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Synthesis of new materials for photo-electrocatalytic reduction of CO₂

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Příprava nových materiálů pro foto-elektrokatalytickou redukci CO₂

Bakalářská práce

Vedoucí práce:

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Praha, 2025

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Abstract

This bachelor's thesis is based on research of new composite materials serving as photo-electrocatalysts for conversion of carbon dioxide into value-added products, solar fuels. Since CO₂ is a prominent greenhouse gas and its excessive emissions are proved to cause global warming, it is crucial to pay a sufficient attention to this topic. In this work, copper (I) oxide was investigated as a photoresponsive material due to (a) its ability to be photoexcited by visible light and (b) its suitable redox potential for CO₂ reduction. The main goal is to overcome the limitations of Cu₂O such as photocorrosion and fast charge recombination. In this regard, this study investigates Cu₂O and TiO₂ *p,n*-heterojunctions, enhanced with non-precious metal-based co-catalysts, multilayered titanium-based MXenes (ml-Ti₃C₂T_x). The research is focused on how the formation of TiO₂ on surface of Ti₃C₂T_x affects the overall performance of multicomponent photocathode in CO₂ reduction reaction (CO₂RR).

The composite photocatalysts were prepared by first electrodepositing Cu₂O over fluorine-doped tin oxide glass support (FTO) and further coating this layer with a layer of TiO₂-ml-Ti₃C₂T_x material. The composite consisting of TiO₂ particles and multilayered Ti₃C₂T_x was prepared by treating Ti₃C₂T_x MXene under varying atmospheres at temperatures above 350°C. This heat treatment led to the *in situ* formation of TiO₂ particles directly on the MXene surface. To characterize the prepared composites, the following methods were utilized: X-ray diffraction, N₂ adsorption, X-ray photoelectron spectroscopy, UV-Vis spectroscopy, and scanning electron microscopy.

Series of photocathodes were assembled and further tested by linear sweep voltammetry and chronoamperometric tests using a 300W Xe-lamp (equipped with 1.5 AM global and UV filter to simulate the natural solar light) in a 0.5M K₂SO₄, 0.5M KHCO₃ electrolyte, saturated with argon or CO₂. Product analysis was conducted under photo-electrocatalytic conditions after 2 hours of irradiation using gas chromatography with TCD and BID detectors.

CO₂RR product analysis revealed that the FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x - 350 °C_N₂ flow photocathode provides CO and acetic acid. This research has brought initial promising results regarding the application of Ti-based MXenes as a cover layer for visible-light-responsive Cu₂O.

Key words: Photo-electrocatalysis, carbon dioxide, copper (I) oxide, MXene, *p,n*-heterojunction semiconductors, solar fuels

Abstrakt

Tato bakalářská práce je založena na výzkumu nových kompozitních materiálů sloužících jako foto-elektrokatalyzátory pro přeměnu oxidu uhličitého na energeticky hodnotné produkty, solární paliva. Vzhledem k tomu, že CO_2 je významným skleníkovým plynem a jeho nadměrné emise prokazatelně způsobují globální oteplování, je nezbytné věnovat tomuto tématu dostatečnou pozornost. V této práci byl zkoumán oxid měďný jako fotoresponzivní materiál z důvodu (a) jeho schopnosti být fotoexcitován viditelným světlem a (b) jeho vhodnému redoxnímu potenciálu pro redukci CO_2 . Hlavním cílem práce je eliminovat nevýhody Cu_2O jako je fotokoroze a rychlá rekombinace náboje. Za tímto účelem se tato práce zabývá *PN* přechodem mezi Cu_2O a TiO_2 , za přítomnosti kokatalyzátoru, který neobsahuje ušlechtilý kov, ale je založen na bázi MXenu (karbidu titanu), konkrétně $\text{ml-Ti}_3\text{C}_2\text{T}_x$. Tato závěrečná práce zkoumá, jak formace TiO_2 na povrchu $\text{Ti}_3\text{C}_2\text{T}_x$ ovlivňuje celkové chování a efektivitu vícesložkové fotokatody při redukční reakci CO_2 (CO_2RR).

Kompozitní fotokatalyzátory byly připraveny v rámci několika kroků, počínaje elektrodopozicí Cu_2O na sklíčko pokryté oxidem cíničitým dopovaným fluorem. Dalším krokem bylo pokrytí vzniklého nosiče s katalyzátorem vrstvou kompozitního materiálu $\text{TiO}_2\text{-ml-Ti}_3\text{C}_2\text{T}_x$, který byl připraven modifikací MXenu $\text{Ti}_3\text{C}_2\text{T}_x$ v různých atmosférách při teplotách nad 350°C . Vystavení materiálu vysokým teplotám vedlo k *in situ* tvorbě částic TiO_2 přímo na povrchu MXenu. K charakterizaci připravených kompozitních materiálů byly použity následující metody: rentgenová difrakce, adsorpce N_2 , rentgenová fotoelektronová spektroskopie, UV-Vis spektroskopie a skenovací elektronová mikroskopie.

Zkoumané fotokatody byly po sestavení dále testovány pomocí lineární voltametrie a chronoamperometrických testů s použitím 300W Xe-lampy (vybavené 1,5 AM globálním a UV filtrem pro simulaci přirozeného slunečního světla) v 0.5M K_2SO_4 , 0.5M KHCO_3 elektrolytu nasyceném argonem nebo CO_2 . Analýza produktu byla provedena po 2 hodinách ozařování za foto-elektrokatalytických podmínek pomocí plynové chromatografie s TCD a BID detektory.

Tyto experimenty ukázaly, že fotokatoda $\text{FTO/Cu}_2\text{O/TiO}_2\text{-ml-Ti}_3\text{C}_2\text{T}_x$ - 350°C - N_2 flow poskytuje CO a kyselinu octovou. Závěrem lze říci, že tento výzkum přinesl první slibné výsledky týkající se použití titanových MXenů jako krycí vrstvy pro Cu_2O , materiál excitovatelný viditelným světlem.

Klíčová slova: Foto-elektrokatalýza, oxid uhličitý, oxid měďný, MXeny, *PN* přechody v polovodičích, solární paliva

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List of Abbreviations

2D	Two-dimensional
Ac	Acetate
CB	Conduction band
CO ₂ RR	CO ₂ reduction reaction
EC	Electrocatalysis
E _F	Fermi level
FE	Faraday efficiency
FTO	fluorine doped tin (IV) oxide
GC	Gas chromatography
HDPP	High-density polypropylene
HER	hydrogen evolution reaction
LSV	Linear sweep voltammetry
ml-	multilayered
MSE	Mercury sulphate electrode, Hg/Hg ₂ SO ₄
NHE	Normal Hydrogen Electrode
NMR	Nuclear magnetic resonance
PC	Photocatalysis
PEC	Photo-electrocatalysis
PPE	Personal protective equipment
PTFE	polytetrafluorethylene
PVC	Polyvinylchloride
PVDF	Polyvinyl difluoride
PXRD	X-ray powder diffraction
RHE	Reversible hydrogen electrode
sat.	saturated
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
UV-Vis	Ultraviolet-visible
VB	Valence band
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

1 Introduction

Due to the rapid industrial development since the Industrial Revolution, CO₂ emissions have been increasing at an unsustainable rate, even though scientists have been warning the public about the potentially catastrophic consequences for more than sixty years.¹ The emissions of CO₂ have increased from 16Gt in 1970 to 37.8 Gt in 2024.^{2,3} It has been proven that CO₂ creates 70 % of the greenhouse gas worldwide and it is general knowledge that greenhouse gas excess causes global warming.² This large environmental issue further leads to other problems as glacier melting, sea-level rise, and ocean acidification.

Besides the problems described from an ecological point of view, there are other challenges from an economical and practical point of view in general in a very close connection. This is the lack of C-sources, as the fossil C-sources are certainly not infinite, while there is an increasing demand for them.

This work focuses on the development of a catalyst for the conversion of CO₂ into value-added products, which could be an effective solution to the mentioned problems. Utilization of CO₂ as a source of carbon is one of the possible strategies to mitigate its impact on the environment. Photo-electrocatalytic CO₂ reduction is one of the attractive approaches producing so-called solar fuels. In this application, a catalyst is a part of a photoelectrode. Utilization of produced solar fuels on a larger scale instead of their fossil fuel alternatives could contribute to diminishing global warming and the shortage of carbon sources.

Many photocatalytic studies have focused on TiO₂-based materials, which require UV light for photoexcitation. This work focuses on developing a composite catalyst capable of driving the reaction under the visible part of natural sunlight. The photoactivity of the catalyst is provided by copper (I) oxide (*p*-type semiconductor). The main advantages of Cu₂O are its ability to be photoexcited by a visible part of electromagnetic spectra thanks to its convenient band gap of 2-2.2 eV, as well as its suitable conduction band potential for CO₂ reduction to various products.⁴ However, there are also a few drawbacks, such as a photocorrosion and a fast charge recombination. These shortages are addressed within the research for this bachelor's thesis. Special attention is given to the formation of *p,n*-heterojunctions, which is the main strategy to effectively enhance the charge separation. Moreover, employing a non-precious metal based co-catalyst could also contribute to the charge separation and overall performance enhancement.

For the role of co-catalyst, multilayered MXene (ml-Ti₃C₂T_x) is a highly promising candidate, as it shows (I) a metallic conductivity, which further enhances the electron-hole

separation; (II) a suitable Fermi level for CO₂RR; and (III) it has a surface area with abundant Ti active sites. Additionally, thanks to its titanium content, it is able to be partially oxidized resulting in *in situ* growth of TiO₂ (*n*-type semiconductor) on the surface of ml-Ti₃C₂T_x. This composite, TiO₂-ml-Ti₃C₂T_x, is unique because of its intimate contact between the two phases (*n*-type semiconducting TiO₂ and metallic ml-Ti₃C₂T_x).

1.1 Aims of the work

This thesis aims to develop Cu₂O based composite photoelectrodes for the photo-electrocatalytic conversion of CO₂ into solar fuels under natural sunlight, primarily in the visible range. During electrode preparation, efforts were made to enhance stability, efficiency, and tune selectivity compared to the bare Cu₂O photocatalyst, which shows a great potential for CO₂RR.

The partial objectives of this thesis are followed:

- Preparation of Cu₂O electrodeposits on fluorine doped tin (IV) oxide (FTO) glass support
- Preparation and modification of Ti-based metallic MXenes as co-catalysts
- Preparation of composite photocathodes composed of Cu₂O and modified MXenes
- Characterization of the synthesized materials and the prepared electrodes using a series of characterization methods
- Photo-electrochemical characterization of the prepared cathodes
- Analysis of CO₂RR products
- Evaluation of the effect of MXene modification on the overall photo-electrocatalytic activity of the Cu₂O/MXene composite electrode.

2 Theoretical part

2.1 CO₂ as an alternative source of carbon for circular economy

An impulse to form a topic for this thesis was the fact that anthropogenic CO₂ emissions have been growing faster every year, causing one of the main environmental problems of today – global warming. Due to this, the linear economy based on the assumption that fossil C-based sources are infinite must be replaced by the circular economy. It counts with carbon recycling and aims to form a so-called man-made C-cycle (overall recycling of C from CO₂ coming from human production back to the C-source).⁵ However, there are several challenges in CO₂ utilization, mainly its outstanding stability coming from its high standard Gibbs free energy of formation ($\Delta G_f^0 = -396 \text{ kJ/mol}$).⁵ The energy required for CO₂ conversion into value-added products depends on the final oxidation state of carbon in the products, e.g., the formation of carbonates requires less energy than the formation of a high-energy C–C or even C–H bonds.⁵ Besides the thermodynamic aspects, there is also the slow kinetics of the CO₂ reduction reaction due to the necessary rearrangement of the linear molecule of CO₂ into bent anion radical and resulting product molecules.⁶

To overcome these issues, engaging a catalyst into the reaction is a possible path, as it changes the reaction mechanism and therefore, the activation energy of CO₂ is reduced. The catalyst is adjusting the reaction pathway, facilitating electrons transfer or making the reaction proceed through different intermediates. The structure, distribution and chemical properties of active sites of the catalyst are also able to affect the adsorption and desorption of reactants, intermediates and products, which additionally affects mentioned aspects.

Products of CO₂ reduction that are formed in a reaction employing solar energy as a renewable source are usually called solar fuels. To give a correct definition of the term solar fuels, the general term fuels should be defined, first.

Fuels are substances capable of storing chemical energy, which can be released through combustion or other chemical processes to generate heat, mechanical power, or electricity.⁷ Common examples include fossil fuels (coal, oil, and natural gas), and renewable alternatives such as biofuels (e.g., bioethanol produced via sugar fermentation, bio-oil derived from vegetable oils) and hydrogen. Another greener alternative is a nuclear energy, although this can be problematic, as there is still a question of nuclear power plants construction. This aspect is very time consuming and economically demanding.

Solar fuels, on the other hand, is a category of fuels generated using solar energy as the primary input.⁸ Through processes such as photocatalysis and photo-electrocatalysis, solar energy is converted into chemical energy stored in compounds like hydrogen, methane, or alcohols.^{5,19} In contrast to conventional fuels, which depend on finite resources and contribute to greenhouse gas emissions, solar fuels exploit the energy from the sun, and they have typically lower carbon footprint, making them a promising alternative in addressing energy and environmental challenges.

While photo-electrocatalysis and other alternatives for carbon recycling are still in research, there are other possibilities of CO₂ utilization, that are already used in practice. Carbon dioxide is used in the chemical industry for the preparation of several chemicals, including urea, carbonates and methanol.⁵ CO₂ for this purpose is captured mostly from power plants and industrial processes, or it can be captured by DAC technologies (Direct Air Capture), although this approach is not economically favourable.⁵

2.2 Electrocatalysis, photocatalysis and photo-electrocatalysis for CO₂ reduction into value-added products

Photocatalysis (PC) is a catalytic reaction which is initiated by UV, visible or IR electromagnetic irradiation of the catalyst or its reaction mechanism is affected by light. Compared to electrocatalysis and photo-electrocatalysis, no external potential nor current is applied to the PC system. Photocatalysis is explored for various applications, e.g. water-splitting (hydrogen production), nitrogen fixation, CO₂ reduction, organic pollutants degradation, etc.^{10,11}

Electrocatalysis (EC) is a catalytic reaction that takes place at the electrolyte-electrode interface, where the bonds in the reactants, ionic intermediates and products are rebuilt through electron transfer to or from a non-reactive electrode.¹² During electrocatalysis, the reaction runs as two half-reactions, reduction on a cathode and oxidation on an anode. The electrode's surface serves as an electrocatalyst in some specific cases or is covered with one.¹² It is possible to perform an electrocatalytic reaction in a two-compartment reactor, where most of the half-reaction products are separated by a membrane and the communication between the electrodes is mainly provided by the wiring. Photo-electrocatalysis (PEC) is a process that involves both defined. This type of catalysis will be described later.

For CO₂ conversion, the water-splitting reaction is often used in parallel as a proton source for hydrocarbon formation. In a photocatalytic setup, the catalyst must be able to perform both water oxidation to O₂ and H⁺, as well as CO₂ reduction, since all occur on the same material. In electrocatalytic and photo-electrocatalytic setup, the material only needs to be suitable for CO₂ reduction because water splitting occurs at the anode.

2.2.1 Photocatalysis (PC)

One of the mentioned CO₂ processing approaches is photocatalysis. It is usually described separately for homogeneous and heterogeneous systems. Photocatalysis in heterogeneous system consists of five sub-processes which are depicted in Figure 1.:⁶

- 1) Initial absorption of light by photosensitive material (semiconductor photocatalyst) is followed by the excitation of electrons from the valence band (VB) into the conduction band (CB), which creates electron-hole pairs.
- 2) At the same time, CO₂ is adsorbed on the catalyst surface, which is a crucial step for successful reaction progress. It is affected by the properties of the catalyst surface, e.g., its alkalinity or acidity, since CO₂ shows Lewis acidity.

- 3) Then, the photogenerated charge is separated (details in chapter 2.2.3.2). This step can be complicated or entirely blocked by charge recombination. Here, it depends on the kinetics of this competing process, which is affected by many, especially structural, factors of catalysts, such as crystallinity, dimension, surface properties, etc.⁶
- 4) The following step is an electrochemical process. Redox reaction takes place as two half-reactions: oxidation of water to O₂ and protons by holes in VB and reduction of CO₂ by electrons in CB into value-added products (e.g., CO, CH₄, HCOOH, CH₃OH)¹³.
- 5) The last step is product desorption. This step has to be fast enough, otherwise, the catalyst is poisoned, and the reaction is terminated.

Photocatalytic reactions can take place both in a liquid and in a gas phase (CO₂ and H₂O vapours react directly with a catalyst).

In a catalytic experiment in a homogenous setup, there is usually a photosensitizer (a substance that absorbs light and converts it into another form of energy, which is then transferred to a catalyst itself), a molecular catalyst, and an electron donor (a substance that donates electrons while itself being oxidized and consumed in the process).¹⁴ There are three options of catalyst-photosensitizer arrangements: i) a mixture of photosensitizer and catalyst in the same phase, ii) the photosensitizer and catalyst combined into one large molecule, or iii) the catalyst meets both functions (light energy absorption and accommodating the reaction). Homogeneous photocatalysts (mostly complexes of metals, such as Ru, Rh) suffers from several disadvantages including the instability of the utilized precious metal molecular catalysts, their high cost, the use of sacrificial electron donor, as well as low efficiency of CO₂ conversion.⁹ Altogether, with the knowledge we have so far, homogeneous photocatalysis is less useful strategy of the described.

Heterogeneous photocatalysis is a more promising method, utilizing semiconductor materials as catalysts. A semiconductor capable of absorbing a specific region of the light spectrum (e.g., visible light) must have an appropriate band gap. This band gap corresponds to the energy required to excite electrons from the VB to the CB. For visible light, the estimated band gap ranges from 1.8 to 2.0 eV.⁶ At the same time, the edge of the conduction band has to be more negative than the standard reduction potential of carbon dioxide conversion (depending on the particular reaction). The valence band has to be more positive than the standard reduction potential of water splitting.¹⁵

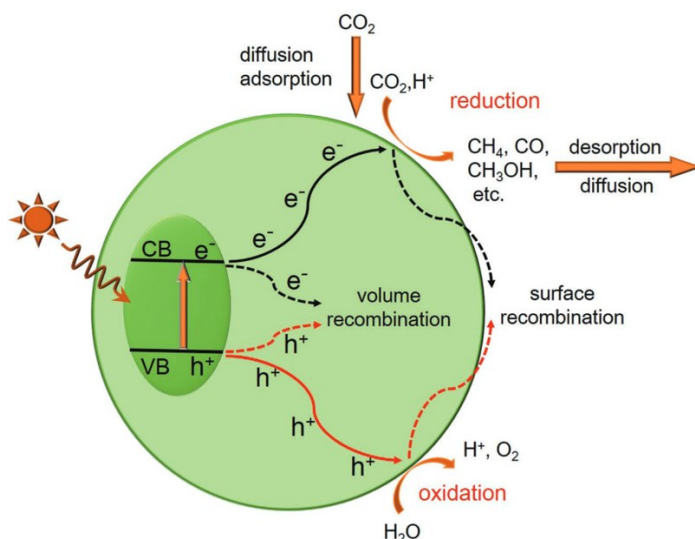


Figure 1: Scheme of five sub-processes of CO_2 reduction by photocatalysis. Adopted from⁶.

2.2.2 Electrocatalysis (EC)

Electrocatalytic conversion is another approach to carbon dioxide reduction. The reaction is driven by an external electric field. Aiming at the carbon neutrality of the process, the electric energy should come from a sustainable sources e.g., from photovoltaic cells, or wind, hydro, and geothermal power plants.^{16,17}

Figure 2 illustrates the typical electrochemical two-compartment cell. The voltage is applied to the electrodes, where carbon dioxide is reduced at the cathode and water is simultaneously oxidized to oxygen and hydrogen protons at the anode.^{6,17} Anodic and cathodic space is separated by a proton exchange membrane. It enables penetration of only protons originating in H_2O oxidation from the anodic part to the cathodic part, where they can be combined with CO_2 on the cathode. When the voltage is applied to the circuit, the multielectron process of CO_2 reduction itself takes place on the electrolyte/cathode surface interface¹⁸.

Similar to photocatalysis, electrocatalysis can be divided into four sub-processes¹⁸:

- 1) Firstly, CO_2 dissolved in an electrolyte is adsorbed¹³ onto a cathode's surface.
- 2) Secondly, reduction of CO_2 and oxidation of water occurs on electrodes.
- 3) Thirdly, the transport of electrons through a circuit and protons through the proton exchange membrane takes place.
- 4) Lastly, same as for photocatalysis, reaction products (e.g., CO , CH_4 , CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$, C_2H_4)¹³ desorb from the catalyst's surface in the cathodic part and O_2 desorbs from the anodes' surface.

A disadvantage of this method is a low selectivity for individual products and the competing hydrogen evolution reaction occurring on the cathode at higher overpotentials (η).¹⁷

The definition of overpotential is

$$\eta = E' - E, \quad (2.1)$$

where η is overpotential, E is an equilibrium potential of a specific chemical reaction and E' is the applied potential. In electrocatalysis, it reflects the additional voltage needed to drive a redox process in an electrochemical cell.¹⁹

When comparing electrocatalysis to photocatalysis, electrocatalysis offers an advantage in the separation of the cathodic and anodic compartments. This separation facilitates the isolation of oxygen produced during water oxidation and thus prevents the oxidation of the CO₂ reduction products. Additionally, electrocatalysis provides significant flexibility in the experimental setup. The electrocatalysts used for anode and cathode preparation can be combined, thereby further enhancing the overall performance of the reaction cell.⁶ The advantage of photocatalysis over electrocatalysis is the wireless configuration, which prevents energetic losses.²⁶ Another advantage is the independence from additional electric energy supply.

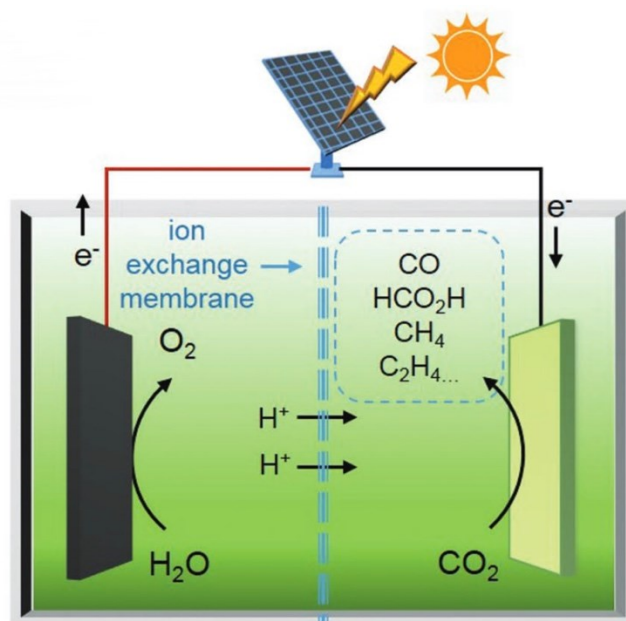


Figure 2: Scheme of reduction of CO₂ on electrocatalysts powered by a photovoltaic cell. Adopted from⁶

2.2.3 Photo-electrocatalysis (PEC)

Photo-electrocatalysis (PEC) is a chemical process integrating both photochemistry and electrochemistry driven by a combination of light and applied potential. This fusion of electro- and photocatalysis is enabled by the presence of a photoactive semiconductor catalyst serving

as a photocathode (Figure 3b), photoanode (Figure 3a) or both (Figure 3c). Unlike in EC set up, the photoelectrode in PEC is irradiated from a source of light. As a difference from PC set up, the photocatalyst is a part of a photoelectrode connected to an external voltage. Therefore, it is usually immobilized rather than dispersed in the system, as is often done in PC. In the cathodic compartment, there is an inlet for CO_2 and an outlet for the reaction products. An outlet is also present in the anodic compartment to release (or collect) the formed oxygen. Both these compartments are separated by a proton exchange membrane.

Both mentioned types of catalysis contribute to the improvement of efficiency, economy and ecology of the whole process.

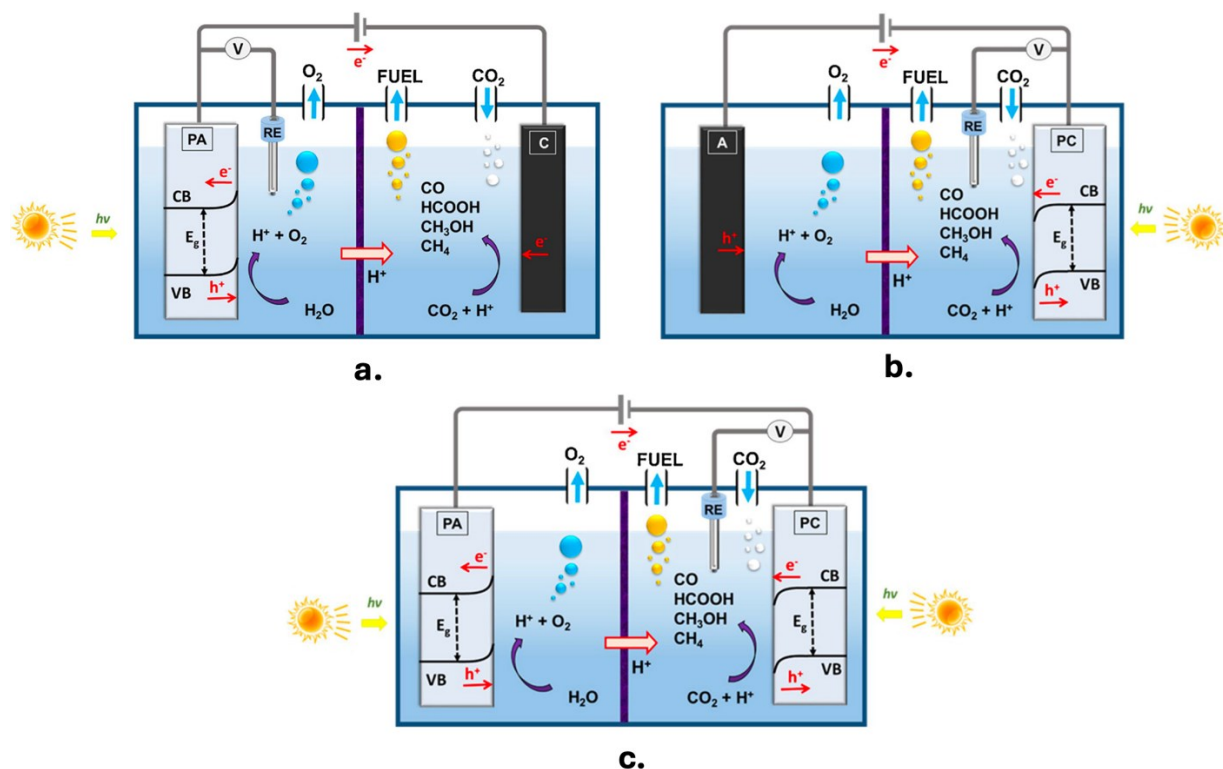


Figure 3: A schematic diagram illustrates the three-electrode configuration of a PEC cell designed for CO_2 reduction. The cell is divided into two compartments by a proton-exchange membrane and includes a. an illuminated photoanode (PA) and a cathode (C); b. an illuminated photocathode (PC) and an anode (A); c. an illuminated photoanode (PA) and photocathode (PC), along with a reference electrode (RE). The illustration also highlights the movement of photogenerated charge carriers and protons. Adopted from⁹

The fundamental principle behind photo-electrocatalysis involves the photoexcitation of electrons in semiconductor catalysts through its irradiation, the electrons' migration and utilization, while charge separation and transfer are facilitated by applied external potential. Absorption of the photons' energy by electrons in the semiconductor's valence band generates electron-hole pairs that are further separated and transported by external potential to the surface of the catalyst, where the reaction takes place.¹³

The system studied in this thesis is illustrated in (Figure 3 b) where the photoactive composite is the photocathode, and the platinum counter electrode serves as an anode. Similarly to previous EC and PC processes, photo-electrocatalysis (PEC) can be divided into several steps described below: ¹³

- 1) The photoexcitation of electrons in a semiconducting catalyst and the creation of a charge carrier happens on a photocathode.
- 2) Charge separation by external voltage is performed.
- 3) Water is oxidized at the anode (Pt). Formed protons travel to the cathode compartment through the proton exchange membrane and electrons travel towards the cathode through the external circuit.
- 4) Lastly, reduction reaction of CO₂ and H⁺ takes place on the photocathode's surface.

Compared to PC, the PEC systems facilitate faster electron transfer. This improves process efficiency by mitigating charge recombination and photocorrosion of the catalyst. Both of the mentioned factors are affected by lowering reaction overpotentials.¹³ Another improvement compared to PC is the two-compartment layout – the same as for EC, the proton exchange membrane present in PEC cells prevents migration of reaction products between compartments and, therefore, oxidation of products.¹⁷ Considering the comparison of EC and PEC, sunlight, as an additional energy source for carrier generation, significantly lowers the electric energy consumption, making the process more sustainable and financially demanding.¹⁷ Ideally, in both systems, the externally applied potential originates from a sustainable source.

Drawbacks of PEC compared to EC are usually connected with the transport of photogenerated charge carriers. These challenges could be especially charge recombination and photocorrosion of photoelectrode due to slow kinetics of CO₂ reduction and thus electron accumulation on the electrode surface.

2.2.3.1 Products and reaction mechanisms of photo-electrocatalytic reduction of CO₂

The following description of proposed mechanisms and products of this process refers to the case of reaction in an aqueous solvent, which is also commonly used as a proton source. Nevertheless, it is important to note that it is possible to perform PEC reduction of CO₂ in both nonaqueous and aqueous environments, although CO₂ is more soluble in nonaqueous solvents, e.g., methanol.¹⁴

There are several proposed mechanisms of CO₂ reduction, however, none of them have been fully confirmed, yet. The mechanism of CO₂ reduction is influenced by its pH-dependent dissociation. In acidic conditions, dissolved CO₂ predominates; near-neutral pH, HCO₃⁻

becomes dominant; under alkaline conditions CO_3^{2-} is the primary species. According to the present form, different products can be yielded.¹⁴ The conversion of CO_2 usually involves transfer of one proton and one electron during one step and the whole process occurs in multiple steps (Table 1). The single-electron reduction of CO_2 into $\text{CO}_2^{\bullet-}$ and subsequent reaction with H^+ is also described as one of the possibilities (reaction (2.4) in Table 1).^{9,20}

To facilitate or even enable CO_2RR , various homogenous and heterogenous catalysts are used. Focusing on the heterogenous ones, mechanisms of the PEC reduction of CO_2 and, therefore, products of this reaction differ in several aspects, especially the particular structure of the used catalyst, the applied voltage and the pH of the solution.¹⁴ According to Kumar et al.¹⁴, the most common products of CO_2RR on heterogeneous semiconductor catalysts are HCOOH and CO . Moreover, HCOH , CH_3OH , CH_4 and $\text{CH}_3\text{CH}_2\text{OH}$ were reported a few times.⁹

Table 1: Standard potentials related to CO_2 reduction and water oxidation vs Normal Hydrogen Electrode (NHE) at $\text{pH} = 0$. adopted from ⁹

Reaction	E^0 [V] vs NHE at $\text{pH} = 0$	Equation number
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0	(2.2)
$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{e}^- + 4\text{H}^+$	-1.23	(2.3)
$\text{CO}_2 + \text{e}^- \rightarrow \text{CO}_2^{\bullet-}$	-1.90	(2.4)
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	-0.20	(2.5)
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.11	(2.6)
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.07	(2.7)
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	0.03	(2.8)
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 3\text{H}_2\text{O}$	0.08	(2.9)
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$	0.08	(2.10)
$2\text{CO}_2 + 14\text{H}^+ + 14\text{e}^- \rightarrow \text{C}_2\text{H}_6 + 2\text{H}_2\text{O}$	0.14	(2.11)
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	0.17	(2.12)

The photo-electrocatalytic reduction of CO_2 can yield a range of diverse products, predominantly C1 and C2 hydrocarbons or oxygen-containing organic compounds with a great variation but low selectivity for each of them. The low selectivity and efficiency in targeted product formation can be overcome by establishing the right reaction path and adsorption of intermediates that favour C-C coupling through a convenient choice of catalyst. According to the literature, catalysts based on Cu_2O exhibiting strong binding energy for carbon monoxide

and low protonation energy barriers are particularly effective for generating methanol or methane.¹³ As example, the reduced graphene oxide coated with Ag/Cu₂O composite exhibited excellent performance during photocatalytic reduction of CO₂ with water into methane with a formation rate of 82.6 $\mu\text{mol/g/h}$ and selectivity 95.4% towards methan.²¹

As CO₂ conversion is a complex multi-electron and multi-proton transfer reaction, numerous challenges remain regarding competing side reactions such as hydrogen evolution reaction (HER). This can lead to lower Faradaic efficiency (FE).¹³ Faradaic efficiency of a product is a ratio of charges transferred to the product relative to the total charges passed through the circuit; it is defined by Equation (2.13)²²:

$$FE (\%) = \frac{Q_{prod}}{Q_{total}} \cdot 100 \quad (2.13)$$

Other shortages to the photo-electrocatalytic process are the high reaction potential and overpotentials, and, most importantly, the instability of catalysts, which have been developed so far. To overcome the last-mentioned inconvenience, many strategies are being developed, e.g., the synthesis of composite material, protective layers, doping, engineering of crystal and surface structure or creation of heterojunction semiconductors. Semiconductors properties and effect on catalytic performance differ with their chemical identity, but also with specific crystallography structure, thickness of the layer, etc.²

Photo-electrocatalysts for CO₂RR discovered by this point are a diverse group of materials, whose working principles and chemical identity differ substantially. The group of heterogeneous catalysts includes for instance metal oxides (TiO₂, ZnO, Cu₂O, CuO etc.), SiC, sulphides, iodides, tellurides, selenides, nitrides, carbon-based materials, other.^{23,24} Examples of semiconductor catalysts commonly studied in PEC are displayed in Figure 4 .

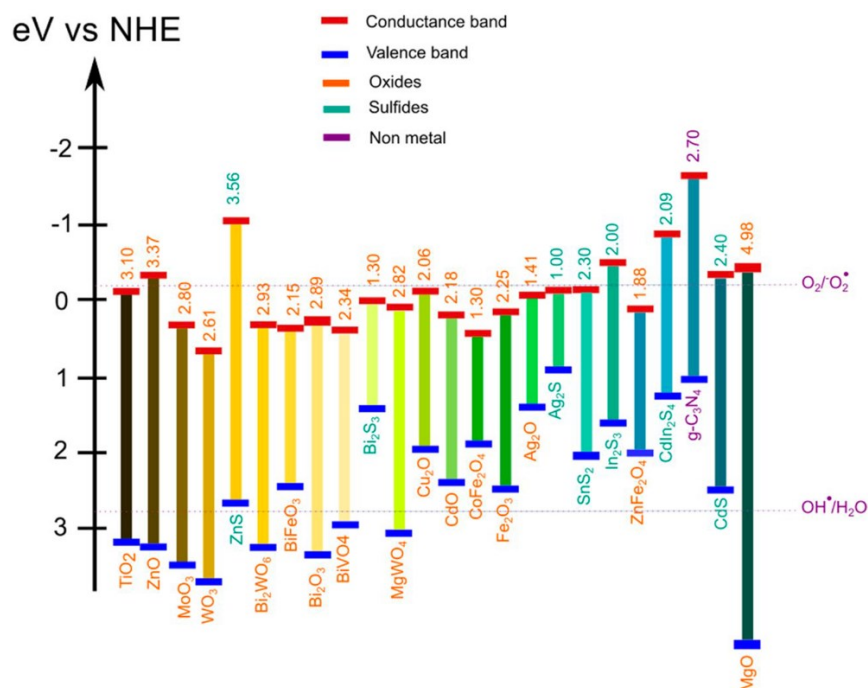


Figure 4: An example of semiconductor materials commonly used to prepare heterojunction catalysts and their bandgap energy levels. Adopted from¹⁰

2.2.3.2 Semiconductor heterojunctions as an example of PEC catalysts

Materials can be categorised based on their conductivity into three major groups: conductors, insulators, and semiconductors (Figure 5).

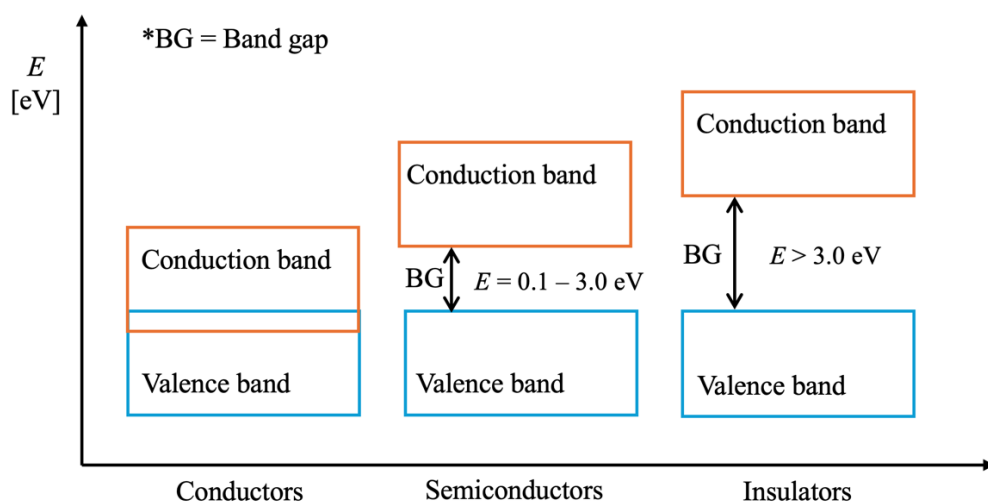


Figure 5: Scheme of energy band structure of conductors, semiconductors and insulators and the range of their band gap energies²⁵

For purposes of photo-electrocatalysis, semiconductors exhibit the most intriguing properties. A material can be classified as a semiconductor based on the width of its band gap. In conductors, the valence and conduction bands practically overlap, resulting in no detectable

band gap. In contrast, insulators possess a large band gap, which prevents their valence band electrons from being excited into the conduction band. Semiconductors possess a moderate band gap that allows electron excitation under thermal energy or light. The excitation of an electron leads to the formation of an electron-hole pair (Figure 6).

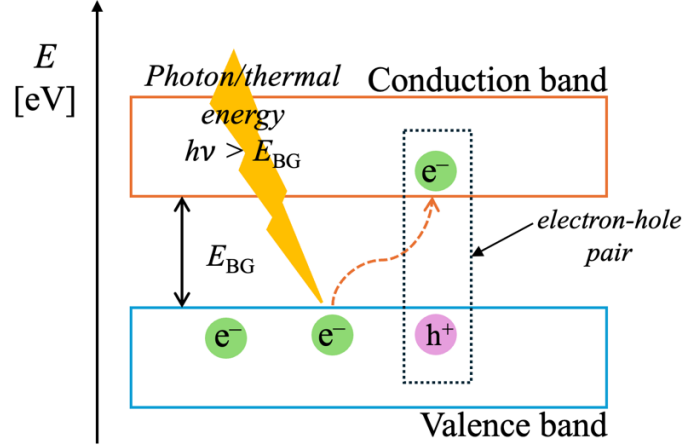


Figure 6: scheme of creation of electron-hole pair by excitation of valence band electron in conduction band

There are three types of semiconductors (Figure 7): intrinsic semiconductors and extrinsic semiconductors, which are further sorted into *p*-type semiconductors (having a lack of electrons and where the holes serve as the main charge carrier), and *n*-type semiconductors (having an excess of electrons that facilitate conduction).²⁶

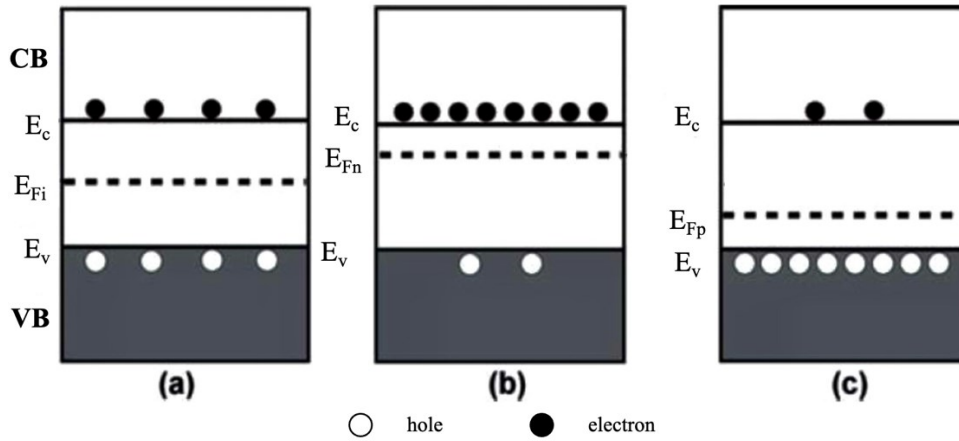


Figure 7: a) Scheme of intrinsic semiconductor; b) scheme of *n*-type semiconductor; c) scheme of *p*-type semiconductor. Here, E_{Fi} , resp. E_{Fn} , resp. E_{Fp} is Fermi level for intrinsic, *n*-type, and *p*-type semiconductors, respectively. Adopted from ²⁶.

In relation to this topic, the term Fermi level (E_F) is a concept that represents the energy level at which the probability of finding an electron is 50% (Figure 7).²⁷ In other words, the Fermi level means the likelihood of energy states being occupied in both the valence and

conduction bands. In intrinsic semiconductors, the Fermi level is precisely in the centre between the valence and conduction band, as, by definition, the creation of one free electron also creates one positive hole.²⁷ *P*-type and *n*-type semiconductor differs. As *n*-type semiconductors are specific by the excess of electrons over holes, the probability of an electron occupying the conduction band is higher than for intrinsic semiconductors, shifting the Fermi level towards the conduction band (Figure 7b). Contrarily, the Fermi level of *p*-type semiconductors lies nearer to the valence band, as this type of material has an excess of positively charged holes in its valence band (Figure 7). The value of E_F also anchors the band structure of the material to a certain value, which is useful information while using semiconductors as PEC catalysts, since every reaction requires a specific reaction potential (amount of energy that has to be supplied).^{27,28}

In photo-electrocatalysis, the coupling of extrinsic semiconductors to create heterojunction has shown significant advantages. A type of heterojunction can be established according to the two materials utilized. One can recognise *p,p*-; *n,n*- and *p,n*-heterojunctions, while the last one is the most promising combination for PEC purposes.²⁹ Many catalysts are based on this principle.

Heterojunctions can be sorted into 3 types, according to their energy band structure (Figure 8):³⁰

In type-I, the band gap of one semiconductor is positioned within the band gap of another semiconductor with a broader band gap, causing both electrons and holes to migrate from the semiconductor with a broader band gap to the material with a narrower one.

In type-II, the energy bands of the two semiconductors are misaligned, causing photo-generated electrons to move in the direction of the lower energy valence band and holes in the opposing direction.

In type-III, the valence band of one semiconductor lies above the conduction band of the other, with no overlapping energy levels within the band gap. Here, the electrons from semiconductor B (Figure 8) scavenge the holes in semiconductor A.

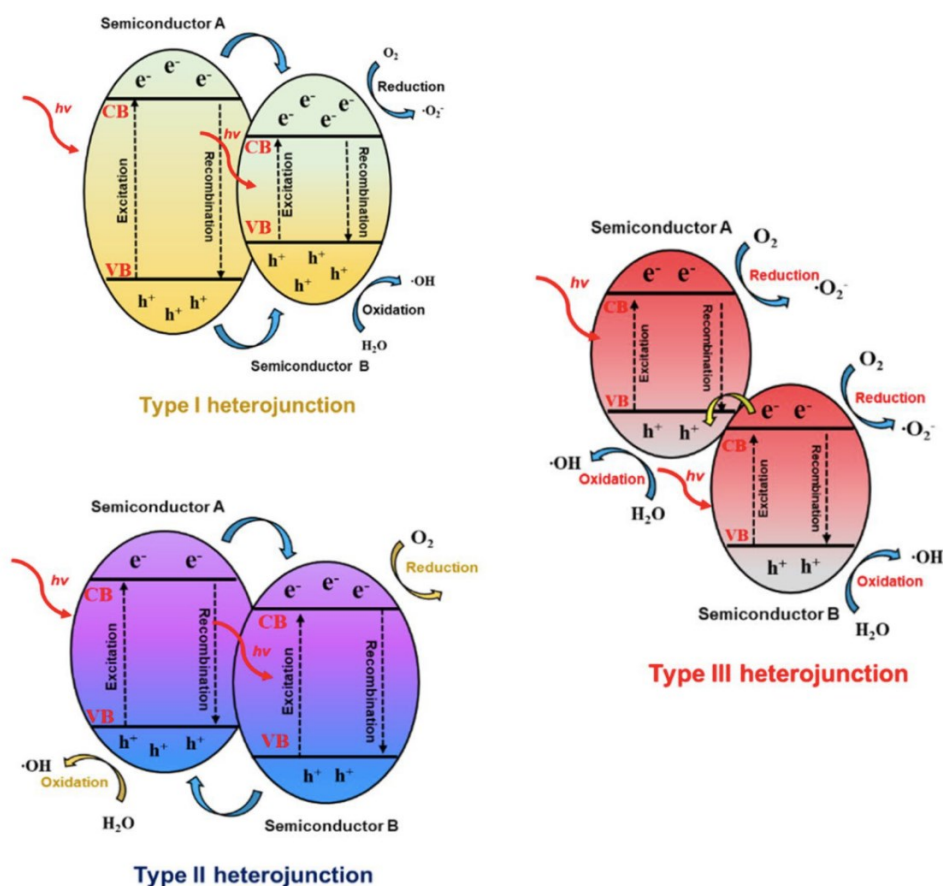


Figure 8: Three types of heterojunctions according to their energy band structure. Adopted from ¹⁰.

As mentioned above, to perform the photo-electrocatalytic reaction, the potential of the edge of the semiconductor's conduction band must be more negative than the reaction potential of the target reaction. This condition is met by Cu_2O in CO_2 reduction reactions (CO_2RR) (Figure 9).

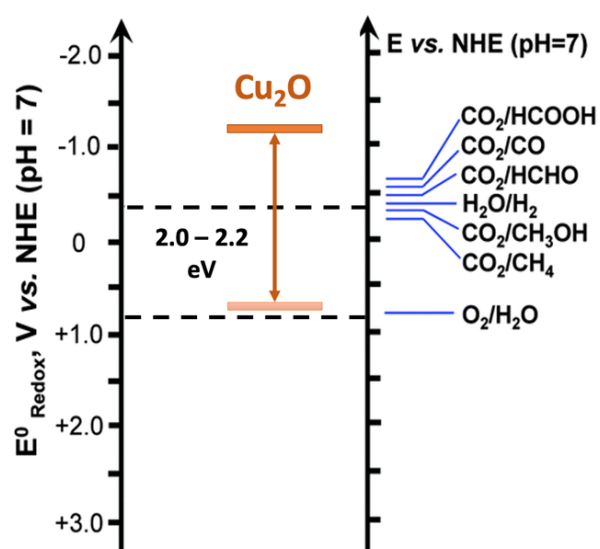


Figure 9: Scheme of Cu_2O band structure and possible products of CO_2RR with this semiconductor used as photo-electrocatalyst + their formation potential. Pale line is for VB and intense line for CB.

2.3 Copper (I) oxide

In this work, copper (I) oxide is studied as the primary photoactive layer of photocathodes used for conversion of CO₂ into value-added products. As copper is the 28th most abundant element in Earth's crust³¹, copper (I) oxide is an inexpensive and additionally environmentally friendly and easily preparable material. Due to this, and particularly for its semiconducting properties and ability to absorb visible light, this oxide has gained significant attention in the field of photo-electrocatalysis.

2.3.1 Structure and properties of Cu₂O

In Cu₂O, copper ions occupy a face-centred cubic sublattice and are linearly coordinated by two oxygen atoms, while oxygen atoms reside in a body-centered cubic sublattice and are tetrahedrally coordinated by copper atoms (Figure 10). At atmospheric pressure, two of these identical lattices are interpenetrating and shifted by $\frac{1}{4}$ of the cube diagonal, composing a cubic Bravais lattice.¹

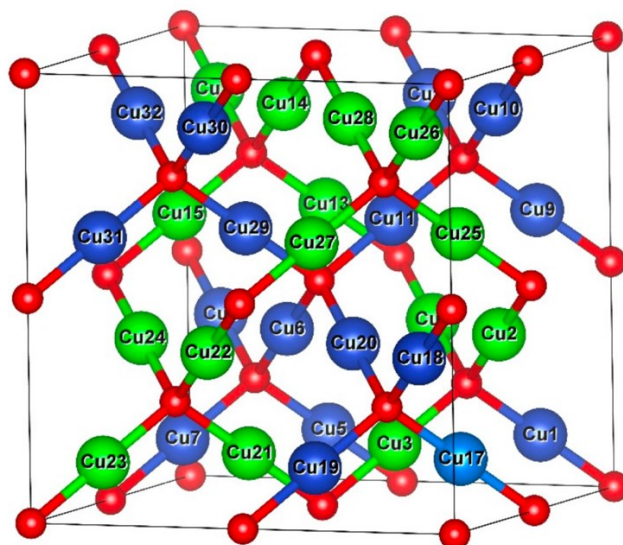


Figure 10: $2 \times 2 \times 2$ Cu₃₂O₁₆ supercell consisting of two interpenetrating sub-lattices (Cu atoms of one of them are depicted in blue, one of them in green; O atoms are depicted in red). Adopted from ⁴.

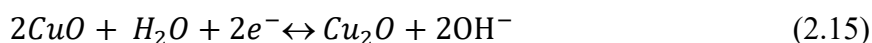
The described structure of copper (I) oxide is specific by randomly placed vacancies of Cu, produced as the material crystallizes, not requiring subsequent doping. Reportedly, the low-coordinated Cu sites work as active centres for the photo-electroreduction of CO₂.¹³ The formation of the mentioned vacancies is enabled by their low formation enthalpy, while the formation enthalpy of charge-compensating O vacancies is significantly higher. Due to this, Cu₂O is a great *p*-type semiconductor, although most binary oxides are *n*-type

semiconductors.³² The hole concentration can differ according to the preparation method used.³³ Moreover, holes in this oxide are mostly delocalised on the very top of the valence band,³¹ leading to high charge carrier mobility.³⁴

The ability of Cu₂O to absorb visible light thanks to its convenient band gap of around 2 eV⁴ provides a significant advantage over other metal oxides and sulphides studied for use in CO₂RR, such as TiO₂, ZnO, or ZrO₂. The band gaps of these n-type semiconductors are mostly greater than 3 eV, which corresponds to absorption in the UV region.³⁵

Furthermore, several articles mention the high Faraday efficiency of this catalyst in creating C₂ products, which is a crucial step in the preparation of longer hydrocarbon chains or value-added hydrocarbons with larger molecular masses in general.¹³

On the other hand, it is important to note some disadvantages of Cu₂O as a photoresponsive material for photocathodes. Firstly, photocorrosion (Equations (2.14) and (2.15)) occurs because this catalyst's own reduction and oxidation potentials lie between its valence and conduction bands.



This reaction competes with the desired CO₂ conversion, and it also results in a low stability of the photocatalyst. Secondly, rapid charge recombination leads to low efficiency in mobilizing charge carriers for the CO₂RR.

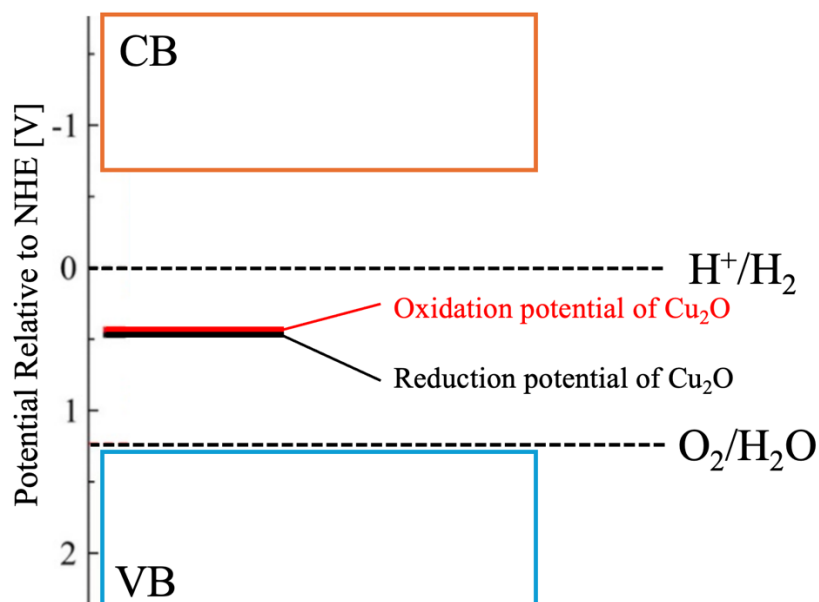


Figure 11: Scheme of band structure of Cu₂O with its reduction and oxidation potential and redox potential of H⁺/H₂ and O₂/H₂O marked.³⁶

To overcome these limitations, in the PC field, various strategies can be employed, including surface or morphology modification, the incorporation of heterojunctions or composite structures, and the loading or doping of metals, particularly silver, alkali metals, palladium, or copper. Another approach specific to EC is defect engineering. When a metal is integrated into the semiconductor structure as a conductor, its work function can vary based on particle shape, size, and specific crystal facets.⁴ It leads to the formation of varying Schottky barriers at the heterojunctions. A Schottky barrier is a potential energy barrier formed at the interface between a metal and a semiconductor due to the difference in their work functions, influencing charge transfer.³⁷ Consequently, electrons can migrate from Cu₂O to the metal while simultaneously being effectively prevented from returning to Cu₂O. This mechanism significantly influences the catalytic performance of the photo-electrocatalyst by reducing rapid charge recombination. Another approach involves doping Cu₂O with suitable anions to raise its valence band to more positive values, thereby improving the catalyst's ability for water oxidation.¹³ However, this serves as an advantage for the use of Cu₂O as a catalyst in photocatalysis rather than photo-electrocatalysis.

2.3.2 Preparation of Cu₂O

Numerous preparation methods have been developed most of which are still being optimized. This work focuses on the preparation of thin layer of copper (I) oxide by electrodeposition method.

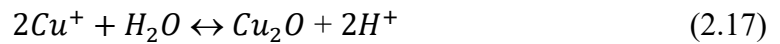
There are several methods to produce a relatively homogenous thin layer of copper (I) oxide for photo-electrochemical purposes. Some of them are more suitable for industrial conditions, while others require more precise laboratory techniques.

The mostly studied methods are electrodeposition, thermal oxidation of copper substrates, and the conversion of copper films into Cu(OH)₂ nanowires by immersion in an (NH₄)₂S₂O₈ solution, which is subsequently thermally reduced, oxidized in KOH and dehydrated into Cu₂O³³. There are a few other, less employed methods like copper-amine complex reduction under microwave irradiation from its glucose solution³⁸, solvothermal³⁹ and sol-gel⁴⁰ precipitation methods, thermal evaporation⁴¹, sonochemical synthesis⁴², chemical vapour deposition⁴³, wet chemical routes⁴⁴, sputtering⁴⁵, and hydrothermal⁴⁶ methods. Each preparation method results in a layer of Cu₂O with slightly different structures.

2.3.3 Electrodeposition of Cu₂O

Electrodeposition of copper (I) oxide is one of the most utilized and intensively studied synthesis methods of this photoactive material, as it is scalable, relatively inexpensive, environmentally friendly and applicable on a larger scale.⁴⁷ The substrate for this synthesis can be, for instance, a copper wire or glass slide covered with a conductive layer of a semiconductor (e.g., SnO₂, In₂O₃, Cd₂SnO₄). Copper (I) oxide is then cathodically reduced from an alkaline Cu(II) solution in three electrodes system, where a wire or glass support is connected as a working electrode.⁴⁸

The electrodeposition of Cu₂O is a two-step process. Initially, Cu²⁺ ions are reduced to Cu⁺ ions (Equation (2.16)), followed by the precipitation of Cu⁺ ions to form Cu₂O due to a limited solubility of Cu⁺ ions in an alkaline solution (Equation (2.17)).⁴⁹



For enhanced photocatalytic activity of Cu₂O photocathodes, crystal orientation is crucial and can be easily optimized via this method. The morphology and crystal orientation can be effectively managed by utilizing additives (e.g., complexing ligands), adjusting the pH, modifying the bath temperature and the applied current or potential.⁵⁰ As follows from Equation (2.17), the deposition of Cu₂O is directly affected by the solution's pH. Copper (I) oxide is stable within a narrow range of conditions, particularly regarding pH and applied potential as evident from Pourbaix diagram (e.g., approximately 0.2 – 0.4 V in pH = 5 or –0.3 to –0.15 V in pH = 14, while under pH = 3 Cu₂O is not stable at all).⁴

All these factors are accounted for in several electrodeposition methods varying in copper precursor solution used and potential (potentiostatic methods) or current (galvanostatic methods) applied.⁴ The copper source used for a precursor solution preparation can be, e. g. 0.01 M Cu(NO₃)₂ + 0.01 M NH₄NO₃⁵¹; 0.02 M Cu(Ac)₂ + 0.1 M CH₃COONa + 1.5 M KCl⁴⁹; Cu foil + 280 gL⁻¹ NaCl + 0.1 gL⁻¹ Na₂Cr₂O₇ (pH adjusted between 8 and 12 with 0.1 M NaOH)^{52,4}. However, the most widely used and most promising in terms of photocurrent density exhibited by prepared photoelectrodes is the combination of 0.5 M Cu₂SO₄ + 3 M lactic acid + NaOH to adjust pH to basic values^{53,54}. The last-mentioned approach is therefore employed within this work.

It has been proven that even very fine changes in deposition parameters and conditions can affect the thin film's structure and orientation.⁴ Furthermore, the orientation has an

influence on the photoelectrode's performance. As a catalyst, Cu₂O shows facet-dependent activity.⁵⁵

2.3.4 Cu₂O as a catalyst for photo-electrocatalytic CO₂RR and its enhancement

Depending on the preparation method, a certain amount of low-coordinated Cu⁰ particles may be present in the copper (I) oxide structure, influencing the formation of specific products. These could be active sites for CH₄ formation, compared to Cu⁺ centres favouring the production of CO.⁵⁶ Furthermore, according to Yang et al. Cu⁰ as a metal centre promotes electron transfer. Combined with Cu⁺ that additionally facilitates C–C coupling by enhancing CO• and CH_xO intermediates adsorption, the Cu⁰ sites produce CH₄ and C₂H₅OH.^{57,58,13} Due to this, the ratio of Cu oxidation states on the Cu₂O surface must be ideally tuned to gain the optimal result.¹³

To address the shortcomings of Cu₂O as a photo-electrocatalyst (especially photocorrosion), a few strategies have been developed. These can be listed as follows:^{4,13}

- addition of a protective overlayer (which usually involves creation of a heterojunction),
- doping of the photoactive material,
- combining Cu₂O with a suitable co-catalyst,
- modifying or functionalizing the Cu₂O surface by organic and inorganic chromophores,
- introduction of carbon-based composites.

Named strategies are based on a principle of removing the photogenerated electrons from Cu₂O to prevent them from reducing the copper (I) oxide itself.⁴

2.3.4.1 Cu₂O/TiO₂ composite: *p,n-heterojunction semiconductor catalyst for PEC*

The idea behind constructing the *p,n*-heterojunction between Cu₂O and the protective overlayer constructed of *n*-type semiconductor is to effectively separate the photogenerated holes and electrons. For purposes of this work, titanium dioxide serves as an *n*-type semiconductor. TiO₂ also has a wide band gap, which makes it more stable than narrow band gap semiconductors.⁵⁹ To simulate the natural solar light, the developing catalyst is exposed to a visible part of the spectrum only, meaning the TiO₂ is not excited. The combination of Cu₂O and TiO₂ can be described as a *p,n*-heterojunction created by reduction *p*-type and oxidation *n*-type¹⁰ semiconductor (Figure 12), where the copper (I) oxide serves as an absorbing material and titanium dioxide as a stabilising material.⁵⁹ In this setup, when excited, electrons from Cu₂O transfers and concentrate in CB of TiO₂.⁶⁰ This should lead to an effective hindrance of charge recombination and also prevent photocorrosion.

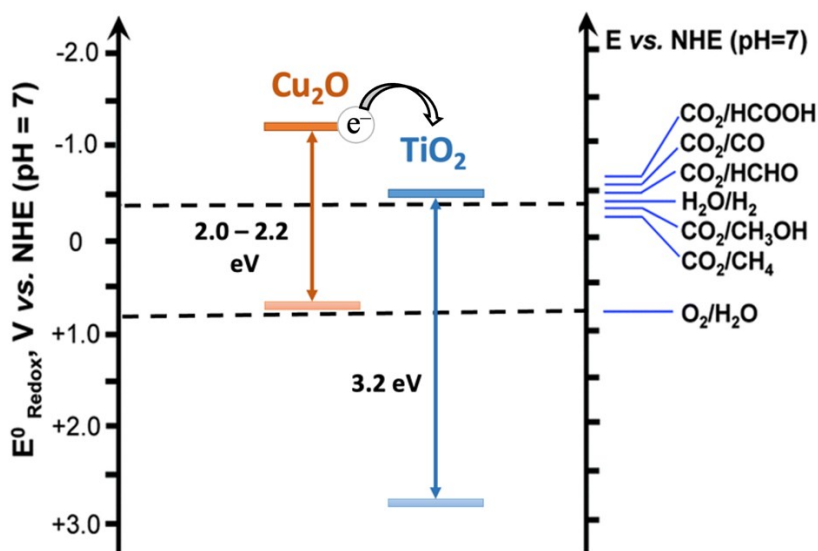


Figure 12: Scheme of band structure of the p,n-heterojunction between Cu_2O (reduction p-type semiconductor) and TiO_2 (oxidation n-type semiconductor) illustrating the possible electron transfer. The possible products of this p,n-heterojunction semiconductor used as photo-electrocatalyst are also depicted according to their formation potential. Pale lines are for VB and intense lines are for CB.

2.4 Co-catalysts in CO_2RR

One of the attractive strategies for improving the stability and overall performance of a semiconductor catalyst for PEC CO_2RR is employing a co-catalyst. Co-catalyst is a secondary catalyst that, when combined with a primary catalyst or semiconductor, enhances the efficiency and/or stability of the primary catalyst by providing additional active sites, promoting charge separation, and/or lowering activation energy of substrate (here CO_2) by adjusting the reaction mechanism.^{61,62}

The process of photo-electrocatalytic reduction of CO_2 starts with a creation of an electron-hole pair by photoexcitation of electrons in a semiconducting catalyst, followed with a charge separation by external voltage. After that, charge carriers are transported to the electrodes' surface, where cathodic reduction of CO_2 takes place as the last step.^{13,63} When the redox reactions are too slow, the charge carriers may recombine. Therefore, this is the point where the co-catalyst mainly plays its crucial role, fastening the electrode half-reaction and elevating the kinetics of the whole process.^{63,61} In other words, it can extract electrons from a semiconductor's valence band and facilitate their transport between the semiconductor and the reactant-containing solution. For this, the co-catalyst utilizes photogenerated electrons to drive the reaction forward.^{64,65} To achieve this, the co-catalyst Fermi level should be lower than the bottom edge of the semiconductor's conduction band.⁶⁵ This enhances charge separation and can also reduce photocorrosion. (Figure 13)

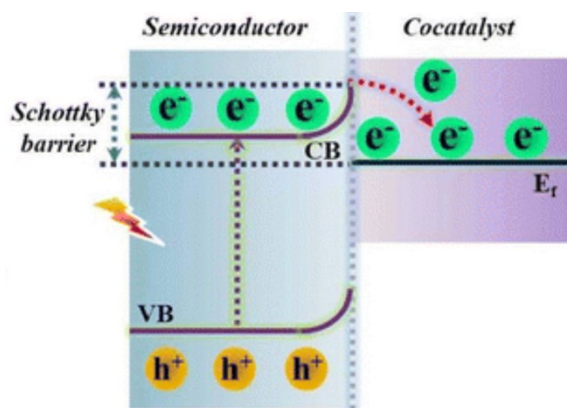


Figure 13: Scheme of band structure of a semiconductor/co-catalyst composite. Adopted from ⁶⁶.

The co-catalyst is able to provide additional active sites of different nature compared to photocatalyst surface.⁶⁷ Moreover, the catalyst also affects product selectivity, e.g., Au and Ag usually produce H₂ and CO only while non-precious metals (e.g., Sn, Cu, Bi) can produce HCOOH, CO, C₂H₄ etc.⁶⁸ The principle and the specific functioning are individual and can differ slightly for every pair of a co-catalyst and a photo-electrocatalyst.⁶⁴ Due to the described advantages, the construction of a multicomponent photoelectrode for PEC appears as a promising solution for several shortcomings of the catalysts used so far.⁶⁹

Various chemical species can act as a co-catalyst:

- metals (Sn, Cu, Ru, Co, Bi, Pt, Rh, Au, Ag, Pd, Ni)^{62,68},
- metal oxides, hydroxides⁶¹, sulphides, phosphides⁶² and complexes⁶³,
- non-metals, such as nanocarbon materials (nanotubes, nanosheets)^{61,62}
- metal carbides of MXene type⁶⁷.

There are numerous methods of co-catalyst loading, including impregnation, electrostatic adsorption and low-temperature heat treatment, hydrothermal treatment, controlled ink-jet printing, etc.⁶² The listed methods are known as direct addition.⁶² Another method of co-catalyst preparation results in a so-called composite type of co-catalyst, prepared by *in situ* growth methods like calcination.⁶²

2.4.1 MXenes

MXenes belong to the family of 2D materials.⁷⁰ These materials are two-dimensional carbides, nitrides, or carbonitrides of the transition metals, which can exhibit either a structured form or create a solid solution (Figure 14).⁷¹ Additionally, their layers are terminated with surface groups like O=, OH-, NH-, F-, Cl-, Br-, S-, Se-, Te- or their mixture depending on the

preparation procedure.⁷² MXenes were first obtained from its precursor, the MAX phase, in 2011 and continue to be the subject of intensive research today.⁷¹

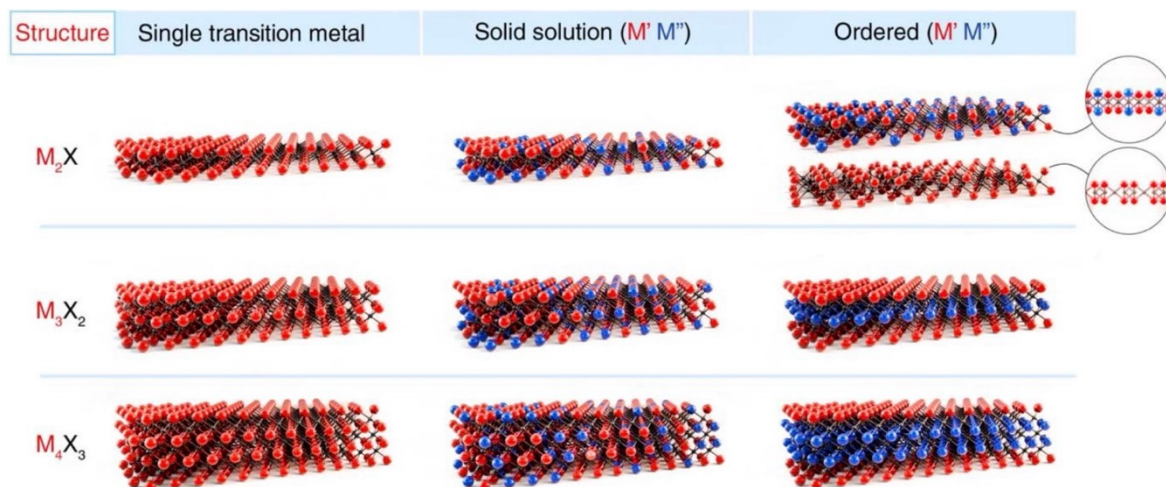


Figure 14: An example of a possible arrangements of metal atoms (depicted in red and blue) in various MXenes structure. C atoms are represented by black dots in the middle of metal tetrahedron. The terminal groups are not depicted in this scheme. Adopted from⁷³.

Given the extensive variety of these materials, their properties vary widely based on specific compositions. This diversity enhances their potential applications across multiple fields including electronics⁷⁴, energy storage (batteries and supercapacitors)⁷⁵, catalysis⁷⁶, water purification through filter components⁷⁷, and even medicine (Ta₄C₃T_x combined with NIR radiation is studied for its promising potential in cancer treatment⁷⁸). The properties of these materials are actively researched due to their ability to be modified relatively easily through compositional adjustments. Another significant advantage of MXenes is the abundant availability of their constituent elements, which results in low production costs.

2.4.1.1 Structure of MXenes

MXenes can be represented by the general formula $M_{n+1}X_nT_x$, where n ranges from 1 to 4, indicating the number of carbon or nitrogen layers and $n + 1$ denotes the number of transition metal layers in the material's structure. In this formula, M stands for the transition metal, X represents carbon (the most common element in this position) or nitrogen, and T is a general designation for the surface termination group, that strongly depends on the preparation method, while mostly they are a mixture of several chemical moieties (as mentioned above) in various ratios.⁷⁹

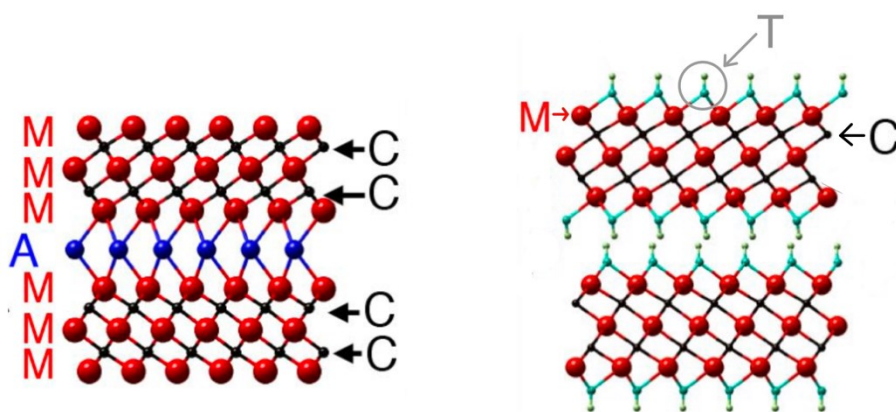


Figure 15: A scheme of MAX phase (left) and $M_3C_2T_x$ MXene (right) structure. Adopted from ⁷⁹.

A specific example of this formula is $Ti_3C_2T_x$ (the most studied MXene⁸⁰), where $x = 2$. This MXene is also the subject of the research in this work. It is composed of two carbon layers alternating with three layers of titanium, with T– denoting the terminal group depending on the MXene synthesis. The MXenes produced to date typically consist of 3, 5, or 7 layers, corresponding to the following structural types: M_2X , M_3X_2 , and M_4X_3 .^{79,73}

MXenes are typically prepared from their precursor, MAX phase. In MAX designation, M stands for a transition metal layer, A for A group (usually III.A or IV.A group of the periodic table) element layer and a C or N for carbon or nitrogen (or the mix of both) layer.⁷¹

Non-equal strength of the chemical bonds between these layers, especially the stronger X–M bond and weaker X–A, resp. A–M bonds, are crucial for etching – selective removal of the A layer, which is most frequently used as a preparation method of MXenes.^{70,73}

2.4.1.2 Method of MXenes preparation

To obtain MXene material of desirable structure and quality, one can apply several methods. Historically, the first preparation method was etching of the parent MAX phase by immersing it in a concentrated (and later diluted) hydrofluoric acid solution.⁸¹ As HF is a highly hazardous chemical, safer methods have been developed with time. One of these approaches is the utilization of fluoride salt (such as LiF, KH, NaF, CsF, FeF₃, CaF₂, etc.) in combination with hydrochloric acid or sulfuric acid. This enables the *in situ* creation of HF.⁸² However, both these methods are based on the same principle. The weakly bonded A layer is selectively dissolved by HF, creating AlF₃ and H₂, leaving M and X layers loosely stacked and their surface covered with termination groups depending on the method used. At this state, the obtained substance is called a multilayered (ml-) MXene.⁸³ Depending on the preparation method,⁷⁹ ml-MXene can have several morphology types. Most known is an accordion-like morphology caused by extensive hydrogen evolution via the reaction of the Al layer with HF.⁸² Furthermore,

thanks to the excessive formation of flammable hydrogen gas and the reaction exothermicity, it is crucial to set up and follow safety protocols, particularly personal protective equipment.⁸⁴

Next to the etching by HF, which can be both directly added or *in situ* formed, few alternative methods have been developed these days. For instance, hydrothermal treatment of the parent MAX phase in an environment of NaOH solution also selectively dissolves Al layer.^{85,86} Another example of such method is electrochemical etching, controlled by selecting favourable electrolyte, temperature, time and voltage.⁸⁷ There is also a preparation process, which does not involve water as a solution. The combination of NH_4HF_2 salt and propylene carbonate as an etching agent provides a high-quality ml-MXene with intercalated organic molecules.⁸⁸ Slightly different is a strategy of molten salt etching, which is a solution-free procedure at high temperatures.⁸⁷ Aside the listed, there are also approaches based on a completely different principle. These are utilizing non-MAX phases as a precursor. It is e. g., chemical vapour deposition.⁶⁷

2.4.1.3 MXenes properties

Like other materials, MXenes' properties are shaped by their chemical composition: internal layer arrangement, interlayer organization, the elements occupying the X and M positions, the bond strength and reactivity between these elements, and the surface groups present.

In several aspects, MXenes are similar to metals. For instance, the outstanding electrical and thermal conductivity of some of these structures⁸⁹ is one of the most appealing characteristics of these materials.⁶⁷ The electric conductivity of their parent MAX phases is, in some cases, even higher than that of the corresponding pure metal.⁷⁰ Furthermore, their resistance increases with temperature, given by the principle of electron transport comparable to the one in transition metals⁷³. However, there are exceptions where some MXenes exhibit semiconducting properties⁹⁰, depending on the transition metal within the structure and also the surface termination groups⁸⁹. A typical example of a conductor among MXenes is $\text{Ti}_3\text{C}_2\text{T}_x$, while Mo_2CT_x , and $\text{Mo}_2\text{TiC}_2\text{T}_x$ (out-of-plane MXene containing a mixture of Ti and Mo layers), is an exception as it is a semiconductor.⁹¹ When examining the electrically conductive properties of MXenes, it is crucial to differentiate between the in-plane conductivity, which is estimated one order of magnitude higher than the conductivity vertical to the MXenes layers, given by more difficult electron transport in the second-mentioned direction.⁹²

Indirectly, the optical properties of MXenes are important for PEC applications because, although they do not directly generate charge carriers upon absorbing visible light,

the absorption-induced heating (photothermal effect) enhances the material's conductivity. Thereby, the mobility of charge carriers increases, facilitating more efficient capture of photogenerated electrons by MXene acting as a co-catalyst.⁷⁶

Shekhirev et al. wrote, that considering MXenes' thermal stability, their degradation temperatures differ from 375 °C to 860 °C in a protective atmosphere (e.g., N₂, inert gases).⁹³ Due to this, MXenes are considered thermally stable materials. Experimentally, a relation has been found between thermal resistance and the number of layers in these materials: the thicker the layer, the more thermally stable the MXene is.⁹³

Due to the layered structure of MXenes, the versatility of metals in the M position, and adjustable termination groups, these materials can be tailored to optimize their photocatalytic properties, such as their band gap, and surface chemistry.⁶⁷

Properties of Ti₃C₂T_x MXene crucial for this work are as follows⁶⁷:

- metallic conductivity,
- suitable position of Fermi level for PEC CO₂RR purposes,
- hydrophilicity (as the PEC reactions are performed in aqueous environment),
- thermal, chemical and mechanical stability,
- surface area with abundant active sites.

2.4.2 MXenes as co-catalysts in CO₂RR

Paired with a semiconductor catalyst, MXenes are perfect candidates for a role of PEC CO₂RR co-catalysts thanks to their many advantageous properties.^{76,67} As described above, they are characterised by outstanding metallic conductivity⁸⁹, which is one of the co-catalyst's required properties. Furthermore, Ti₃C₂T_x MXene's Fermi level position is suitable for CO₂RR, as this energy matches the formation potential of most value-added products of CO₂ reduction (Table 1). The calculated⁷⁶ position of Ti₃C₂T_x Fermi level is -0.04 vs NHE, while e.g., the energy of TiO₂ CB is -0.25eV vs NHE. Due to this, an MXene co-catalyst paired with a semiconductor catalyst creates a Schottky barrier. This contributes to an effective separation of photogenerated charge carriers and lowers charge recombination and photocorrosion. Moreover, if the difference between co-catalyst's Fermi level and the semiconductor's lower edge of the conduction band is not too large, electron transfer is further promoted. Thanks to MXene's layered structure, they also work as an electron reservoir, which facilitates the multielectron reaction required during CO₂ reduction.⁶⁷ The variability of termination groups offer various active adsorption sites.⁶⁷

Moreover, $\text{Ti}_3\text{C}_2\text{T}_x$ is particularly appealing due to its capability to form the described composite-type co-catalyst when subjected to high-temperature treatment. When exposed to a high-temperature treatment in the presence of oxygen, rice crust-like structured TiO_2 is *in situ* formed on $\text{Ti}_3\text{C}_2\text{T}_x$ surface. Thus, it creates the composite of a *n*-type semiconductor catalyst and MXene co-catalyst in intimate contact.⁷⁶ In this work, we applied this material for the creation of a *p,n*-junction with Cu_2O . The idea of *p,n*-heterojunction Cu_2O semiconductor catalyst combined with the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene co-catalyst having a surface covered with TiO_2 particles is depicted in Figure 16 together with the energies of lower edges of components CB and MXenes Fermi level.

In principle, electrons from copper (I) oxide's VB (light orange in Figure 16) are photoexcited into its CB (dark orange) upon visible light irradiation. These excited electrons then transfer into the CB of TiO_2 (dark blue), which has a lower energy level, making this shift thermodynamically favourable. A similar electron transfer occurs from the CB of TiO_2 into MXene, as its Fermi level (green) is at an even lower energy.

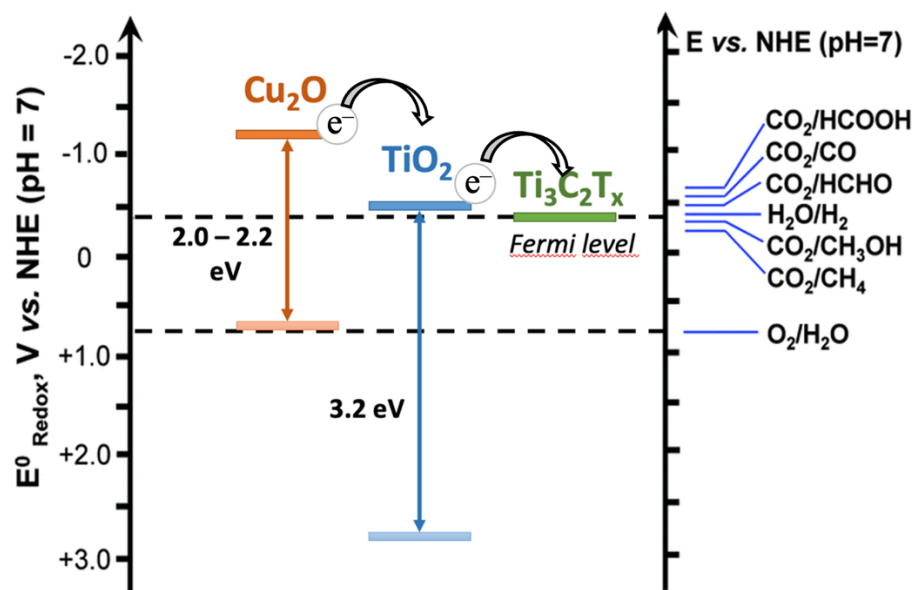


Figure 16: Scheme of band structure of the *p,n*-heterojunction catalyst and $\text{Ti}_3\text{C}_2\text{T}_x$ as a co-catalyst illustrating the possible electron transfer. The Fermi level of MXene co-catalyst is depicted in green.

2.5 Material and catalysis products characterization methods

2.5.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive bulk characterization method used to investigate the crystal structure of materials. It provides information about crystallite size, lattice arrangement, purity and phase composition by analysing the unique diffraction patterns generated when monochromatic X-rays interact with a sample's crystal lattice. The interaction of X-rays with the periodically arranged atoms in a crystal results in constructive interference at specific angles. Powder X-ray diffraction (PXRD) is commonly employed due to its ease of sample preparation. The peak intensities in the diffractogram also offer a quantitative analysis of specific phases in the material.⁹⁴

The method relies on Bragg's law (Equation (2.18)), which correlates the diffraction angle at which constructive interference occurs with the spacing between atomic planes.

$$n\lambda = 2d \sin \theta \quad (2.18)$$

Where n is for integer number (diffraction order); λ is the wavelength of the radiation; d is for the distance between the planes and θ is for incident angle. By comparing diffraction data with known patterns, the crystalline structure and purity of a sample can be determined.⁹⁴

2.5.2 Gases adsorption

Gas physisorption is commonly used to analyse the textural properties of porous or layered materials, including specific surface area, pore volume, and pore size distribution. A sample is exposed to a gas (typically N₂ or Ar) at a controlled temperature, and the adsorbed gas volume is recorded as a function of pressure, generating an adsorption isotherm. Gas molecules interact with the surface via weak van der Waals forces. An example of a method used for analysis of the isotherm to calculate a surface area is the Brunauer-Emmett-Teller (BET) model.⁹⁵

2.5.3 UV-VIS spectroscopy

UV-Vis spectroscopy is a widely used tool for investigating the electrons' transitions within a material by measuring the absorption and transmission of UV and visible regions of the electromagnetic spectrum. When a sample is exposed to UV-Vis irradiation, electrons transition between energy levels. These transitions occur as bands in the plot of absorbance against wavelength. The band gap can be estimated from the measured spectrum through graphical methods like the Tauc plot.⁹⁶

It plots $(\alpha h\nu)^\gamma$ (direct band gap) or $(F(R)h\nu)^\gamma$ (indirect band gap) versus photon energy $(h\nu)$, where α is the absorption coefficient, h is Planck's constant, ν is frequency, and γ depends on the nature of transition – for direct band gap it is $\gamma=2$, for indirect band gap it is $\gamma=1/2$. In this work, UV-Vis spectroscopy in diffuse reflectance mode was used. $F(R)$ is calculated by the Kubelka-Munk function to transform reflectance spectra into absorbance values⁹⁶:

$$F(R) = \frac{(1 - R)^2}{2R} \quad (2.19)$$

where R is reflectance. Optical band E_g is then calculated by Tauc equation for absorbance

$$(\alpha h\nu)^\gamma = A(h\nu - E_g) \quad (2.20)$$

or Tauc equation for reflectance

$$(F(R) \cdot h\nu)^\gamma = A(h\nu - E_g) \quad (2.21)$$

where A is energy independent constant.

2.5.4 Electron microscopy

Electron microscopy is an analytical technique for visualising the morphology of materials at high magnification. The two most common types are scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM was employed in this work. SEM scans a sample with a focused electron beam. Interaction of the sample and this beam generates secondary and backscattered electrons, as well as X-rays. Detectors capture these signals to create images. Secondary electrons reveal surface topography, while backscattered electrons show compositional contrast based on atomic number differences. SEM is used to analyse surface morphology, particle size, and texture.⁹⁴

2.5.5 Gas chromatography (GC)

Gas chromatography is a separation method used to separate and quantify volatile substances in a mixture. A sample is injected into an inlet, preheated, and then it proceeds to a column, where components in a mobile phase (gas) are separated based on affinity for the stationary phase in the column (usually capillary). Once analytes exit the column, a detector (e.g., FID, BID or TCD) determines their concentration, creating a chromatogram. In photo-electrochemical CO₂ reduction, GC is utilized for analysing reaction products. Compounds like methane, ethylene, formic acid, CO or H₂ can be identified by comparing retention times with known standards. However, the compounds identification is limited by situations, when more compounds have the same retention times and for an accurate identification other methods like NMR or MS are required.

To analyse both hydrocarbons and non-hydrocarbon gases, a combination of more detectors is required. The flame ionization detector (FID) works by ionizing organic molecules, such as methane (CH_4) and ethylene (C_2H_4), in a hydrogen flame. This process generates a current proportional to the carbon content of the analytes. FID has limited sensitivity to non-hydrocarbon gases like CO and CO_2 .

In contrast, the thermal conductivity detector (TCD) operates by measuring the difference in thermal conductivity between the carrier gas, typically helium, and the analytes. Unlike FID, it can detect inorganic gases like CO, CO_2 , and H_2 , as well as light hydrocarbons, without requiring chemical modification. However, TCD is generally less sensitive than FID.

The barrier discharge ionization detector (BID) utilizes a plasma generated by a high-voltage AC discharge in helium to ionize the molecules of the analyte as they are eluted from the column. A current proportional to the analyte concentration is generated, as the separated ions go through the detector. It is possible to identify a wide range of compounds, including both inorganic gases and hydrocarbons, unlike with both FID and TCD. Moreover, BID offers higher sensitivity than TCD.^{97,98}

2.5.6 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) enables surface-sensitive (to the depth of 1–3 nm) analysis of elemental composition and oxidation states. Its surface sensitivity results from the short mean free path of photoelectrons ejected via the photoelectric effect. Standard XPS functions under ultrahigh vacuum (UHV) to prevent electron scattering. The development of near-atmospheric pressure (NAP)-XPS extends this method's application to *in situ* measurements under gas environments (up to a few hundred pascals). NAP-XPS employs both laboratory (e.g., Mg K α) and synchrotron X-ray sources. As this method utilizes X-rays, which is a high-energy photon beam, it reveals also inner-level electrons in spectra (e.g., O 1s, N 1s).⁹⁴

2.5.7 Photo-electrochemical characterization

2.5.7.1 Chronoamperometric tests

Chronoamperometry is an electrochemical technique monitoring current over time at a constant potential. It is a method used for evaluating photocathode's photo-response and stability in PEC systems. Applying a constant potential while measuring current under illumination reveals charge carrier generation and long-term performance.

In photo-electrochemical CO₂ reduction, chronoamperometry evaluates photocathode performance and stability. By applying a constant potential under light and monitoring current, efficiency and degradation over time can be evaluated.

2.5.7.2 Linear sweep voltammetry tests

Linear sweep voltammetry is a method used for electrode behaviour analysis by varying potential at a fixed rate and measuring the current response. It helps to evaluate the photocathode's stability in terms of charge carriers' recombination rate at specific potentials.

For CO₂RR, comparing light and dark scans assesses the effect of illumination on the electrode's photo-response. Dark scans, recorded without irradiation, measure the dark current. Light scans, performed under illumination, evaluate the photocurrent by comparing the results of these two. Chop tests, where light is periodically covered and uncovered, help analyse charge recombination by monitoring the immediate photocurrent drop at the start of each light period.

3 Experimental part

3.1 List of used Chemicals

Chemicals	Abbreviation	Purity/ concentration	Manufacturer
Copper (II) sulphate pentahydrate	$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$	$\geq 98,5\%$	VWR CHEMICALS
Hydrofluoric acid	HF	38-40 %	Lachner
Lactic acid in H_2O solution		90%	VWR CHEMICALS
MAX phase ≤ 40 micron	Ti_3AlC_2		Carbon Ukraine
Perfluorinated resin solution containing Nafion		5% in propanol	Sigma-Aldrich
Potassium hydrogen carbonate	KHCO_3		Sigma-Aldrich
Potassium sulphate	K_2SO_4	100%	VWR Chemicals
Sodium hydroxide	NaOH	P.A.	LACHNER
Titanium dioxide	TiO_2		Euro support

3.2 Procedures

3.2.1 Safety protocols and personal protective equipment⁸⁴

As in this work hydrofluoric acid was used for MXene synthesis, safety protocols and personal protective equipment have to be mentioned. Hydrofluoric acid is a highly corrosive, tissue-damaging and poisonous chemical. It causes acid burns due to high H^+ concentration alongside with way more dangerous liquefactive necrosis caused by lipophilic F^- anions. Exposure of body surface wider than 1 % leads to serious consequences like hyperkalemia, hypocalcemia, hypomagnesaemia and multiple organ failure. According to the concentration of HF solution one is affected with, the occurrence of the burn takes from a few seconds to two days (diluted solution). In case of exposure, the first step is to minimise the exposed area and exposure duration, followed by immediate rinsing of the affected area using the emergency shower or eyewash and removing contaminated clothing. The next step is to apply calcium gluconate gel, solution, or slurry and seek immediate hospital care, especially in case of inhalation of HF vapours.

To prevent any of the mentioned, special personal protective equipment (PPE) must be worn. Besides commonly used laboratory goggles, coat, closed-toe shoes and long pants, special acid-resistant gloves, and a plastic face shield must be utilized as well. As glass and metals are not HF-resistant, all laboratory equipment used for synthesis utilizing HF, as well as PPE, must be made of resistant materials, such as HDPP, thick PVC, natural rubber, Neoprene or PTFE.

The HF-containing waste must be properly disposed of, usually in a sealed-lid container made of listed materials that is labelled properly. The container must not be filled completely to leave a space for gas formation.

3.2.2 Etching

Multilayered $Ti_3C_2T_x$ was prepared by selective etching of the Al layer from the Ti_3AlC_2 parent phase with the solution of 20 % hydrofluoric acid. The reaction was held in a round-bottomed polypropylene centrifuge tube, which was placed in an ice bath. To prepare 20% solution 20.63 mL of deionised water was pipetted into the tube and then 18.25 mL of HF was added. The stirring was provided by a crossed stirring bar and the speed was set at 300 rpm. The solution was cooled down to 0 °C in an ice bath.

2 grams of Ti_3AlC_2 MAX phase was added very slowly into the acid solution in a time interval of at least one hour. The ice bath was kept at a temperature of 0 °C for the whole

adding procedure. Subsequently, the reaction mixture was left to warm up to ambient temperature (approximately 25 °C) and stirred overnight (for 16 hours at least).

The next day, the suspension was divided into four 250 mL tubes, the product was separated by a series of 5-minute-long centrifugation cycles at 3500 rpm, and it was rinsed with deionized water until almost neutral pH of supernatant. Obtained ml-Ti₃C₂T_x was then vacuum-filtered using PVDF membrane filters and rinsed with water once again. Both wet and vacuum oven-dried samples of the product were analysed using powder XRD.

3.2.3 Preparation of TiO₂-ml-Ti₃C₂T_x composite

The TiO₂-ml-Ti₃C₂T_x composite made of multilayered two-dimensional MXene covered with particles of TiO₂ was prepared by high-temperature treatment of ml-Ti₃C₂T_x. A combination of various conditions was used:

- Temperatures: 350 °C, 400 °C and 450 °C;
- Gas atmosphere: air flow, nitrogen flow, air atmosphere.

It was performed in a calcination oven with a connection to gas cylinders. The temperature step was set to 1 °C per minute, and the time of calcination was set to 4 hours in all the cases. Prepared materials were labelled as TiO₂-ml-Ti₃C₂T_x_temperature used for the calcination_atmosphere during calcination (e.g., TiO₂-ml-Ti₃C₂T_x_350°C_air flow). Series of various electrodes was prepared and further tested in the photo-electrocatalytic reactions.

3.2.4 Characterization of prepared materials

Powder X-ray diffraction (PXRD) analysis was performed using a Bruker AXS D8 Advance diffractometer, equipped with a DLYNXYE XE-T detector, in the Bragg–Brentano configuration. The measurements utilized Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$), generated at 30 mA and 40 kV. Diffraction data were obtained via continuous scanning over a 2θ angular range of 1–70°.

A Micromeritics 3-FLEX static volumetric apparatus was employed to obtain N₂ adsorption/desorption isotherms at –196 °C. Before the sorption experiments, the materials were degassed using a Micromeritics Smart VacPrep at 200 °C for 8 hours.

Surface morphology was examined using a JEOL JSM-IT800 scanning electron microscope (SEM), with images captured using a secondary electron detector. An accelerating voltage of 1 kV was employed during imaging. Samples were prepared by depositing them onto conductive carbon tape affixed to the SEM holder.

XPS analysis was conducted by RNDr. Tomáš Hrbek (MFF UK) to investigate the surface chemical composition of the samples. Spectra were recorded on an X-ray photoelectron spectrometer utilizing a non-monochromatized Mg K α X-ray source (1253.6 eV) and a Phoibos 150 hemispherical analyser (SPECES GmbH, Germany), operated in FAT (Fixed Analyzer Transmission) mode.

Diffuse reflectance ultraviolet-visible (UV-vis) spectra were measured in a wavelength range of 190 – 400 nm on a Cary 300 UV-Vis spectrophotometer. BaSO₄ was used as a reference. The spectra were processed using the Kubelka-Munk function.

3.2.5 Electrodes preparation

The electrode used for CO₂RR was prepared by electrodeposition of Cu₂O from copper (II) solution on fluorine-doped tin (IV) oxide (FTO) glass and further covered with layers of MXene Ti₃C₂T_x or TiO₂-Ti₃C₂T_x by spray-coating.

3.2.5.1 FTO glasses cleaning

Before electrodeposition of Cu₂O on FTO, FTO glasses were cleaned to remove especially organic contaminants using the RCA-1 Silicon Wafer Cleaning method. Firstly, 39 mL of 25% ammonium hydroxide solution was mixed with 195 mL of deionized water. The obtained solution was heated up to 70 ± 5 °C. After that, the solution was removed from the hotplate and 39 mL of 30 % hydrogen peroxide solution was added. FTO glass pieces were soaked for 15 minutes in this mixture. Then, FTO glass pieces were rinsed with deionized water and left to dry at 150 °C on a hotplate (the active side always directed upwards).

3.2.5.2 Potentiostatic electrodeposition of Cu₂O on FTO

Cu₂O was electrodeposited on FTO glass used as a conductive support. The top of the FTO glass was covered with Cu tape for better conductivity and connectivity with potentiostat (Figure 17). It was wired as a working electrode in a three-electrode system. It was immersed in a 0.5M Cu₂SO₄ 3M lactic acid solution prepared by dissolving 4,9767 g of Cu₂SO₄ · 5 H₂O in 38,8 mL of deionised H₂O and adding 11.2 mL of 90% lactic acid. The pH of the solution was adjusted either to the value of 9 or 10,5 by the addition of solid NaOH. For the electrodeposition process, the temperature of the solution was set to 65 °C, and it was stirred during the procedure. Voltage of – 0.64 and – 0,9 V vs Hg/Hg₂SO₄ (MSE), respectively, was then applied for 30 minutes. A platinum electrode was used as a counter electrode, and a mercury sulphate electrode Hg/Hg₂SO₄ (MSE) was used as a referent electrode. The FTO glass

was weighted before and after the electrodeposition to assess the electrodeposited amount of Cu_2O .

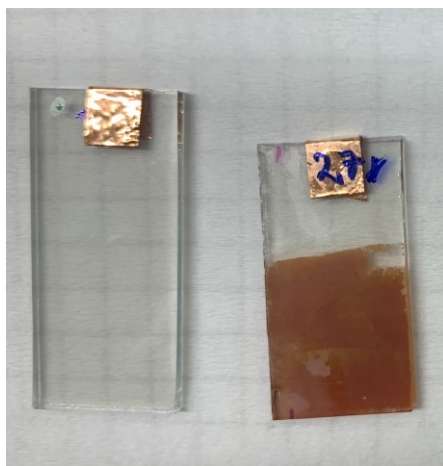


Figure 17: Photo of a FTO glass equipped with a Cu tape before the electrodeposition (on the left) and FTO glass coated with Cu_2O after electrodeposition (on the right)

3.2.5.3 Spray-coating

A suspension of MXene was prepared by dispersing 0.1 g in a mixture of 1 mL water and 0.23 mL of Nafion (5 wt % in isopropanol) using ultrasound. In one case, less concentrated suspension was prepared by mixing 10 mg of $\text{TiO}_2\text{-ml-Ti}_3\text{C}_2\text{T}_x$ with 1 mL of water and 23 μL of Nafion solution to compare the performance based on the amount of composite material present. After the electrodeposition of Cu_2O on FTO, the final $\text{TiO}_2\text{-ml-Ti}_3\text{C}_2\text{T}_x$ layer was sprayed on the electrode from its water suspension using a FENGDA BD-207K air-brush gun. The upper part (without Cu_2O) of the electrode was covered with Teflon tape, and FTO/ Cu_2O glass was then put on a 150 $^\circ\text{C}$ hot plate for 30 min to desorb organic impurities. After that, this glass was attached to the hotplate with scotch tape, the temperature was lowered to 110 $^\circ\text{C}$, and the suspension was spray-coated on the part covered with Cu_2O . The prepared electrode was left to dry on the hot plate for the next 30 minutes at 110 $^\circ\text{C}$ to ensure evaporation of water and isopropanol present in the Nafion solution. The electrode was weighted before and after the spray-coating to determine the mass of applied MXene per covered area.

3.2.6 Photo-electrochemical tests

Photo-electrochemical tests were performed using CH Instruments (Austin, TX, USA) 660D Workstation and two-compartment cell. The irradiation of electrodes was provided by a solar simulator (Newport-81094 Model equipped with the 300 W Xe-lamp and the AM 1.5 Global (2x2 inch) filter and UV filter). During measurements, the light intensity was adjusted to 100 $\text{mW}\cdot\text{cm}^{-2}$ with the calibrated reference cell (Portable Radiometer, International Light

Technologies Model 1400 with SEL623 and the thermopile detector with NIST Traceable Calibration).

3.2.6.1 Linear sweep voltammetry tests

On the prepared photo-electrocatalysts, linear sweep voltammetry tests were conducted in a 0.5M K₂SO₄ 0.5M KHCO₃ electrolyte (87,12 g of K₂SO₄ and 50,05 g of KHCO₃ in 1 L of deionised water, prepared in 1L volumetric flask), saturated first with argon and then with CO₂. The dependence of current density on applied potential was tested in a range of potential from 0 to 0.64 V vs RHE (reversible hydrogen electrode) at three modes: in dark mode, under light irradiation and in chopped mode (the shutter is repeatedly open for 3 seconds and closed for 3 seconds). A platinum electrode was used as a counter electrode, and a mercury sulphate electrode Hg/Hg₂SO₄ (MSE) or Ag/AgCl was used as a referent electrode.

After saturation of the electrolyte for 20 minutes, pH was measured to adjust the range of potential. Applied potential depends on the pH of the solution according to the equation:

$$E_{MSE} = E_{RHE} - E_{MSE}^{\circ} - 0.0592 \cdot pH \quad (3.1)$$

Where E_{MSE} is applied potential vs MSE, E_{RHE} is applied potential vs RHE, E_{MSE}° is the standard potential of MSE ($E_{MSE}^{\circ} = 0.65$ V), and pH refers to the pH of the electrolyte after Ar or CO₂ saturation. If recalculating to values measured vs Ag/AgCl reference electrode, E_{MSE} would be substituted with $E_{Ag/AgCl}$ and E_{MSE}° with $E_{Ag/AgCl}^{\circ}$ ($E_{Ag/AgCl}^{\circ} = 0.22$ V).

At dark tests, we measured dark photocurrent density without exposing the working electrode to light. For light tests, 300W Xe-lamp with 1.5 AM and UV filters was utilized as a source of light. Lastly, we carried out chopped tests. We measured the electrode's response by light shining for 3 seconds alternating with a dark period of the same duration.

These tests were performed in a two-compartment reactor with an anodic part from glass and the cathodic part from Teflon (Figure 18).

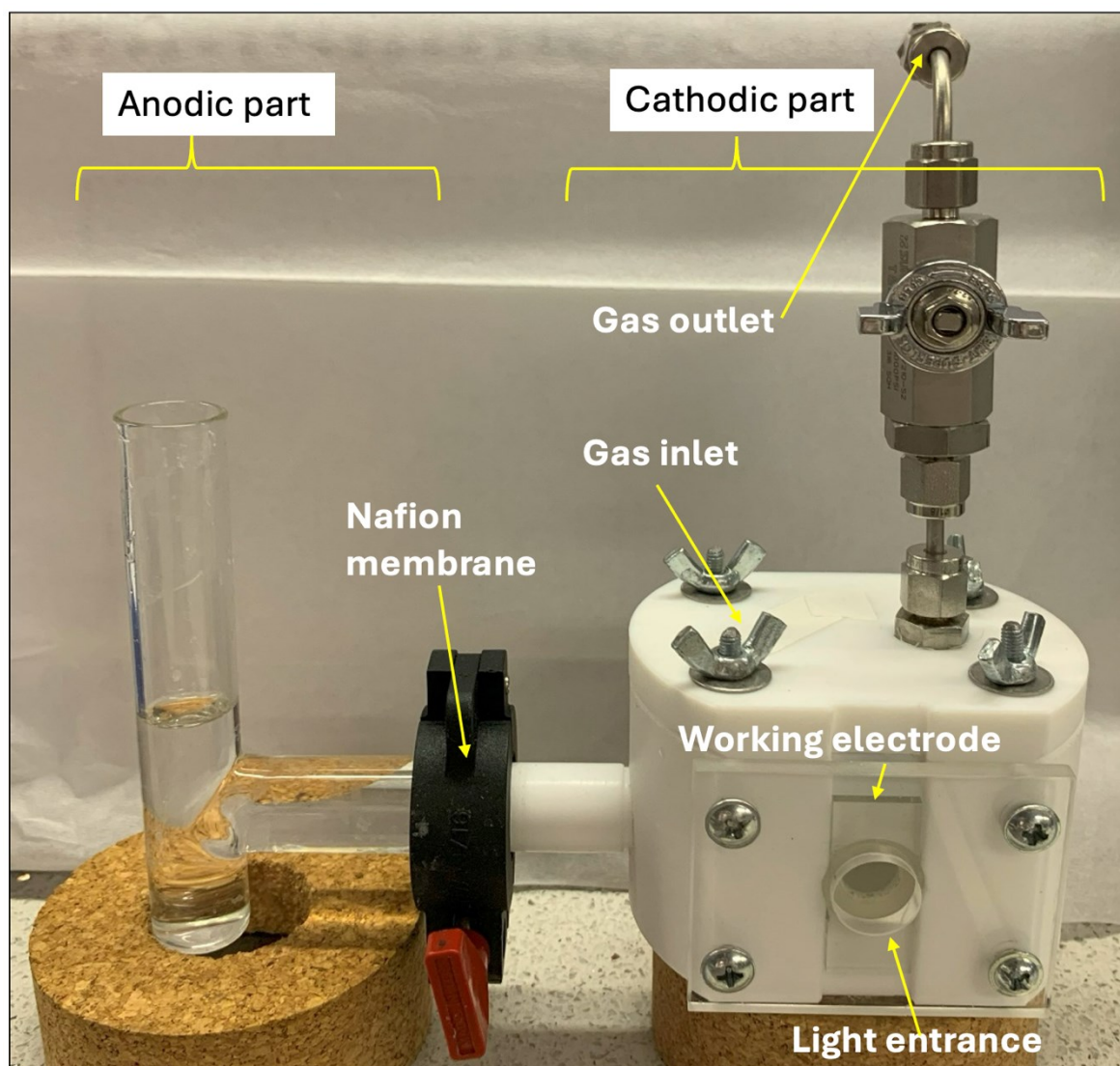


Figure 18: A photo of a two-compartment reactor used for photo-electrocatalytic tests.

Both compartments are separated by a proton-ion exchange Nafion membrane (Nafion 117; thickness, 0.007 inches) enabling the transfer of protons only. The reactor is filled with electrolyte, in our case, 0.5M KHCO_3 0.5M K_2SO_4 solution.

Each of the three tests is performed twice under argon saturation and twice under carbon dioxide saturation (80 mL/min for 20 minutes prior to the experiment). Argon displaces dissolved oxygen and other gases from the electrolyte, while carbon dioxide then participates in a reaction. The gas inlet is enabled also during the experiment (20 mL/min), while the excess of gas escapes freely, as the reactor is not sealed for this type of tests.

3.2.6.2 Chronoamperometric tests

The photocurrent density dependence on time was measured at a specific potential (0.24 V vs RHE) applied for 30 minutes. Performing the chronoamperometric test, the shutter

of a solar simulator lamp was closed three times for 15s periods approximately after 5, 15 and 25 minutes to evaluate the photoresponse and compare electrode performance at both dark and light conditions.

3.2.6.3 Long-term product analysis test

This analysis was conducted during my short visit of IC²R laboratories at Bari in Italy with the help of Domenico Caringella. This internship was organised as a part of the European Horizon project DESIRED. PEC CO₂ reduction tests were conducted in a two-compartment reactor (due to confidentiality concerning the project, this reactor cannot be described in further detail) with the compartments separated by Nafion membrane (Nafion 117; thickness, 0.007 inches). Prepared photocathodes calcined before the test for 30 minutes at 150 °C were utilized as a working electrode. Ag/AgCl (sat. KCl) electrode was employed as a reference electrode, Pt plate as a counter electrode. Solution of 0.5M KHCO₃ + 0.5M K₂SO₄ was used as electrolyte.

To remove air from the reactor, it was evacuated three or four times, followed by filling with CO₂. Oxygen was removed from the electrolyte, which was then kept and subsequently transferred to the reactor under N₂. The photocathode was irradiated for a period of 2 h with 300 W Xe lamp. The CO₂RR test was performed at applied potential of 0.24 V vs RHE. After 2-hour period, the lamp was turned off and the gas phase from the reactor was directly injected into GC (GC-2023 Nexis Shimadzu equipped with TCD and BID detectors, Mol-sieve and Q-Bond us as columns with He as a carrier gas). 5 mL of the electrolyte was sampled in a vial with a septum. This sample was kept at 90 °C for 30 minutes, and head-space gas was then injected into the GC.

3.2.6.4 False positive products of CO₂RR

To obtain representable results, any of the components of the electrode must not be exposed to any organic compounds during the preparation or other treatment. To be sure the product originates from CO₂, the presence of any other carbon source must be eliminated.

There are a few known C sources mentioned in the literature, that should be omitted²⁴:

- photo-electrocatalysts containing carbon;
- chemical contamination from the catalyst preparation (e.g., residues of organic chemicals might be released during the tests);
- equipment contaminants and contamination from the laboratory, including air;
- organic solvents used in any state of testing or electrode preparation;
- contamination introduced by the operator (by touching the equipment; organics from breath – most typically acetone, which is very often detected by GC in trace amounts).

Due to this, protocols adopted to avoid contaminations are listed below:²⁴

- Except for lactic acid and isopropanol present in solution of Nafion, no organic compounds were included during the catalyst's preparation and cleaning of the equipment.
- Special cleaning method was employed to remove organic contaminants from FTO glass pieces (RCA-1 protocol) and equipment used during the whole procedure.
- To confirm that the products of the PEC reactions do not originate from contamination, blank tests were performed by conducting the tests the same way except for changing CO₂ for inert gas like Ar or N₂.
- Special attention was paid to keeping the personal protective equipment clean.
- A face mask was worn by the operator.

Another possibility to confirm the origin of the reaction products is using labelled ¹³CO₂ as a reactant.

4 Results and Discussion

4.1 Material characterization of photoelectrode components

4.1.1 Characterization of Cu₂O layer

A thin layer of Cu₂O was deposited on FTO glass by potentiostatic method at applied potential of 0.36 vs RHE at 65 °C for 30 minutes. This coating was meant to serve as a photoactive component of the photocathode for PEC CO₂RR. As the performance of Cu₂O in PEC CO₂RR (in terms of product formation) strongly depends on the Cu₂O morphology, its layer was carefully analysed by a series of methods. Firstly, the current was plotted against time during the deposition itself (Figure 19). Considering the current density, we estimated the Cu₂O layer thickness, as the deposited amount relates to the current going through the system. This current density depends also on the counter and working electrode's surface area. An average value of a current density during electrodeposition was around -12 mA/cm². However, this method is not sufficiently precise, therefore the amount of the deposited oxide was determined by weighting. The amount of deposited Cu₂O was mostly around 3.5 mg/cm².

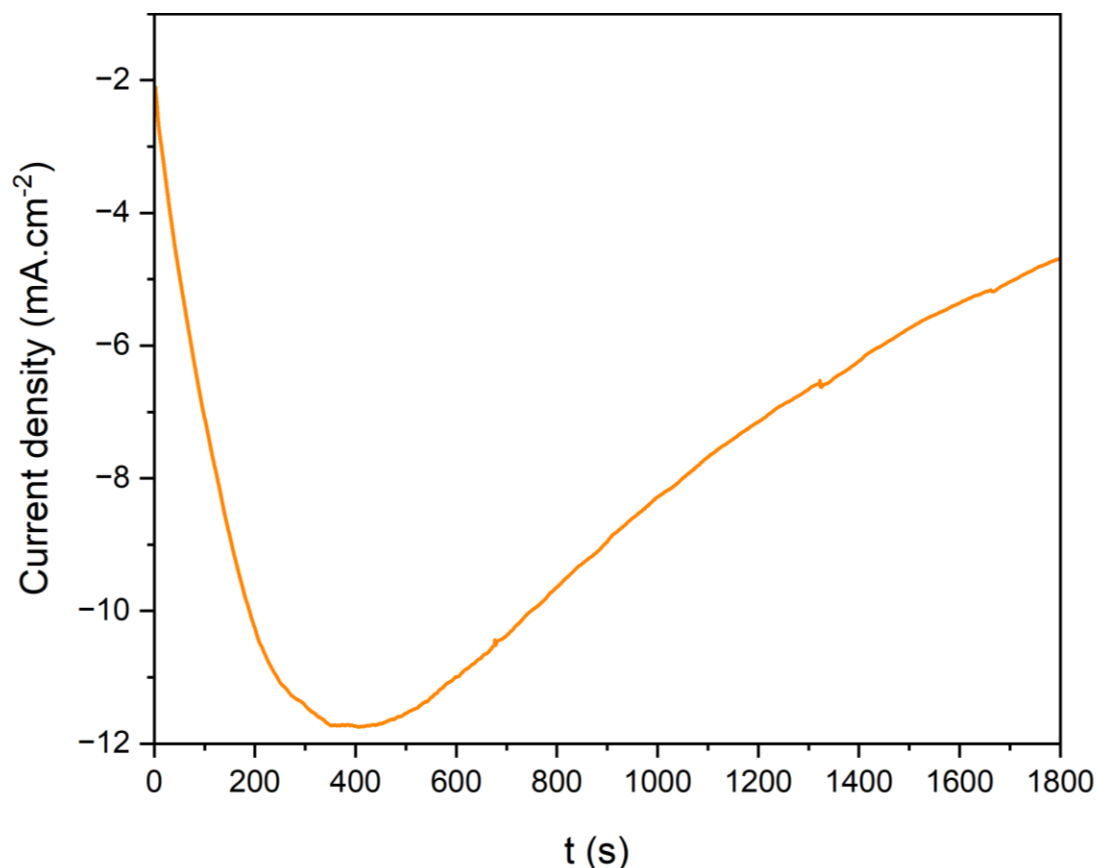


Figure 19: Plotted relation of a current density in time during electrodeposition of Cu₂O over FTO

Prepared FTO/Cu₂O electrodes were further characterized using X-ray diffraction. The diffraction pattern of the Cu₂O layer deposited over FTO glass was collected utilizing an XRD holder, onto which the whole electrode was placed. To be able to recognize a diffraction pattern of the Cu₂O layer in the FTO/Cu₂O pattern, the FTO glass diffraction pattern was also measured for comparison (Figure 19).

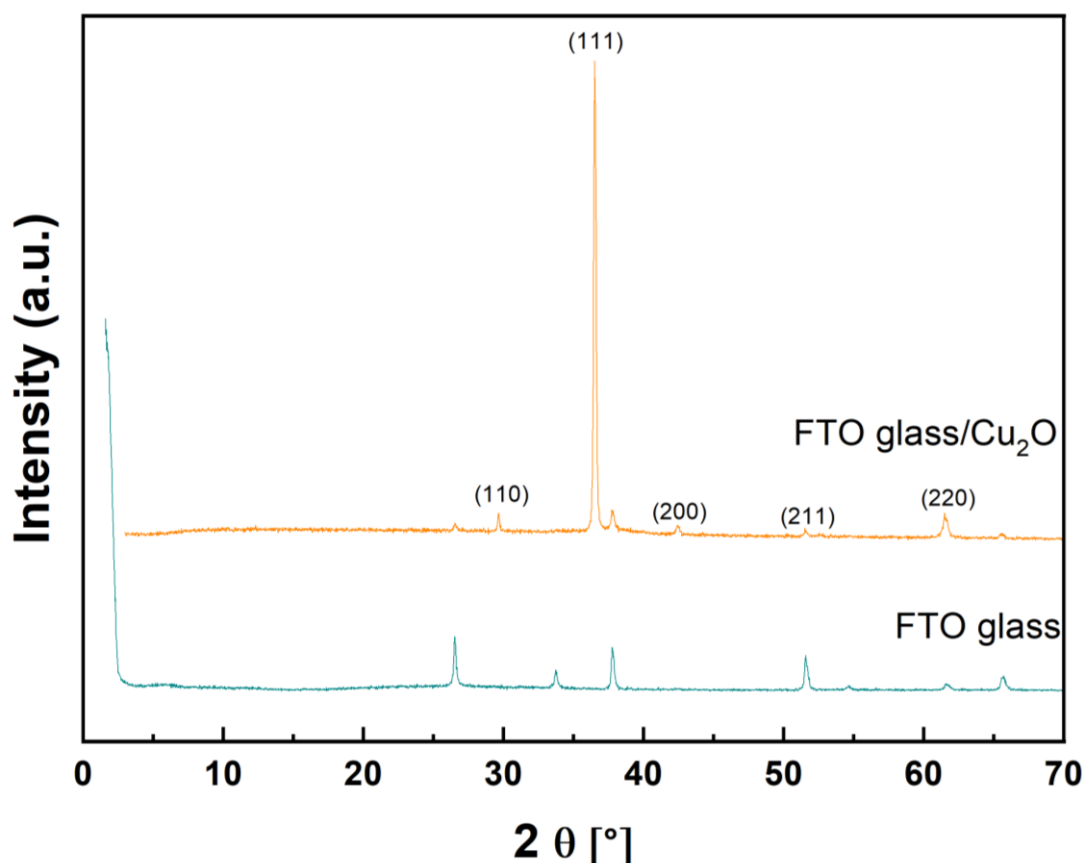


Figure 20: XRD patterns of FTO glass and Cu₂O deposited on a FTO glass

From XRD results, we concluded that the prepared layer of the Cu₂O shows dominantly an octahedral structure (see denoted Miller indexes in Figure 20)⁹⁹. For the copper (I) oxide, the octahedral structure typically has a high intensity ratio of the dominant (111) peak (at around 36 ° 2θ) to the (200) peak (around 44° 2θ).¹⁰⁰ The structure of the photoelectrode was visualised as a top-view using a scanning electron microscope (Figure 21, on the right). On the SEM image the surface exhibits a dense coverage of well-defined, faceted microcrystals with predominantly pyramidal morphologies. The sharp edges suggest controlled crystal growth, consistent with the typical (111) orientation of Cu₂O. A photo of the electrode was also taken (Figure 21, on the left).

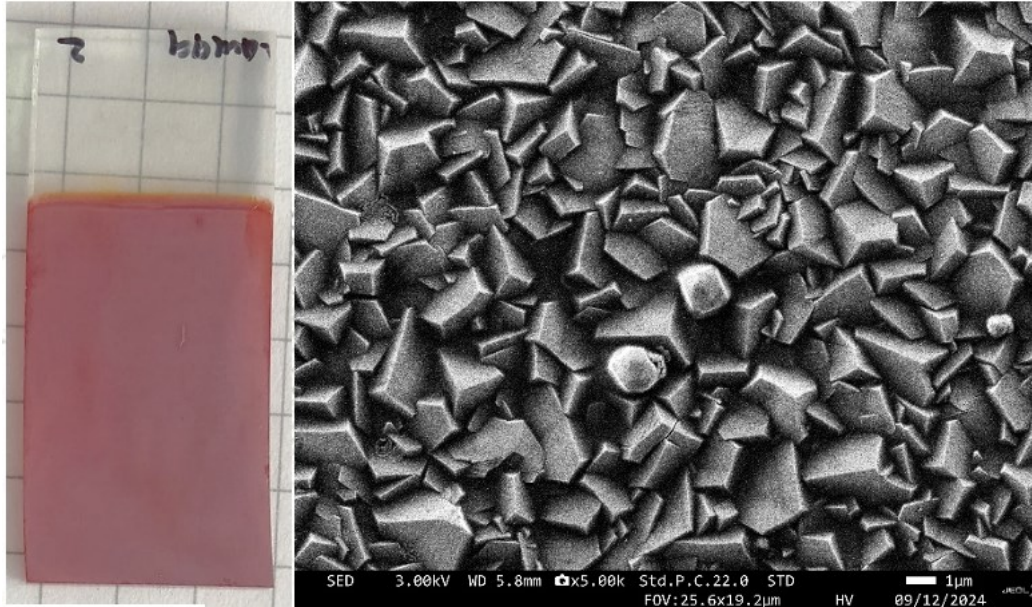


Figure 21: Photo of the FTO/Cu₂O photoelectrode on the left; SEM image of the Cu₂O layer of this electrode on the right

4.1.2 Characterization of MXene-Ti₂O composite

A series of various TiO₂-ml-Ti₃C₂T_x composites were synthesized. The conditions for each synthesis differed in temperature and/or atmosphere in the calcination oven (Table 2).

Table 2: Notation of materials and corresponding preparation conditions

Material	Atmosphere	Temperature [°C]
TiO ₂ -ml-Ti ₃ C ₂ T _x _350°C_N ₂ flow	N ₂ (flow)	350
TiO ₂ -ml-Ti ₃ C ₂ T _x _350°C_air atmosphere	air (static)	350
TiO ₂ -ml-Ti ₃ C ₂ T _x _350°C_air flow	air (flow)	350
TiO ₂ -ml-Ti ₃ C ₂ T _x _400°C_air flow	air (flow)	400
TiO ₂ -ml-Ti ₃ C ₂ T _x _450°C_air flow	air (flow)	450

It resulted in a different amount of TiO₂ formed by oxidation of Ti-atoms in ml-Ti₃C₂T_x MXene. As a first method to examine the structure of prepared materials, powder X-ray diffraction (PXRD) was used.

In Figure 22, PXRD patterns of materials prepared at 350 °C under various atmospheres (static air atmosphere, flow of N₂, and flow of air) are depicted. Figure 23 shows the comparison of PXRD patterns of the materials prepared at 350 °C, 400 °C and 450 °C under air flow.

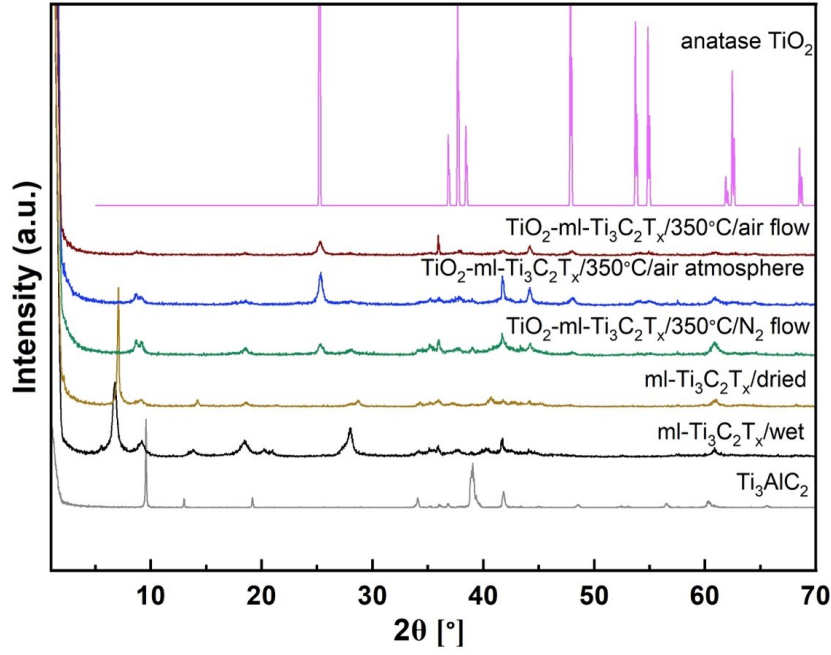


Figure 22: PXRD patterns of composite $\text{TiO}_2\text{-ml-Ti}_3\text{C}_2\text{T}_x$ prepared by a high-temperature treatment at 350 °C in the flow of nitrogen gas, flow of air and static air atmosphere. For comparison, the diffraction patterns of parent MAX phase (Ti_3AlC_2) and $\text{ml-Ti}_3\text{C}_2\text{T}_x$ directly after etching (wet) and after drying under vacuum (dried) are also included.

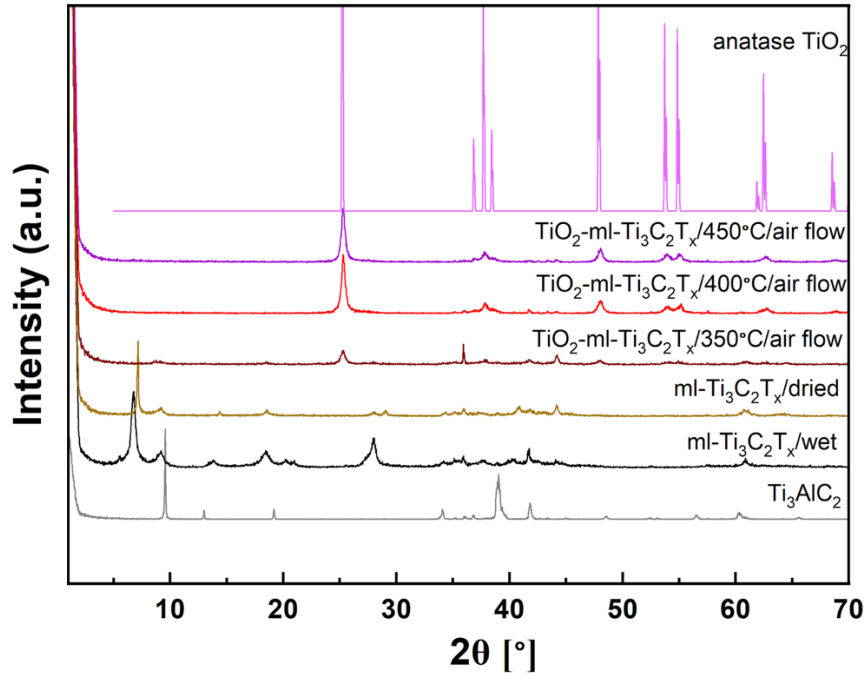


Figure 23: PXRD patterns of composite $\text{TiO}_2\text{-ml-Ti}_3\text{C}_2\text{T}_x$ prepared by a high-temperature treatment at 350 °C, 400 °C and 450 °C under air flow. For comparison, the diffraction patterns of parent MAX phase (Ti_3AlC_2) and $\text{ml-Ti}_3\text{C}_2\text{T}_x$ directly after etching (wet) and after drying under vacuum (dried) are also included.

When investigating the structure of MXene prepared from its parent MAX phase by etching, one should keep in mind several aspects. Firstly, the success of obtaining the multi-layered MXene $\text{ml-Ti}_3\text{C}_2\text{T}_x$ was evaluated based on a shift of a peak around $7^\circ 2\theta$, which signalled the change in interlayer spacing. In a freshly etched wet $\text{ml-Ti}_3\text{C}_2\text{T}_x$, this peak shifts towards lower angles. It is a consequence of removal of the Al layer from the Ti_3AlC_2 and simultaneous intercalation of H_2O molecules and coverage of the surface with terminal groups. After drying of $\text{ml-Ti}_3\text{C}_2\text{T}_x$, this peak shifts slightly back towards the higher angles, as a part of the intercalated H_2O molecules is being removed. However, the interlayer spacing is still larger than in the parent MAX phase due to the presence of the mentioned terminal groups. Secondly, the peaks at higher angles corresponding to the interlayer spacing either vanish completely, or lower in intensities.⁹³

After the thermal treatment of $\text{ml-Ti}_3\text{C}_2\text{T}_x$ the formation of TiO_2 is evident in all materials (Figure 22 and Figure 23) due to the dominant peak around $25^\circ 2\theta$, as this diffraction peak is typical for titanium dioxide. The share of TiO_2 and therefore the peak's intensity gets higher with rising temperature, which indicates the temperature effect on the oxidation of Ti to TiO_2 . This fact was also confirmed by the increase in the weight of the sample after calcination due to the formation of TiO_2 and the change in colour from dark grey/black to lighter shades. The presence of $\text{ml-Ti}_3\text{C}_2\text{T}_x$ in each composite from Figure 22 was confirmed by the presence of interlayer diffraction peaks, especially that at 6.8 , 7.1 and around $8.7^\circ 2\theta$. Peaks at mentioned angles are visible on the patterns collected from measurements of wet and dried $\text{ml-Ti}_3\text{C}_2\text{T}_x$ and on those calcined at 350°C , too.

Scanning electron microscope images of the prepared composite materials are depicted in Figure 24. All the images show the typical MXenes accordion-like morphology. No significant differences were observed among the samples calcined at 350°C under different atmospheres. However, in a close detail, the surface of materials calcined at 400 and 450°C seems to be covered by small rice-crust-like particles. This type of morphology was reported for $\text{TiO}_2\text{-ml-Ti}_3\text{C}_2\text{T}_x$ calcined at high temperatures.⁷⁶

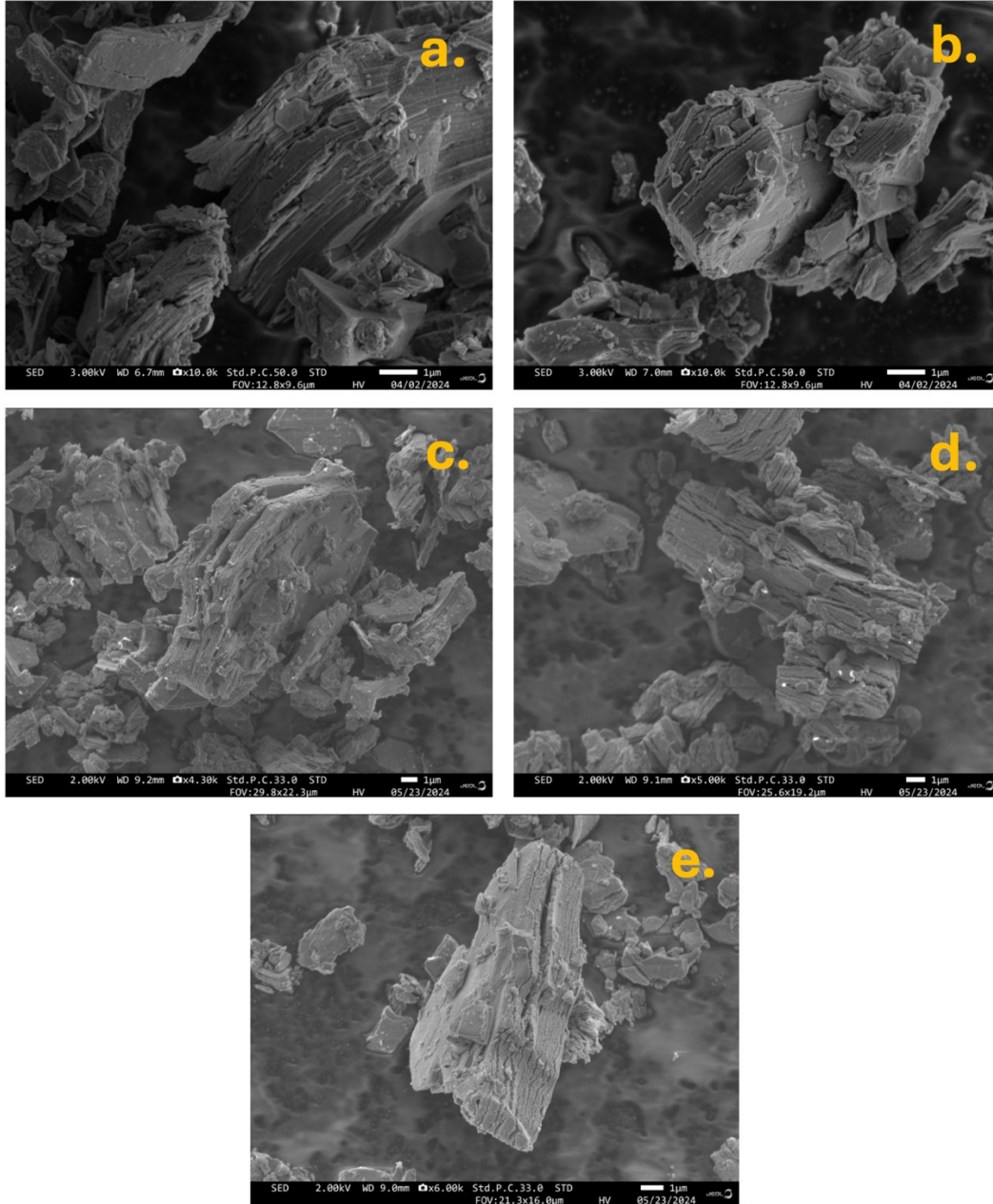


Figure 24: SEM images of $\text{TiO}_2\text{-ml-Ti}_3\text{C}_2\text{T}_x$ composite materials prepared by calcination under nitrogen flow at 350 °C (a.), under static air atmosphere at 350 °C (b.), and under air flow at 350 °C (c.), 400 °C (d.) and 450 °C (e.).

The X-ray photoelectron spectroscopy was employed as a surface-sensitive technique. The O 1s, T 2p and C 1s spectra of ml- $\text{Ti}_3\text{C}_2\text{T}_x$ and all calcined materials were measured (Figure 25). The C 1s spectra of ml- $\text{Ti}_3\text{C}_2\text{T}_x$ revealed a broad peak at around 282 eV confirming the presence of the multilayered MXene, as this peak corresponds to Ti-C-Ti component.¹⁰¹ After deconvolution of band at 455 eV in the Ti 2p spectrum (Figure 26) several distinct peaks were recognized and assigned according to the literature. This band is created by a fusion of 455.2, 456.3 and 457.4 eV assigned to C-Ti(O/OH), C-Ti²⁺-(O/OH) and C-Ti³⁺-(O/OH)

components, respectively.⁹⁶ This band is also present only in a spectrum of the uncalcined multilayered MXene, confirming the information obtained from the C 1s spectrum. The band with the position around 455 eV belongs to C-Ti-O/F, MXenes' usual termination groups.¹⁰¹ Peaks of Ti 2p region at 459 and 466 eV suggest the presence of TiO₂ in the sample, which can be formed in a small amount also during the etching.

On the contrary, the mentioned peak at 282 eV in C1 spectrum vanished in spectra of all calcined materials (regardless of the preparation conditions), as well as the peak of Ti 2p region at 459 eV. It should be noted that XPS is a surface characterization technique with a typical analysis depth of only a few nanometres (approximately 5–10 nm, depending on the material and photoelectron energy). Therefore, these results do not necessarily rule out the presence of MXene within the bulk of the composite material.

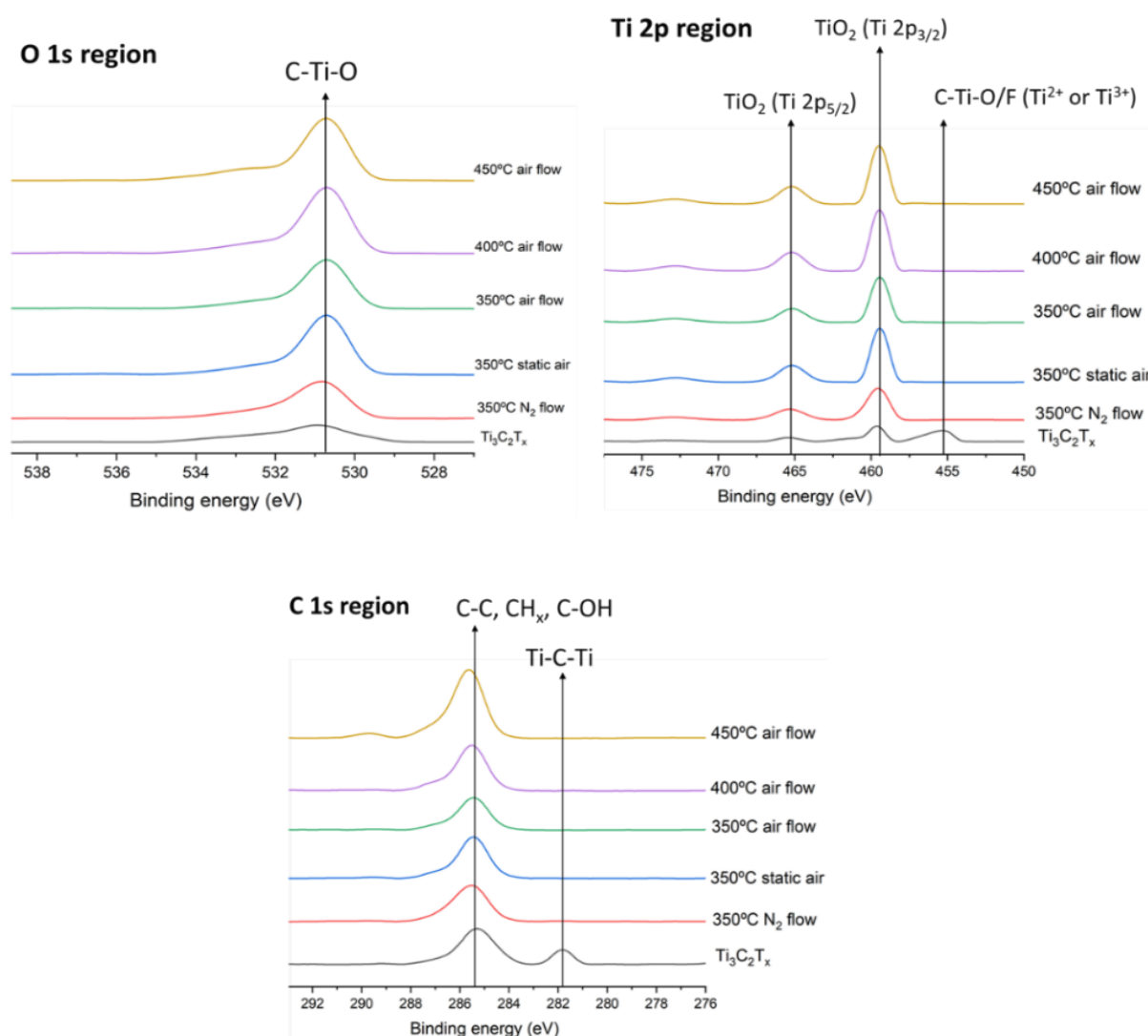


Figure 25: XPS spectra of multilayered Ti₃C₂T_x and composite materials prepared by calcination under various atmospheres at 350 °C, 400 °C and 450 °C

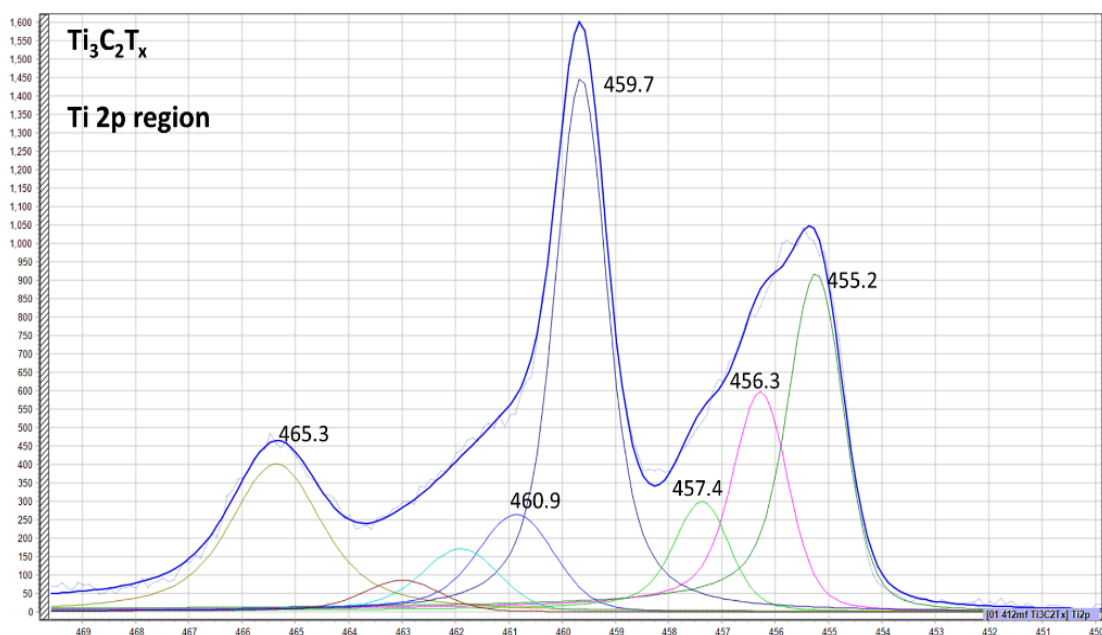


Figure 26: Deconvolution of XPS spectra in Ti 2p region for multilayered $\text{Ti}_3\text{C}_2\text{T}_x$ MXene (before any calcination)

The composites were further investigated using UV-Vis spectroscopy. UV-Vis spectra at a wavelength range from 200 to 900 nm were measured in a reflectance mode and the obtained data were recalculated to absorbance values using the Kubelka-Munk function. The resulting plots are summarized in Figure 27. From the obtained curves, the presence of titanium dioxide in each composite can be estimated, as white coloured TiO_2 absorbs in the UV range only, while dark grey/black multilayered MXene absorbs in the whole range of measurement, similar to metals. Both pure TiO_2 and ml- $\text{Ti}_3\text{C}_2\text{T}_x$ are included in the plot as a reference. With a supposed extent of oxidation, the absorbance of visible light decreases. The composite materials treated with higher temperatures (400 and 450 °C) do not absorb in the visible range at all. The ml- $\text{Ti}_3\text{C}_2\text{T}_x$ calcined at 350 °C under N_2 shows a higher absorption of visible light than the freshly etched ml- $\text{Ti}_3\text{C}_2\text{T}_x$.

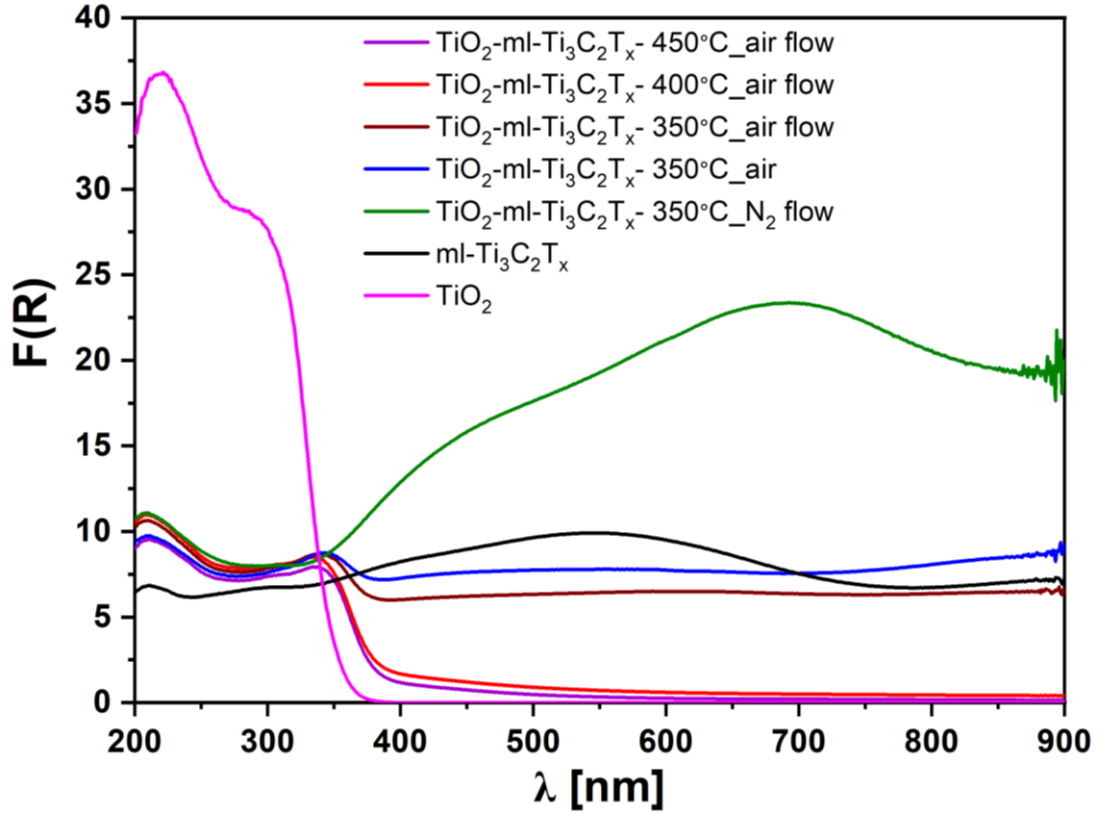


Figure 27: UV-Vis spectra of multilayered $ml-Ti_3C_2T_x$ and composite materials prepared by calcination under various atmospheres at 350 °C, 400 °C and 450 °C

The measured spectra were utilized to calculate the band gap values of all composites, as well as $ml-Ti_3C_2T_x$. These values were determined using a Tauc plot. Obtained plots are summarized in Figure 28 and the determined values of band gap energies are listed in Table 3. Multilayered $Ti_3C_2T_x$ itself is typically classified as a metallic type of conductor, not a semiconductor. However, the conducting properties of MXene can be affected by the termination groups present on the material's surface.¹⁰³ Here, the $ml-Ti_3C_2T_x$ shows signs of a band gap of 1.2 eV.

TiO_2 , which is formed on the $Ti_3C_2T_x$ surface, is an indirect band gap semiconductor, therefore Tauc plot for indirect band gap calculation was used for determining the BG of prepared composites.⁹⁶ Observing the increasing values of BG in Table 3, it is evident that there is a correlation between the BG value and the increasing temperature during the calcination of MXene. In conclusion, the higher the extent of $ml-Ti_3C_2T_x$ oxidation, the closer the band gap value of prepared composite material is to the BG value of the TiO_2 band gap.

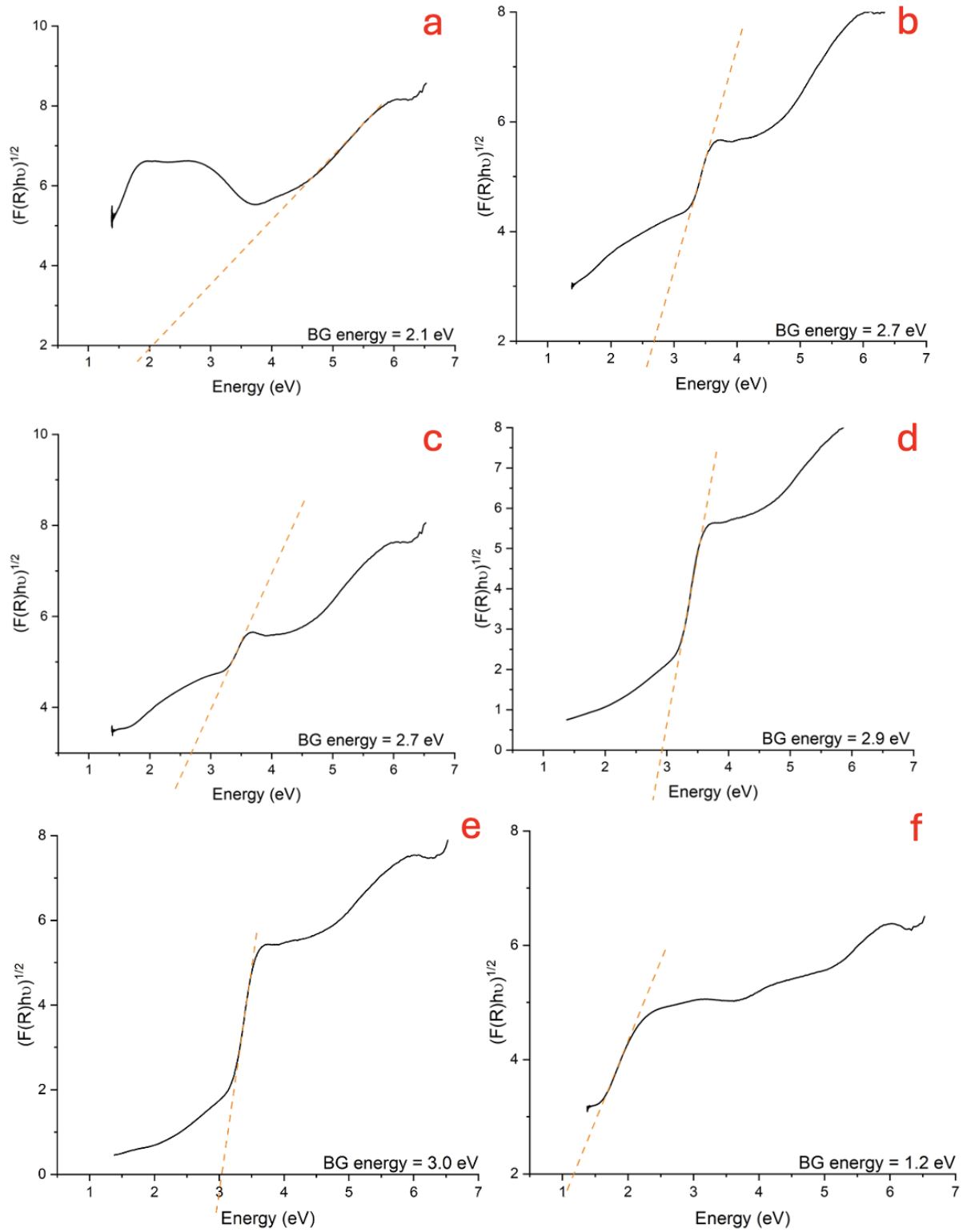


Figure 28: Tauc plots of composite materials prepared by calcination under nitrogen flow at 350 °C (a), under static air atmosphere at 350 °C (b), and under air flow at 350 °C (c), 400 °C (d) and 450 °C (e) and non-calcined multilayered $Ti_3C_2T_x$ (f). BG = band gap

Table 3: Indirect band gap energy values from plots of multilayered $Ti_3C_2T_x$ and composite materials prepared by calcination under various atmospheres at 350, 400 and 450 °C.

Material	Band gap energy [eV]
ml- $Ti_3C_2T_x$	1.2
TiO_2 -ml- $Ti_3C_2T_x$ _350 °C_ N_2 flow	2.1
TiO_2 -ml- $Ti_3C_2T_x$ _350 °C_ air atmosphere	2.7
TiO_2 -ml- $Ti_3C_2T_x$ _350 °C_ air flow	2.7
TiO_2 -ml- $Ti_3C_2T_x$ _400 °C_ air flow	2.9
TiO_2 -ml- $Ti_3C_2T_x$ _450 °C_ air flow	3.0

Nitrogen physisorption was used to examine the changes in textural properties of prepared composites BET method. The adsorption and desorption isotherms of all materials are captured in Figure 29.

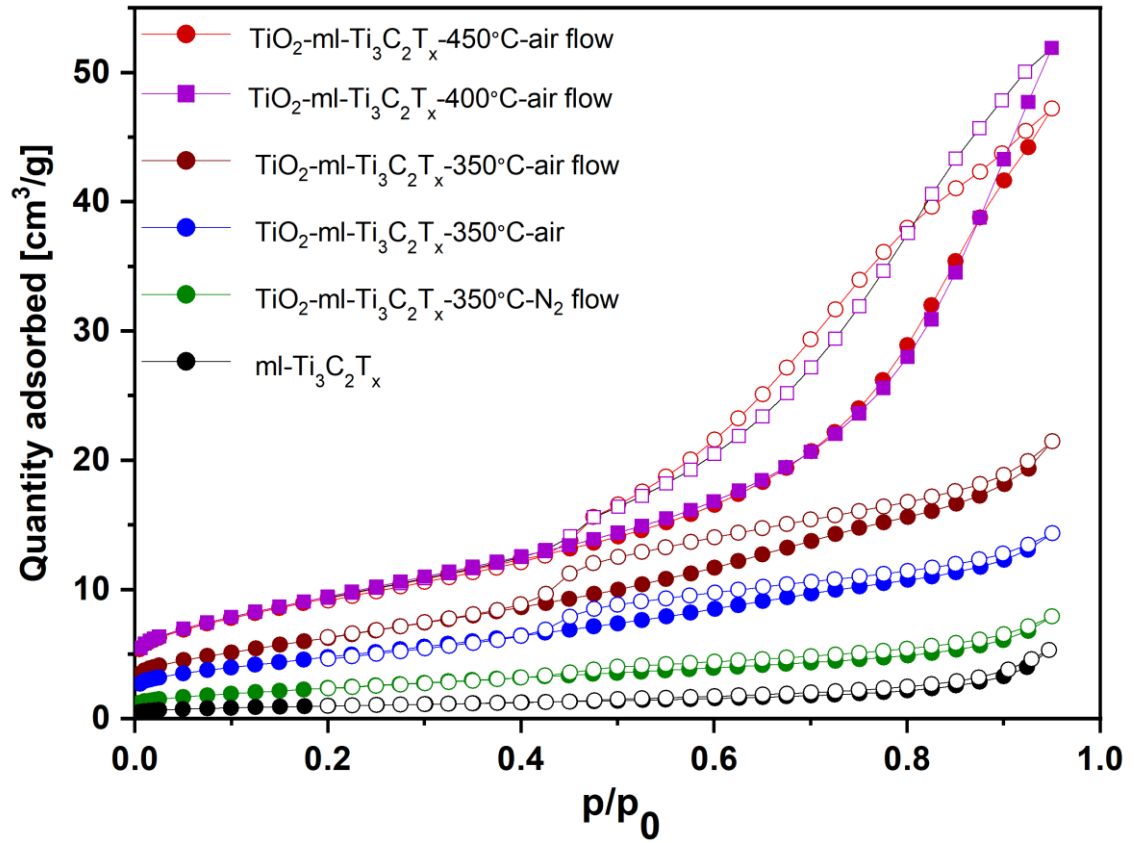


Figure 29: Adsorption and desorption isotherms of ml- $Ti_3C_2T_x$ and TiO_2 -ml- $Ti_3C_2T_x$ composites measured by nitrogen physisorption

Table 4: Values of surface areas evaluated by BET method

Material	BET [m ² /g]
ml-Ti ₃ C ₂ T _x	4
TiO ₂ -ml-Ti ₃ C ₂ T _x _350 °C_N ₂ flow	9
TiO ₂ -ml-Ti ₃ C ₂ T _x _350 °C_air atmosphere	17
TiO ₂ -ml-Ti ₃ C ₂ T _x _350 °C_air flow	23
TiO ₂ -ml-Ti ₃ C ₂ T _x _400 °C_air flow	34
TiO ₂ -ml-Ti ₃ C ₂ T _x _450 °C_air flow	33

It is important to note that, since MXenes are nonporous, the surface area of the prepared composites was not expected to be particularly high. Accordingly, the obtained BET values are relatively low compared to those of porous materials commonly used as catalysts or catalyst supports. Multilayered Ti₃C₂T_x exhibits only a very small surface area of 4 m²/g. With increasing temperature, the values of BET surface area goes up to 34 m²/g. In the isotherm of materials calcined at 400 and 450 °C a hysteresis loop is clearly distinguished. Based on that, we concluded that these two materials probably differ from others by the presence of the interparticle voids and spaces, which were probably formed by the high temperature treatment causing oxidation of the surface and forming of TiO₂.

To conclude the characterisation of prepared TiO₂-ml-Ti₃C₂T_x materials, although XPS results may indicate that MXene phase is not present, powder XRD patterns confirmed the retention of the Ti₃C₂T_x structure in all samples calcined at 350 °C. In addition, SEM images showed no unusual features indicating the presence of an isolated TiO₂ phase. Thus, the combination of XRD, SEM and XPS methods revealed an intimate contact between *in situ* grown TiO₂ and the surface of Ti₃C₂T_x. Furthermore, UV-Vis spectroscopy and Tauc plot analysis indicate that higher calcination temperatures result in band gap values that more closely approach that of pure TiO₂.

4.1.3 Characterization of FTO/Cu₂O/Ti₂O-MXene electrodes

Following the materials characterisation, the final multicomponent electrodes were characterised via photo-electrocatalytic tests. The electrodes were labelled as FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x_temperature calcination_atmosphere indicating the conditions of their preparation, e.g., FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x_350°C_air flow. Two types of tests were performed, the linear sweep voltammetry (LSV) and the chronoamperometric tests. LSV tests were conducted

to examine the photoelectrodes' response to illumination in terms of the photocurrent density in relation to the potential applied and the presence of light. Chronoamperometric tests were utilized to evaluate the photocurrent density in time and thus the stability of the photoelectrode.

4.1.3.1 Linear sweep voltammetry tests results

LSV tests were carried out after the saturation of two gases – argon and CO₂. The relation between the generated photocurrent density vs applied potential was observed in three modes (light, dark, chopped). The tests after saturation with argon served as a blank experiment to examine whether carbon dioxide takes part in the reaction. The ideal case here is the photocurrent being more negative after saturation with CO₂ than with argon pointing to reaction of CO₂ on the surface of photocathode. Figure 30 depicts the plot of recorded photocurrent against the potential applied. In this picture, all three modes are shown after both argon (dashed lines) and carbon dioxide (full lines) saturation. From this relation, several aspects can be evaluated.

Firstly, the dark-current (blue line) represents the stability of the non-illuminated electrode. Ideally, this line should be constant and as close to zero as possible. If the dark-current significantly diverges from zero, it indicates that the reaction proceeds even in the absence of photo-excited charge carriers. It may indicate the instability of the electrode and some changes on the electrode surface.

Secondly, the light-current (red line) indicate the photoactivity of the photocathode under illumination. The research aims to prepare the photocathode providing high negative photocurrent densities, which indicate efficient charge separation, with minimized electron-hole recombination losses. At low applied potentials, negative photocurrent also suggests low energy supply requirements, enhancing the energy efficiency of the CO₂ reduction process.

Lastly, from the signal collected during the chopped mode, the electrode stability and charge recombination rate can be evaluated. Ideally, the light period parts of the signal should copy the light mode line and the dark period parts of the chopped mode signal should copy the dark mode line. If one of these requirements is not fulfilled, it can indicate some issues with stability and fast charge recombination. The charge recombination can be revealed also by the presence of spikes on the chopped mode line right at the beginning of the light period. These are caused by intense photoexcitation of the electrons by exposure to light, however, a certain part of the photogenerated electron-hole pairs recombine immediately. In Figure 30, the light and the dark periods of the chopped mode plot are highlighted, as well as the charge recombination spike.

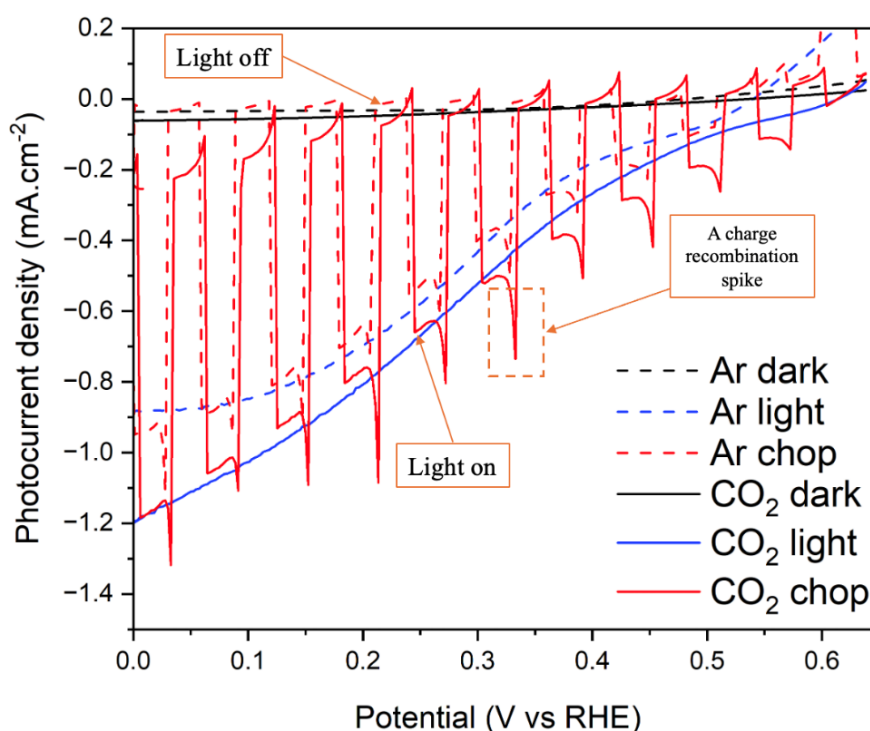


Figure 30: Linear sweep voltammetry of FTO/Cu₂O electrode in electrolyte saturated with argon (dashed lines) and with CO₂ (full line).

Figure 30 shows the results of LSV tests of FTO/Cu₂O photocathode. From this graph, it can be concluded that the reaction is probably taking place in the system after saturation of the electrolyte with the CO₂, as the photocurrent in both the light mode line and the light period of the chopped mode line is more negative than the one of both mentioned for the system after saturation with argon.

Figure 31 captures a summary of the chopped mode LSV results after saturation with CO₂ collected for the electrodes prepared from materials calcined at 350 °C at various atmospheres. From the graph it is evident that the FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x_350°C_N₂ flow electrode provides the highest negative photocurrent, and a decent dark current, which is quite close to zero. Other photocathodes do not reach such negative values and in the case of the one calcined under air flow (brown line), the dark current is significantly decreasing. All the results were also compared with the bare FTO/Cu₂O photocathode (orange line in all the graphs). The additional layer of TiO₂-ml-Ti₃C₂T_x over FTO/Cu₂O enhances the electrodes' performance in terms of both photocurrent response and stability particularly for material prepared under nitrogen atmosphere (green line). Moreover, the LSV chopped mode line of the FTO/Cu₂O photocathode is distinct by the spikes at the beginning of the dark period, not only the light one.

These dark phase spikes are particularly eliminated in the case of FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x_350°C_N₂ flow (green line).

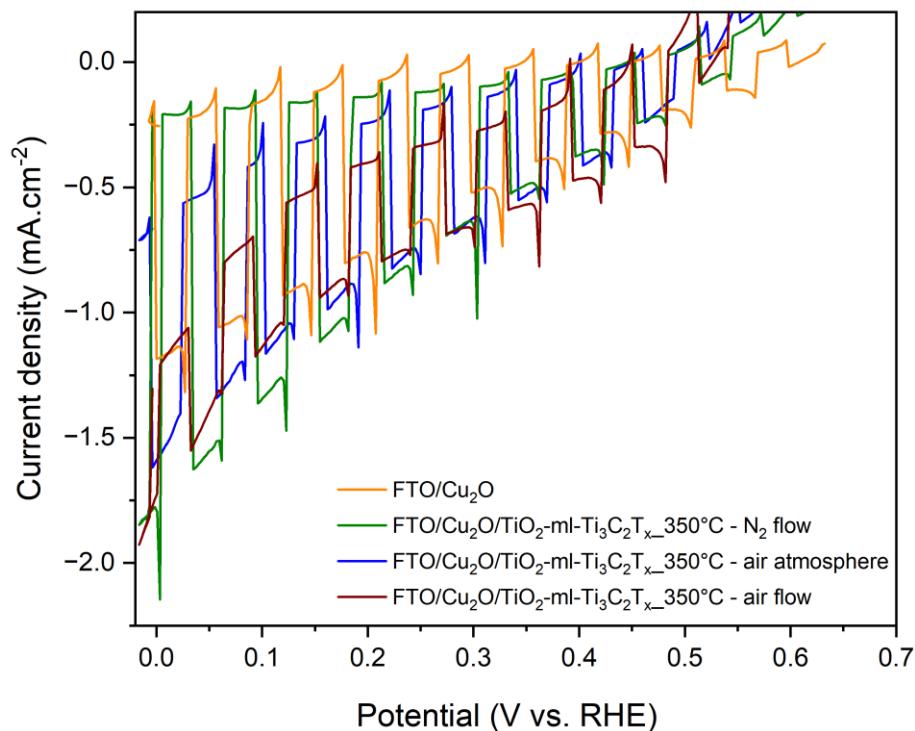


Figure 31: Results of chopped mode linear sweep voltammetry tests of the FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x_350°C electrodes after saturation of the electrolyte with CO₂.

Figure 32 shows the comparison of LVS results for photocathodes with composites prepared under air flow at 350, 400 and 450°C. The dark currents are decreasing with decreasing applied potential. The photocurrent densities are less negative for higher temperatures (400, 450 °C) compared to the material prepared at 350 °C (brown). Considering these results, photocorrosion likely occurs. Interestingly, there are not any spikes that would signalize the charge recombination.

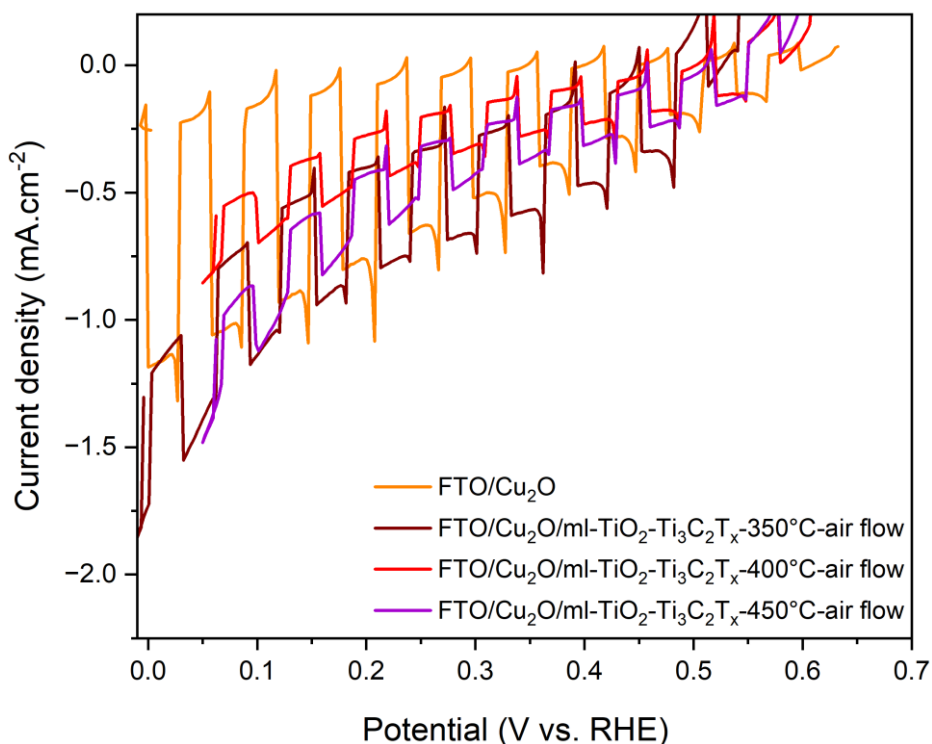


Figure 32: Results of chopped mode linear sweep voltammetry tests of the FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x_air flow electrodes after saturation of the electrolyte with CO₂.

For comparison, FTO/Cu₂O/TiO₂ photocathode was prepared by spray-coating of a suspension of commercially available titanium dioxide over FTO/Cu₂O. This electrode was evaluated using LSV (Figure 33). Under tested conditions, TiO₂ layer cannot be photoexcited as we simulate natural light by using solar simulator with AM 1.5 filter and additionally UV filter. Therefore, Cu₂O serves as an absorbing material and TiO₂ as a stabilising material as discussed above in Chapter 2.3.4.1. In this system, we expect a transfer of photoexcited electrons from Cu₂O towards conduction band of TiO₂.

In LSV curve FTO/Cu₂O/TiO₂ exhibits lower photocurrent density under illumination and an unstable dark current compared to FTO/Cu₂O. However, the charge recombination spikes were minimal, indicating good charge carrier stability, which is the desired outcome when employing Cu₂O/TiO₂ heterojunction. This result supports the validity of the theoretical assumptions underlying this thesis.

To conclude the results from LSV, the FTO/Cu₂O/TiO₂-Ti₃C₂T_x composite photocathodes exhibited improved stability and photo-electrochemical activity compared to Cu₂O/TiO₂. Moreover, the photocathode FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x_350°C_N₂ flow revealed higher negative photocurrent densities, low dark current and minimal spikes in comparison with bare FTO/Cu₂O.

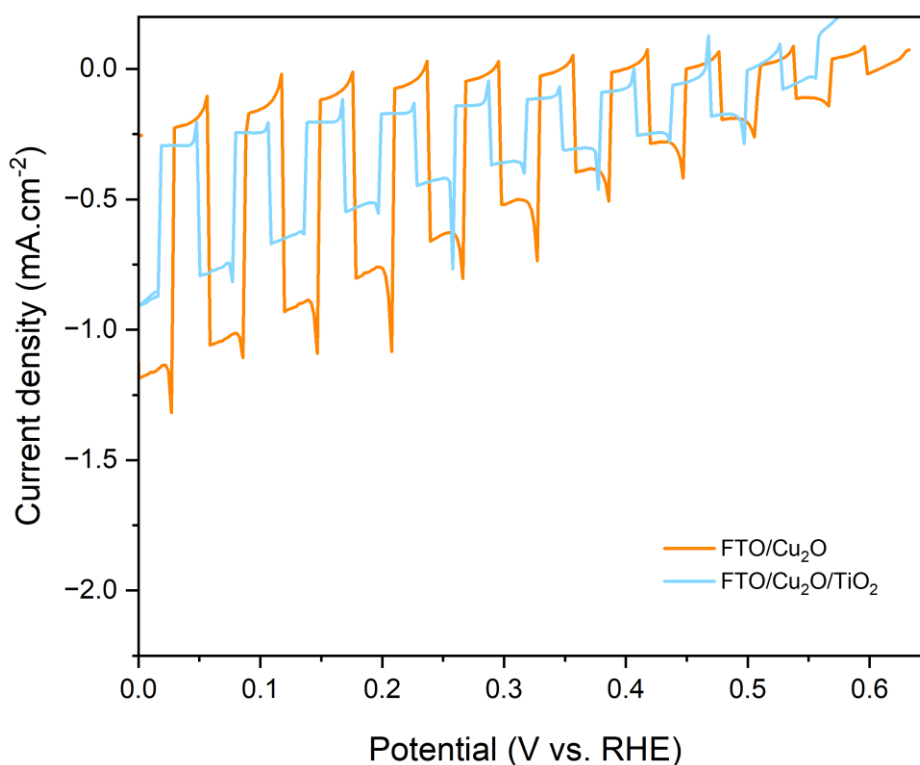


Figure 33: Results of chopped mode linear sweep voltammetry tests of the FTO/Cu₂O/TiO₂ electrode after saturation of the electrolyte with CO₂.

4.1.3.2 Chronoamperometric tests results

Chronoamperometric tests were conducted in a two-compartment reactor after saturation of the electrolyte with CO₂. The measurements were done to evaluate the photocurrent response of each photocathode after a longer period (30 minutes) at a constant potential applied. During these tests, the shutter was closed three times around the fifth, fifteenth and twenty-fifth minute to observe also the changes in a dark current and evaluate the photoresponse of electrode.

Figure 34 shows the results of all photoelectrodes. Additionally, we prepared FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x_350°C_N₂ flow electrode from diluted suspension of TiO₂-ml-Ti₃C₂T_x_350°C_N₂ to assess the effect of amount of spray-coated material on the performance (in the Figure 34 distinguished as *dil.*, light green colour line). In the case of the bare FTO/Cu₂O electrode, the photocurrent density was observed to decrease over time, which, in combination with a simultaneous decline in dark current, typically indicates ongoing photocorrosion processes. This behaviour is commonly associated with the reduction of Cu (I) to metallic copper, resulting in the formation of conductive copper species on the electrode surface, which can alter the electrochemical properties of the material and further contribute to its degradation.

All the electrodes with the additional layer of the $\text{TiO}_2\text{-ml-Ti}_3\text{C}_2\text{T}_x$ composite demonstrated relatively stable photocurrent densities over a 30-minute illumination period and maintained consistent photoresponsiveness throughout the entire duration of the experiment. This indicates their ability to sustain charge separation and transport under continuous light exposure, suggesting relative stability in photoelectrochemical conditions. The results indicate that the most promising samples are FTO/ Cu_2O /TiO₂-ml-Ti₃C₂T_x_350°C_N₂ flow (dark green line) and FTO/ Cu_2O /TiO₂-ml-Ti₃C₂T_x_350°C_air atmosphere (dark blue line). These photocathodes give the most negative stable photocurrent density around 0.7 mA/cm². On the other hand, the photocathode prepared from the diluted suspension of TiO₂-ml-Ti₃C₂T_x_350°C_N₂ flow material (light green colour) shows only very small photocurrent densities but stable dark current. Thus, we can conclude that the amount of applied material plays a crucial role, as well as the identity of this material.

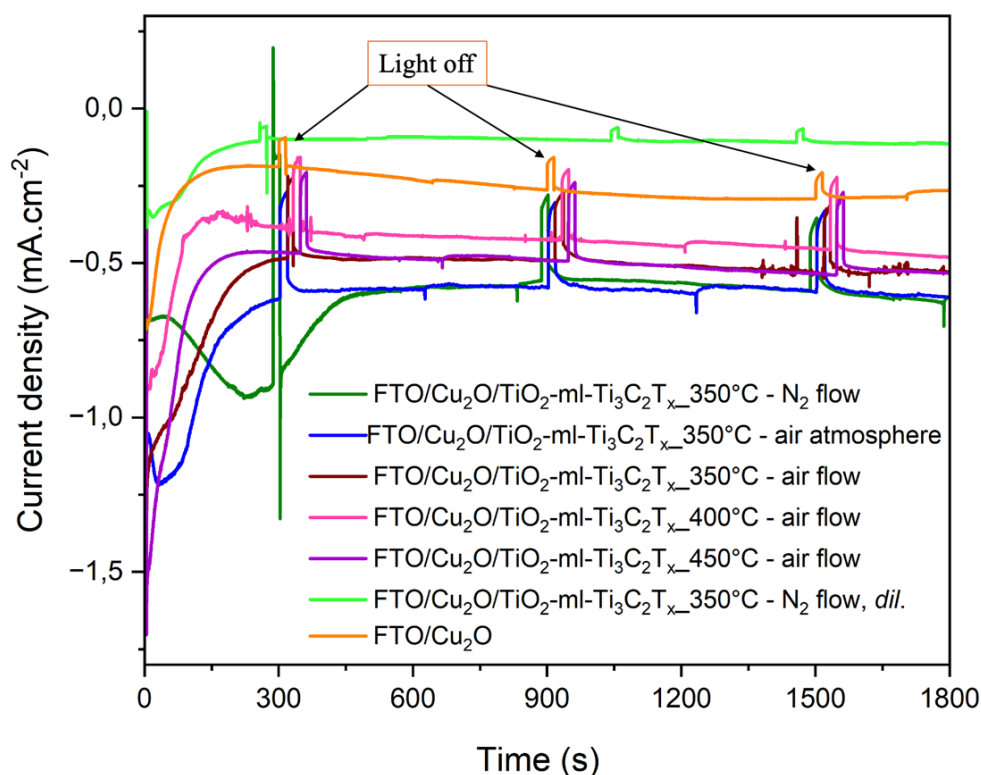


Figure 34: Results of chronoamperometric tests of the FTO/ Cu_2O /TiO₂-ml-Ti₃C₂T_x photoelectrodes after saturation of the electrolyte with CO₂ under applied potential of 0.24V vs RHE

Photos of each electrode were taken before and after the catalytic tests from both the front and back sides to document photocorrosion. Photocorrosion manifests as a change in the colour of the Cu_2O layer and is mainly visible from the back side, as the front side is covered with a $\text{TiO}_2\text{-Ti}_3\text{C}_2\text{T}_x$ composite layer. The first electrode shown in Figure 35 (top left) is a bare FTO/ Cu_2O . Since this electrode lacks any protective layer, photocorrosion is most pronounced

and clearly visible in this case by turning into almost black colour. In comparison, FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x electrodes exhibit a slightly less photocorrosion as indicated by less intensive dark colouring. However, as observed in the change in colour, there is not any significant difference between them (Figure 35).

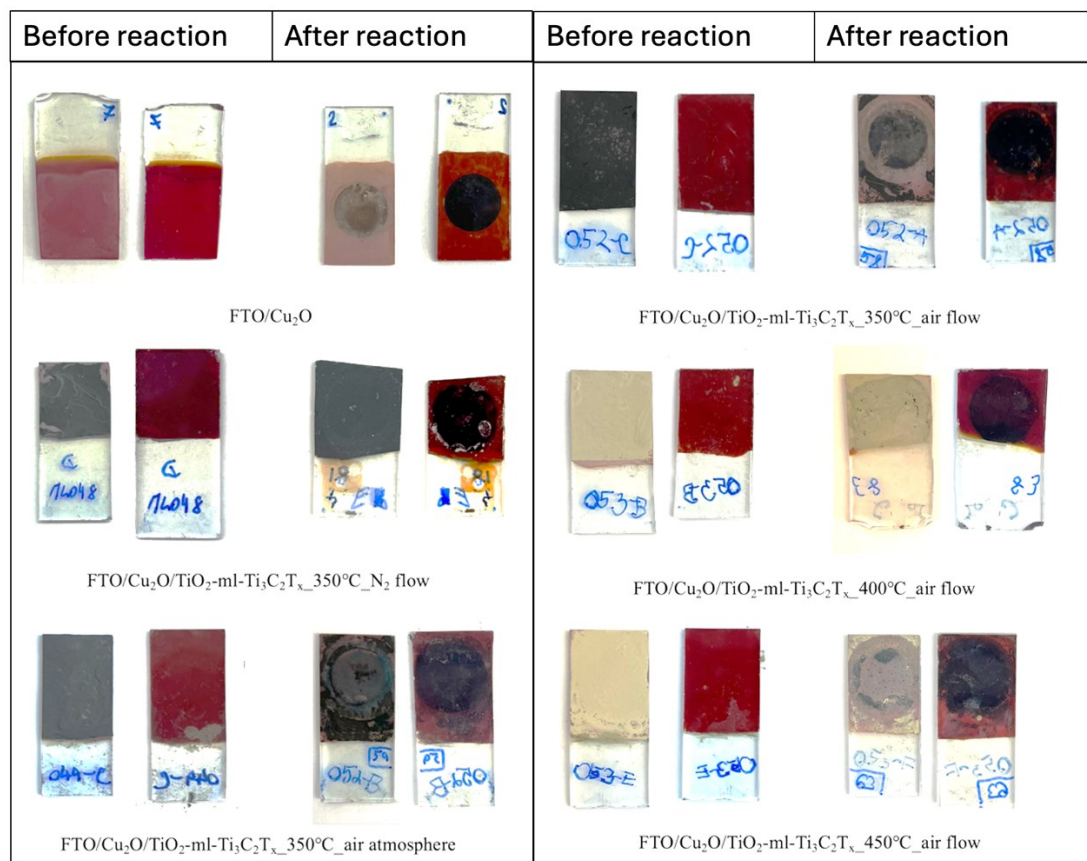


Figure 35: Photos of electrodes from the front (on the left) and back (on the right) side before (on the left) and after (on the right) the reaction

To further investigate the changes of the photoactive Cu₂O layer after chronoamperometric tests, XRD patterns of each electrode before and after reaction were acquired (Figure 37 to Figure 41). The occurrence of photocorrosion was evaluated by comparing the diffraction patterns of the electrodes to the bare FTO/Cu₂O, and theoretical patterns of Cu and CuO (which are the typical products of photocorrosion).

In the case of the bare Cu₂O layer on the FTO electrode, after the reaction we observe a new peak at 43 °2θ which is specific for metallic Cu. It confirms that FTO/Cu₂O undergoes

photocorrosion during the reaction. Moreover, SEM images of the photocathode after the reaction (Figure 36) clearly reveal the formed cubic copper species.

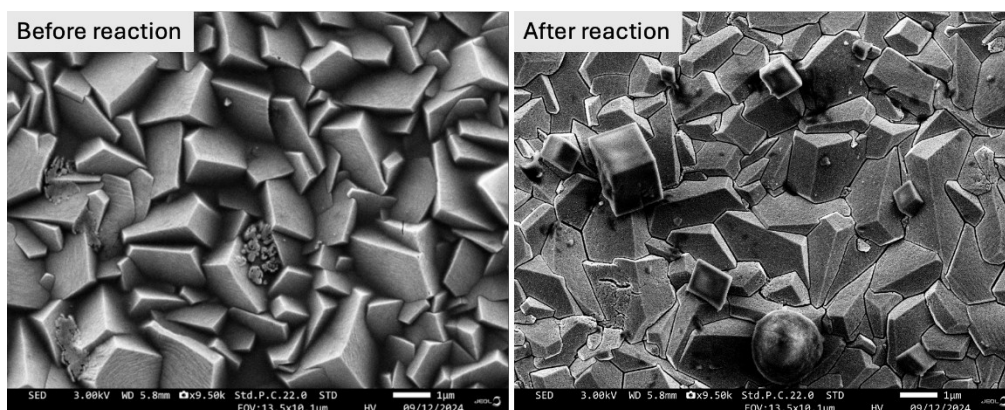


Figure 36: SEM image of the Cu_2O layer of the FTO/ Cu_2O electrode before reaction (on the left) and after reaction (on the right)

Figure 37 compares the FTO/ Cu_2O /TiO₂-ml-Ti₃C₂T_x-350°C _N₂ flow electrode before and after photocatalytic testing. A new diffraction peak attributed to metallic Cu appears at approximately 43° 2θ. Although the photoelectrochemical tests showed promising stability, these observations suggest the occurrence of photocorrosion in some extend.

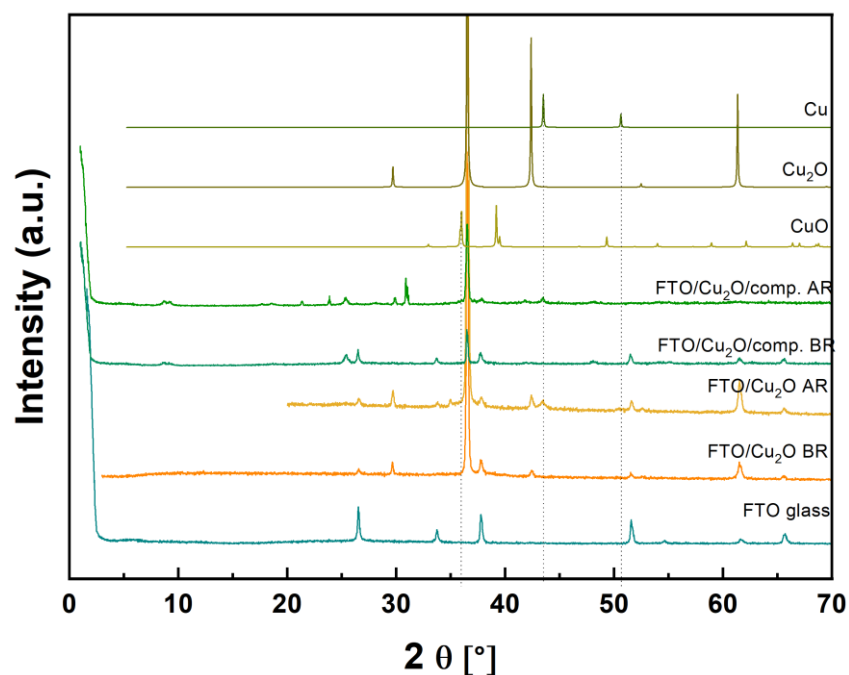


Figure 37: Diffraction patterns of FTO glass, FTO/ Cu_2O electrode, FTO/ Cu_2O /TiO₂-ml-Ti₃C₂T_x-350°C _N₂ flow electrode (labelled in the figure as FTO/ Cu_2O /comp.) before (BR) and after the reaction (AR). The theoretical patterns of CuO, Cu_2O and Cu species are included as well.

Figure 38 displays the comparison of electrode FTO/ Cu_2O /TiO₂-ml-Ti₃C₂T_x-350°C _air atmosphere before and after the test. Interestingly, the presence of photocorrosion products is

not clear. This can be either caused by small particles of copper species which are under the detection limit of XRD or by analysing the area which was not perfectly aligned with the reaction exposed area.

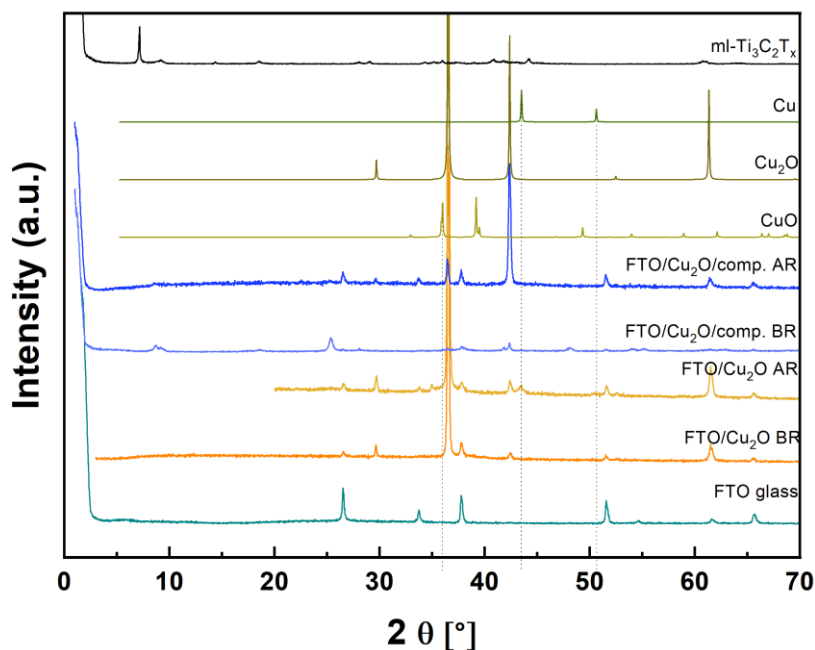


Figure 38: Diffraction patterns of FTO glass, FTO/Cu₂O electrode, FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x-350°C_{air} atmosphere electrode (labelled in the figure as FTO/Cu₂O/comp.) before (BR) and after the reaction (AR). The theoretical patterns of CuO, Cu₂O and Cu species and pattern of ml-Ti₃C₂T_x powder are included as well.

In the Figure 39, the electrode FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x-350°C_{air} flow is shown before and after the catalytic test. Similar as in the case of FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x-350°C_{air} atmosphere (Figure 38), no clear signs of photocorrosion were observed, probably due to the same reasons as described above.

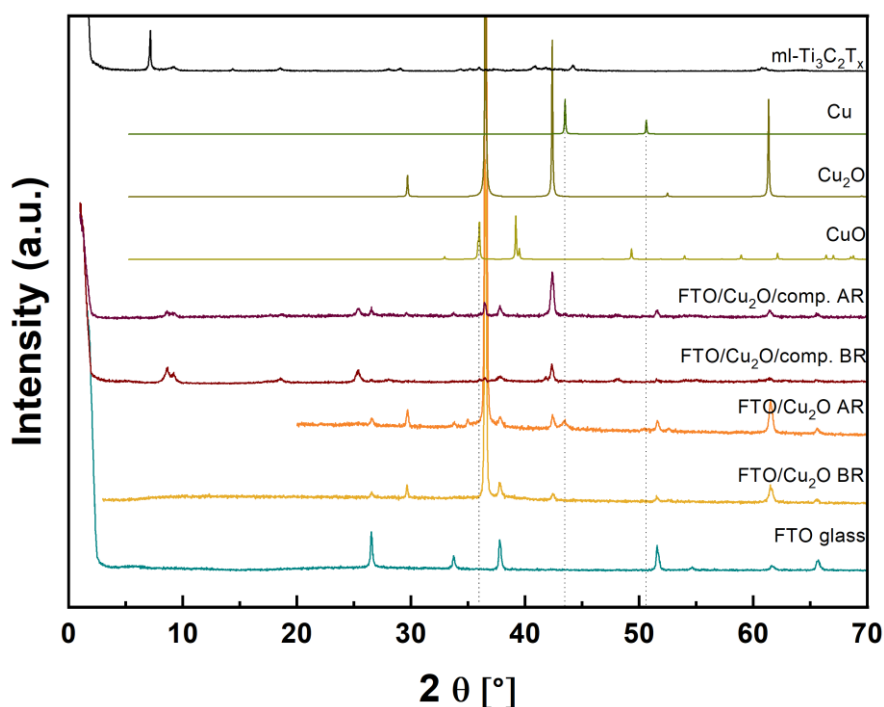


Figure 39: Diffraction patterns of FTO glass, FTO/Cu₂O electrode, FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x-350°C_{air} flow electrode (labelled in the figure as FTO/Cu₂O/comp.) before (BR) and after the reaction (AR). The theoretical patterns of CuO, Cu₂O and Cu species and pattern of ml-Ti₃C₂T_x powder are included as well.

The photocorrosion can be also observed in the diffraction patterns in the Figure 40 and in the Figure 41. They illustrate the structural comparison before and after the reaction of the electrodes FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x-400 °C_{air} flow and FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x-450 °C_{air} flow. Both photocathodes show signs of photocorrosion with visible peak at 43 °2θ corresponding to Cu.

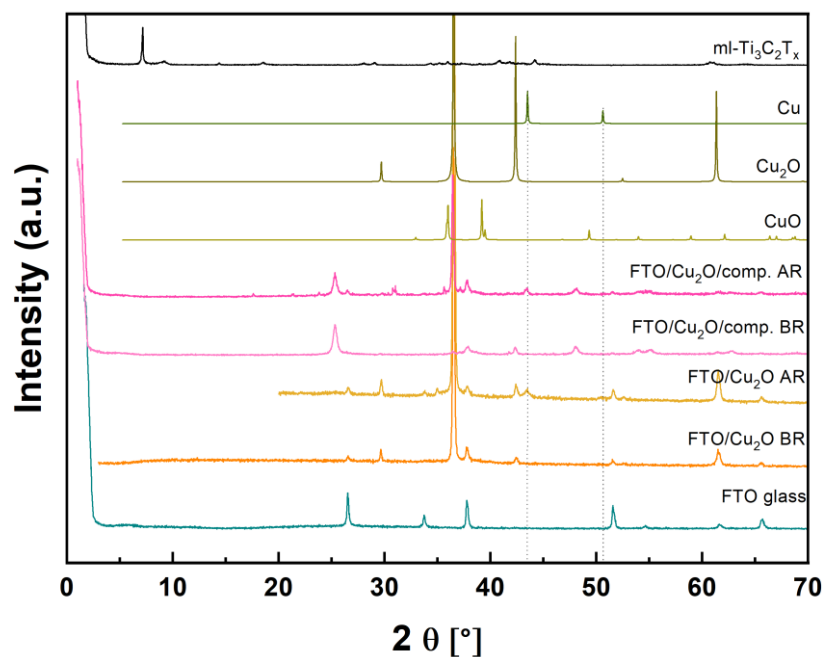


Figure 40: Diffraction patterns of FTO glass, FTO/ Cu_2O electrode, FTO/ Cu_2O /TiO₂- $ml-Ti_3C_2T_x$ -400°C air flow electrode (labelled in the figure as FTO/ Cu_2O /comp.) before (BR) and after the reaction (AR). The theoretical patterns of CuO, Cu_2O and Cu species and pattern of $ml-Ti_3C_2T_x$ powder are included as well.

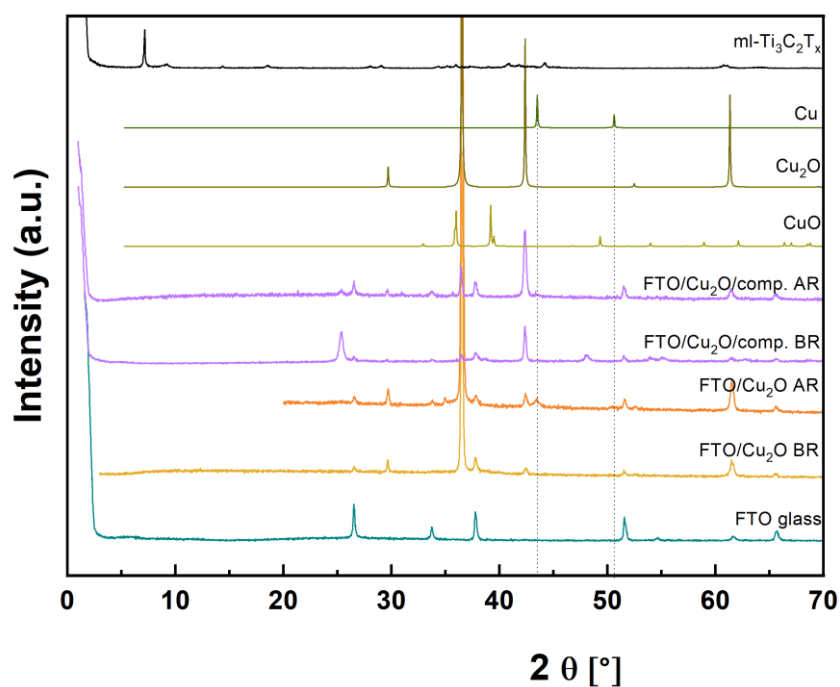


Figure 41: Diffraction patterns of FTO glass, FTO/ Cu_2O electrode, FTO/ Cu_2O /TiO₂- $ml-Ti_3C_2T_x$ -450°C air flow electrode (labelled in the figure as FTO/ Cu_2O /comp.) before (BR) and after the reaction (AR). The theoretical patterns of CuO, Cu_2O and Cu species and pattern of $ml-Ti_3C_2T_x$ powder are included as well.

4.1.4 Catalytic tests and product analysis

Based on the LSV and chronoamperometric results, the selected materials were submitted for CO₂RR product analysis performed during my short stay in IC²R laboratories in Bari, Italy (a workspace of our partner group in the DESIRED project). The tests were performed using the DESIRED reactor. This reactor is being developed during the DESIRED project. It is designed to be utilized for PEC CO₂RR, therefore it is equipped with a septum system for sampling the liquid and the gas phase, which keeps it gas tight. Long term product analysis tests were carried out for a period of two hours at applied potential of 0.24 vs RHE.

The tests were performed on FTO/Cu₂O, FTO/Cu₂O/Ti₃AlC₂, FTO/Cu₂O/ml-Ti₃C₂T_x and FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x_350 °C_N₂ flow. The nitrogen treated composite was chosen among all prepared materials based on the promising results from LSV and chronoamperometric tests. Blank tests without CO₂ in the electrolyte were performed as well to confirm the origin of the C products (the same protocol, but the electrolyte was saturated with N₂ instead of CO₂). Blank experiments did not provide any products, which confirms that CO₂ serves as only source of carbon of the obtained products.

The results of performed experiments are summarized in Table 5. As the reaction takes place on a very small scale (the total volume of the reactor is about 50 ml), the products are noted without quantification at this stage of the research. The goal was mostly to identify the products of CO₂RR, not to quantify them.

Table 5: Electrodes tested in IC²R in long term product analysis tests and corresponding products

Sample	Products
FTO/Cu ₂ O	CO, acetic acid
FTO/Cu ₂ O/Ti ₃ AlC ₂	CO
FTO/Cu ₂ O/ml-Ti ₃ C ₂ T _x	CO, acetic acid
FTO/Cu ₂ O/TiO ₂ -ml-Ti ₃ C ₂ T _x _350 °C_N ₂ flow	CO, acetic acid

Based on GC analysis, carbon monoxide and acetic acid were identified as the main products when FTO/Cu₂O was employed as a photocathode. Acetic acid is not a typical product observed in CO₂ reduction reactions when Cu₂O is used as a catalyst. The usual products formed on Cu₂O include carbon monoxide, methane, and ethanol (as discussed in Section 2.3.4). The FTO/Cu₂O electrode coated only with the initial MAX phase (Ti₃AlC₂) produced carbon monoxide as the only detectable product. Electrodes coated with multilayered Ti₃C₂T_x

and $\text{TiO}_2\text{-ml-Ti}_3\text{C}_2\text{T}_x_{350\text{ }^\circ\text{C_N}_2}$ flow MXenes produced CO and acetic acid. This suggests that the surface modification with the MAX phase may influence the product distribution, potentially suppressing further reduction steps that would normally lead to multi-carbon or more reduced compounds. However, the addition of ml-MXene or its partially oxidized form ($\text{TiO}_2\text{-ml-Ti}_3\text{C}_2\text{T}_x_{350\text{ }^\circ\text{C_N}_2}$ flow) restores the ability to form acetic acid (a C₂ product), which is a desirable feature for photocatalytic CO₂RR, as it indicates the facilitation of C–C bond formation.

The difference between the bare FTO/Cu₂O, FTO/Cu₂O/ml-Ti₃C₂T_x and FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x_{350 °C_N₂} flow can be potentially found based on the quantification of the formed products. However, a detailed quantitative analysis has not been completed yet, therefore it is not included in this thesis. Another distinction could be the possible formation of additional products, which may not be detectable using the current GC-based analytical method. Some compounds, particularly non-volatile, may remain unobserved (e.g., organic acids like acetic or lactic acid, that can create salts), highlighting the need for complementary techniques such as ¹H NMR or mass spectrometry (MS) connected to GC to fully characterize the formed products.

The initial set of experiments provides valuable information on overall photocathodes stability and helps forming an initial understanding of their activity and selectivity. Nevertheless, all experiments must be repeated multiple times to eliminate the possibility of false positive results and to validate the observed selectivity and activity of each electrode. These experiments will be the focus of our future research. The next step is to establish a product analysis setup in our laboratory with our reactor, based on experience from IC²R laboratories. The products will be determined by a combination of methods GC (with FID and TCD detectors), GC-MS and ¹H NMR (with water signal suppression). This work has started, however, as the results have not been completed, they are not a part of this work. This multiple analysis method approach will allow us to identify all possible products of the CO₂RR, not only gaseous products and volatile compounds with low boiling points.

5 Conclusion

During the research for this bachelor's thesis, a series of multicomponent photoelectrodes were prepared by spray-coating of synthesised TiO_2 -ml-MXene composite materials over electrodeposited Cu_2O . Prepared electrodes were characterized by linear sweep voltammetry (LSV) tests, chronoamperometric tests and in photo-electrocatalytic CO_2RR .

Cu_2O layer was deposited onto FTO glass via electrodeposition from CuSO_4 solution containing lactic acid, at pH 10.5 and an applied potential of 0.36 V vs. RHE. This method typically resulted in Cu_2O mass of 3.5–4 mg/cm^2 . SEM analysis confirmed the formation of crystals with an octahedral morphology.

Multilayered MXene was synthesized by etching Ti_3AlC_2 MAX phase using HF solution. The resulting ml- $\text{Ti}_3\text{C}_2\text{T}_x$ was then thermally treated at 350 °C, 400 °C, and 450 °C under various atmospheric conditions, including nitrogen flow, static air atmosphere, and air flow. This process yielded five distinct materials. The materials were fully characterized by methods of PXRD, nitrogen sorption, XPS, UV-Vis spectroscopy (with a Tauc plot method), and SEM. Characterization results confirmed the *in situ* formation of TiO_2 on the MXene surface after thermal treatment. The amount of TiO_2 increased with both temperature and oxygen availability during the calcination (as indicated by PXRD). It also led to a gradual increase in the band gap energy as indicated by UV-Vis spectroscopy and Tauc plot analysis. This confirmed that higher oxidation degree correlates with the increased band gap values (from 1.2 eV for ml- $\text{Ti}_3\text{C}_2\text{T}_x$ up to 3.0 eV for TiO_2 -ml- $\text{Ti}_3\text{C}_2\text{T}_x$ _450 °C_air flow). PXRD and XPS showed TiO_2 formation on the surface of MXene, while SEM indicated intimate contact between these two phases without separate TiO_2 particles.

The composite materials were subsequently spray-coated onto pre-fabricated FTO/ Cu_2O electrodes, resulting in the preparation of the following photocathodes:

- FTO/ Cu_2O / TiO_2 -ml- $\text{Ti}_3\text{C}_2\text{T}_x$ _350°C_N₂ flow
- FTO/ Cu_2O / TiO_2 -ml- $\text{Ti}_3\text{C}_2\text{T}_x$ _350°C_air atmosphere
- FTO/ Cu_2O / TiO_2 -ml- $\text{Ti}_3\text{C}_2\text{T}_x$ _350°C_air flow
- FTO/ Cu_2O / TiO_2 -ml- $\text{Ti}_3\text{C}_2\text{T}_x$ _400°C_air flow
- FTO/ Cu_2O / TiO_2 -ml- $\text{Ti}_3\text{C}_2\text{T}_x$ _450°C_air flow

The composite photocathodes were further characterized by LSV and chronoamperometric tests. Electrochemical characterization via LSV identified FTO/ Cu_2O / TiO_2 -ml- $\text{Ti}_3\text{C}_2\text{T}_x$ _350 °C_N₂ flow electrode as the most promising photocathode, showing the highest negative photocurrent, low and stable dark current, and overall good

stability in a long period chronoamperometric tests. Based on the LSV, chronoamperometric measurements, XRD analysis (before and after the tests), and visual observations, it can be concluded that FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x composite photocathodes exhibit improved stability against photocorrosion compared to FTO/Cu₂O. It is therefore expected to maintain its activity for a longer period. Furthermore, testing FTO/Cu₂O/TiO₂ electrode as a reference confirmed better performance of composite FTO/Cu₂O/TiO₂-MXene electrodes.

Product analysis was conducted after PEC CO₂RR using GC with TCD and BID detectors. The tests were performed on FTO/Cu₂O, FTO/Cu₂O/Ti₃AlC₂T_x, FTO/Cu₂O/ml-Ti₃C₂T_x, and FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x-350°C_N₂ flow photocathodes. The goal was to evaluate the added value of (a) layers sprayed on top of Cu₂O and (b) high temperature treatment of ml-Ti₃C₂T_x. Most of the electrodes provided CO and acetic acid as main products. Acetic acid is not a typical product of FTO/Cu₂O electrode. The advantages of FTO/Cu₂O/TiO₂-ml-Ti₃C₂T_x-350°C_N₂ flow over the bare FTO/Cu₂O could be in the quantity of the formed products and the potential to detect non-volatile compounds. These compounds could be problematic to identify using solely the current GC protocol, which analyses the headspace of electrolyte heated to 90 °C.

The obtained results provided useful data on the photoelectrodes' properties, particularly their activity and stability. The ongoing work has been focused on repeating experiments for reproducibility and elimination of false positive products. We are currently conducting a detailed product analysis by combination of methods GC (with FID and TCD detectors), GC combined with mass spectrometry (GC-MS) and ¹H NMR analysis of electrolyte, all under the conditions of our laboratory.

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