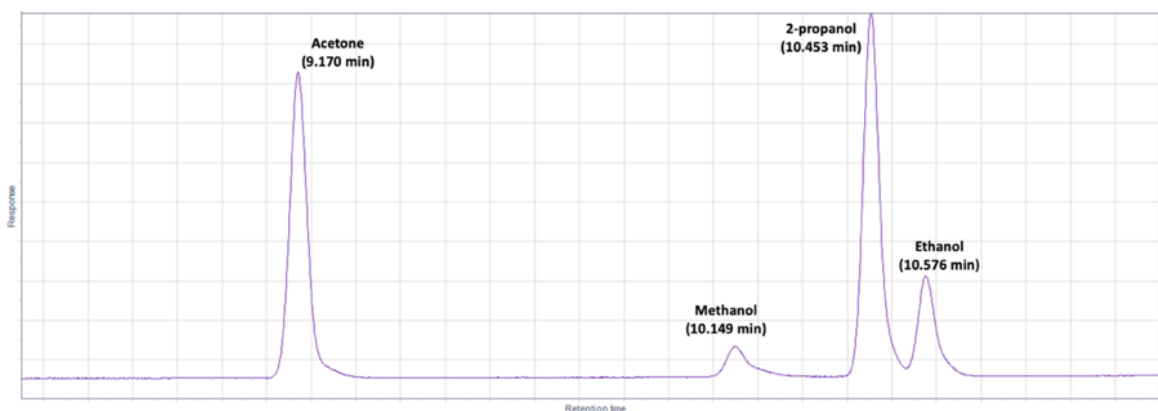


Figure 59: GC calibration mixture of chosen organic compounds.

Firstly, the GC analysis of the gas phase did not show presence of any products. Either no detectable gas phase products were formed, or it might be a result of a leakage from the reactor or the closed gas circuit. Only CO₂ as a reactant and air gases (nitrogen and oxygen), were determined.

For all the tested electrolytes the GC analysis showed two peaks at a retention time approximately 5.4 min and 11.6 min. These two peaks were observed even in the blank test of the pure deionized water used for electrolyte preparation and also in the blank test of the air from the laboratory. However, the blank test without injection did not reveal any peaks. Therefore, these two peaks have been considered some kind of contamination from the air in the laboratory, in which the PEC apparatuses and GC instrument are located.

In the case of liquid phases GC analysis, the results of quantitative analysis are summarized in the Table 7. Unfortunately, most of the measured areas of the peaks were below the lowest point of the calibration curve, and therefore they cannot be approached with complete certainty.

Table 7: The amounts of produced calibrated chemicals obtained in the analysis of electrolytes after chronoamperometric tests via GC. The values denoted in red were below the lowest point of the calibration curve. The values denoted in the green were in the calibration range.

Electrode	Acetone (ppm)	Ethanol (ppm)	Methanol (ppm)
FTO/Cu ₂ O	2.6	9.7	—
FTO/Cu ₂ O/*BEA	2.8	4.1	6.2
FTO/Cu ₂ O/FAU-Y	2.6	—	—
FTO/Cu ₂ O/Zn-FAU-Y	2.6	5.4	—
FTO/Cu ₂ O/MCM-41	—	—	—
FTO/Cu ₂ O/KIT-6	4.19	4.6	3.2

The results are always compared to the result of the bare FTO/Cu₂O electrode (see Figure 60d and Figure 61c). In the case of bare FTO/Cu₂O electrode, we detected considerable peak for ethanol (corresponding to approximately 9.7 ppm) and a peak for acetone.

In the Figure 60, the chromatograms of FTO/Cu₂O/zeolites electrodes are compared. In the case of FTO/Cu₂O/*BEA electrode (see Figure 60a), peaks for acetone, methanol and ethanol were identified based on their retention times. Besides the identified peaks, another 3 unknown peaks can be perceived in the chromatogram with the approximate retention times: 11.3, 12.2 and 15.1 min.

In the case of FTO/Cu₂O/FAU-Y electrode (see Figure 60b) only the peak for acetone can be observed.

In the case of FTO/Cu₂O/Zn-FAU-Y electrode (see Figure 60c) the peak for ethanol is visible with high intensity (corresponding to approximately 5.4 ppm) and a peak for acetone can be seen. Besides the identified peaks also an unknown peak around 5.7 min retention time is visible. The short retention time suggest that it might be a volatile substance.

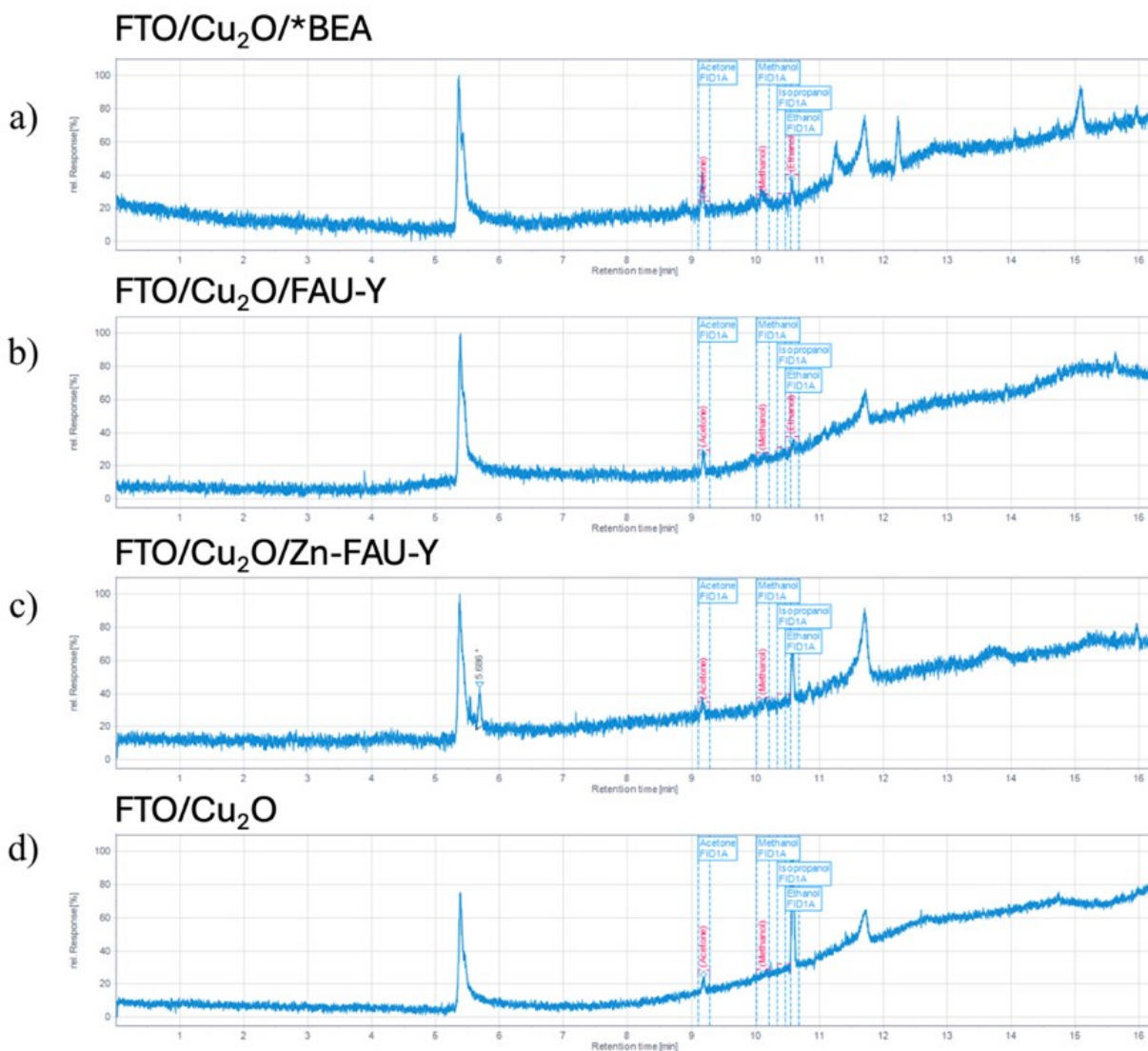


Figure 60: GC analysis of the electrolyte after the chronoamperometric measurements of electrodes spray-coated with zeolites: a) FTO/Cu₂O/*BEA b) FTO/Cu₂O/FAU-Y electrode, c) FTO/Cu₂O/Zn-FAU-Y electrode, d) FTO/Cu₂O electrode.

The same analysis of the electrolyte was also performed for the electrodes FTO/Cu₂O covered with the mesoporous materials. In the case of FTO/Cu₂O/KIT-6 electrode (see Figure 61a) three identified peaks (acetone, methanol and ethanol) can be observed in the small intensities. Besides these peaks, also one more peak with retention time around 5.6 min can be seen (the same peak as seen in the case of FTO/Cu₂O/Zn-FAU-Y, see Figure 60c). Low retention time suggests that it could be some volatile organic substance. In the case of FTO/Cu₂O/MCM-41 electrode (see Figure 61b) only a peak for acetone with small intensity can be noted.

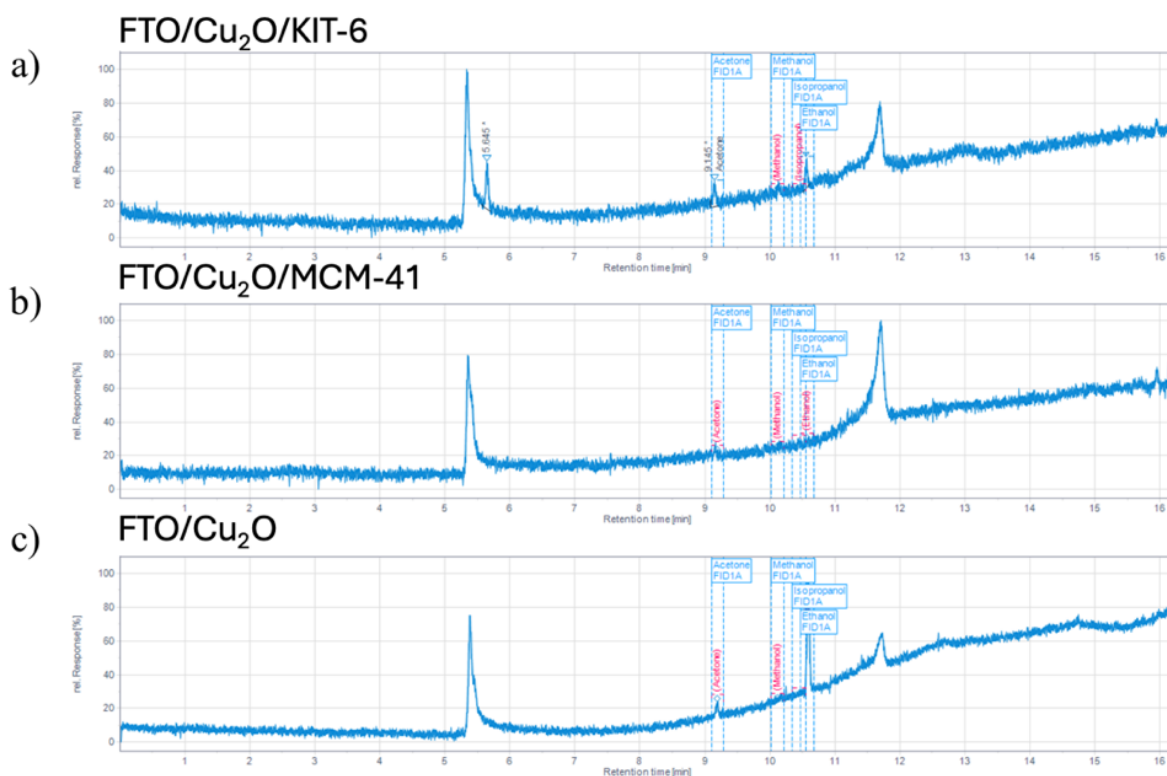


Figure 61: GC analysis of the electrolyte after the chronoamperometric measurements of a) FTO/Cu₂O/KIT-6 electrode, b) FTO/Cu₂O/MCM-41 electrode, c) FTO/Cu₂O electrode.

GC analysis can be further complemented with the ¹H NMR spectroscopy to determine other produced non-volatile compounds and unidentified compounds observed in the chromatograms.

5.4.3.2. Proton nuclear magnetic resonance (¹H NMR)

¹H NMR spectroscopy analysis was performed from the electrolyte after the chronoamperometric measurements. The pure electrolyte was analysed as well to detect possible contaminants (see Figure 62). The calibration of this method was again done similarly to GC, via preparation of the solutions of common products/contaminants (methanol, ethanol, isopropanol, acetone, lactic acid, acetic acid and formic acid) in the used electrolyte. The chemical shifts distinguished in the real samples were then compared with the chemical shifts of individual compounds in these standard solutions. All standard solutions were prepared in the electrolyte solution (0.5M KHCO₃, 0.5M K₂SO₄). It is important to note that the electrodes FTO/Cu₂O/*BEA and FTO/Cu₂O/FAU-Y were tested in the different batch of electrolyte solution than the rest of the electrodes (FTO/Cu₂O/Zn-FAU-Y, FTO/Cu₂O/MCM-41 and FTO/Cu₂O/KIT-6). Consequently, the

electrolyte measured on ^1H NMR, was the one used for the rest of the electrodes (FTO/ Cu_2O /Zn-FAU-Y, FTO/ Cu_2O /MCM-41 and FTO/ Cu_2O /KIT-6).

No signals were observed with the chemical shift above 5 ppm, what discards the presence of hydrogen linked directly to carbonyl or carboxyl groups. The spectrum was divided into 4 ranges of chemical shift (4.5 – 3.0, 2.5 – 1.5, 1.55 – 1.0 and 1.0 – 0 ppm) to perceive existing peaks more closely.

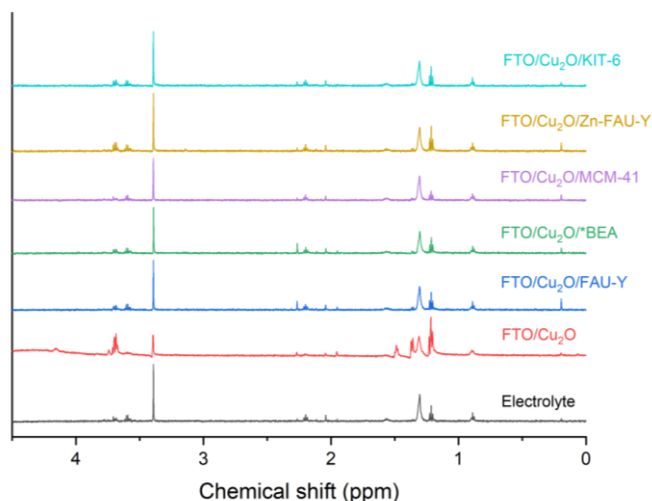


Figure 62: Spectra of ^1H NMR analysis of all prepared multicomponent electrodes, as well as bare FTO/ Cu_2O electrode and pure electrolyte.

In the range of 4.5 – 3.0 ppm chemical shift (see Figure 63), a singlet at 3.39 ppm (corresponding to methanol) and a quartet at 3.69 ppm (from ethanol) can be observed in all the samples, including the electrolyte. Since the signals for methanol and ethanol are of similar intensities as in the pure electrolyte, it can be assumed that these peaks are contaminants. However, the quartet corresponding to ethanol seems to be of higher intensity in the case of bare FTO/ Cu_2O electrode. Together with results from GC (see Figure 60d), it confirms the formation of ethanol in the PEC CO_2RR process over the FTO/ Cu_2O . The quartet seems to be also of a higher intensity in the case of the FTO/ Cu_2O /Zn-FAU-Y electrode. It is consistent with the GC analysis of the electrolyte where peak for ethanol was clearly distinguished (see Figure 60c).

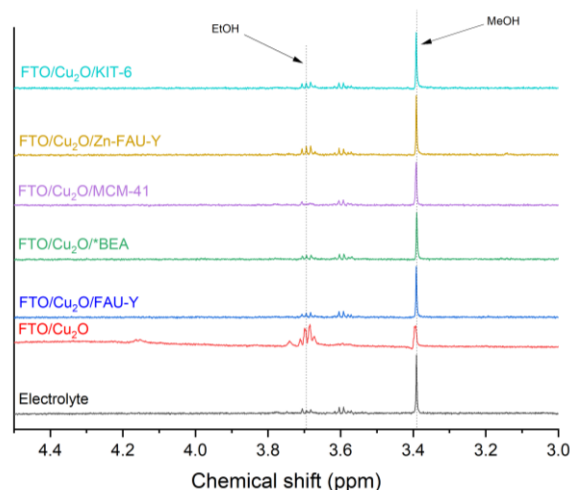


Figure 63: ^1H NMR spectra for all the prepared electrodes in the range of chemical shift of 4.5 – 3.0 ppm.

In the range of 2.5 – 1.5 ppm chemical shift (see Figure 64), the presence of singlet at 2.26 ppm (coming from acetone) seems to be of higher intensities in the case of electrodes, when compared with the pure electrolyte. This peak has the highest intensities in the case of FTO/Cu₂O/*BEA and FTO/Cu₂O/FAU-Y electrodes, however, these two electrodes were tested in the different electrolyte than the rest of the electrodes. Notably, to prevent contamination of the electrolyte by acetone from the operator's breath, we routinely wear a respirator during handling of the electrolyte and samples. Still, we can observe amounts in level of ppm in all samples but in similar concentrations, which would indicate the air contamination (see Table 7).

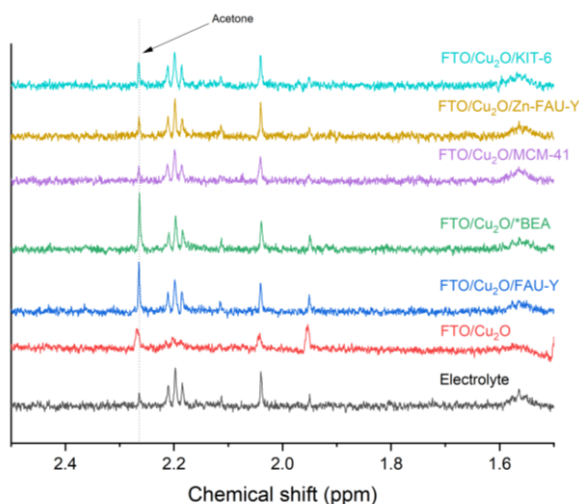


Figure 64: ^1H NMR spectra for all the prepared electrodes in the range of chemical shift of 2.5 – 1.5 ppm.

In the range of 1.5 – 1.0 ppm (see Figure 65), multiple peaks can be observed. First, a triplet at close to 1.5 ppm, which has not been identified yet. This signal is only present in the bare FTO/Cu₂O electrode. Another doublet at 1.36 ppm corresponds to lactic acid/lactate and is mostly visible in the case of bare FTO/Cu₂O electrode. After revision of the protocol done for this particular sample, we confirmed that the presence of lactic acid/lactate is the result of contamination. Also, this conclusion was further confirmed by another team member via blank tests – bare FTO/Cu₂O was tested in Ar saturated electrolyte in PEC condition. The ¹H NMR analysis of the electrolyte from this blank test did not show any lactic acid/lactate nor ethanol present in the sample. Thus, the results confirm that the only product over bare FTO/Cu₂O is ethanol. In the case of all other electrodes, this doublet (corresponding to lactic acid/lactate) is only of minimal intensities if at all.

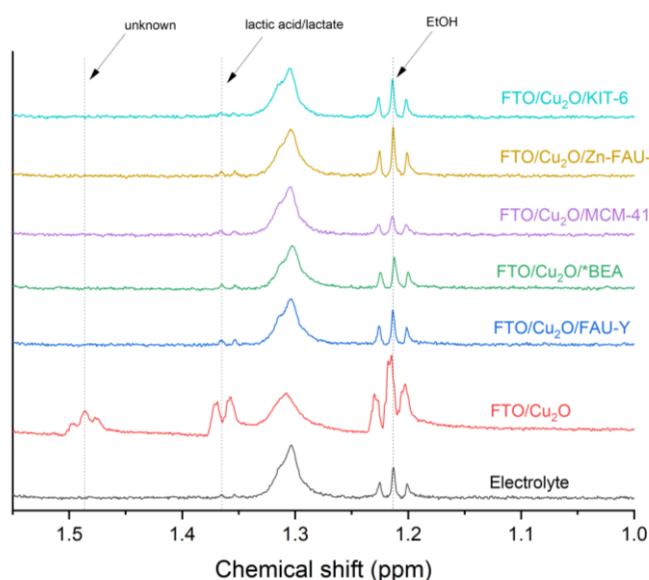


Figure 65: ¹H NMR spectra for all the prepared electrodes in the range of chemical shift of 1.55 – 1.0 ppm.

In the range of 1.0 – 0 ppm chemical shift (see Figure 66), there is a triplet at 0.88 ppm with similar intensities in all the samples and therefore it is assumed to come from unknown impurity of the electrolyte. Another singlet can be observed at 0.19 ppm in all samples but with different intensities. It is practically negligible in the pure electrolyte; therefore, it might come from CO₂RR. Since it has a low chemical shift, it is assumed that it comes from H that is far from any electronegative group or multiple C-C bonds, meaning that it comes from an aliphatic compound. The peak being a singlet, suggests that there are no adjacent C with H. This singlet might also be a result of silicone fat used in the ¹H NMR apparatuses.

Nevertheless, the nature of this compound must be further confirmed and investigated by repeating the experiments and combination of GC, ^1H NMR, and GC-MS.

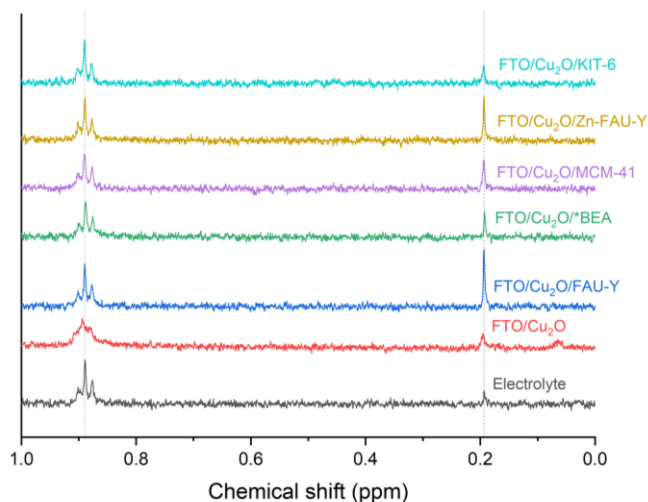


Figure 66: ^1H NMR spectra for all the prepared electrodes in the range of chemical shift of 1.0 – 0 ppm.

To conclude the results of product analysis, the electrode with bare FTO/ Cu_2O produced ethanol (in the amount approximately 9.7 ppm), which was confirmed by both GC and ^1H NMR analysis method.

In the case of FTO/ Cu_2O /Zn-FAU-Y electrode, the GC showed the production of ethanol in considerable amount (around 5 ppm), which was also corroborated via ^1H NMR analysis. The GC analysis of FTO/ Cu_2O /Zn-FAU-Y revealed another peak at retention time of 5.6 min, which was also observed in the case of FTO/ Cu_2O /KIT-6. Its identification has been in progress. In the case of FTO/ Cu_2O /KIT-6 electrode the ethanol was also revealed in small concentration (below 4.5 ppm) through GC analysis.

It is also important to note that the amounts of produced chemicals are in ppm level because the overall volume of electrolyte in the reactor is only about around 50 ml. Additionally, the tests ran only for 2 hours. Another significant note to consider is the small exposed area of the electrode (constantly 0.71 cm^2) together with the amount of individual layers of prepared electrodes, since as afore-mentioned it has a direct impact on the efficiency of the electrode.

6. Conclusion

The purpose of this thesis was the enhancement of the catalytic properties of Cu_2O , which was employed as the photoactive material for PEC CO_2RR . The series of porous materials (microporous zeolites and mesoporous silica materials) were used as a protective overlayer over the Cu_2O .

Cu_2O electrodes were successfully prepared via electrodeposition on the FTO glass from the Cu^{2+} solution of $\text{pH} = 10.5$ under applied potential of 0.36 V vs RHE for 30 minutes. The average coverage of FTO was in the range of $3.5 \text{ mg/cm}^2 - 5.0 \text{ mg/cm}^2$.

The porous materials, both microporous (*BEA, FAU-Y and Zn-FAU-Y) and mesoporous (MCM-41 and KIT-6) were synthesized through hydrothermal synthesis. The crystallization time was optimized for individual syntheses (mainly in the case of FAU type materials). The materials were then thoroughly characterized via various methods, including PXRD, adsorption of nitrogen, SEM, EDX, ICP-MS and in the case of Zn-FAU-Y also STEM. All the syntheses were through characterization confirmed as successful. The surface area and pore volume of the synthesized zeolites *BEA and FAU-Y correlated with the reported values. However, in the case of the Zn-FAU-Y, it exhibited nearly half the BET surface area ($S_{\text{BET}} = 330 \text{ m}^2/\text{g}$) and pore volume ($V_{\text{total}} = 0.20 \text{ cm}^3/\text{g}$), when compared with the synthesized FAU-Y ($S_{\text{BET}} = 731 \text{ m}^2/\text{g}$, $V_{\text{total}} = 0.37 \text{ cm}^3/\text{g}$). The synthesis was therefore repeated with the seeding method. Unfortunately, the results of nitrogen adsorption for seeded Zn-FAU-Y were even worse ($S_{\text{BET}} = 211 \text{ m}^2/\text{g}$, $V_{\text{total}} = 0.10 \text{ cm}^3/\text{g}$) than the non-seeded Zn-FAU-Y. From the Si/Zn molar ratio obtained from ICP analysis, it was noted that the seeded sample contained more Zn than the non-seeded one ($\text{Si}/\text{Zn}_{\text{non-seeded}} = 13.1$ vs $\text{Si}/\text{Zn}_{\text{seeded}} = 9.60$). The XRD pattern indicated only the presence of faujasite structure. The STEM and EDX elemental mapping also corroborated that Zn is not aggregated in the form of some clusters (like ZnO), but rather it is uniformly distributed through the material. Therefore, further analysis of the material, and possibly repeated synthesis would be needed to explain the decreased surface area and pore volumes in this zincoaluminosilicate counterpart of FAU-Y.

Regarding the PEC characterization of the prepared multicomponent electrodes, it was done through two types of tests: linear sweep voltammetry (LSV) and chronoamperometric

tests paired with product analysis afterwards. The results from LSV tests showed that all prepared multicomponent electrodes produced less negative photocurrent densities than bare FTO/Cu₂O, but significantly reduced the charge recombination spikes which are prominent in the case of bare Cu₂O. The most promising results produced the electrodes with overlayer of materials *BEA, Zn-FAU-Y and MCM-41.

The long-term photocurrent stability was assessed via chronoamperometric tests. Unlike the bare FTO/Cu₂O, the electrodes with a zeolitic overlayer produced more negative photocurrent densities (lower than -0.35 mA/cm^2), being consistent during the 2-hour measurement. In the case of mesoporous materials overlayer the photocurrent densities came close to the 0 mA/cm^2 by the end of the measurement (similar results as for bare FTO/Cu₂O).

The product analysis after the chronoamperometric measurement was done by GC analysis of gas and liquid phase (electrolyte) from the cathodic compartment of the reactor and by ¹H NMR of the electrolyte. No products were observed in the GC analysis of the gas phase. In the case of electrolyte from bare FTO/Cu₂O electrode, the formation of ethanol in amount around 9.7 ppm was confirmed by both the GC and the ¹H NMR.

In the case of FTO/Cu₂O/Zn-FAU-Y electrode, the GC revealed the amount around 5 ppm of formed ethanol, which was also supported via ¹H NMR. The GC analysis of FTO/Cu₂O/Zn-FAU-Y revealed another peak at retention time of 5.6 min, which was also observed in the case of FTO/Cu₂O/KIT-6. Its identification has been in progress. In the case of FTO/Cu₂O/KIT-6 electrode, the GC revealed also the formation of ethanol in amount below 4.5 ppm.

The outcome of this research showed that the overlayer of crystalline microporous zeolites have larger impact on the photostability of the Cu₂O when compared with the overlayer of mesoporous materials. The protective overlayer of *BEA zeolite, with 12-membered pore rings and 3D channel system, significantly reduced the presence of charge recombination spikes in the LSV measurements suggesting faster charge transfer and surface reaction with CO₂. The electrode FTO/Cu₂O/*BEA also exhibited stable value of photocurrent density throughout the 2-hour chronoamperometric measurement reaching -0.35 mA/cm^2 . The overlayer of Zn-FAU-Y having 12-membered pore rings, 3D channel system and supercages, also improved the photostability of Cu₂O, with comparable results

to overlayer of *BEA. Interestingly, the performance was similar despite significantly lower surface area and pore volumes of FTO/Cu₂O/Zn-FAU-Y. Moreover, the protective overlayer of zeolite *BEA changed the distribution of the products formed during the CO₂RR PEC – from ethanol in the case of the bare FTO/Cu₂O to both ethanol and methanol when covered with *BEA zeolite. It points to the effect of microporous material present on the surface of photoactive Cu₂O on the reaction mechanism. This topic will be studied as the subject of the future research.

7. References

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