

Aerosol-assisted Chemical Vapour Deposition of Delafossite CuFeO_2 Thin Films and Optimisation of Functional Properties

This thesis is submitted in partial fulfilment of the requirements for the Degree of
Doctor of Philosophy (Chemistry)

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Declaration

I, Xinyue Zhang, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm this has been indicated in the thesis.

Abstract

Semiconducting metal oxides play a vital role in water splitting and gas sensing, offering a multifunctional approach to sustainable energy production through solar energy utilization and emissions control.

The focal point of this endeavour was to synthesize and modify Delafossite-structure CuFeO_2 thin films for application as a photocathode for water splitting and in gas sensor devices. Delafossite CuFeO_2 is a p-type metal-oxide semiconductor (MOS) with hole conductivity resulting from non-stoichiometric structure due to Cu-deficiency in the Cu-layer and O-interstitials.

In this project, high-purity CuFeO_2 thin films consisted of a single crystal phase with meticulously controlled thickness and morphology have been synthesised via aerosol-assisted chemical vapour deposition (AACVD) wherein various parameters including precursors, substrates, solvent, deposition temperature, gas flow rate, and post-annealing conditions are optimized. The deposition conditions are gentle and scalable for mass production, boasting remarkable efficiency.

As a photocathode, the band gap of the thin film Delafossite CuFeO_2 has been measured at ~ 1.8 eV (indirect). The highest photocurrent density of CuFeO_2 thin films measured in 1M NaOH electrolyte with 10% 0.1M $\text{Na}_2\text{S}_2\text{O}_8$ was $\sim 240 \mu\text{A}/\text{cm}^2$ at 0.4 V vs Reversible Hydrogen Electrode (RHE), with an incident photon to charge carrier efficiency (IPCE) of 4.5%. The mechanism of charge carriers transportation and utilization was explained by Transient Absorption Spectroscopy (TAS), which confirmed the relationship between charge carrier recombination and film thickness and morphology. The data revealed the significance of hole thermalization and charge carrier separation in rationalizing the film performance.

Delafossite CuFeO_2 thin films were engineered for enhanced photoelectrochemical (PEC) water splitting using distinct approaches: post-

annealing treatment in air, heterojunction construction with a CuNiO_x hole transport layer, and surface decoration with a thin Fe_2O_3 film. These strategies led to diverse levels of enhancement in PEC performance and offered valuable insights for future research endeavours aimed at realizing the full potential of CuFeO_2 films as photocathode materials.

Gas-sensing experiments on CuFeO_2 thin films fill the gap in research on CuFeO_2 gas sensors and extended our knowledge of p-type semiconducting metal oxide gas sensors. In this project, CuFeO_2 gas sensors demonstrated diverse responses to oxidized analyte gases across varying temperatures and concentrations. Sensitivity exhibited temperature dependency, with heightened responsiveness notably observed during oxygen and humidity tests. The p-n gas sensing behaviour shifted in response to analyte gases with oxygen (in nitrogen) volumetric ratios ranging from 1% to 20%, highlighting the impact of thermal treatment on the phase and surface oxygen composition of the CuFeO_2 gas sensors. Further research should be conducted in this area to thoroughly characterize the sensitivity, selectivity, and reusability of CuFeO_2 gas sensors, to gain a deeper understanding of the gas-sensing mechanism, and to enhance the overall gas-sensing performance of CuFeO_2 .

Impact Statement

Amidst the escalating global wave of automation and technological advancement, gas sensors have emerged as an indispensable asset across diverse sectors. These include the identification of explosive and harmful gases for security, monitoring hazardous gases in industries, regulating fermentation processes in food production, and diagnosing patients through in-vitro detection in medicine. This surge in applications has fuelled substantial interest in the exploration and innovation of gas sensor materials in recent decades.

Beyond ensuring gas safety, the escalating concern over deteriorating air quality, mainly stemming from the combustion of non-renewable fossil fuels, has prompted a significant environmental discourse. Photoelectrochemical (PEC) water splitting stands as a cost-efficient and eco-friendly avenue to harness solar energy, transforming it into a renewable resource of hydrogen.

This project focused on the fabrication of Delafossite CuFeO_2 thin films via aerosol-assisted chemical vapour deposition and utilization as gas sensing materials and photoelectrochemical water splitting materials to solve the listed two problems together.

The well-developed AACVD deposition method has been used beyond this thesis, published and referenced by other researchers in the field of thin film deposition. During this PhD project, the idea of adjusting thin films' morphology, including surface area and grain size, was proposed and discussed with researchers in a similar field at the international conference and symposium and later on considered in other researchers' projects. The research topic and findings in **Chapters 3** and **Chapter 5** were presented in the UCL final year PhD talk and obtained the Clark prize in 2022.

Research Paper Declaration Form

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Five years ago, as I eagerly applied for UCL's Master's course, I was fueled by a determination to pursue a Ph.D. My admiration for acknowledged scientists, contributing to humanity's development, spurred me on. Fast forward five years, having completed my Master's degree and penned my Ph.D. thesis, I've come to the realization that reaching the end of a Ph.D. is merely the beginning of an academic journey. While I may not have been the top student throughout my academic career, I take pride in earning the title of Doctor and in the modest contribution I've made to the advancement of science and technology. It seems, in academia, the journey from "Dr." to "Einstein" is rather longer than expected - a bit like trying to navigate the London Underground during rush hour: slow progress, occasional delays, but ultimately, an exciting ride!

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Abbreviations

AACVD Aerosol-assisted chemical vapour deposition

AFM Atomic force microscopy

ALD Atomic layer deposition

APCVD Ambient pressure chemical vapour deposition

AGSS Alumina gas sensor substrate

CFO Copper iron oxide

Cu(acac)₂ Copper (II) acetylacetonate

DMF dimethylformamide

DMSO Dimethyl sulfoxide

EDX Electron dispersive X-ray spectroscopy

EIS Electrochemical impedance spectroscopy

EP Ellipsometric porosimetry

ESA Excited state absorption

Fe(acac)₃ Iron (III) acetylacetonate

FeCl₂•4H₂O Iron (II) chloride tetrahydrate

FTO Fluorine doped tin oxide

H₂SO₄ Sulfuric acid

HER Reversible hydrogen electrode

I current

IPCE Incident photo-to-current efficiency

ITO Indium tin oxide

j current density

K₂HPO₄ Potassium hydrogen phosphate

KH₂PO₄ Potassium dihydrogen phosphate

LSV Linear sweep voltammetry

MBE Molecular beam epitaxy

MFC Mass flow controller

MOS metal oxide semiconductor

Na₂SO₄ Sodium sulphate

Na₂S₂O₈ Sodium persulfate

Ni(acac)₂ Nickel (II) acetylacetonate

NaHCO₃ Sodium bicarbonate

PDF Pair distribution function

PLD Pulsed laser deposition

PEC Photoelectrochemical

RF-sputtering radio-frequency sputtering

RMS Root mean squared

sccm Standard cubic centimetres per minute

SCE Saturated calomel electrode

SE Stimulated emission

SEM Scanning electron microscopy

STL surface-limited-trap

TAS Transient absorption spectroscopy

UV-Vis Ultraviolet-visible spectrum

VOC Volatile organic compounds

XPS X-ray photoelectron spectroscopy

XRD X-ray diffraction

XRF X-ray fluorescence

Chapter 1. Introduction

1.1 Overview of water splitting

1.1.1 Research background and trend of photoelectrochemistry and water splitting

1.1.1.1 Research background in photoelectrochemistry

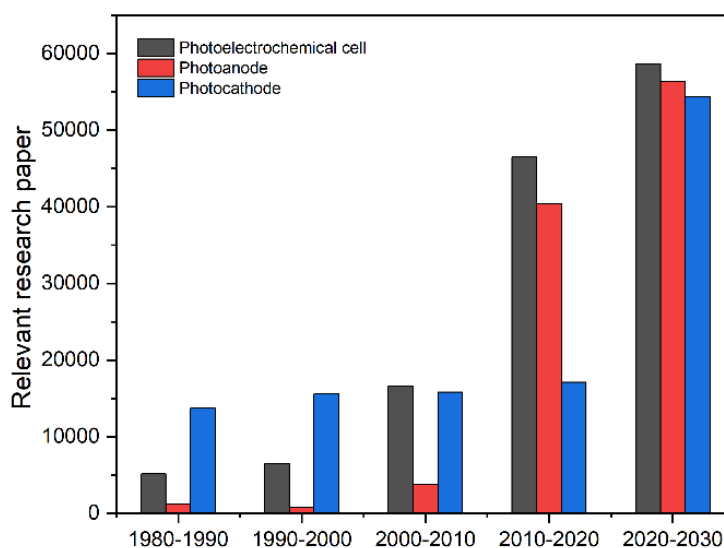


Figure 1. Research trends of photoelectrochemistry in the recent 50 years

The field of photoelectrochemistry began to take shape in the early 20th century. However, in recent years, the application of photoelectrochemistry has extended beyond solar energy conversion, and it now plays a crucial role in other cutting-edge technologies, including environmental remediation and photocatalytic degradation of pollutants (**Figure 1**). These diverse and impactful applications underscore the versatility and significance of photoelectrochemistry in addressing pressing societal challenges.

After the 26th UN Climate Change Conference of the Parties (COP26) in Glasgow, an accelerated transition to clean power has become one of the most important goals for the world to react to the Paris Agreement and secure global net-zero by mid-century. The development of clean, cheap, and renewable solar energy is

regarded as one of the most significant opportunities to prevent environmental degradation.

1.1.1.2 Introduction of photoelectrochemical water splitting

Within the area of photoelectrochemistry, photoelectrochemical water splitting received a great amount of attention due to its ability to harvest solar energy and split water (H_2O) into renewable fuel hydrogen (H_2) and clean, environmentally friendly byproduct oxygen (O_2) through electrochemical reactions occurring at the surface of the semiconductor material.

The study of photoelectrochemical water splitting is of paramount importance due to 1) the sustainability of producing clean energy hydrogen that can be used as a fuel for various applications, including transportation, electricity generation, and industrial processes; 2) the environmental benefits of reducing harmful greenhouse gases or pollutants during its utilization; 3) promising energy conversion efficiency compared to conventional water electrolysis methods; 4) material and technological advancements in materials science, nanotechnology, and electrochemistry, which paves the way to the development of efficient and stable photoelectrodes using semiconductor materials with nanostructured architectures and surface engineering techniques; 5) feasibility of energy storage and grid balancing, which offers a potential solution to the challenge of integrating intermittent renewables into the grid and achieving grid stability.

1.1.1.3 Latest research on metal oxide semiconducting materials used for photoelectrochemical water splitting

To maintain, utilize and expand the advantages of PEC water splitting, many materials have been studied in the last century. The research on semiconducting metal oxides has experienced particular growth due to their desirable stability, abundance, and the ability to be engineered at the nanoscale for improved performance.

Traditional materials like titanium dioxide (TiO_2) and zinc oxide (ZnO) were commonly investigated for their potential as photoelectrodes or photocatalysts. In 1972, Honda and Fujishima¹ first proposed a photocatalytic water-splitting mechanism using TiO_2 irradiated under UV light. Since then, numerous studies have been conducted on water splitting using metal oxide semiconducting photoelectrodes, and the mechanism has been well-developed.

The 2000s saw an upsurge in exploring nanostructured metal oxides, including zinc oxide nanowires² and titania nanotubes³, aiming to enhance light absorption and charge separation properties. In recent decades, multi-metal oxides, such as perovskite oxides, strontium titanate^{4,5} (SrTiO_3), bismuth ferrite⁶ (BiFeO_3), Spinel oxides (CuBi_2O_4)⁷, Delafossite oxides (ABO_2)⁸⁻¹⁰ emerged as promising candidates for photocathodes due to their tuneable bandgaps and good charge transport characteristics.

1.1.2 Mechanism of PEC water splitting

There are four steps in solar-induced PEC water splitting, including 1) light absorption where sunlight is absorbed by the photoelectrode material, promoting electrons from the valence band to the conduction band; 2) photoexcitation where electrons are generated in the conduction band and leaving holes in the valence band; 3) photogenerated charge separation (against charge recombination), under appropriate band bending conditions near surface, these electrons and holes can be separated to drive the reduction and oxidation reactions; and 4) generating hydrogen and oxygen on the (photo)cathode and (photo)anode, respectively¹¹.

The water-splitting process typically occurs in a photoelectrochemical cell, where the constructions may vary depending on the number of photoactive electrodes and reaction compartments¹². Generally, a single photoelectrode cell consists of a working photoelectrode, a counter electrode, and a reference electrode immersed in an electrolyte.

When light is incident on the photoelectrode, it generates electron-hole pairs (e^-/h^+), and these charge carriers facilitate the oxidation or reduction reaction of water molecules at the interface between (photo)electrode's surface and electrolyte to produce oxygen or hydrogen gas simultaneously, with the assistance of a small amount external bias. When the photoelectrode is immersed in the electrolyte, the electrochemical potential (Fermi level) is disparate across the interface.

At the semiconductor-liquid junction, charge transfer occurs to maintain the electrostatic equilibrium, where the Fermi level of the electrons in the semiconductor and the redox potential of the electrolyte are aligned at the interface of the semiconductor/electrolyte junction, resulting in a downward band bending in the p-type photoelectrode and an upward band bending in an n-type photoelectrode.

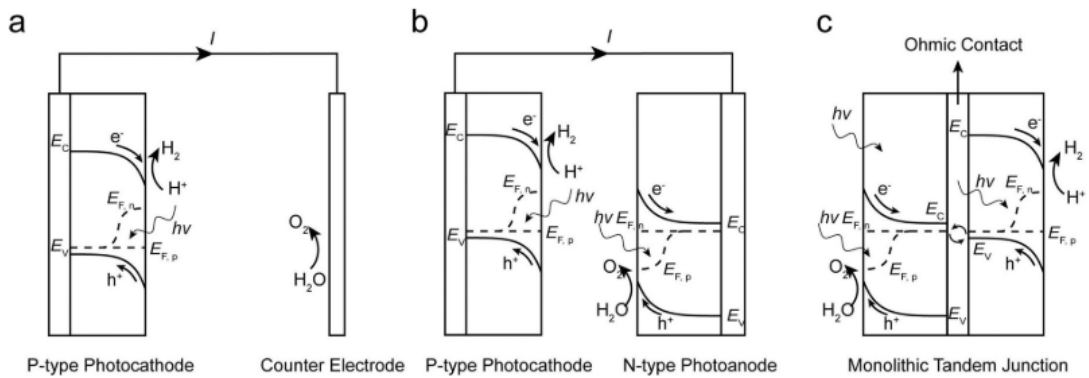


Figure 2. Schematic of three types of PEC cell with a p-type photocathode: a) P-type photocathode and counter electrode as anode; b) p-type photocathode and n-type photoanode; c) monolithic tandem junction¹³

The basic operation of three typical PEC cells consisting of a p-type photocathode is shown in **Figure 2**.

When a p-type semiconductor is used as a photocathode with a counter electrode in the dark background, the charge transfer produces a space-charge layer on the p-type semiconducting photoelectrode, while a compact layer (Helmholtz) followed by a diffuse layer (Gouy-Chapman) is formed on the electrolyte side¹⁴.

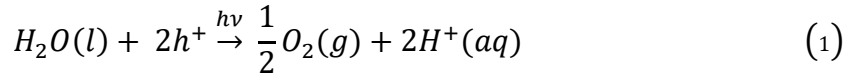
Additionally, there exists a distinctive area within the semiconductor where charge equilibration occurs, resulting in the removal of charge. Beyond this region, the semiconductor maintains electrically neutral. Hence, this layer is identified as the space charge region or depletion layer, because the layer is depleted of the majority carriers¹⁴. A crucial feature of semiconductors employed in photoelectrochemical water splitting is the inherent electric field present in the space charge region or depletion layer, where band bending takes place.

Under illumination, the photogenerated charge carriers are separated by the space-charge region. Electrons are transported to the semiconductor-electrolyte interface to be consumed in the reduction reaction. In contrast, the holes are transported to the counter electrode and participate in the water oxidation reaction.

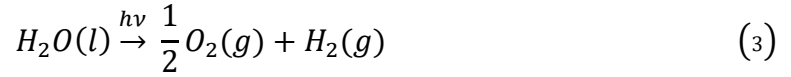
Photogenerated charge carriers (electrons and holes) created within the semiconductor by incident light are affected by this built-in electric field. Electrons are repelled by the downward-bent conduction band and attracted to the electrolyte, while holes are repelled by the upward-bent valence band and attracted away from the interface. This spatial separation of charge carriers creates a potential difference, known as the photovoltage, between the semiconductor and the electrolyte. A photovoltage is generated during this process under illumination in response to splitting the initial Fermi level into separated quasi-Fermi levels for electrons ($E_{F,n}$) and holes ($E_{F,p}$), as shown in **Figure 2**. The maximum of the photovoltage is determined by the band bending degree.

Water splitting is an endothermic reaction in which the enthalpy change of $\Delta H^0 = 238 \text{ kJ/mol}$ (As shown in **Equation 1**). Based on the Nernst equation, the according standard reversible potential $\Delta E^0 = 1.23 \text{ eV}$. Therefore, photon energy larger than 1.23 eV ($\lambda < 1000 \text{ nm}$) is required to drive the water splitting reaction under 1 sun's light intensity¹⁵. The general reaction can be described as:

Oxygen evolution reaction (OER):



Hydrogen evolution reaction:



In the whole water-splitting process, four electron-hole pairs are required to produce two hydrogen molecules and one oxygen molecule. Band positions of the conduction band and/or the valence band are of great importance to drive the reaction. The valence band edge of the photoanode needs to be more positive than the potential of water oxidation reaction (H_2O/O_2). In contrast, the conduction band edge of the photocathode needs to be more negative than the potential of water reduction reaction (H_2O/H_2)¹².

1.1.3 Influencing factors in the semiconducting metal oxides for the application of PEC water splitting

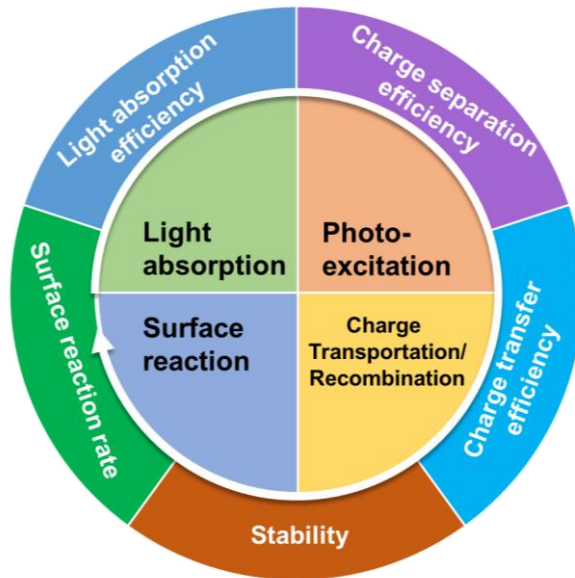


Figure 3. Crucial factors of photoelectrode materials affecting PEC performance

To improve a MOS material's performance for photoelectrochemical water splitting, the influenced factors can be considered from the four processes: light absorption, photoexcitation, charge transportation/recombination, and surface reaction.

When considering the promising materials used as photoelectrodes to ensure the desired efficiency of solar energy conversion, the following aspects as shown in the **Figure 3** need to be carefully considered¹⁶: (1) suitable conduction and valence band position; (2) relatively small band gap; (3) reasonable competition between electron and hole pair separation and recombination rate; (4) surface reaction rate and efficiency, and (5) long-term stability.

Table 1. Factors affecting the performance of photoelectrodes and modification methods

Process	Methods	Effect after modification	Ref.
Light absorption	Doping	Reduce the band gap and extend the light absorption range	17
	Introduce optics-based elements	Increased light utilization rate	19
	Heterojunction or homojunction structure	Combine with materials with narrow band gaps to extend the light absorption range	20
Photoexcitation	Electrical field effect by heterojunction or homojunction	Increased photogenerated charge separation efficiency	21
	Doping	Boost electrical conductivity and carrier density	22
	Photothermal effect by increased temperature	Accelerate bulk charge separation	20
Charge transportation	Cocatalyst	Increase charge transfer efficiency	23
	Hole transport layer	Increase charge transfer rate and reduce charge carriers recombination	12,24
Surface reaction	Cocatalyst	Increase OER or HER rate	25
	Protection layer	Maintain surface stability and reduce photo corrosion	23
	Tuning electrolyte composition	Maintain surface stability and reduce photo corrosion	26

To enhance the PEC performance and boost the material's PEC performance, strategies from five different aspects, such as enhancing light harvesting efficiency, improving charge separation efficiency, increasing charge transport rate, increasing photoelectrode stability and slowing down the charge recombination rate^{17,18} were proposed and used in past studies on semiconducting metal oxides

for photoelectrochemical water splitting. Methods are briefly summarized in **Table 1**. Examples have been introduced in detail in **Chapter 1.4**.

1.2 Overview of gas sensing

1.2.1 Market trend of semiconducting metal oxide gas sensor

The gas sensor market is projected to reach USD 2.76 billion at an 8.14% compound annual growth rate (CAGR) by 2030, according to a global forecast report from Market Research Future published in May 2023²⁷.

The market demand for gas sensors is from various industries ranging from medicine, defence and military, energy, aerospace, etc., and the applications can monitor air pollution, chemical processes, and exhaust from combustion engines. For example, gas sensors have become an indispensable tool in various technological fields, including the detection of explosive and harmful gasses in the security field, the inspection of harmful and hazardous gases in the industrial fields, the control of the fermentation process in the food industries, and the in-vitro detection and diagnosis of patients in the medical field²⁸.

The standard technologies used for gas sensor production are electrochemical^{29–32}, photoionization detection (PID)³³, solid-state/metal-oxide-semiconductors (MOS)^{34–37}, infrared-red (IR)^{38,39}, laser, zirconia^{40,41}, holographic⁴², or others such as paramagnetic^{43,44}, flame ionization detection (FID)⁴⁵, chemiluminescence^{46–48}, carbon nanotubes^{49–51}, polymers^{52,53} and ultraviolet²⁷.

In the past decade, solid-state gas sensors, particularly those based on semiconducting metal oxides, have gained remarkable prominence and emerged as a highly prolific research area in the gas sensor field⁵⁴, with advantages such as high sensitivity, selectivity, wide detection range of target gases (up to 150 different types of gases and vapours including oxidizing and reducing gases⁵⁵), fast response and recovery, low cost, miniaturization and integration, and long-

term stability^{55–58}. However, some limitations remain, such as cross-sensitivity to humidity, temperature dependence, and the need for periodic calibration⁵⁹.

1.2.2 Background of semiconducting metal oxide used for gas sensor

1.2.2.1 Types of metal oxide semiconductors used for gas sensor

To date, different MOSs have been studied for the application of gas sensors. These MOSs can be divided into n-type and p-type MOSs based on their electronic behaviour and the dominant charge carriers within the materials.

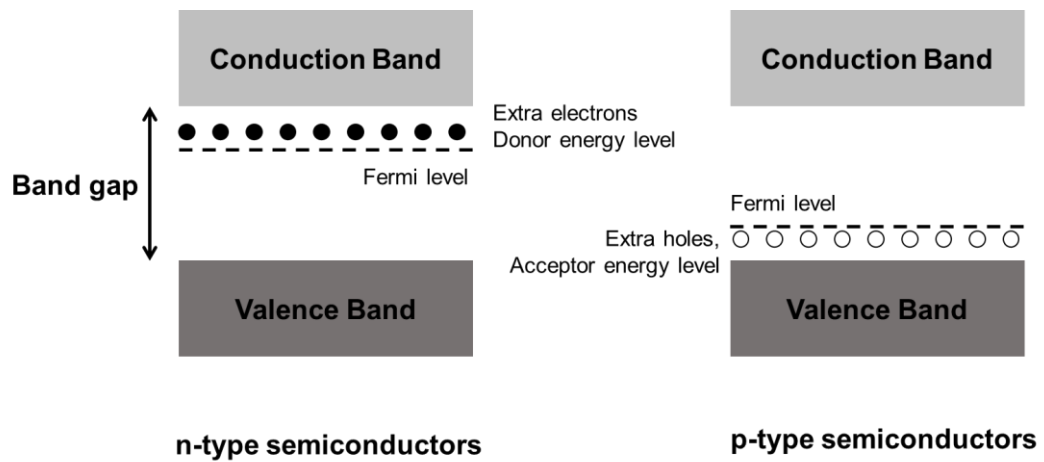


Figure 4. Energy bands in n-type and p-type semiconductors

As shown in **Figure 4**, in n-type semiconductors, the dominant charge carriers are electrons, achieved by incorporating dopant elements that introduce additional electrons into the semiconductor lattice. The presence of these extra electrons enhances the conductivity of the material. In p-type semiconductors, the dominant charge carriers are positive holes created by introducing dopant elements that create electron vacancies. These holes contribute to the overall conductivity of the material. In the energy diagram, the dopant introduces an energy level near the conduction band in the n-type MOS, which allows electrons to move more freely. In contrast, in the p-type MOSs, the dopant introduces an energy level near the valence band, facilitating the movement of holes.

The general properties of MOSs used for gas sensing can be divided into surface conductance materials and bulk conductance materials according to the operating temperatures: 1) Materials following surface conductance effects can usually be operated at a lower temperature (400-600°C). At lower temperatures, the bulk defect effect is slow, and conductance change is due to the formation and removal of surface oxygen; 2) Materials following the bulk conductance effect need to be operated at relatively high temperatures over 700°C⁶⁰ to respond to oxygen partial pressure changes and show the equilibrium between atmosphere and bulk stoichiometry³⁴.

1.2.2.2 Influencing factors in the semiconducting metal oxides gas sensor

According to the gas sensing mechanism, MOS's gas sensing performance is primarily dominated by three gas sensing factors: receptor function, transducer functions, and utility (**Figure 5**).

Receptor function refers to the crucial ability of the MOS's oxide surface to interact with the target gas effectively. The surface oxygen of MOS itself plays a significant role in this function and ultimately influences the material's gas-sensing performance. Therefore, modifications such as adjusting stoichiometry, adding surface additives, controlling crystallite faceting, and introducing dopants can effectively alter the surface oxygen's characteristic or composite. Testing environmental adjustments of operating temperatures, local oxygen partial pressure and the analyte gases in the air ambient can also profoundly influence the redox property and gas adsorption/desorption involved with surface oxides, impacting the receptor function.

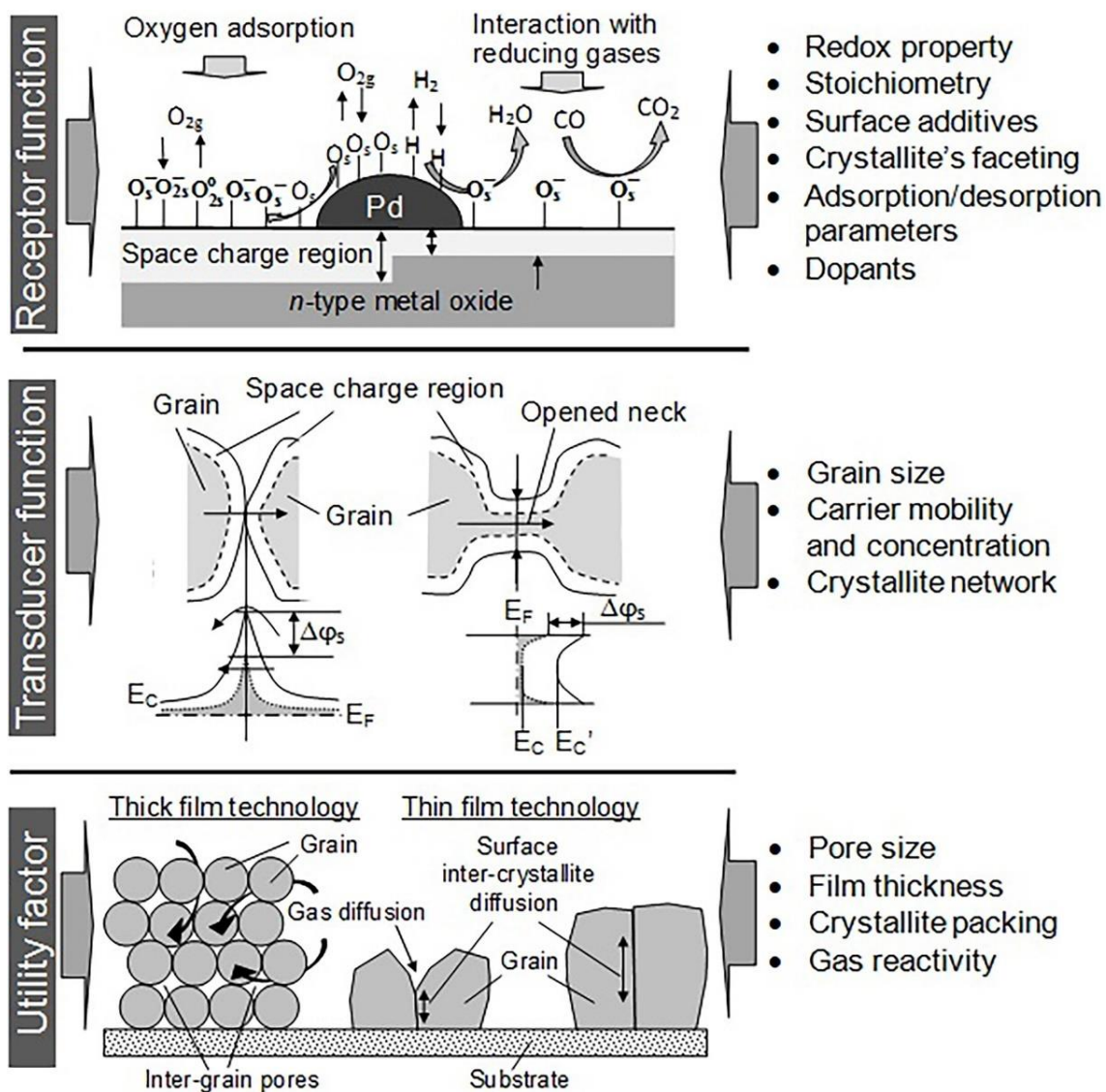


Figure 5. Illustration of three gas sensing factors: receptor function, transducer function, utility factor and associate material engineering factors in the context of semiconducting metal oxide gas sensors^{34,61,62}

Transducer function refers to the ability to convert a signal caused by the chemical interaction of the oxide surface (resistance change/ work function change) into an electrical signal. This function can be influenced by the particle size and grain boundaries, which a double-Schottky barrier model can be used to explain⁵⁸. The gas sensing signal - the resistance change - depends on the barrier height and then the concentration of the analyte gas⁶².

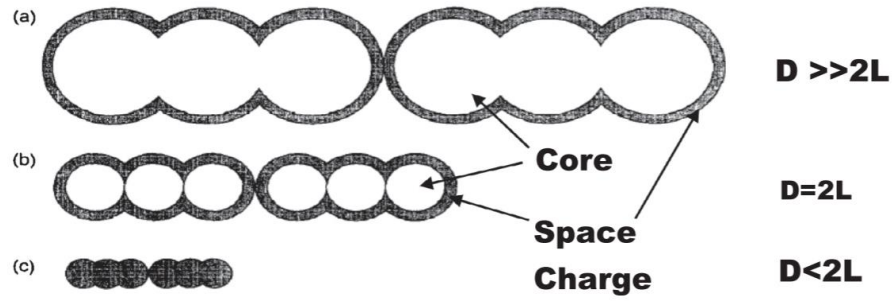


Figure 6. Illustration of dominant factors between grain size (D) and the diffusion length (L) on the conductance in MOS gas sensors a) $D \gg 2L$, grains boundary control; b) $D = 2L$, neck control; c) $D < 2L$, grain control^{34,58}

During the formation of a space charge layer, the concentration of charge carriers in volume is decreased only in the 'shell' (electron depletion layer for n-type and hole accumulation layer for p-type MOS). Therefore, three types of conductance mechanisms were proposed (**Figure 6**): 1) For large crystallites, the grain size $D \gg 2L$ (space charge layer), the conductance is limited by the Schottky barrier at grain boundaries, which is known as grain boundary control. 2) When grain size is comparable to $2L$ ($D = 2L$), every conducting channel in the neck between grains becomes small enough to influence the total conductivity, which is regarded as neck control. 3) When $D < 2L$, every grain is fully involved in the space charge layer, and the electron transport is affected by the charge on the grain surface, where the gas sensing response is controlled by grains⁵⁸.

Utility, as the last factor, refers to the accessibility of oxides to the analyte gas and the competition between redox rate (analyte gas and oxide) and diffusion rate (analyte gas diffuses into inner bulk). If the redox is much faster than the diffusion, the analyte gas molecules cannot access the grains at inner sites. The contact area will decrease, resulting in a reduced gas-sensing signal. Therefore, in this step, MOS material's porosity, crystallite packing, and film thickness can significantly impact gas diffusion. In contrast, the detection gas's reactivity determines the competition between redox reaction and gas diffusion rate.

1.2.2.3 Evaluation of sensing performance

Generally, the gas sensor's performance is evaluated by 3 'S'⁶³ and 3 'R'^{58,64,65}: selectivity, sensitivity, stability, response time, recovery time and reversibility, together with the fabrication cost³⁴. Selectivity is the ability of gas sensors to identify a specific gas in a mixture of gases. Sensitivity is the smallest amount of target gas that can be detected. Stability is the ability of a gas sensor to reproduce the same results for a certain period. Response time is the period until the concentration of target gas reaches a specific value to when a sensor generates a corresponding signal. Recovery time is the period required for a sensor signal to return to its initial value after the concentration of the target gas changes from a specific value to zero. Reversibility refers to the ability of a gas sensor to return to its original state after exposure to a target gas. An ideal gas sensor should have high selectivity, sensitivity, stability and reversibility while having low response and recovery time^{58,63,65}.

Table 2 showed how three gas sensing factors are used to adjust the properties of materials, which can guide the construction and development of MOS gas sensor. The different effects provide a certain complexity for the gas sensor design and engineering, which requires optimising the different parameters to build the equilibrium and consider the trade-offs. For example, numerous experiments on nanostructured metal oxide films (especially n-type MOS⁵⁹) revealed a significant boost in sensitivity when the average grain size was reduced within several nanometres^{66–70}. However, nanostructured oxides with small grains are subject to degradation due to the high reactivity⁵⁸. In this case, the trade-off of film grain size on sensitivity and stability needs to be considered according to specific application requirements.

Table 2. Parameters impacting the gas sensing performance of semiconducting metal oxide gas sensors: a summary of sensitivity, selectivity, and stability ⁵⁸

	Parameters
Sensitivity	1) Grain size and grain boundary ^{66–68} 2) Microstructure and porosity ^{69–74} 2) Doping ^{75–81}
Selectivity	1) Prepare materials specifically sensitive to a single compound and low cross-sensitivity to other compounds ⁵⁸ . 2) Modulation of sensor temperature ^{82–86} 3) Using sensor arrays ^{87,88}
Stability	1) Post-annealing treatment 2) Reducing working temperature 3) Adding dopants

1.2.3 Recent research progress

The most typical sensor materials are SnO_2 ^{71,72} and ZnO ^{73,74}, which exhibit n-type gas sensing performance. Accordingly, n-type gas MOS sensors have been widely studied, including TiO_2 ^{75,76}, WO_3 ^{77,78}, In_2O_3 ^{79,80}, Fe_2O_3 ^{81,82}, etc. Compared with n-type MOS, p-type MOS received less attention. The investigation and development of p-type MOS, such as NiO ^{83–85}, CuO ^{86–88}, Co_3O_4 ^{89,90}, Cr_2O_3 ^{91,92}, and Mn_3O_4 ⁹³ are still in progress. Besides single-metal oxide semiconductor materials, researchers also discovered the gas sensing potential in multi-metal oxide semiconductors, including Perovskite⁹⁴, Spinel⁹⁵, and Delafossite^{12,95–99} materials. The underexploited potential of p-type gas sensors relates to:

- High selectivity, as many p-type MOS materials such as NiO , CuO , Cr_2O_3 and Mn_3O_4 have been extensively used as catalysts to improve the selective oxidation of various volatile organic compounds (VOCs)^{100–103}.
- Low dependency on humidity. In past research, Kim¹⁰⁴ et al. used NiO as a dopant to reduce the humidity impact on SnO_2 -based gas sensors. By adding 1.27 w.t% NiO , the response and recovery time were significantly reduced. In the hollow sphere NiO -functionalized SnO_2 , the response and

recovery time can be reduced to even ultrafast level ($\leq 5\text{s}$)¹⁰⁵, with sufficient gas response ($R_a/R_g = 2.58$ to 50 ppm $\text{C}_2\text{H}_5\text{OH}$).

- Low-temperature dependence of conduction when operating in the high-temperature range^{94,106,107}

1.3 Introduction of Delafossite CuFeO_2 and related semiconducting metal oxides

1.3.1 Introduction of Delafossite CuFeO_2 semiconducting metal oxides

Delafossite CuFeO_2 is an intriguing compound that belongs to the ternary metal oxide family with a formula of ABO_2 , where A is a monovalent metal element such as Cu, Ag, Pt, and Pd while B is a trivalent metal element such as Fe, Cr, Al, Ga or In^{98,108–122}. The crystal structure of Delafossite metal oxides consists of the alternative stacking layer of O-A-O ‘dumbbells’, where the A cation is linearly connected with O^{2-} anion in the *c*-direction and lead to the monovalent state, and edge-shared BO_2 octahedra, where the B occupies the middle of the octahedral block¹²³ along the *a*-direction, showing the trivalent state.

The Delafossite structure can also be described as two alternating layers consisting of a planar layer of A-site cations in a triangular pattern and a layer of edge-sharing BO_2 octahedra flattened with respect to *c*-direction. The different stacking orientation of these two layers results in the formation of two polytypes¹²⁴: hexagonal 2H, with $P6_3/mmc$ space group symmetry, and rhombohedral 3R type with $R\bar{3}m$, as shown in **Figure 7**.

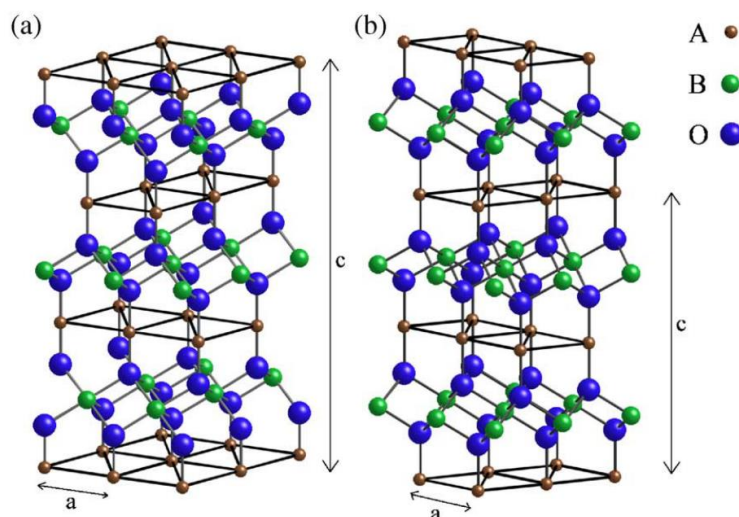


Figure 7. Crystal structure of two polytypes of Delafossite CuFeO_2 : (a) 3R polytype with $R\bar{3}m$ space group symmetry; (2) 2H polytype $P6_3/mmc$ space group symmetry

Due to the native p-type conductivity resulting from Cu-deficiency in the Cu-layer (and/or interstitial oxygen)¹²³, Delafossite CuFeO_2 received much attention for various applications. The research landscape concerning Cu(I) based Delafossite semiconducting metal oxide is witnessing substantial growth and diversification in the material or thin film's synthesis, characterization, modification, material engineering and the potential applications in electronics, magnetics, spintronics, photoelectronic, etc.^{125–130}

1.3.2 Recent studies on Delafossite CuFeO_2 semiconducting metal oxides used as photocathode

Among cuprous Delafossite, CuFeO_2 has a relatively small band gap ($E_g \approx 1.5$ eV, shown in **Figure 8**). It has received many attentions as a promising candidate of the photocathode due to the small band gap, favourable conduction band position (~ -0.4 V vs RHE), relatively good charge carrier mobility ($0.2 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$) and relatively long lifetime (200 ns) for photogenerated charge carriers¹³¹.

Compared with the other Cu-based semiconducting metal oxides, CuFeO_2 has relatively good stability because of its Delafossite structure and hole thermalization

process (**Figure 8**)^{113,129}. Hole thermalization occurs when an electron transfer from the higher lying Cu 3d states to backfill the photogenerated holes in the lower lying O 2p states. Photogenerated electrons and holes were found to be separated at the atomic scale near Fe and Cu¹¹³. Since there is no direct covalent bonding between Cu and Fe, the suppress direct electron-hole recombination is less favourable and provides stability in the Delafossite CuFeO₂ structure.

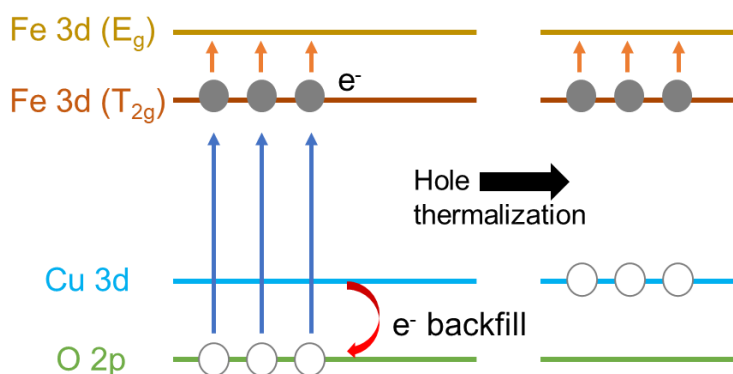


Figure 8. Energy diagram of CuFeO₂ and the illustration of hole thermalization phenomenon¹²⁹

According to first-principles calculations, the lowest optical transition in CuFeO₂ relates to Cu 3d + O 2p → Fe 3d charge transfer. This transition is found to be more favourable compared than Cu self-reduction (from Cu⁺¹ to Cu⁰). Less reactive Cu minimize the occurrence of detrimental reactions (such as oxygen evolution reaction, dissolution of CuO into the electrolyte, formation of reactive oxygen species etc), and therefore provided a better stability^{132,133,129,125, 106}.

Theoretically¹⁰⁸, CuFeO₂ is expected to have a strong light absorption ability for proton reduction¹³⁰, with maximum efficiencies of ~33% to 35% and the maximum photocurrent density of ~40 mA cm⁻² to ~45 mA cm⁻².

Prevot et al. also discovered the good charge transport properties in the bulk of Delafossite CuFeO₂ photocathode and a long lifetime (~200 ns) of charge carriers¹³¹.

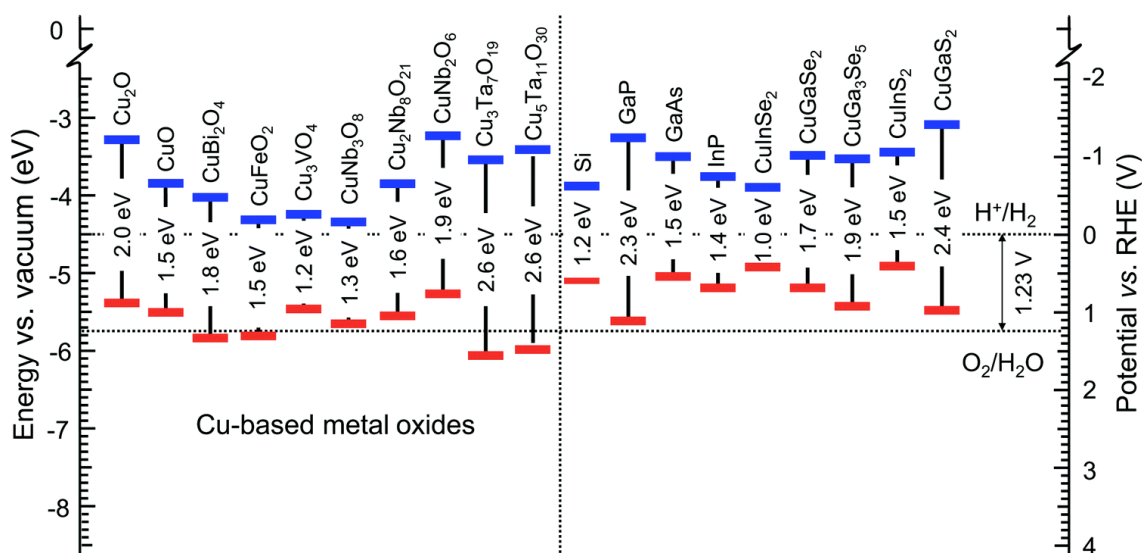


Figure 9. Energy band diagram of several Cu-based semiconducting metal oxides together with a wide range of semiconductors. The dotted lines represent the redox potentials of water splitting.

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However, in the case of a practical CuFeO_2 photocathode, the maximum photocurrent density achieved is much lower than the theoretical value. The material presents limited photovoltage and photocurrent density in the absence of sacrificial electron removers, highlighting kinetic limitations^{19,23,134,135}.

Considering the whole process of photochemical water splitting and CuFeO_2 electric property, the bottleneck of CuFeO_2 as a photocathode is rapid electron-hole recombination rate at the surface¹³¹, fast electron-hole recombination rate in the bulk¹³⁶, and low minority-carrier diffusion length¹³⁷. A high surface state density ($\sim 10^{14} \text{ cm}^{-2}$) was found in the previous research¹³¹ which is positioned 0.35 eV above the conduction band, and causes substantial Fermi level pinning at the semiconductor-liquid junction, limiting the photovoltage to roughly 0.35 V regardless of the electrolyte, therefore exhibiting poor HER catalytic activity in CuFeO_2 photocathode.

These surface states were found to act as electron traps, causing an inversion of the depletion layer upon filling, both in the dark background and under illumination, leading to rapid electron-hole recombination at the surface. A sufficient density of

these surface states located close to the valence band edge prevents the photovoltage from reaching the value anticipated from an ideal semiconductor-liquid junction as the Fermi energy in the bulk of the semiconductor equilibrates with the energy of these states rather than with the electrolyte, which causes a so-called Fermi level pinning^{138,139}.

If the surface states could be passivated, the maximum photovoltage for water reduction could be ~0.8 eV and make CuFeO₂ a suitable candidate photocathode for water splitting.

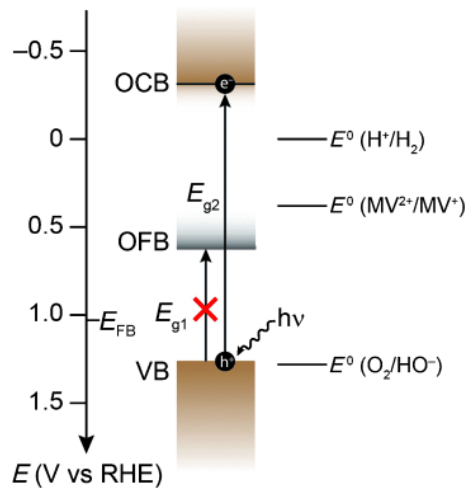


Figure 10. Band energy diagram of CuFeO₂ under the flat-band condition proposed by Prevot et al.²³, the optically forbidden band (OFB) is not accessible from the valence band (VB) by a transition of energy E_{g1} , whereas a transition induced by a photon of energy E_{g2} can excite an electron to the optical conduction band (OCB)

A multiple-band structure therefore was proposed in Delafossite CuFeO₂ films as shown in **Figure 10**, in which the direct transition band gap can be observed at ~1.2 eV, ~2.2 eV and ~3.0 eV as the thickness changes¹⁴⁰. Prevot et al. also proposed the band gap diagram of CuFeO₂ under flat-band conditions, in which the intermediate band (optically forbidden band) is not accessible from the valence band. However, a transition can be induced by lower energy and excite an electron to the optical conduction band²³, which also explains the rapid electron-hole recombination rate.

In recent years, many studies have been conducted on the synthesis, characterization, and modification of Delafossite CuFeO_2 to enhance its photocathode water-splitting performance. The literature listed in **Table 3** summarizes diverse attempts over these years and the corresponding results of their photoelectrochemical activity.

Many modifications on the Delafossite CuFeO_2 , including heterojunction^{141,142}, surface decoration with noble metal catalyst²³, post-annealing treatment¹⁴³, oxygen vacancy insertion¹⁴⁴, etc., have been investigated (**Table 3**).

Table 3. Research progress on PEC performance of CuFeO₂ photocathode

Photocathode	Synthesis method	Year	Electrolyte	Photocurrent density (mA/cm ²)	Refs.
Mg-doped CuFeO ₂	Solid state reaction	2013	0.1 M NaHCO ₃	1.0 @ -2V vs SCE	22
CuFeO ₂ thin film	Sol-gel	2015	1M NaOH with saturated Ar	0.025 @ 0.4V vs RHE	23
			1M NaOH with saturated O ₂	1.05 @ 0.4 V vs RHE	
Oxygen-intercalated CuFeO _{2+δ} thin film	Spin coating with post-hybrid microwave annealing in air	2016	1M NaOH	1.3 @ 0.4V vs RHE	135
410 nm CuFeO ₂ -decorated microsphere 2D silica photonic crystal	Pechini method	2017	1M NaOH saturated with oxygen	0.2 @ 0.6 V vs RHE	145
Fe ₂ O ₃ wrapped CuFeO ₂ thin film	Sol-gel	2018	0.1 M Na ₂ SO ₄	0.274 @ 0 V vs Ag/AgCl	146
CuFeO ₂ thin film	Solution-based ultrasonic spray pyrolysis process (USP) followed by a short hybrid microwave annealing treatment (HMA)	2019	1M NaOH with O ₂ saturated	0.65 @ 0.4 V vs RHE	143
CuFeO ₂	Spin-coating + air annealing	2019	1M NaOH degassed of oxygen	0.04 @ -0.5V vs Ag/AgCl	21
CuFeO ₂ thin film	Reactive co-sputtering	2019	0.1M KHCO ₃ +saturated CO ₂ (pH=6.8) with 0.1 M Na ₂ S ₂ O ₈	0.85 @ 0.4 V vs RHE	113
CuFeO ₂ thin film	Hydrothermal and silk-screen printed	2020	1M NaOH	0.010 @ -0.4V vs NHE	147
CuFeO ₂ thin film	Electrochemical deposition with post-annealing in air at 550°C	2021	1M NaOH	Up to 0.3	144
CuFeO ₂ thin film	Aerosol-assisted ambient pressure chemical vapour deposition	2021	1M NaOH with 0.5 M Na ₂ S ₂ O ₈	Up to 2.5	110
CuFeO ₂ with highly exposed {001} crystal facets	Hydrothermal with post-annealing	2023	0.1 M Na ₂ SO ₄	0.008 @ 0 V vs Ag/AgCl	148

1.3.3 Recent studies on Delafossite CuFeO_2 semiconducting metal oxides used as gas sensors

P-type Delafossite CuFeO_2 is a p-type metal oxide semiconductor (MOS) with hole conductivity resulting from its non-stoichiometric structure due to Cu-deficiency in Cu-layer and excess O-interstitials, which shows high potential as a gas sensing material. In previous studies, Delafossite CuFeO_2 have been used to detect oxygen¹⁴⁹ and ethanol¹²³ and has shown high sensitivity and quick response, whilst the detection performance towards other reducing and oxidizing gases and its response to moisture have received very little attention.

In 2013, Ruttanapun et al. constructed CuFeO_2 in a disc shape with a diameter of 12 mm and thickness of 2.5 mm from compressed powers obtained from the solid-state reaction. The target gas was $\text{C}_2\text{H}_5\text{OH}$ (70%) and was tested at 150°C in a vacuumed chamber (10^{-3} torr). The results exhibited a rapid response of the CuFeO_2 gas sensor towards alcohol in 2-4 minutes with high sensitivity ranging from 1.7 to 1.93 when calculated using $R_{\text{gas}}/R_{\text{air}}$, in which R_{gas} is the resistance after inputting the target gas, R_{air} is the resistance before inputting the target gas (**Figure 11 (Left)**)¹²³.

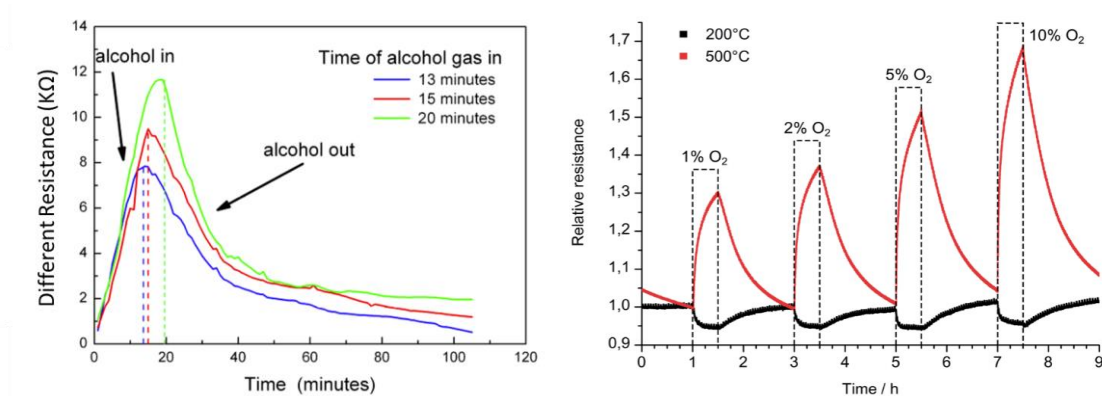


Figure 11. (Left) The different resistance of CuFeO_2 with inputting time of alcohol gas¹²³; (Right) The response of CuFeO_2 towards oxygen gas at 200°C and 500°C under variable concentration¹²⁸

PatZsch et al. reported the p-n type gas sensing behaviour transition in Delafossite CuFeO_2 inorganic nanowires the following year (**Figure 11** (Right)). In their research, the CuFeO_2 nanowires synthesized by electrospinning with post-calcination were used to detect oxygen target gas at 200°C and 500°C and showed p-type and n-type gas sensing behaviours, respectively¹²⁸.

There are only a few studies on the Delafossite CuFeO_2 gas sensor, and the mechanism has not been explained clearly. However, the gas-sensing properties of Delafossite CuFeO_2 's derivatives have been discussed and can provide some insights into the sensing ability and properties of Delafossite CuFeO_2 and its derivatives.

In 2010, Chapelle et al. reported a semiconducting copper oxide and spinel ferrite nanocomposite thin films synthesized from radiofrequency sputtering from a Delafossite CuFeO_2 target with post-annealing in air to detect CO_2 target gas. The concentration of CO_2 target gas was varied up to 5000 ppm at different operating temperatures ranging from 130 – 475°C , with the frequency ranging from 0.5 – 250 kHz. The results showed a high response of 50% ($R_{\text{air}}/R_{\text{CO}_2} = 1.9$) at 250°C for a CO_2 concentration of 5000 ppm (**Figure 12** (Left))¹⁵⁰.

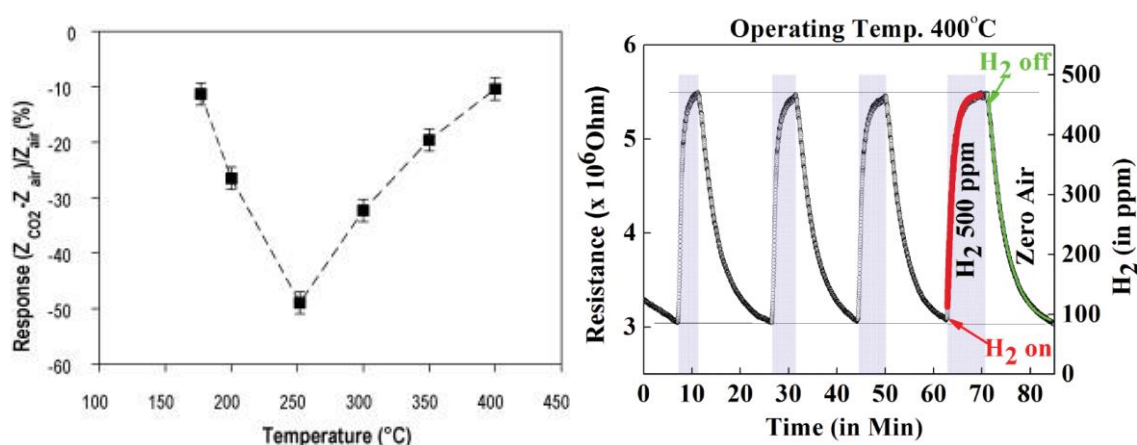


Figure 12. (Left) Response of $\text{CuO-CuFe}_{3-x}\text{O}_4$ (with $0 \leq x \leq 1$) nanocomposite sensing layer towards CO_2 operating at different temperatures, the measurement was conducted with alternating air and CO_2 frequency of 700 Hz, nanocomposite sensing layer's thickness is of 50

nm¹⁵⁰; (Right) Response and recovery of 25 nm CuO-CuFe₂O₄ thin film sensor towards H₂ at the operating temperature of 400°C with 100 cc/min H₂ flow rate¹⁵¹

Later on, in 2018¹⁵¹, De et al. reported the ethanol and hydrogen gas sensing properties of CuO-CuFe₂O₄ nanostructured thin film developed via a similar route as Chapelle's team (radio-frequency sputtering from Delafossite CuFeO₂ ceramic target with a thermal oxidation process). The sensing properties towards ethanol and hydrogen gas were examined in dry air with an operating temperature ranging from 250°C to 500°C. The composite CuO-CuFe₂O₄ thin film (25 nm) showed the highest response (79%) towards 500 ppm hydrogen when the operating temperature was 400°C. The shortest response time was ~60 s and ~90 s for H₂ and ethanol, respectively (**Figure 12 (Right)**).

1.4 Performance improvement strategies

Despite distinct working mechanisms, several parameters, including film morphology, degree of crystallinity, grain size, dopants, and heterojunction construction, among others, were observed to exhibit varying degrees of correlation with the gas sensing performance and photoelectrochemical (PEC) water splitting performance of MOS materials. Consequently, these parameters and the performance improvement strategies of these two applications were collectively discussed in this project.

Recent advances in the design and performance control of Delafossite CuFeO₂ used for gas sensing and PEC water splitting, followed by the discussion of the strategies employed for improving the performance of gas sensing and photocathodes, were summarized as follows.

1.4.1 Tuning morphology and crystal facet

Film morphology and crystal facets can significantly impact gas sensing performance and PEC water splitting efficiency through several key aspects,

including surface area, surface reactivity, charge carrier transportation efficiency, band structure, influence from active sites of defects and dopants, and light absorption efficiency, which can be illustrated using recent advances.

Li et al. synthesized a series of hexagonal CuFeO_2 nanosheets with different grain sizes and thicknesses via the hydrothermal method. The PEC measurement in 0.1 M Na_2SO_4 electrolyte showed enhanced photocurrent density from $\sim 1.4 \mu\text{A}/\text{cm}^2$ to $\sim 8 \mu\text{A}/\text{cm}^2$, resulting from increased charge separation efficiency due to the highly exposed (001) crystal facets¹⁴⁸.

Besides Delafossite CuFeO_2 , Guo et al. synthesized and compared TiO_2 nano-branched and nano-wall structures. The result showed that the nano-branched TiO_2 showed 40% higher hydrogen generation efficiency resulting from extended light absorption, reflection and refraction efficiency¹⁵², indicating the effectiveness of microstructure construction.

Thirumalairajan et al. prepared Delafossite CuAlO_2 nanoparticles⁹⁷ in the shape of flowers and hexagons from the hydrothermal method, with different surface areas of ~ 59.8 and $70.8 \text{ m}^2/\text{g}$, respectively. The ozone gas sensing results indicate that CuAlO_2 with hexagonal morphology exhibited superior ozone detection for 200 ppb at 250°C , with a response and good recovery time of 25 s and 39 s compared to the flower morphology (28 s and 69 s).

1.4.2 Doping

Doping refers to the deliberate introduction of impurities into a semiconductor material to alter its electrical properties³⁴. Doping is a crucial process in semiconductor manufacturing because the electrical properties of the material can be tailored, enabling the design and production of complex electronic devices with specific functionalities³⁴.

Regarding doping studies in PEC water splitting, a suitable dopant can be a significant approach to enhance light absorption efficiency and accelerate charge separation and transfer by regulating the band structure¹⁵³.

Deng et al. synthesized and summarized the structural, optical and photoelectrochemical properties of p-type Ni-doped CuFeO₂ via hydrothermal methods. In their research, the indirect band gap of Delafossite CuFeO₂ was narrowed down from 1.03 eV to 0.59 eV after Ni doping. The corresponding charge carrier concentration was promoted from 7.95×10^{19} to $1.14 \times 10^{20} \text{ cm}^{-3}$, together with the anodic shift of flat band potential. The narrowed band showed the promoted light absorption ability, and the transient decay time of 6% Ni-doped CuFeO₂ was prolonged from 5 s to 11 s, showing a lower charge carrier recombination rate than pure CuFeO₂. Furthermore, the EIS spectra in this study revealed reduced charge transfer resistance and increased interfacial carrier transfer efficiency for Ni-doped CuFeO₂. As a result, the photocurrent density was significantly promoted from $\sim 15 \mu\text{A}/\text{cm}^2$ to $\sim 30 \mu\text{A}/\text{cm}^2$ in a 120 s chopped light test with a 60 s interval, all carried out in a 0.2 M Na₂SO₄ electrolyte¹³⁶.

In addition, Mg-doped CuFeO₂ was synthesized as a photocathode for photoelectrochemical reduction of CO₂ and was reported by Gu et al²². The addition of Mg²⁺ dopants is found to substantially enhance the conductivity of the material, which was also reported by Wutting et al.¹⁵⁴ However, the increased conductivity in Mg-doped CuFeO₂ does not promote the PEC performance of CuFeO₂ and, in contrast, shows a reduced PEC performance resulting from increased Cu defect¹⁵⁴.

Two fundamental mechanisms, widely used in semiconducting metal oxide gas-sensing materials, were proposed by Yamazoe¹⁵⁵ and Morrison¹⁵⁶ based on chemical or electronic sensitization of semiconducting metal oxides by noble metal

additives and were named as spillover and Fermi-level control sensitization mechanism (**Figure 13**), respectively¹⁵⁷.

In the case of electronic sensitization, the additive, in its oxidized state, acts as a strong acceptor for electrons of the host semiconductor. This induces an electron-depleted space-charge layer near the interface, and the redox state/chemical potential is changed by reaction with the analyte gas¹⁵⁷.

In the case of chemical sensitization, it results from a catalytic surface reaction. It is assumed that the deposited noble metals clusters catalysts provide preferred adsorption and activation sites for the target gas from which activated fragments are spilled onto the semiconductor to react with the ionosorbed oxygen. As a result, the surface coverage with oxygen, and therefore eV_{surface} , is reduced and accompanied by a change in conductance, while the catalyst itself remains unchanged¹⁵⁷.

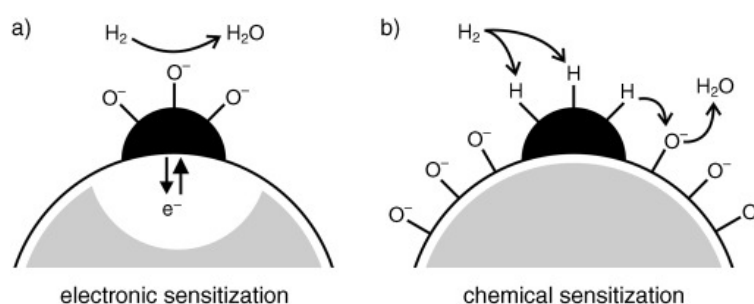


Figure 13. Sensitization mechanism of metal/metal oxide loaded on semiconducting metal oxides by a) Fermi-level control and b) spillover¹⁵⁷

1.4.3 Surface decoration (loading)

Like doping, surface decoration refers to selectively modifying the surface by depositing nanoparticles, nanostructures or other functional materials. It, therefore, leads to a significant change in the material's properties and behaviours. Both PEC water splitting and gas sensing applications involve the surface reaction in the solid-gas or solid-liquid interface. Therefore, surface decoration plays an important role as a performance improvement strategy.

In Prevot, Guijarro and Sivula's research²³, they modified CuFeO₂ photocathode's surface by atomic layer deposition (ALD) with a standard combination of aluminium-doped ZnO (AZO) and TiO₂, together with the photo-electrodeposition of a Pt cocatalyst. The loading of Pt cocatalyst dramatically enhanced the photocurrent for water reduction, reaching 0.4 mA/cm² at 0 V vs RHE.

Similarly, Cheng deposited Fe₂O₃ wrapped CuFeO₂ photocathode on ITO glass and loaded Pt cocatalysts onto the surface, after which the total charge transfer resistance across the front photoelectrode/electrolyte interface reduced significantly, which corresponded to smaller resistances for charge transfer and resulted in the improved PEC activity (**Figure 14**)¹⁴⁶.

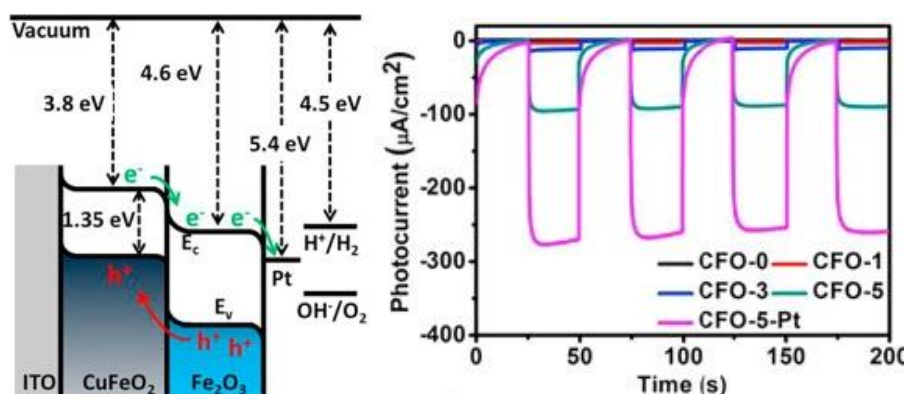


Figure 14. (Left) Energy band diagram of CFO photocathode wrapped with Fe₂O₃ layer and Pt co-catalyst. (Right) PEC performance of CFO photoelectrodes with different amount of wrapped Fe₂O₃ layer (CFO-0 to CFO-5) and CFO-5 photoelectrode loaded with Pt co-catalyst¹⁴⁶

When loading some noble metal nanoparticles, such as Au and Ag, they exhibit a strong localized surface plasmon resonance effect, which can demonstrate a strong light absorption in the UV-vis region and play an important role in improving the light absorption capacity of photoelectrode¹⁵³. In gas sensing applications, loading noble metal particles has effectively increased gas response and selectivity⁵⁹.

Kong et al. deposited Ag on Delafossite CuCrO₂ via thermal evaporation (**Figure 15**)¹¹⁸. The as-deposited Ag nanoclusters formed isolated islands on top of CuCrO₂

thin film, generating divalent copper ions. This enhanced the Ag/CuCrO₂ active interface, improving electrical conductivity and electronic structure while reducing adsorption energy with more oxygen vacancies. As a result, gas response to 100 ppm VOCs, like formaldehyde (38.7%), methanol (56.8%), and acetone (76.3%), increased significantly.

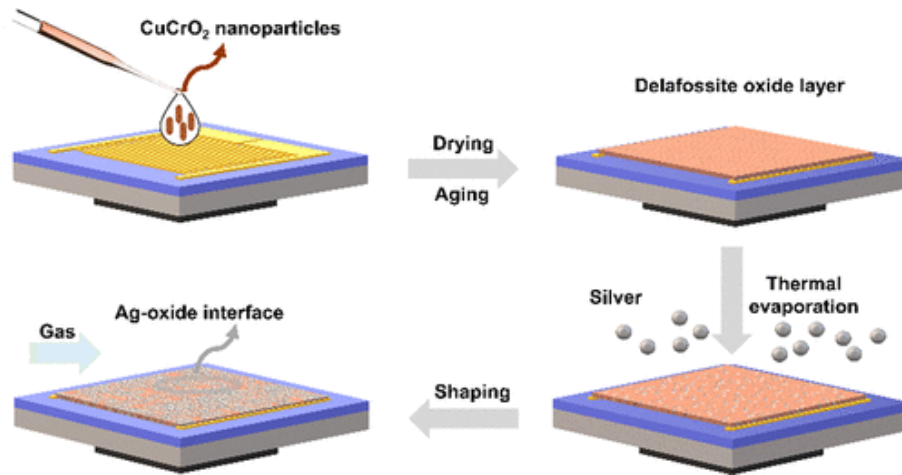


Figure 15. Schematic illustration of Ag/CuCrO₂ hybrid device synthesized by thermal evaporation

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1.4.4 Heterojunction and homojunction

It is widely accepted that forming a junction structure within semiconducting metal oxides is an effective way to solve the problems of low light absorption efficiency and severe recombination of photo-generated carriers for the application of PEC water splitting¹⁵³, while effectively enhancing the sensor response with shorter response time and recovery time for the gas sensing application¹⁵⁸.

Heterojunction refers to the interface between two different MOS materials, which can boost the charge carrier separation and transport and extend the light absorption efficiency via design and matching band structure¹⁵³. Homojunctions consist of the same semiconductor with two different layers of the same MOS materials with different doping concentrations or crystal facets, which benefit the charge carrier separation across the interface due to the lesser lattice mismatch and the continuity of chemical bonding¹⁵³.

Jiang et al.²¹ boosted the CuFeO₂'s photocathodic performance by constructing a CuFeO₂/CuO heterojunction. The charge recombination was inhibited while the charge separation efficiency was promoted due to the extended lifetime of photoinduced charge carriers resulting from the interfacial electric field effect. A photocurrent of 50 $\mu\text{A}/\text{cm}^2$ after 600 s irradiation of white light at -0.5 V vs Ag/AgCl was observed in 1M NaOH. A more than threefold increase over the pure CuFeO₂ photocathode was observed.

According to Cheng et al.¹⁴⁶, a Fe₂O₃-wrapped CuFeO₂ layer on ITO glass was fabricated on ITO glass by electrophoretic and sol-gel methods, and the FeCl₃ gel penetrated through the CuFeO₂ layer, enhancing the connection and conductivity between CuFeO₂ particles and CuFeO₂/ITO glass interface. The inserted Fe₂O₃ thin layer then worked as a buffer layer, eliminating the surface electron traps and improving the PEC activity.

In 2008, Derbal et al. prepared a CuFeO₂/SnO₂ heterojunction¹⁵⁹ for effective hydrogen evolution. This heterojunction structure was found to have its conduction band (~ -1.09 V vs RHE) located below that of SnO₂ (~ -0.86 V vs RHE) at pH ~ 13.5 , which is more negative than the H₂O/H₂ level leading to the thermodynamically favourable H₂ evolution under visible irradiation.

In 2017, Karmakar et al. constructed a CuFeO₂-ZnO p-n heterojunction¹⁶⁰ photoanode. The reconstructed photoanode was found to have a higher photoconversion efficiency than pristine ZnO nanorods under visible solar light illumination and also resolved the limitations from charge carrier separation and transportation efficiency due to the interfacial band alignment (**Figure 16**).

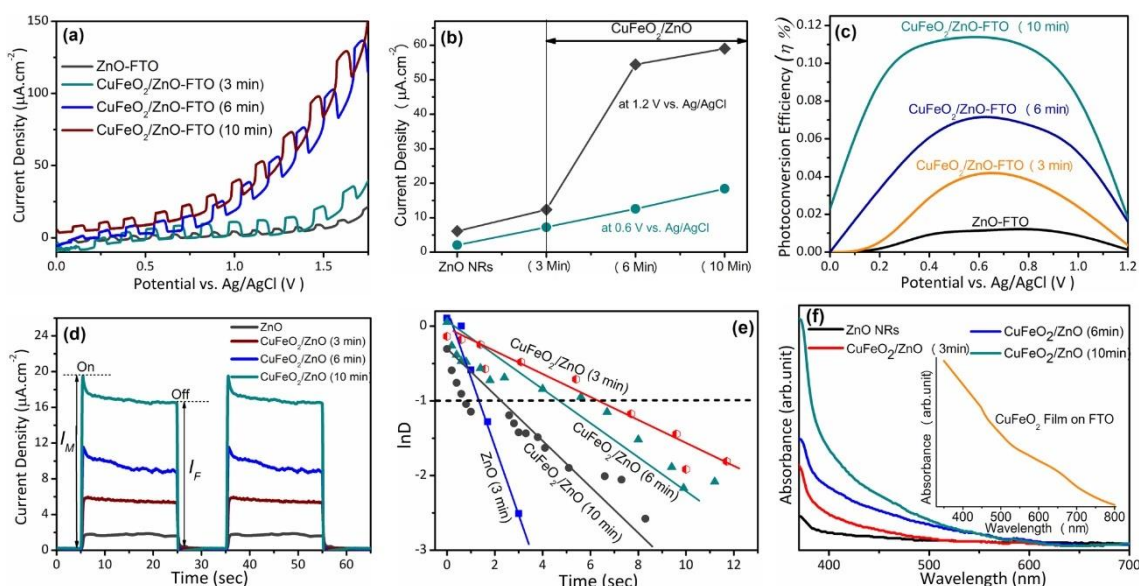


Figure 16. (a) Linear sweep voltammetry curves for the photoelectrodes performed under chopped visible light. (b) Variation of photocurrent density with the thickness of the p-type nanolayer for the as-designed nano-heterostructures. (c) photoconversion efficiency of the electrode. (d) photoswitching activity of the electrodes. (e) $\ln D$ versus transient decay time plot and (f) UV-vis absorption spectra of the as-prepared electrodes. ¹⁶⁰

1.4.4.1 Overview of CuO/Cu₂O semiconducting metal oxides used for photoelectrochemical water splitting

Due to their unique physical and chemical properties, copper oxides (CuO and Cu₂O) have attracted much attention in the fabrication of energy conversion devices, electrochemical sensors, and optoelectronic devices.

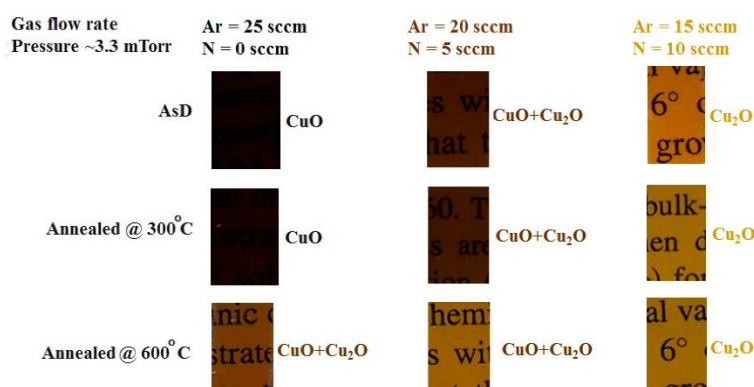


Figure 17. Change of colour due to the different ratio of CuO and Cu₂O in the films deposited in the in situ nitrogen environment¹⁶¹

As shown in **Figure 17**, CuO thin films appear black or dark brown, while Cu₂O thin films appear reddish-brown, derived from the different band gaps between 1.4-2.0 eV. The electronic structure and bonding arrangements, which are influenced by respective crystal structures and oxidation states of copper.

The mixture of CuO and Cu₂O exhibited different colours according to the various mixed ratios, due to changes in the electronic structures and optical properties of the mixture. The light absorption ability of mixtures containing various ratios of CuO and Cu₂O differs, consequently manifesting in distinct film colors.

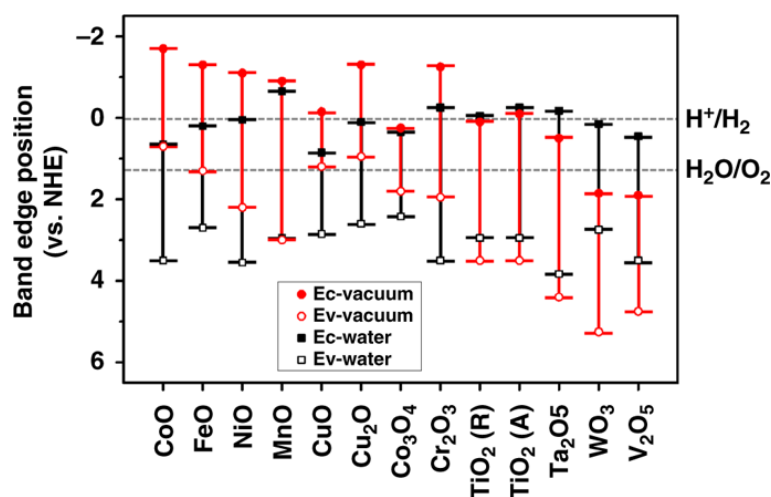


Figure 18. Band edge positions of transition metal oxides in vacuum and water measure in previous experiment¹⁶²

Overall, both CuO and Cu₂O showed promising potential in constructing highly efficient photocathodes due to the narrow bandgap (~1.5 eV for CuO and ~1.7-2.0 eV for Cu₂O depending on the deposition conditions^{161,163}, band diagram of CuO and Cu₂O is shown in **Figure 18**), as well as their abundance in the earth crust, non-toxicity and scalability for industrial produce. However, the chemical instability of CuO and Cu₂O has limited their PEC performance. Researchers have been focusing on addressing these issues: surface protection, interfacial engineering, and co-catalyst modification¹².

In 2016, Bera et al. synthesized a mixed-phase Delafossite structure consisting of p-type CuFeO_2 and CuO on the FTO-coated glass (**Figure 19**). The result presented how CuO acted as a p-type semiconductor and a provider of defect states that improved the p-type conductivity in the CuFeO_2 film, indicating its promising potential in the semiconductor technology¹⁶⁴.

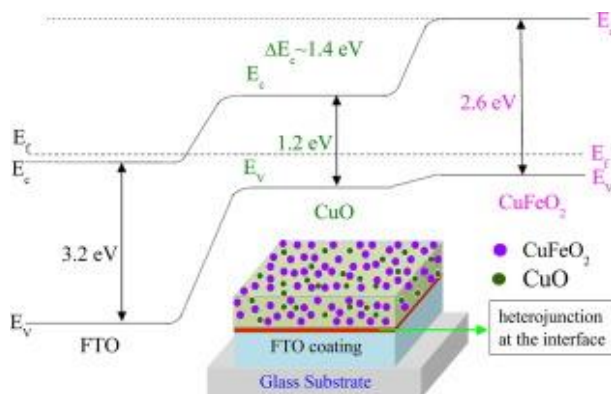


Figure 19. Energy band diagram of $\text{CuFeO}_2/\text{CuO}$ deposited on FTO-glass substrate¹⁶⁴

Later on, in 2019, Jiang et al. constructed a $\text{CuFeO}_2/\text{CuO}$ heterojunction (**Figure 20**) via a facile spin coating method and evaluated it for the application of photoelectrochemical water reduction. The interfacial electrical field effectively extends the lifetime of photoinduced charge carriers. It enhances the charge separation efficiency, which improved from $\sim 40 \mu\text{A}/\text{cm}^2$ to $\sim 80 \mu\text{A}/\text{cm}^2$ at -0.5 V vs Ag/AgCl in 1 M NaOH electrolyte²¹.

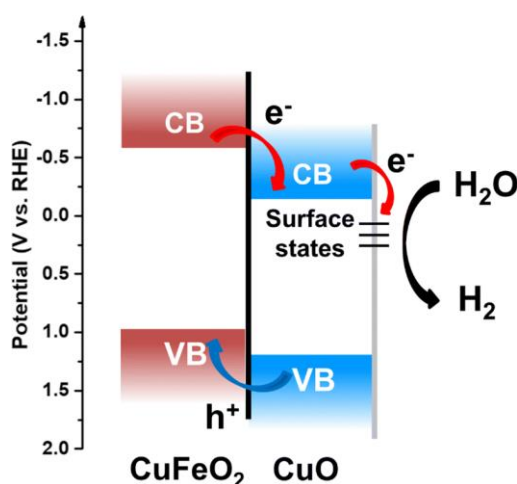


Figure 20. Energy band diagram and illustration of the photoinduced charge transfer process between CuO and CuFeO_2 in the $\text{CuFeO}_2/\text{CuO}$ photocathode²¹

Noticeably, Bera et al. constructed CuO and CuFeO₂ with a sequence of FTO-glass → CuO → CuFeO₂¹⁶⁴, while in Jiang et al.'s study²¹, CuO was deposited on top of CuFeO₂ film.

At the same time, Yuan et al. proposed the CuO/CuFeO₂ thin film photoelectrode for CO₂ reduction to form alcohol¹⁶⁵, in which the methanol and ethanol were both observed when the applied potential is set between -0.50 to -0.80 V vs SCE. The highest concentration of methanol and ethanol occurred at the applied potential of -0.70 and -0.63 V vs SCE, respectively.

This year, Lu et al. constructed a 0D/1D CuFeO₂/CuO nanowire heterojunction array¹⁶⁶ by dipping method for improved photoelectrocatalytical reduction of CO₂ to ethanol in the water and triethanolamine electrolyte (water: triethanolamine=9:1) with pre-purged O₂. A high faradic efficiency of 66.73% was achieved, and the heterojunction formed between CuFeO₂ and CuO was proposed as shown in

Figure 21.

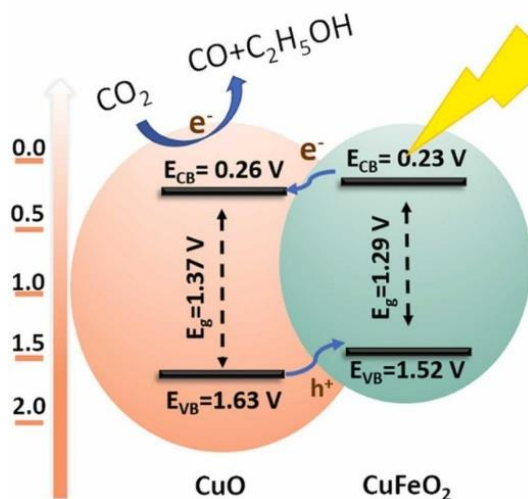


Figure 21. Band energy position and illustration of charge transportation between CuO and CuFeO₂ in the CuO/CuFeO₂ photocathode¹⁶⁶

To better understand the complex defect in the mixed phase copper iron oxide, Fugate et al. studied CuO/CuFeO₂ mixed phase via visible light transient

absorption spectroscopy and density functional theory (DFT). Their results showed that there is a 'surface state' existing in CuFeO₂ acting like an electron trap, where the separation of charge carriers are inhibited and the recombination was fast. The lifetime of these charge carriers can be longer if this 'surface state' can be removed and the electrons are not trapped on the surface to inhibit the charge separation. In the study, researchers found that hole thermalization can significantly facilitate charge separation and slow down the charge carrier recombination. Introducing Cu vacancies can enhance the photoelectrochemical performance by facilitating charge separation kinetics. In contrast, introducing oxygen interstitial will switch the relative position of O 2p and Cu 3d valence band state, inhibiting the charge separation by inter-band hole thermalization. They also suggested that the interfacial charge transfer from CuFeO₂ to CuO is not responsible for enhanced carrier lifetimes since there is no evidence for electron injection from CuFeO₂ to CuO, suggesting that charge separation at the heterojunction interface does not play a role in the carrier lifetime or photochemical performance enhancement¹⁴⁴.

1.4.4.2 Overview of NiO semiconducting metal oxides

Nickel oxide is an oxide containing divalent nickel and is a p-type semiconducting metal oxide with an excess of positive charge carriers that contribute to its electrical conductivity. It has a wide bandgap, typically around ~3.6 eV^{167–170}, making it suitable for absorbing visible light and some ultraviolet light. Generally, nickel oxide is stable, non-toxic, and relatively abundant, making it an attractive candidate for various applications, particularly in photoelectrochemistry, gas sensing^{171–173}, and energy storage^{174–176}.

In a recent study, NiO has been studied as a promising material for photoelectrochemistry, such as being used as a p-type semiconductor layer in solar cells^{177–180} and has been used as a photocatalyst^{181–183} for water splitting,

photodegradation of organic pollutants^{184–186}, and CO₂ reduction^{187–190} to produce renewable fuels.

Also, NiO thin film combined with CuO/Cu₂O photoelectrode greatly enhanced the photoelectrochemical performance in CuO/Cu₂O as a hole extraction layer¹⁹¹.

According to Senobari et al. in 2018¹⁹², the calcination temperature plays an important role in CuO-NiO nanoparticle photoactivity. In their research, the calcination temperature ranges from 200°C to 800°C and the higher the calcination temperature, the better the photoactivity due to the increased crystallinity. They also found that the pre-mixed catalyst performed better than the post-mixed system due to a better formation of the mixed crystallite.

In 2020, Santos et al.¹⁹³ reported a CuO/NiOx thin film-based photocathode as the application for photoelectrochemical water splitting, in which the presence of NiOOH in the NiOx acted as an electron trapper, favouring the generation of electron-hole pairs. The best CuO/NiOx film exhibited a photocurrent density of -1.02 mA cm⁻² at 0 V vs RHE. All measurements were carried out in 0.5 M Na₂SO₄ solution when pH equals 6.

In the same year, Li, Wei and Yang conducted an ITO/NiO/Cu₂O photocathode, and it demonstrated a photocurrent density of -1.68 mA/cm² at -0.6 V vs RHE. At the same time, the measurements were carried out in 0.1M Na₂SO₄ aqueous solution.

The application of NiO as a hole selective/transport layer is not limited to CuO/Cu₂O photoelectrode but shows its effectiveness in other photocatalysts and photoelectrodes.

In 2019, Lee et al. used Cu-doped NiO₂ as an effective hole selective layer (HSL) to successfully enhance the photochemical water splitting efficiency in Sb₂Se₃ photocathode¹⁸⁰.

In the same year, NiO nanowires¹⁹⁴ were reported as an effective hole transfer layer for the CdSe-sensitized photocathodes, greatly enhancing the light capture efficiency and promoting the charge carrier transfer rate.

Recently, Han et al. reported a one-pot-oxidation synthesized NiO/CuFeO₂ heterojunction photocathodes consisting of a Cu: NiO layer and Ni: CuFeO₂ layer on top of the FTO substrate. The combination of the Cu: NiO hole selective layer (HSL) and Ni: CuFeO₂ active layer significantly promoted the separation of photogenerated carriers, and the composite photocathode exhibited a high photocurrent density of $\sim 0.9 \text{ mA/cm}^2$ at 0.2 V vs RHE in 0.1 M Na₂SO₄ electrolyte¹⁹⁵.

1.4.4.3 Overview of CuFe₂O₄ and NiFe₂O₄ semiconducting metal oxides

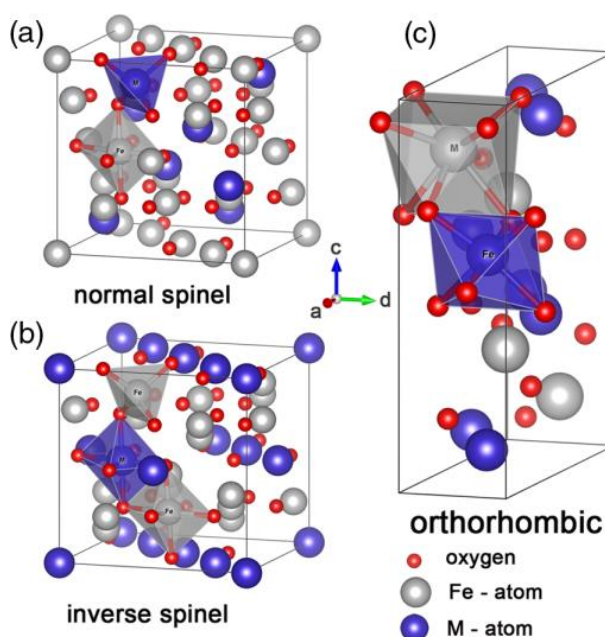


Figure 22. Crystal structures of spinel ferrites: (a) normal spinel, (b) inverse spinel, and (c) orthorhombic, each crystal structure demonstrates three crystallographic sites¹⁹⁶

Spinel ferrites with the formula of AB₂O₄ have a crystal structure consisting of interstitial spaces with octahedral and tetrahedral sites. The distribution of cations in the cubic lattice can be varied, depending on the magnetic properties, and form either a normal type of spinel, in which A fills the tetrahedral sites. B fills in the

octahedral site, or a reverse spinel, in which cation B fills half of the tetrahedral site and cation A fills in the octahedral site¹⁹⁷, as shown in **Figure 22**.

Ferrite spinel is one of the most promising photocathode candidates for PEC water splitting due to its earth abundance, non-toxicity and stability in aqueous electrolytes. The narrow band gaps and suitable band positions allow them to drive the redox reaction over the surface¹⁹⁸.

In the ferrite spinel family, CuFe_2O_4 attracts the most attention with a band gap of $\sim 1.5\text{-}1.9$ eV. Theoretically, the photocurrent density can reach ~ 27 mA/cm² while its solar-to-hydrogen efficiency can reach $\sim 33\%$ ¹⁹⁹.

In the past study, CuFe_2O_4 thin films were successfully deposited via many methods, including spray pyrolysis²⁰⁰, electrochemical deposition²⁰¹, pulsed laser deposition (PLD)²⁰², RF-sputtering²⁰³, liquid-phase deposition²⁰⁴, sol-gel²⁰⁵ etc. In the case of photoelectrochemical performance, the highest photocurrent density was achieved at ~ 1.82 mA/cm² after a flamed-annealed process in which the film had a higher degree of porosity, while in the traditional process, it was at ~ 0.52 mA/cm² at 0.4 V vs RHE in the Ar purged 1M NaOH electrolyte²⁰⁵.

In addition, the construction of the heterojunction between amorphous MnO_2 with CuFe_2O_4 on the ITO surface via electrochemical deposition has been investigated in 0.5 M Na_2SO_4 electrolyte for the hydrogen evolution reaction (HER)²⁰⁶. The CuFe_2O_4 /amorphous MnO_2 with a ratio of 1:4 produced 502.8 $\mu\text{mol H}_2$ in 90 min, which was higher than $\text{CuFe}_2\text{O}_4/\text{TiO}_2$ (130 $\mu\text{mol/h}$) and $\text{CuFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ (76 $\mu\text{mol/h}$)¹⁹⁹.

NiFe_2O_4 is an inverse spinel ferrite and exhibits ferromagnetic nature with a curie temperature of 858 K, where half of the Fe^{3+} ions occupy tetrahedral sites, and the remaining ions occupy the octahedral sites. NiFe_2O_4 has a similar band gap to CuFe_2O_4 ²⁰⁷ (**Figure 23**).

Recent studies on NiFe_2O_4 used as a photocathode mainly focused on hydrogen generation²⁰⁸, heterojunction construction²⁰⁹ or morphology modifications²¹⁰ to improve its PEC water-splitting performance.

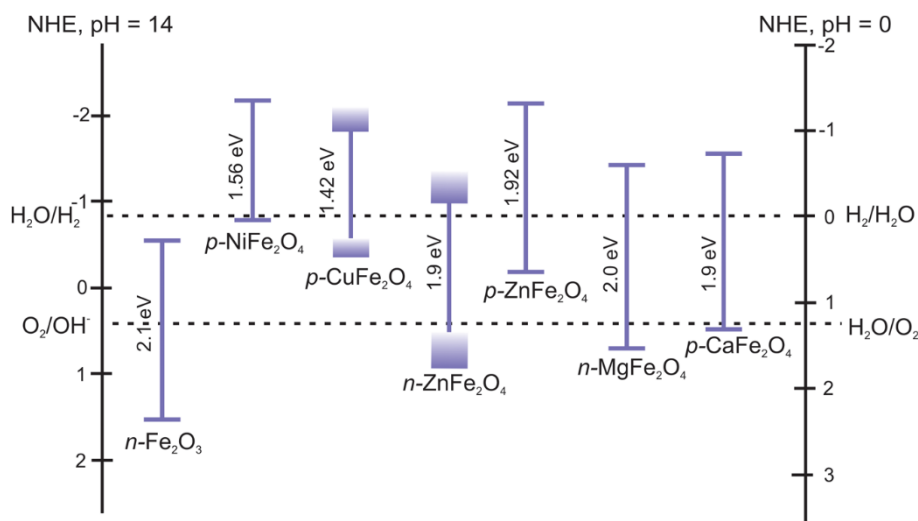


Figure 23. Band diagram of spinel ferrites in contact with aqueous solution referenced with NHE (right pH=14, left pH=0 relative to the standard potentials for the reduction and oxidation of water)¹⁹⁶

In 2013, Rekhila et al. prepared a p-type NiFe_2O_4 photocathode via the sol-gel method to produce hydrogen under visible light²⁰⁸. Under ideal conditions (neutral electrolyte with $\text{S}_2\text{O}_3^{4-}$ acts as hole scavenger, the rate of H_2 production attains $0.68 \times 10^{-3} \text{ mlmg}^{-1} \text{ min}^{-1}$ with a quantum efficiency of 0.53%.

In 2021, Maitra et al. fabricated highly porous NiFe_2O_4 nanoflake arrays by low-temperature surfactant-assisted solvothermal phase change-induced temperature-controlled etching process²¹⁰. The PEC performance of NiFe_2O_4 nanoflake photocathode with 77% inverse spinel exhibited the highest photocurrent density of -0.139 mA/cm^2 at 0 V (vs RHE) and -2.57 mA/cm^2 at -1 V (vs RHE) with the highest IPCE achieved 18.7%.

However, according to the comparison study conducted by Kumar et al. among CuFe_2O_4 , NiFe_2O_4 , and ZnFe_2O_4 , the photoelectrochemical performance of NiFe_2O_4 is less effective than CuFe_2O_4 on organic compound photodegradation

(though better than ZnFe_2O_4) due to smaller surface area, larger band gap, and fewer holes for trapping more oxygen molecules to produce oxidizing species and OH radicals²⁰⁷, which probably explains why NiFe_2O_4 received less attention than ternary copper oxide on PEC water splitting.

1.4.5 Oxygen vacancies and oxygen interstitials

Oxygen vacancies are a ubiquitous defect in semiconducting metal oxides, and their concentration can be affected by synthesis, processing and operating parameters²¹¹. The generation of oxygen vacancies can alter the physicochemical properties of materials compared to their stoichiometric counterpart, such as conductivity, content of active sites, adsorption/desorption process, contact angle, etc²¹².

The primary role of oxygen vacancies in the gas sensing applications is based on a modulation of the amount of surface absorbed oxygen or the baseline resistance²¹¹, while in the MOS materials for PEC water splitting, the introduction of oxygen vacancies can significantly influence the charge separation, the light absorption, charge transfer, and the surface reaction kinetics^{213,214}.

Creating oxygen vacancies in a specific material usually involves introducing deliberate defects by removing oxygen atoms from the crystal lattice. The standard techniques include thermal annealing, ion implantation, reducing atmospheres, plasma treatment, electronic methods, chemical doping, or ion exchange²¹³.

Tong et al. investigated the oxygen vacancy defects in a p-type Delafossite CuCrO_2 gas sensor. The study revealed that singly ionized oxygen vacancies ($\text{Vo}^\bullet$) played a more significant role than grain size in enhancing charge exchange at the VOCs/ CuCrO_2 interface. $\text{Vo}^\bullet$ defects suppressed the hole concentration in the sensor channel and provided active sites for the chemisorption of environmental oxygen and VOCs. This synergetic effect led to increased sensitivity. The defect-

rich CuCrO₂ gas sensor also demonstrated excellent reproducibility and stability at an operation temperature below 325°C²¹⁵.

Jeong et al. treated as-deposited CuFeO₂ thin films using novel hybrid microwave annealing (HMA). Compared with traditional thermal annealing, hybrid microwave annealing introduces more oxygen vacancies, increasing the charge carrier density and thus improving the charge transportation properties. The HMA-treated CuFeO₂ photocathode exhibited a photocurrent density of ~1.3 mA/cm² at 0.4 V vs RHE, showing a significant improvement (over four thresholds) compared with CuFeO₂ without any thermal treatment (~0.3 mA/cm² at 0.4 V vs RHE)¹³⁵.

In contrast to oxygen vacancies, oxygen interstitials refer to the process that excess oxygen is inserted into the lattice of a material, which also creates a defect in the material and influences the material's properties and behaviours via various ways, including the effects in band broadening²¹⁶, lattice volume, electrical and optical properties, charge carrier diffusion and migration and probably reduced stability.

Point defects are imperative to the physical properties of oxides for electronics such as fatigue and domain wall pinning in ferroelectrics²¹⁷. If the components are smaller, the available length for point defects in materials to diffuse can be reduced, which shorten the time needed for point defects to spread throughout the samples compared to bulk materials, where they essentially become fixed in place²¹⁸. According to Skjærvø et al.'s study, the interstitial oxygens can govern the concentration of charge carrier holes, control the thermal and atmospheric history and provide a simple and fully reversible approach to tune the electrical properties, which can be a source of p-type electronic conductivity.²¹⁹ Yengantiwar et al. prepared Delafossite CuFeO₂ photocathodes by direct liquid injection chemical vapour deposition, in which the p-type conductivity was confirmed to result from Cu vacancies and interstitial imperfections (oxygen interstitials). Moreover, the

more oxygen interstitials, the higher the p-type conductivity the CFO films achieved

130

In the study of Fugate et al., DFT calculations of Delafossite CuFeO_2 indicate that Cu vacancies can enhance photochemical performance by facilitating charge separation. Meanwhile, oxygen interstitials are predicted to switch the relative positions of O 2p and Cu 3d valence band states, inhibiting the charge separation by inter-band hole thermalization¹⁴⁴. Therefore, introducing oxygen interstitials or vacancies represents a potential approach to influence both the gas-sensing performance and the PEC activity of CuFeO_2 thin films.

1.5 Introduction of deposition methods for Delafossite CuFeO_2

1.5.1 Thin film deposition methods

Thin films can be deposited by many techniques. Previously, common techniques such as chemical vapour deposition (CVD), atomic layer deposition (ALD), physical vapour deposition (PVD), including evaporating and sputtering, molecular beam epitaxy (MBE), spin coating, dip coating, electroplating, sol-gel, pulsed laser deposition (PLD) are widely discussed and developed in both research and industrial production. A material can have multiple synthetic routes, which can vary greatly depending on the availability of required reaction conditions.

Some examples in **Table 4** show several deposition methods for Delafossite CuFeO_2 thin films.

Table 4. A summary of CuFeO₂ thin film deposition methods in the previous study

Deposition method	Cu precursor	Fe precursor	Solvent	Carry gas	(Post) annealing conditions	Refs.
Sol-gel	Cu(CH ₃ COOH) ₂ •H ₂ O	Fe(NO ₃) ₃ •9H ₂ O	Ethanol	N ₂	500°C in air for 1h	220
Pulsed laser deposition	Polystalline CuFeO ₂ target		/	/	600°C under an O ₂ partial pressure of 1.33×10 ⁻² Pa	140
Electrospinning	Copper (II) oximate complex	Iron (II) oximate complex	11 w.t.% PAN (PAN in DMF)	Air and argon	750°C for 6h	128
RF-sputtering	Cu ₂ O	Fe ₂ O ₃	/	argon	450°C in N ₂ for 4h	112
Solid state reaction	Cu ₂ O	Fe ₂ O ₃	/	/	950°C for 12h and 1000°C for 12h	221
Magnetron co-sputtering	Cu target	Fe target	/	9:1 Ar/O ₂	600°C in Ar for 6h	113
Hydrothermal	Cu(NO ₃) ₂ •3H ₂ O	FeCl ₂	H ₂ O, NaOH, NH ₃ •H ₂ O, absolute alcohol	/	160°C-100°C for 12-48 h	222
	Cu ₂ O•H ₂ O	FeOOH	Fused NaOH	/	210°C, 2-5 days	223
	Cu(NO ₃) ₂ •5H ₂ O	Fe(NO ₃) ₃ •9H ₂ O	H ₂ O, NaOH, propionaldehyde, absolute ethyl alcohol	/	80°C for 12h	147
Electrochemical	Copper (II) nitrate	Iron (III) perchlorate	DMSO, potassium perchlorate	/	650°C in Ar for 1h	224
Atmospheric pressure plasma annealing	Copper (II) acetate monohydrate	Iron (III) nitrate nonahydrate	Ethanol, triethanolamine	/	500°C in air for 1h	225
Direct liquid injection CVD	Copper (II) acetylacetonate	Iron (III) acetylacetonate	DMF	/	450°C, 500°C, 550°C for 45-90 min	130
AACVD	Copper (II) nitrate (hemi) pentahydrate	Iron (III) acetylacetonate	methanol	air	623K, 673 K and 723 K	226
APCVD	Copper(II) chloride; Copper(II) nitrate trihydrate; Copper(II) acetylacetonate	Fe(III) chloride; Iron(III) nitrate nonahydrate; Iron(III) acetylacetonate	CH ₃ CN	air	650°C in Ar for 1 h	110
Spin coating	Cu nitrate	Fe (III) nitrate	acetic acid, 2-methoxyethanol, polyethenalglycol	air	900°C in N ₂ for 2h	227

Different deposition methods are compared based on their fundamental deposition techniques, and the results are summarized in **Table 5**.

Table 5. Comparison of MBE, PLD, CVD and ALD for thin film deposition

Deposition method	Deposition temperature (°C)	Deposition pressure (mbar)	Area of Coverage	Purity of film	Time taken for 100 nm film	Cost
MBE	400-800	10^{-10} - 10^{-9}	Small	Poor	60 min	High
PLD	25-800	10^{-9} - 10^{-5}	Small	Poor	30-60 min	High
CVD	200-500	10^{-3} - 10^3	Large	Fair	10 min	Low
ALD	50-200	10^{-3} - 10^3	Large	Good	300 min	Low

1.5.2 Aerosol-assisted chemical vapour deposition (AACVD)

1.5.2.1 The process of AACVD

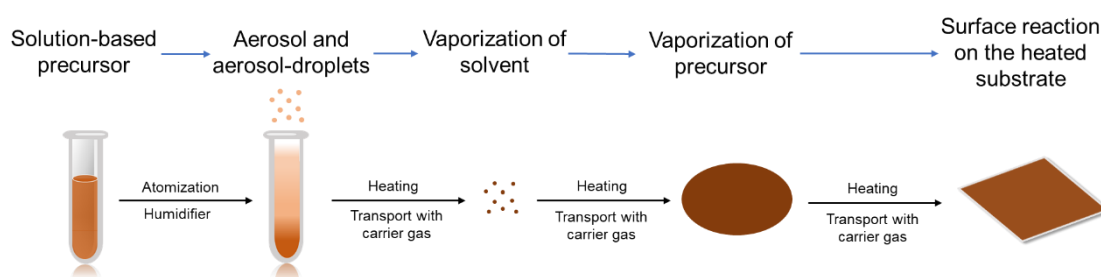


Figure 24. Schematic of typical AACVD processes for thin film deposition^{228,229}

A typical AACVD deposition process (**Figure 24**) starts from atomising a liquid precursor solution in a glass flask to the fine sub-micrometre-sized aerosol droplets. These droplets will be transported by the carrier gas and heated up in a hot reactor chamber to undergo rapid evaporation, where the solvent will be vaporized or decomposed, forming the precursor vapour. The precursor vapour will then start its surface reaction on the top of the heated substrate and form the desired thin film^{228,229}.

There are two types of film growth strategies. They are distinguished into homogeneous and heterogeneous reactions when the vaporised precursor forms a thin film on the heated surface²²⁸.

The heterogeneous reaction occurs when the vaporized precursor and their gaseous intermediate species can be absorbed onto the heated substrate and initiate substantial decomposition and chemical reactions. External reactive gases can be introduced into the reaction zone directly to assist the chemical reactions. The films grown in this way are desired, which generally exhibit high quality and good adhesive strength ²²⁸.

If the decomposition temperature is relatively high, the primary decomposition and chemical reaction may occur in the vapour phase, where the fine particles (with the size ranging from nanometres to micrometres depending on the processing conditions) will be formed during homogeneous nucleation and absorb on the substrate and films typically exhibit higher porosity. External reactive gases can also be introduced to the homogeneous reaction ²²⁸.

1.5.2.2 Controlling factors of film growth in the AACVD

The homogeneous and heterogeneous reactions primarily determine the thin film's morphology and microstructure. During the AACVD process, the pattern of gas-phase reaction is decided by various factors, including precursor^{230–233}, solvent²³⁴, substrate, temperature^{233,235,236}, and gas flow rate²³⁷.

Figure 25 illustrates how these factors influence AACVD deposition on film morphology (microstructure), film growth position and film growth rate.

Deposition temperature affects the amount of elements deposited on the substrate (kinetics) and strongly influences the deposition orientation (film morphology). When the deposition temperature is lower than the optimal temperature for a film, it will initialize the film to deposit in the middle of the substrate. In contrast, if the deposition is higher than the optimal deposition temperature, the film tends to grow at the edges where the temperature is relatively low.

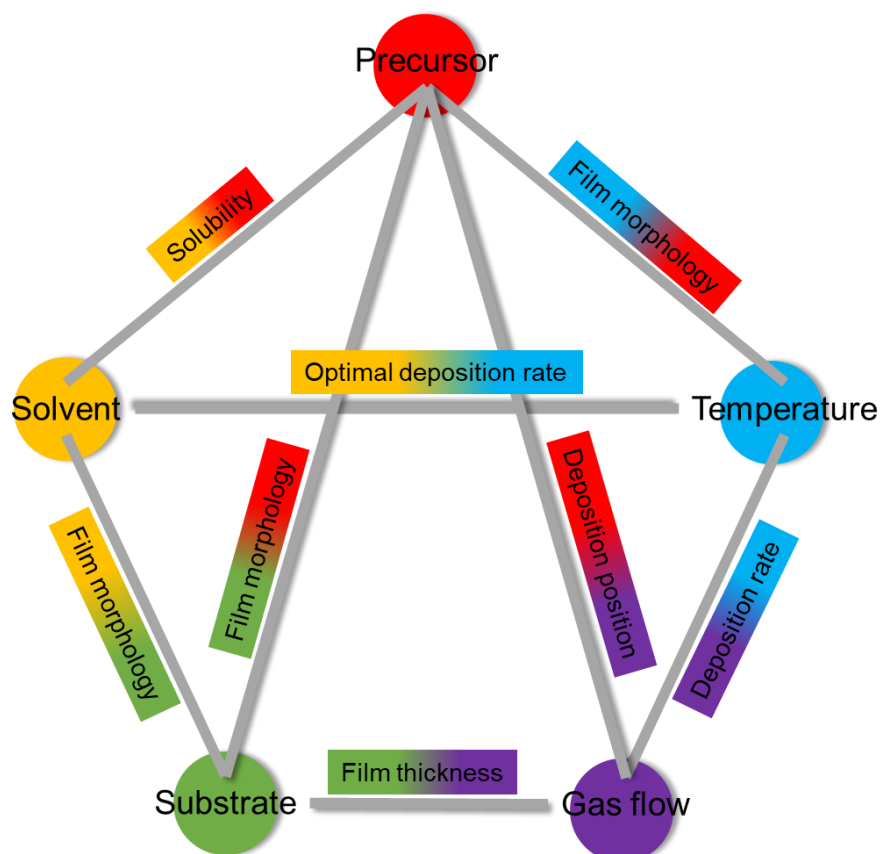


Figure 25. Illustration of various influenced factors and effects during AACVD deposition

For a dual or multi-precursor AACVD deposition, the controlling factors coordinately work more precisely. This is because different precursors typically have different preferences on the influenced factors. In order to get a specific elemental ratio or film morphology, factors including precursor, solvent, substrate, carrier gas flow rate, and temperature need to be carefully adjusted.

1.5.2.3 AACVD's advantages over traditional CVD

In the CVD process, the precursor is required to be decomposed at elevated temperatures on the surface of a substrate to enable the deposition of the required thin film. In traditional CVD, a good (typically liquid) precursor volatility is needed such that the precursor will be readily volatile at temperatures well below its decomposition to allow efficient precursor transport.

In contrast, AACVD is a solution-based technique that reduces the requirement of volatility for precursors, although also requiring solubility of the precursor in a carrier solvent²³⁸.

Compared with traditional CVD, AACVD²²⁹, has the following potential advantages:

- 1) A wider range of precursors for high-quality CVD thin films at low cost due to the replaced requirement of precursor's volatility by solubility²²⁸.
- 2) Simplification of the transportation and vaporization of precursor via the generation of precursor aerosol²²⁸.
- 3) Higher deposition rate, typically several orders of magnitude higher than vacuum deposition methods²²⁹.
- 4) A more flexible reaction environment since AACVD can be conducted in an atmospheric or open atmosphere.
- 5) More ready control of stoichiometry in the thin films synthesized from dual- or multi-precursors.

1.5.2.4 Thin films deposited via AACVD and their applications

Metal oxide or semiconducting metal oxide thin films synthesized via AACVD have been widely used in optics^{239–241}, electronics^{242,243}, solid oxide fuel cells^{244–249}, superconductors^{250–254}, gas sensors^{255,256}, catalytical films such as photodecomposition^{257,258} or self-cleaning^{257–260}, or bioactive coatings²⁶¹. In addition, chalcogenide films^{262–264}, metallic films^{265–267}, nanocomposite coatings^{268,269}, carbon nanotubes^{270–272}, and other nanotubes and nanowires such as MoS₂ nanotubes²⁷³ and square SnO₂ tube tubule arrays^{274,275} can also be synthesized through AACVD methods.

1.5.3 Introduction of post-annealing treatment

1.5.3.1 Post-annealing treatment in the MOS thin films

Post-annealing treatment, also known as thermal annealing, is a heat treatment process performed on thin film after deposition. This treatment involves subjecting the thin film to evaluated temperatures for a specific duration. The process is commonly carried out in a vacuum or a controlled atmosphere.

Post-annealing treatment after thin film deposition offers a multitude of advantages, making it a crucial step in optimizing thin film performance for various applications, which can eliminate impurities²⁷⁶, improve crystallinity²⁷⁷, adjust film defects²⁷⁷, enhance electrical properties²⁷⁸, optimize electrical conductivity, relief mechanical stress²⁷⁹, promote uniformity of film thickness²⁷⁸, improve adhesion²⁸⁰, tailor the properties^{278,281,282}, including bandgap adjustments^{278,281} and modification of magnetic characteristics²⁸², control grain growth²⁸², and improve film's stability and reliability²⁸³.

Post-annealing is a versatile and indispensable process that improves thin film quality, performance, and suitability for various technological applications. It is also a standard procedure in the deposition of Delafossite CuFeO_2 . Examples and related annealing conditions can be found in **Table 4** in **Section 1.5.1**.

1.5.3.2 Controlling factors in post-annealing treatment

Various factors determine the outcome of post-annealing treatment and can be categorized into material-related factors, annealing conditions and equipment-related factors.

Generally, annealing conditions can be altered by four parameters.

1) Annealing temperature²⁸³, which determines the extent of atomic diffusion and the degree of structural transformation. A higher temperature can result in more significant changes and introduce unexpected effects such as film degradation.

2) Annealing time²⁸³. A longer annealing time promotes greater diffusion and structural changes. Various annealing times can lead to different degrees of defect adjustment.

3) Heating rate and cooling rate²⁸⁴. The rate at which the temperature increases (heating rate) and decreases (cooling rate) during annealing impacts the material's microstructure and stress. Suitable heating and cooling rates can avoid thermal shock and stress-induced defects in the thin films.

4) Annealing atmosphere²⁸⁵, which affects oxidation or reduction reactions and can influence the final properties of the materials.

1.6 Research aims

The primary objectives of this project can be divided into three stages.

In the first stage, the main objective was to produce pure p-type Delafossite CuFeO_2 thin films through AACVD and post-annealing treatment. During this stage, the thin film growth mechanism of Delafossite CuFeO_2 via AACVD was investigated. AACVD deposition parameters were evaluated and are summarized in detail to describe the deposition methods of Delafossite CuFeO_2 thin films with well-controlled stoichiometry and adjustable film morphology based on an in-depth understanding of AACVD and the post-annealing treatment.

In the second stage, well-tuned Delafossite CuFeO_2 thin films were assembled in the gas sensing equipment, or photoelectrochemical cell, to evaluate their gas sensing or photoelectrochemical water splitting performance, respectively. Different parameters, either from the testing environment such as operating temperature, humidity, analyst gas for gas sensing performance; or electrolyte, pH, gas atmosphere for PEC water splitting, or from CuFeO_2 thin film itself such as film's morphology, grain size, porosity, and microstructure, were evaluated to

illustrate the working mechanism, summarize the optimal conditions and provide future research insights.

In the third stage, research focused on proposing and thoroughly investigating modification methods to enhance the performance of Delafossite CuFeO_2 thin films, specifically targeting the application of photoelectrochemical water splitting. This was approached by thermal annealing in the low-oxygen atmosphere, constructing heterojunctions, and implementing surface decoration. The PEC performance of Delafossite CuFeO_2 thin film was compared before and after modification to illustrate the effectiveness and explain the working mechanisms.

Chapter 2. Experimental Methodology

2.1 Introduction

This chapter presents the materials and chemicals used in the thesis. Thin film synthesis methods are described, including Aerosol-assisted chemical vapor deposition (AACVD) and post-annealing treatment. Techniques used to characterize and analyze material's morphology, structure, electronic, optical and photoelectrical properties are introduced.

2.2 Materials and Chemicals

Table 6. List of consuming materials and chemicals

Materials and Chemicals	Supplier
Copper (II) acetylacetonate, >98%	ACROS Organics
Iron (III) chloride tetrahydrate, >=99.8%	Fisher Scientific
Iron(III) acetylacetonate, 97%	Sigma-Aldrich
Nickel acetylacetonate, 96%	ACROS Organics
Sodium persulfate, 99.5%	M P BIOMEDICALS UK
Potassium phosphate dibasic, ACS reagent, >=98%	Sigma-Aldrich
Potassium phosphate monobasic, ACS reagent, >=99.0%	Sigma-Aldrich
Sodium hydrogen carbonate, >= 99.7%	Fisher Scientific
Sodium sulfate, anhydrous, free-flowing, Redi-Dri, ACS reagent, >=99%	Sigma-Aldrich
Hydrochloric acid solution – 32% Emplura	Sigma-Aldrich
Sodium hydroxide pellet	Fisher Scientific
N ₂ (9.8 m ³ cylinder, oxygen-free)	BOC
O ₂ /N ₂ (2000 ppm oxygen in nitrogen)	BOC
O ₂ (2.83m ³ cylinder)	BOC
Methanol, >=99.8%	Fisher Scientific

Acetonitrile, >=99.8%	Fisher Scientific
Acetone, >=99.5% (GC)	Sigma-Aldrich
Deionized water	Merck, Direct-Q@3UV water purification system
Glass	VWR International, LLC
Quartz	Wuxi Crystal and Optical Instrument Company Limited
Alumina	University of Warwick
AGSS	University of Warwick
ITO-coated quartz (6-8 Ω , 2*2 cm)	South China Science & Technology Company Limited

2.3 Deposition Methods

2.3.1 Aerosol-assisted chemical vapor deposition (AACVD)

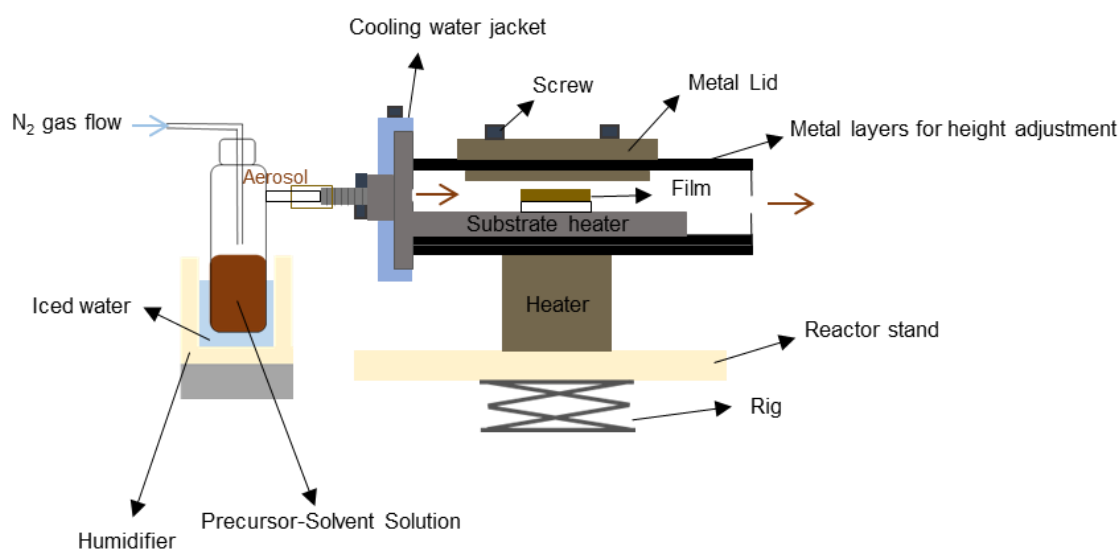


Figure 26. Components and structure of the AACVD equipment

The schematic of the AACVD reactor used in this project is shown in **Figure 26**. In this system, the precursor solvent solution is contained within a glass flask. On one side, it was connected with a mass flow controller (MFC, 0-5000 sccm, Brooks Instrument) to control the gas flow rate of inert carrier gas N₂ (99.99%, BOC). On the other side, it was connected to the reactor. An ultrasonic humidifier (2 MHz,

Johnson Matthey Liquifog) was used to convert the liquid precursor-solvent solution to an aerosol, which was transported by the carrier gas to the reactor chamber. The flask was surrounded with iced water to avoid the heat from the ultrasonic oscillations heating the solution.

The reaction chamber has a space of 3×6×0.4 cm and sits on a substrate heater. The heater was heated by a heating jacket and rod heater that can go from room temperature to 600°C and is controlled by a heating box. Metal inserts can be used to adjust the height of the aerosol-inlet pipe to align the height of the inlet slot in the manifold with the top of the substrate. The manifold is cooled by a circulating water-cooling system (Thermo Haake) to prevent the precursor from decomposing before reaching the substrate. The reaction chamber is not a closed system, and the gas waste and residue are exhausted from the end of the chamber to the fume hood.

In a typical AACVD deposition, a substrate is cleaned and put on the substrate heater in the reaction chamber. The reactor is closed and sealed with rings and screws before heating up to the deposition temperature. The precursors are dissolved in the solvent in the flask, and the flask is assembled with the carrier gas tube and the reactor. Circulated cooling water is used to cool the manifold from the beginning of the experiment. A small amount of carrier gas is introduced before and during heating to keep the substrate surface clean. Once the temperature reaches the set point, the gas flow rate is adjusted to the required amount, and the ultrasonic humidifier is turned on. The aerosol should fill the flask once the humidifier is on with the correct set-up. After passing all the precursor-solvent solution into the reaction chamber over time, the deposition is finished. During the cooling down, the heater and humidifier should be switched off, and the carrier gas should be lowered to the same amount as the heating-up period. Samples should be taken out when the temperature is cooled to room temperature.

2.3.2 Post-annealing treatment

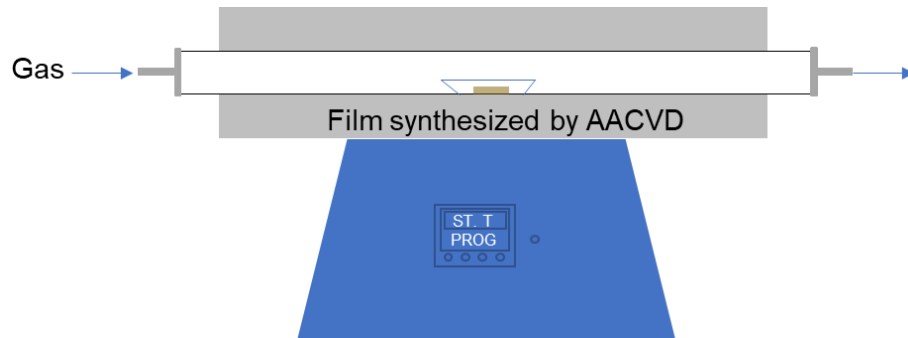


Figure 27. Schematic of post-annealing treatment process in the tube furnace

Following AACVD deposition, the films primarily consist of amorphous metal-oxide mixtures alongside carbon residues derived from the decomposition of organic metal precursors at the deposition temperatures. To get a pure single-crystal phase and remove reaction residues, post-annealing treatment is necessary.

In this stage, films are transported to the crucible (Tangshan High-purity alumina ceramics distribution Co., Ltd)), and then are put in the middle of a furnace (**Figure 27**).

Two furnaces were used during the post-annealing treatment. A chamber furnace (CWF, CARBOLITE GERO) was used for annealing under an air atmosphere in the ambient pressure, whereas a tube furnace was mainly used for annealing under an inert N_2 atmosphere or N_2 mixed with a small amount of air. The tube was capped with tri-clamp fittings and sealing gaskets (Flowsource Process Fittings Ltd) to maintain a pure gas atmosphere. The annealing gas is pumped into a furnace tube with the control of an MFC (Brooks Instrument). Before heating up, the annealing gas was delivered into the tube for 20 min to get rid of the air.

Here, factors including annealing temperature, duration, and ramping rate can be set in the program and conducted automatically. These factors, together with the cooling down and gas atmosphere, have a significant impact on the film's phase and crystal structure, which will be further explained in the next chapter.

2.4 Characterization Techniques

2.4.1 Energy Dispersive X-ray Spectroscopy (EDX)

Energy dispersive X-ray spectroscopy (EDX, Oxford Instrument) was used to detect the elemental composition of the film. A Philips XL30 ESEM and a JEOL JXA-8600 super-probe were used to conduct the analysis. The measurements were carried out under a high vacuum where the electron high tension (EHT) was 20 KV, the beam current was 500 pA, the working distance was 8.5 mm, and the magnification was 1000. Before doing the EDX analysis, the films were coated with a thin layer of conductive carbon (AGAR Scientific Ltd) and stuck to the sample holder stage using copper tape.

2.4.2 X-ray diffraction (XRD)

X-ray diffraction (XRD) was used to study the sample's crystallographic structure. In this thesis, thin film samples on the plain substrate were measured by a Bruker D8 Discover LynxEye diffractometer or PANalytical X'Pert³ thin film analysis diffractometer. Both are equipped with an X-ray diffractometer using Cu K α radiation ($\lambda = 1.540598\text{\AA}$). The operating voltage was 40.00 KV, and the operating current was 40.00 mA. The data was collected with a scanning rate of 1s/step. 2θ ($^\circ$) was set from 10° - 80° and the incident angle θ ($^\circ$) was fixed at 1° /step. The XRD patterns obtained were analysed using Jade software (Version 6.5, Materials Data, Inc.) and then compared with the International Center for Diffraction Data (ICDD) powder diffraction file (PDF) database to confirm the crystal structure and chemical composition.

Microfocus XRD from Bruker D8 Discover diffractometer with a microfocus Cu source and a Vantec area detector was used to characterize the films deposited on the AGSS after gas sensing measurements. 2θ ($^\circ$) was set from 10 - 80° and the incident angle θ ($^\circ$) was fixed at 15° /step. 6 frames were taken.

2.4.3 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurement was conducted to analyze the surface state of thin film samples, including elemental identification, elemental quantification, and surface chemical state identification. An X-ray photoelectron spectrometer (Thermo Fisher Scientific, Neslab ThermoFlex 1400) with a monochromatic Al K α radiation was used to conduct the measurement. The spectroscopies of survey scans were collected in the range of 0-1350 eV, while the scans of required elements were performed multiple times with high resolution. XPS data was analyzed by CasaXPS (2.3.23), in which the binding energies were calibrated by carbon 1s peak at 284.6 eV.

2.4.4 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) investigated film morphology, structure and thickness. All the images were collected using Jeol JSM-6701 and 7600 FEG-SEM (Field Emission Scanning Electron Microscope) with an acceleration voltage of 5-10.00 KV and an acceleration current of 10 mA. Before examination by FESEM, samples were connected to the analysis stub by copper tape and coated with a thin layer of sputtered gold. The images obtained from FESEM were processed using GIMP (GNU image manipulation program, software 2.10.32) to improve the brightness level and contrast.

2.4.5 Raman spectroscopy

Raman spectroscopy is a non-destructive, light-scattering, spectroscopic technique that typically used to provide detailed information about chemical structure, phase and polymorphy, crystallinity and molecular interaction. It is based on the interaction of light whereby a molecule scatters incident light from a high intensity laser source. Most of the scattered light is at the same wavelength as the laser source and doesn't provide useful information (Rayleigh Scatter), while a

small amount of light is scattered at different wavelengths, which depends on the chemical structure of the sample, reflecting the information of the chemical bonds within a material, determining the vibrational modes of molecules, although rotational and other low-frequency modes of systems may also be observed (Raman Scatter)²⁸⁶.

A Raman spectrum features a number of peaks where the wavelength position of the Raman scattered light can provide “fingerprint” information on chemical structure, and the intensity can be used to quantitatively analyse the relative concentration of the components²⁸⁶.

The analysis was carried out using a Renishaw 1000 spectrometer, and the wavelength of the operating laser was 633 nm. All films were analyzed between 50 cm⁻¹ to 1000 cm⁻¹, and the laser power was reduced to 20%. The exposure time was 10 s, and the acquisition was carried out five times. Before and after the analysis, the microscope was used to visually check the condition of the films to check for damage from the laser.

2.4.6 Hall Effect Measurement

The Hall effect is a fundamental physical phenomenon observed in conductive materials when subjected to a magnetic field perpendicular to the direction of current flow. When a current-carrying conductor is placed in a magnetic field, a voltage, known as the Hall voltage, is generated across the conductor perpendicular to both the direction of current flow and the magnetic field.

The Hall effect arises due to the Lorentz force acting on moving charges (electrons or holes) in the presence of a magnetic field. As the charge carriers move through the conductor, they experience a force perpendicular to both their direction of motion and the applied magnetic field. This force causes the charge carriers to

accumulate on one side of the conductor, resulting in a measurable voltage difference across the conductor perpendicular to the direction of current flow.

The Hall effect is commonly used to determine the type (positive or negative) and concentration of charge carriers in a material, as well as their mobility. By measuring the Hall voltage and the applied magnetic field, along with the known current flowing through the conductor, the Hall coefficient can be calculated, which provides information about the density and mobility of charge carriers, and distinguishes the n- and p-type materials.

Hall effect measurement and the Van der Pauw technique were used to determine the semiconductor type, evaluate the free-carrier mobility and measure the hole concentration of the thin films deposited on the quartz substrates (1×1 cm). In the moderate magnetic fields, the Hall coefficient can be described as:

$$R_H = \frac{p\mu_h^2 - n\mu_e^2}{e(p\mu_h + n\mu_e)^2} \quad (4)$$

Where n is the electron concentration, p is the hole concentration, μ_e is the electron mobility, μ_h is the hole mobility, and e is the elementary charge. When $R_H > 0$, the electric field is primarily produced by the positive charge holes, and the material will be identified as a p-type semiconductor.

HMS-3000 hall effect measurement system was purchased from SEL-TEK LIMITED. The input values are listed in **Table 7**.

Table 7. Input values in the hall effect measurement

Film thickness (nm)	Values obtained from SEM.
Operation temperature (K)	300
Operation current (nA)	1.00
Delay (s)	0.100
Magnetic flux density (Wb/m ²)	0.580
Measurement number (Times)	1000

2.4.7 Ultraviolet-visible spectroscope (UV-vis)

Ultraviolet-visible spectroscopy (UV-vis) measures the amount of discrete wavelengths of UV or visible light absorbed by or transmitted through a sample compared to a reference or blank sample. Here, UV-vis spectroscopy purchased from SHIMADZU (UV-2600) was used to measure the absorbance (A) of the CuFeO₂ films deposited on ITO-coated quartz. ITO-coated quartz was used as the background and measured individually compared to the blank background. The wavelength range was 200-1000 nm, and visible light (400-800 nm) was included. In UV-vis measurements, the film is attached to a metal plate with a circular hole in the middle, through which light passes and reaches the detector to complete the measurement. No light passes and is detected through the part outside the circular hole.

The indirect band gap of Delafossite CuFeO₂ on ITO-coated quartz substrate was performed by the Tauc plot method using absorbance spectroscopy through UV-vis analysis:

$$\alpha h\nu = B(h\nu - E_g)^n \quad (5)$$

$$\alpha = 2.303 * A/t \quad (6)$$

$$h\nu \text{ (eV)} = 1240/\lambda(\text{nm}) \quad (7)$$

Where α is the absorption coefficient, $h\nu$ is photon energy, B is the band tailing parameter (a constant), and E_g is the optical band gap. n is determined by the type of transition (direct/indirect; allowed/forbidden transition). In the calculation, n=1/2 is considered a direct band gap, while n=2 is the indirect band gap. The value of α can be calculated via equation (2), where A is the absorbance at each wavelength, and t is the thickness of the film. According to equation (1), extrapolating the point with the highest gradient and the intercept on the x is the band gap. Generally, the absorbance, A, can be used in place of the absorption coefficient, α , in plotting to

obtain the band gap value because the magnitude of this parameter changes the slope rather than the intercept on the X-axis for a given film thickness.

2.4.8 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is a scanning probe microscopy used to collect topography information from the film surface. All AFM measurements were performed in tapping mode on a Keysight 5500 AFM system using SCOUT 70 AFM probes from NuNano Ltd (spring constant 2 N m^{-1} with a resonant frequency of 70 kHz and tip radius of curvature $< 10 \text{ nm}$). AFM tips were oscillated at the first harmonic of their resonant frequency during imaging ($\sim 400 \text{ kHz}$). For each sample, four images were collected, each image $5 \text{ }\mu\text{m}$ in size. A first-order flattening process was applied to the image to remove surface tilt. No further image processing was performed. The root mean squared (R.M.S.) roughness was calculated using the WsXM image analysis software for each image. The average and standard deviation of the four roughness values for the individual images were calculated and used to measure the R.M.S. roughness and associated error for each sample. The four images for each sample were collected at different locations across the sample surface to ensure a consistent measure of the surface roughness.

2.4.9 Ultrafast Time-resolved Absorption Spectroscopy (TAS)²⁸⁷

Transient absorption spectra were recorded using a commercial transient absorption spectrometer (Ultrafast Systems Helios Fire). A regenerative amplifier seeded by a Ti: Sapphire oscillator (Coherent Astrella-HE USP) generated 800 nm femtosecond laser pulses (800 nm, 40 fs, 1 kHz). Tuneable pump pulses were then generated by an optical parametric amplifier (Coherent OPerA Solo). TAS measurements were made using a commercial transient absorption spectrometer (Ultrafast Systems Helios Fire) following photoexcitation at 280 nm, with pulse energies of around 100 nJ at the sample. 800 nm femtosecond pulses were also

directed to a mechanical delay stage before being focused into a sapphire crystal to generate the broadband visible probe. The pump (modulated at 500 Hz, attenuated to 100 nJ) and the probe beam were focussed onto a spot on the sample. After transmitting through the sample, the probe signal was directed to an optical fibre-coupled sensor. Transient spectra were processed using functions built into the software Surface Xplorer, including chirp correction and background noise subtraction. The raw data was corrected and normalized for the thickness for absorbance at the excitation wavelength.

The measurement was done under the supervision of Dr Rhea Kumar, who was a research fellow in Prof. Helen Fielding's group in the Department of Chemistry, UCL. Moreover, the data was co-analysed with Dr. Kumar.

2.4.10 Ellipsometry Porosimetry Analysis

Ellipsometric porosimetry is a method based on spectroscopic ellipsometry for monitoring multilayer adsorption on a thin film surface at gradually increasing relative pressures of a volatile liquid adsorptive (**Figure 28**). Ellipsometry measures the polarization change of light when reflecting from a multilayer structure. The measured response depends on the optical properties and thickness of individual materials.

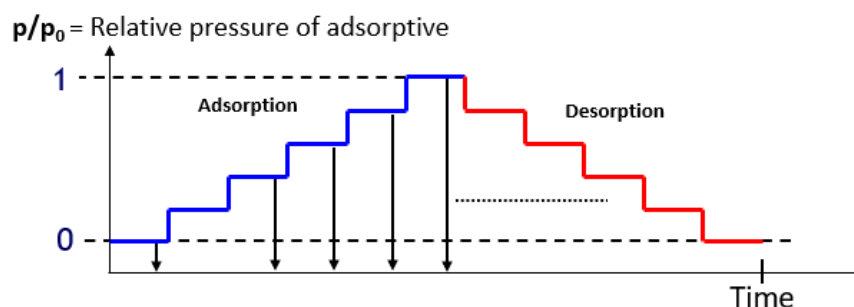


Figure 28. Schematic of the adsorption/desorption cycle in ellipsometric porosimetry

In this project, a SE-2000EP (Semilab, Hungary) ellipsometric porosimeter was used to obtain specific surface area data based on the Brunauer-Emmett-Teller

fitting method²⁸⁸, described previously in detail²⁸⁹. The data was collected and analysed by Mate Furedi, my collaborator, from the Department of Chemical Engineering, UCL. The Tauc-Lorentz and Gaussian dispersion functions were used to construct the optical models of the CFO materials, and the adsorption process was modelled with the Lorentz-Lorenz effective medium approximation. All measurements were carried out in a vacuum chamber setup (described previously²⁹⁰) with varying relative pressures of toluene adsorptive. In order to increase sample reflection and facilitate data analysis, ellipsometric characterisation was performed using CFO materials deposited onto silicon substrates (Microchemicals GMBH, Germany), fabricated following similar conditions to the ones used for the ITO-quartz substrates to facilitate the modelling.

2.4.11 Gas sensing measurement

The gas-sensing workstation (**Figure 29**) was self-built by Prof. Chris Blackman's group. Gas sensor cylinders were connected with MFC to control the gas flow. A cold trap consisting of dry ice and acetone was set up to remove the humidity from gas cylinders. A flask containing deionised water was also built to adjust the analyte gas's humidity, which can be monitored by a humidity sensor (HIH-4602-A/C Series, Honeywell) and finely controlled by the humidity sensor description (**Figure 30**).

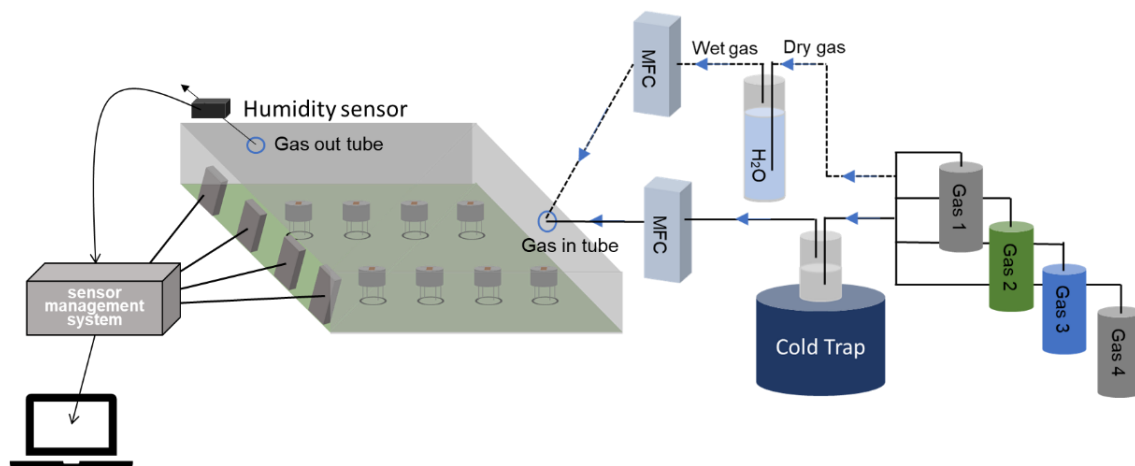


Figure 29. Schematic of gas sensing working station

Then, the analyte gas was carried to the gas sensing box, in which four channels (A, B, C, D) can measure eight sensors at the same time under different conditions. Gas sensor measurements were controlled by the atmospheric sensor management system (AS330, ASsystem).

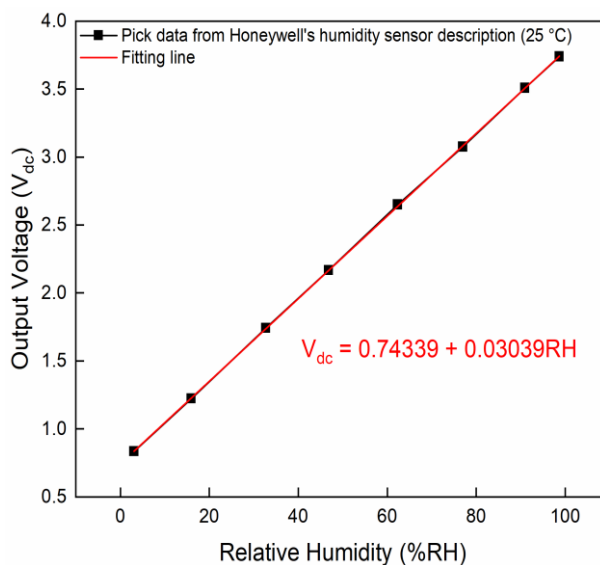


Figure 30. Illustration of the relative humidity and output voltage in the Honeywell humidity sensor²⁹¹



Figure 31. Digital image of gas sensors inserted into circuit board in the gas sensing box

CuFeO₂ thin films deposited on the AGSS were welded in the gas sensor with four legs, in which two legs were connected to the gas sensor management system to control the heating temperature, and the other two legs were used to monitor the films' resistance (**Figure 31**).

In this project, dry N₂ gas was used as background gas. Before each test, dry N₂ gas was purged to create a clean and uniform test environment. Different amount of O₂ gas was purged to test how the material responded to oxidizing gas. Temperature and humidity were also investigated.

2.4.12 Photoelectrochemical measurement

The PEC measurement instrument was built in-house by Dr. Yaoming Li and Dr. Xueming Xia in Prof. Chris Blackman's group. The photo-electrical properties of Delafossite CuFeO₂ thin films deposited on ITO-quartz substrate were evaluated using PEC measurements using the three-electrode system in a cubic quartz cell (**Figure 32**), connecting to a potentiostat (Interface 1000, Gamry). A 75 W USHIO Xe lamp provided the light source with a Newport AM 1.5 G sun illumination (100 mW•cm⁻²) filter. The light intensity was calibrated to one sun by a photodiode (CPC).

In the cubic quartz cell, the CuFeO_2 thin films were used as the photocathodes, Pt mesh was used as the counter electrode, and a Ag/AgCl electrode (in 3M KCl, CHI111) was used as the reference electrode.

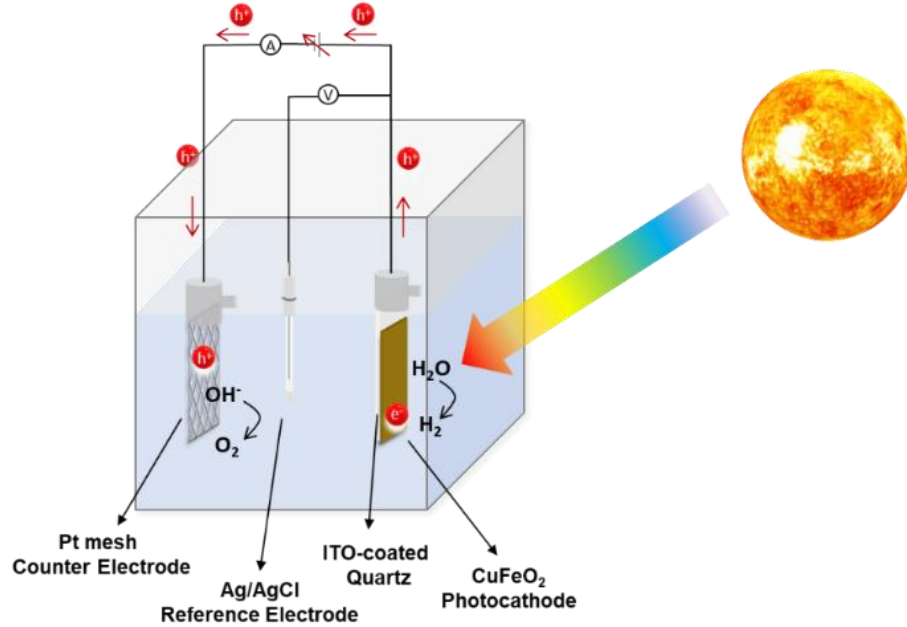


Figure 32. Schematic of photoelectrochemical measurement in the cell

According to the Nernst equation, the as-measured working potential of the 3 M Ag/AgCl electrode can be converted from the reversible hydrogen electrode through the following equation, where, in general, $E^0_{\text{Ag}/\text{AgCl}}$ (in 3M KCl) = 0.210 V at the room temperature (25°C):

$$E_{\text{RHE}} = E_{\text{Ag}/\text{AgCl}} + E^0_{\text{Ag}/\text{AgCl} (3\text{M KCl})} + 0.059 \times \text{pH} \quad (8)$$

Linear sweep voltammetry (LSV) measurements were used to present the current change toward the potential. 1 M NaOH was used as electrolytes as previous research^{147,292293}, and the voltage applied in the PEC measurement ranged from 1-0.2 V vs reversible hydrogen electrode (RHE) with a scan rate of 1 mV/s, 1 mV/E step for all the samples. In the chopped LSV measurement, the light is turned on and off every 10 seconds.

Photocurrent density in a chopped LSV was calculated using the photocurrent density in the dark background minus photocurrent density under illumination, example is shown in Figure 32.

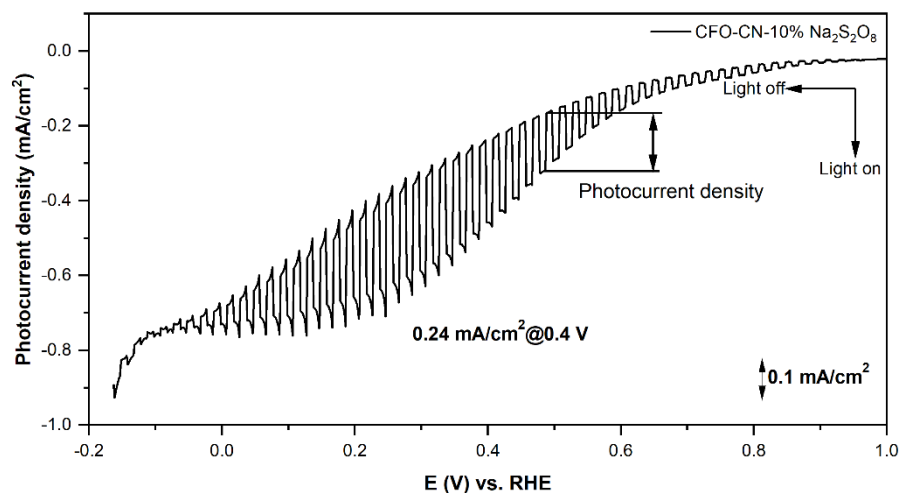


Figure 33. Example of a chopped LSV of ~250 nm CFO-CN film measured with the potential of 1.0 to -0.2 V vs RHE; Electrolyte: 1M NaOH with 10 vol.% 0.1 M Na₂S₂O₈, photocurrent density is calculated as the difference between photocurrent density in the dark environment when light is turned off and the photocurrent density under illumination when light is turned on

Incident photon-electron conversion efficiency (IPCE) was carried out with an adjustable chronometer in the same three-electrode system. 1M NaOH with 10% 0.1 M Na₂S₂O₈ was used as the electrolyte, and the potential was fixed at 0.4 vs RHE.

2.5 Summary

All the AACVD deposition and post-annealing treatments were conducted in the Department of Chemistry at UCL. PEC measurement and gas sensing measurement were run at a self-built PEC working station and gas sensor working station at the Department of Chemistry, UCL, respectively. XRD, XPS, SEM, Hall effect measurement and spectral measurements were carried out at the Department of Chemistry, UCL. Ellipsometry porosimetry measurement was carried out at the Department of Chemical Engineering, UCL. EDX was done at

the Department of Archaeology, UCL. IPCE was carried out at the Molecular Science Research Hub at Imperial College London. CuFeO_2 films deposited on the AGSS were welded to the gas sensors at the University of Warwick.

Chapter 3. Synthesis of Delafossite CuFeO₂ Thin Films via Aerosol-assisted Chemical Vapour Deposition and Post-annealing treatment

3.1 Introduction

This chapter introduced the investigation process of the optimal deposition conditions of Delafossite CuFeO₂ thin film via aerosol-assisted chemical vapour deposition (AACVD), as well as the post-annealing treatment. In the deposition experiments, the optimal conditions for the synthesis on different substrates, such as glass (VWR International, LLC, 76×26 mm), quartz (Wuxi Crystal and Optical Instrument Company Limited, 50×25 mm), alumina (University of Warwick, 25×25 mm), alumina gas sensor substrate (AGSS, University of Warwick, 2×2 mm) and conductive ITO-coated quartz substrate (6-8 Ω, 20×20 mm, South China Science & Technology Company Limited) were investigated and obtained at different stages for different roles.

By adjusting the synthesis methods, Delafossite CuFeO₂ thin films with a well-designed structure were obtained and characterized for their composition, structure, morphology, and optical properties. This chapter summarizes the results as a guide for Delafossite CuFeO₂ thin film deposition for the different applications in future studies.

3.2 Experiment

3.2.1 Deposition of CuFeO₂ thin film via AACVD

To deposit Delafossite CuFeO₂ thin film via AACVD, Cu and Fe precursors were added into the solvent and then sonicated at room temperature until dissolved completely. The mixed precursors were aerosolized with the aerosol transferred by

inert N₂ gas (Oxygen free nitrogen, BOC) to the reaction chamber to grow the mixed metal oxide film on the substrates.

Prior to deposition, glass and quartz were sequentially washed with detergent, tap water, non-ionized water, and acetone. After drying, substrates were cut into the proper size for AACVD deposition. For the alumina and alumina gas sensor substrate (AGSS), high-temperature annealing (~800°C, 1h, air atmosphere) in the tube furnace was used to remove the dirt on the surface before deposition.

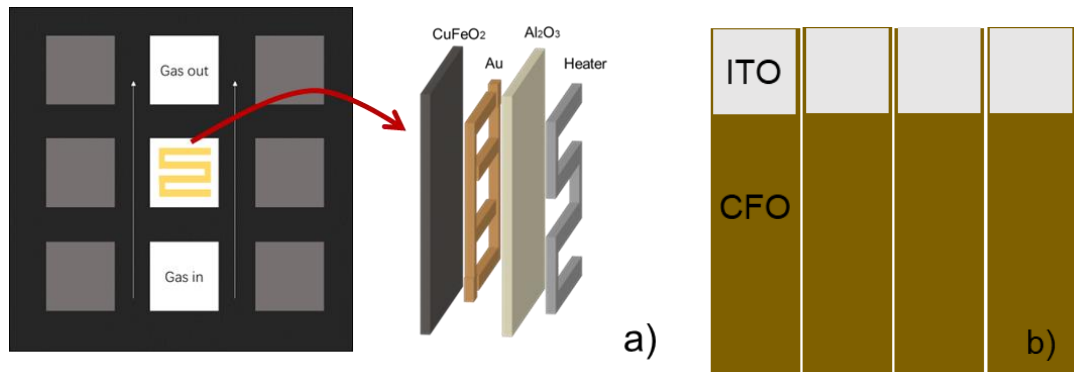


Figure 34. Illustration of film deposition on a) AGSS and b) ITO-quartz substrates

Generally, glass or quartz substrates were used to explore the elemental composition to obtain the film with a Cu/Fe 1:1 relative atomic ratio. Later, quartz substrates were used to study the optimal annealing conditions. Alumina substrate was used as a substitute for alumina gas sensor substrates to study optimal deposition conditions and characterize compositional structural, morphological, and optical properties. The alumina gas sensor substrate consists of three layers, including platinum as a heater, alumina as a deposition substrate, and gold as a conductive electrode, shown in **Figure 34 a)**.

ITO-quartz substrates are conductive and can withstand hours of high-temperature annealing, which were used for PEC measurement. A 5×5 mm² blank space was left in each Delafossite CuFeO₂ thin film sample for conduction (**Figure 34 b)**).

[Cu(acac)₂] (purity>98%, ACOS ORGANICS) was used as Cu precursor. [FeCl₂•4H₂O] (purity>99%, SIGMA-ALDRICH) and [Fe(acac)₃] (purity>=99.9%, ALDRICH) were used as Fe precursors. Methanol (purity>=99.8%, Fisher Scientific) and acetonitrile (purity>=99.8%, Fisher Scientific) were used as solvents. Delafossite CuFeO₂ thin film deposited using [Cu(acac)₂] and [FeCl₂•4H₂O] with methanol as the solvent was denoted as **CFO-ACCL** film. Delafossite CuFeO₂ thin film deposited using [Cu(acac)₂] and [Fe(acac)₃] with methanol as the solvent was denoted as **CFO-ACAC** film. Delafossite CuFeO₂ thin film deposited using [Cu(acac)₂] and [Fe(acac)₃] with acetonitrile as solvent was denoted as **CFO-CN** film.

The deposition effect from precursors, solvents, deposition temperature, carrier gas flow rate, and the amount of precursors was investigated.

3.2.2 Post-annealing treatment

After AACVD deposition, a post-annealing treatment was applied to the film, during which the pure Delafossite crystal structure would be formed. The ceramic tube and crucibles were used in this stage and were cleaned (~800°C, 1h, air atmosphere) to remove the contaminants prior to the use. Before and after the post-annealing treatment, films were analysed by XRD to examine the formation and the transition of the crystalline process.

Annealing temperature, duration, ramping rate, cooling down rate, and gas atmosphere were investigated.

3.3 Results and Discussion

3.3.1 Investigation of the optimal deposition and annealing conditions for CFO-ACCL thin films via AACVD

3.3.1.1 Adjusting Cu/Fe elemental composition in the as-deposited film

To deposit the CFO-ACACL films, $[\text{Cu}(\text{acac})_2]$ and $[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]$ were used as the Cu/Fe precursors, and methanol was used as the solvent.

To begin with, 2.5×2.5 cm glass substrates were used to investigate the optimal deposition conditions. The flow rate was set at 1400 sccm according to our group's experience that when multi-component films are deposited at relatively high flow rates, the elements can be evenly distributed. Different amounts of Cu/Fe precursors were applied while investigating the temperature. In the EDX, five points were collected alongside the diagonal and then were calculated with standard error. For example:

$$\text{Relative Cu at. \%} = \frac{\text{Cu at. \%}}{\text{Cu at. \%} + \text{Fe at. \%}} \quad (1)$$

$$\text{Relative Fe at. \%} = \frac{\text{Fe at. \%}}{\text{Cu at. \%} + \text{Fe at. \%}} \quad (2)$$

$$\text{Standard Error} = \frac{\text{Standard Deviation of Cu at. \%}}{\sqrt{5}} \quad (3)$$

According to the EDX results, when using the same molar amount of the Cu and Fe precursors, iron was always in excess, irrespective of the temperature of deposition (**Figure 35 b**). However, as the temperature increased, the Cu at.% increased in the film. The results showed that at around 400°C , with 0.145 (**Figure 35 e**) or 0.15 mmol (**Figure 35 d**) $[\text{Cu}(\text{acac})_2]$ and 0.13 mmol $[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]$, the atomic ratio of Cu and Fe deposited on the film was closest to the desired 1:1 ratio.

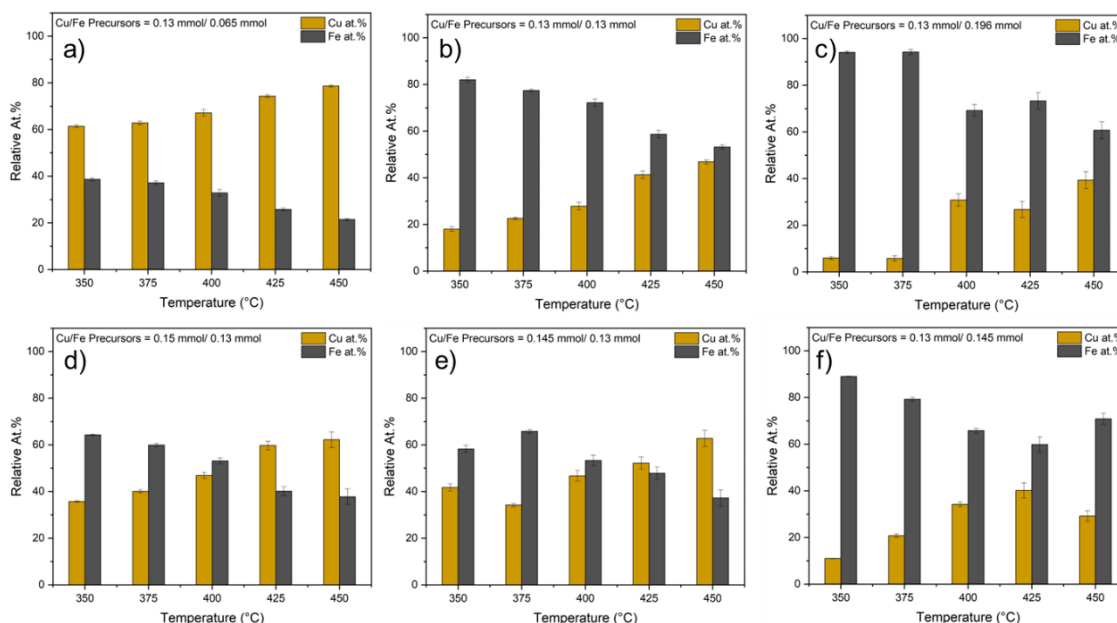


Figure 35. Cu/Fe relative atomic ratios obtained from EDX analysis in the CFO-ACCL films deposited on glass substrate with different deposition temperatures and Cu/Fe precursor amounts; all the films were deposited at five temperatures (350°C, 375°C, 400°C, 425°C, 450°C), gas flow rate was 140 sccm and the amount of Cu/Fe precursors are different in each film: (a) 0.13 mmol/0.065 mmol; (b) 0.13 mmol/0.13 mmol; (c) 0.13 mmol/0.196 mmol; (d) 0.15 mmol/0.13 mmol; (e) 0.145 mmol/0.13 mmol; (f) 0.13 mmol/0.145 mmol

Next, quartz substrates were substituted for glass substrates to continue investigating deposition conditions while also studying (high temperature) annealing conditions required to obtain the Delafossite CuFeO_2 phase. According to the EDX results of the films deposited on the glass substrates, 0.15 mmol, 0.145 mmol and 0.13 mmol of $[\text{Cu}(\text{acac})_2]$ were deposited with 0.13 mmol $[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]$ at different temperatures. The rest of the conditions remained the same. The change in trend of element composition was the same on quartz as on glass substrates (**Figure 36**).

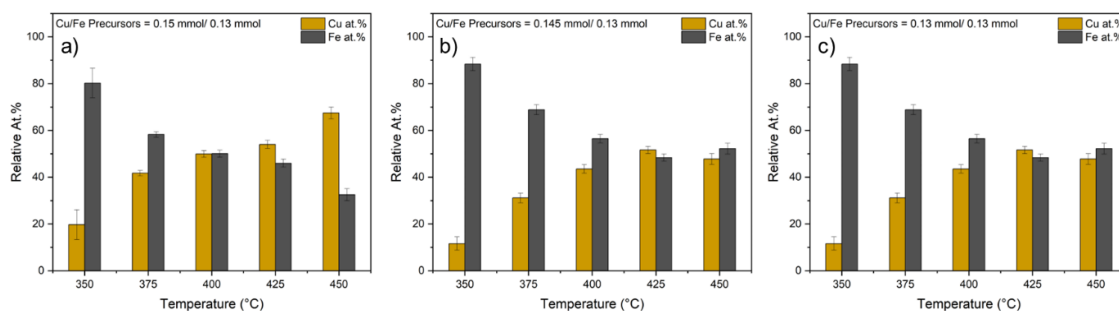


Figure 36. Cu/Fe relative atomic ratios obtained from EDX analysis of CFO-ACCL films deposited on the quartz substrate; all the films were deposited at five temperatures (350°C, 375°C, 400°C, 425°C, 450°C) with gas flow rate of 1400 sccm, the amount of Cu/Fe precursors are different in each film: (a) 0.15 mmol/0.13 mmol; (b) 0.145 mmol/0.13 mmol; (c) 0.13 mmol/0.13 mmol

Further efforts, such as slight changes in Cu/Fe precursors amount and temperature (**Table 8**), were undertaken to achieve the film deposited on quartz with the Cu/Fe ratio closest to 1:1, which was found at 420°C when using 0.15 mmol of $[\text{Cu}(\text{acac})_2]$ with 0.125 mmol $[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]$.

Table 8. Cu/Fe relative atomic ratios obtained from EDX analysis of CFO-ACCL films deposited on quartz substrates with gas flow rate of 1400 sccm, the amount of Cu/Fe precursors of 0.15 mmol/ 0.13 mmol, while the deposition temperature varies from 400°C to 425°C

Sample	n- $[\text{Cu}(\text{acac})_2]$	n- $[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]$	Temperature	Substrate	Flow Rate	EDX Relative Cu/Fe at. %
ACCL-78	0.15 mmol	0.13 mmol	400°C	Quartz	1400 sccm	44.01/55.99 ± 1
ACCL-74	0.15 mmol	0.13 mmol	405°C	Quartz	1400 sccm	42.34/57.66 ± 1
ACCL-71	0.15 mmol	0.13 mmol	410°C	Quartz	1400 sccm	46.25/53.75 ± 2
ACCL-77	0.15 mmol	0.13 mmol	415°C	Quartz	1400 sccm	47.52/52.48 ± 2
ACCL-76	0.15 mmol	0.13 mmol	420°C	Quartz	1400 sccm	48.35/51.65 ± 1
ACCL-73	0.15 mmol	0.13 mmol	425°C	Quartz	1400 sccm	54.48/45.52 ± 2
ACCL-97 (optimal)	0.15 mmol	0.125 mmol	420°C	Quartz	1400 sccm	49.43/50.57 ± 0.4

Subsequently, the influence of carrier gas flow rate was considered. 0.15 mmol $[\text{Cu}(\text{acac})_2]$ and 0.125 mmol $[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]$ were set as fixed precursor amounts, and 420°C was set as the deposition temperature according to the previous study. Films were deposited with N_2 flows ranging from 700 sccm to 1400 sccm. EDX analysis (**Table 9**) illustrates that when the flow rate increased, the amount of Cu or Fe deposited on the film decreased (Si increased), indicating that the films

became thinner with the increased flow rate. Furthermore, increasing the flow rate changed the relative proportions of Cu and Fe deposited on the film (**Figure 37**). However, the effect of flow rate was not so significant compared with the temperature effect and precursor amounts.

Table 9. Elemental distribution (At. %) from EDX analysis of CFO-ACCL films deposited on quartz substrates with different gas flow rate

Sample	Flow Rate (sccm)	O	Si	Cl	Fe	Cu	Total
ACCL-101	700	63.47	27.11	0.17	4.07	5.18	100
ACCL-102	800	63.63	27.44	0.17	3.89	4.86	100
ACCL-103	900	64.54	29.19	0.11	2.90	3.26	100
ACCL-104	1000	64.37	28.93	0.18	3.22	3.29	100
ACCL-105	1100	64.90	29.86	0.08	2.69	2.48	100
ACCL-106	1200	65.32	30.71	0.09	1.90	1.99	100
ACCL-107	1300	65.45	30.96	0.08	1.62	1.91	100
ACCL-108	1400	65.69	31.38	0.04	1.32	1.60	100

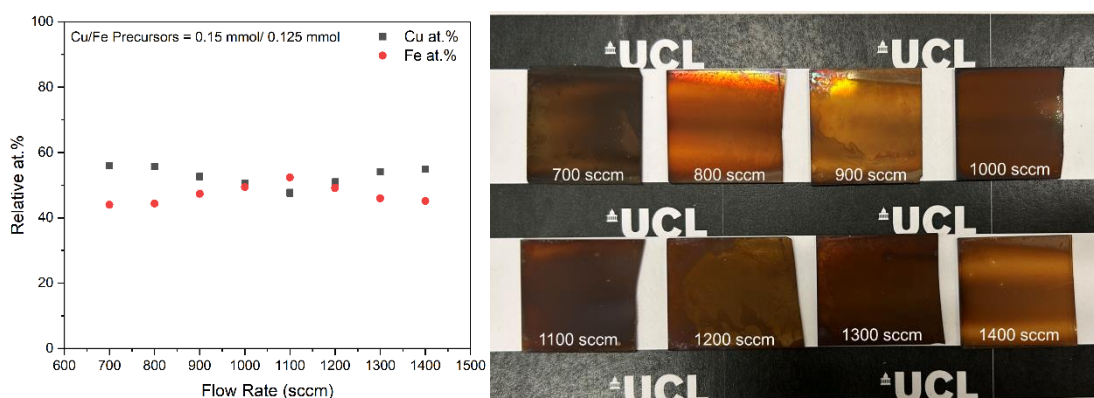


Figure 37. (Left) Cu/Fe elemental distribution analysis from EDX (with error bar, errors are too small to be seen) and (Right) digital photos of CFO-ACCL thin film deposited on quartz substrates with different gas flow rates from 600 sccm to 1500 sccm

In the end, with 0.15 mmol $[\text{Cu}(\text{acac})_2]$ and 0.125 mmol $[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]$, a deposition of 420°C and an N_2 flow rate of 1400 sccm, the optimal deposition conditions on the quartz substrate were found and later confirmed in the post-annealing treatment.

Similar depositions were conducted on the alumina substrates to investigate the optimal deposition conditions. The influence of flow rate was verified when films with different amounts of Cu/Fe precursors were deposited with a flow rate ranging from 1000 sccm to 1400 sccm (**Figure 38**), in which the relative Cu at. % or Fe at. % on the film did not show a noticeable change. Noticeably, in the temperature range of 400-450°C, the temperature effect on Cu and Fe at. % still exists but has significantly reduced.

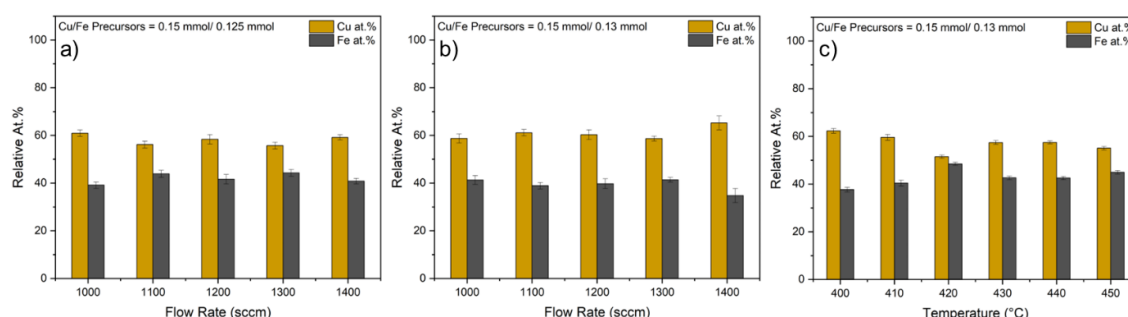


Figure 38. Cu/Fe relative atomic ratios obtained from EDX analysis of CFO-ACCL films deposited on alumina substrates with a) different gas flow rates ranging from 1000 sccm to 1400 sccm, with Cu/Fe precursors of 0.15 mmol/0.125 mmol and deposition temperature of 420°C; b) different gas flow rates ranging from 1000 sccm to 1400 sccm with Cu/Fe precursors of 0.15 mmol/0.13 mmol and deposition temperature of 420°C; c) different deposition temperatures ranging from 400°C to 450°C, with Cu/Fe precursors ratio of 0.15 mmol/0.13 mmol and gas flow rate of 1400 sccm.

The amounts of Cu/Fe precursors were precisely adjusted, and the optimal deposition conditions were found in samples ACCL-220 and 221, where 0.14 or 0.14 mmol $[\text{Cu}(\text{acac})_2]$ and 0.13 mmol $[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]$ were used as precursors. The deposition temperature was set at 430°C, and the flow rate was controlled at 1.4 L/min (**Table 10**).

Table 10. Cu/Fe relative atomic ratios obtained from EDX analysis of CFO-ACCL films deposited on alumina substrates at 430°C with gas flow rate of 1400 sccm; the amount of Cu/Fe precursors varies

Sample	n- [Cu(acac) ₂]	n- [FeCl ₂ •4H ₂ O]	Temperature	Substrate	Flow Rate	EDX Relative Cu/Fe at. %
ACCL-219	0.15 mmol	0.125 mmol	430°C	Alumina	1400 sccm	56.94/43.06 ± 0.7
ACCL-220 (optimal)	0.145 mmol	0.13 mmol	430°C	Alumina	1400 sccm	49.93/50.07 ± 0.8
ACCL-221 (optimal)	0.14 mmol	0.13 mmol	430°C	Alumina	1400 sccm	50.28/49.72 ± 0.5
ACCL-237	0.15 mmol	0.13 mmol	430°C	Alumina	1400 sccm	42.74/57.26 ± 0.9
ACCL-236	0.1525 mmol	0.13 mmol	430°C	Alumina	1400 sccm	49.42/50.58 ± 0.2

According to the above investigations and deposition experience, deposition temperature and the Cu/Fe precursor amounts were slightly adjusted. The optimal deposition conditions for CFO-ACCL on ITO-quartz substrate were achieved with 0.15 mmol [Cu(acac)₂] and 0.13 mmol [FeCl₂•4H₂O] at 450°C with N₂ gas flow rate of 1400 sccm, as presented and verified in **Table 11**.

Table 11. Cu/Fe relative atomic ratios obtained from EDX analysis of CFO-ACCL films deposited on ITO-coated quartz substrates at different deposition temperatures, with gas flow rate of 1400 sccm and the amount of Cu/Fe precursors of 0.14 mmol/ 0.13 mmol

Sample	n-[Cu(acac) ₂]	n- [FeCl ₂ •4H ₂ O]	Temperature	Substrate	Flow Rate	EDX Relative Cu/Fe at. %
PEC-9	0.14 mmol	0.13 mmol	430°C	ITO-Quartz	1400 sccm	42.14/57.86 ± 0.2
PEC-10	0.14 mmol	0.13 mmol	440°C	ITO-Quartz	1400 sccm	46.90/53.10 ± 0.3
PEC-11	0.14 mmol	0.13 mmol	450°C	ITO-Quartz	1400 sccm	48.17/51.83 ± 0.5
PEC-72 (optimal)	0.15 mmol	0.13 mmol	450°C	ITO-Quartz	1400 sccm	50.68/49.32 ± 0.2
PEC-71 (optimal)	0.15 mmol	0.13 mmol	450°C	ITO-Quartz	1400 sccm	49.24/50.76 ± 0.4
PEC-110 (optimal)	0.15 mmol	0.13 mmol	450°C	ITO-Quartz	1400 sccm	50.72/49.28 ± 0.5

3.3.1.2 Investigation of the optimal annealing conditions of CuFeO₂-ACCL film

In section 3.3.1.1, optimal deposition conditions (0.15 mmol [Cu(acac)₂] and 0.13 mmol [FeCl₂•4H₂O] in 30 ml methanol at 450°C with N₂ gas flow rate of 1400 sccm) were obtained to ensure Cu and Fe in the film had the same atomic percentage and were evenly distributed on the substrate. However, the films obtained from this

AACVD process mainly consisted of mixed metal oxides (**Figure 39**) such as Cu, CuO, Cu₂O, Fe₂O₃, or amorphous phases and included carbon contaminants. With these achievements as the basic foundation, the optimal annealing conditions were investigated for the formation of a pure Delafossite CuFeO₂ phase.

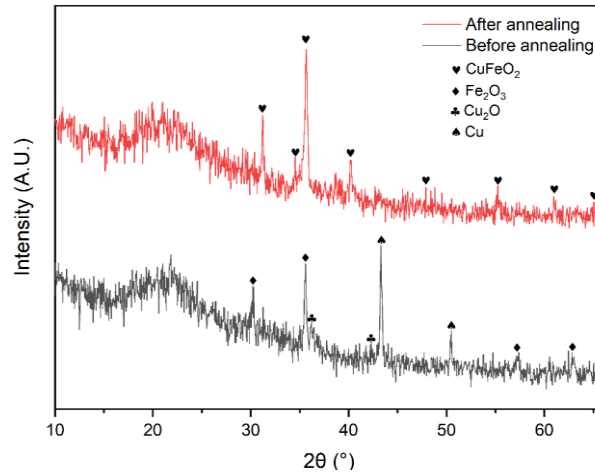


Figure 39. Integrated XRD patterns of CFO-ACCL thin films before and after annealing

In the post-annealing treatment, the annealing temperature, annealing duration, heating rate and cooling rate were initially considered as important factors.

According to the previous research, films containing the same atomic ratio of Cu and Fe were cut into several small pieces. They were annealed under different temperatures (650°C, 700°C, 750°C and 800°C), where the duration was set as 5h and the ramping rate was set as 10°C/min. After naturally cooling down below 100°C, films were taken out to be analysed by XRD.

Figure 41 a) presents the phase change as a result of different annealing temperatures. At 650°C, the films mainly consisted of the amorphous phase, low-intensity peaks of CuO and Fe₂O₃, while Delafossite CuFeO₂ was not formed yet. From 700°C to 750°C, the single Delafossite phase appeared, but at 800°C the peaks had decreased in intensity again. Therefore, the feasible temperature window for the post-annealing treatment is 700°C to 750°C.

The pure Delafossite CuFeO_2 peaks are well matched with standard diffraction patterns from International Centre for Diffraction Data (ICDD), the power diffraction file (PDF) number is 39-0246 (**Figure 72**). The peak positions adhere to rhombohedral $R\bar{3}m$ Delafossite CuFeO_2 , in which the lattice parameters $a=3.035$ Å and $c=17.166$ Å, which are in agreement with the parameters reported in the literature ($a=3.0333$ Å and $c=17.1595$ Å)²⁹³.

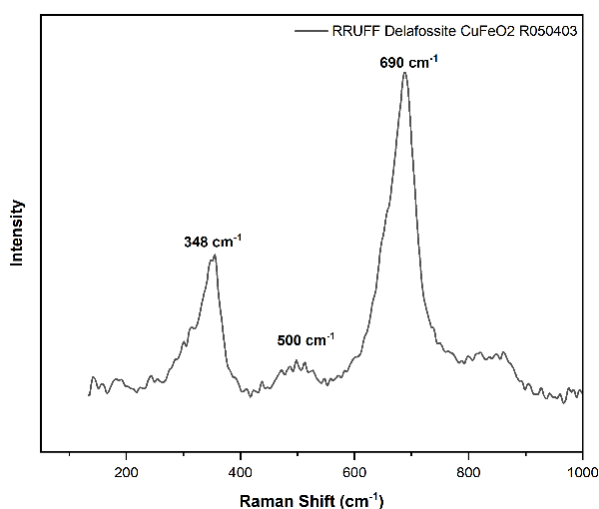


Figure 40. Reference of Raman spectroscopy of CuFeO_2 from RRUFF™ database (ID: R050403.2)

Raman spectroscopy also confirmed this viewpoint (**Figure 42 a**) compared to the reference of Raman spectroscopy shown in (**Figure 40**).

Delafossite-type structures are characterised by the rhombohedral symmetry of the space group C_{3v}^6 and the point group C_{3v} , and these vibrations can be described by the reducible representation by $1A_{1g} + 3A_{2u} + 1E_g + 3E_u$ ²²³.

The A symmetry illustrates the vibrations perpendicular to the c-axis (octahedral structure). The inversion centre located Cu atom, which leads to a result that only even modes (sub-index g, A_{1g} and E_g) are Raman active^{294–296}. While the other odd vibration mode (A_{2u} and E_u) have only acoustic vibrations, which is invisible in the Raman spectroscopy. Therefore, the peak located at 348 cm^{-1} can be allocated to E_g vibration and peak located at 690 cm^{-1} to A_{1g} vibration mode. The peak located

at 500 cm^{-1} can be related to a surface plasmonic resonance of the material mixture²²³.

Annealing duration was also investigated by the XRD and shown in **Figure 41 b)**. A phase transition was observed during the first hour of annealing. The Delafossite phase did not show significant changes with increasing duration from 1 hour to 9 hours. In the Raman spectroscopy, pure Delafossite phase even appeared after 40 min's annealing (**Figure 42 b)**). The Raman peak intensities slightly grow with the increased duration and then remain constant after 1 hour. To ensure the completion of the phase transition, the annealing time was set to 5 hours in further experiments.

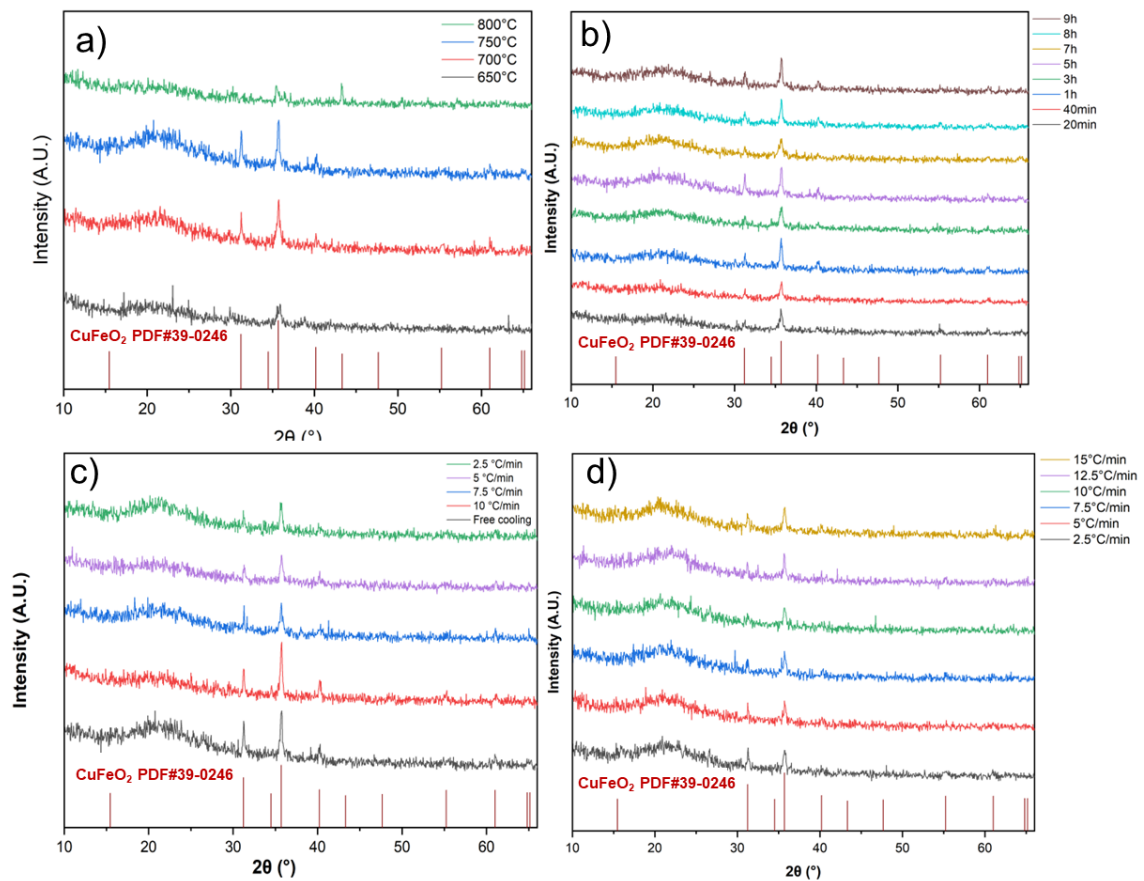


Figure 41. Integrated XRD patterns of CFO-ACCL thin films deposited on quartz substrates for the investigation of a) annealing temperature; b) annealing duration; c) cooling rate; d) ramping rate

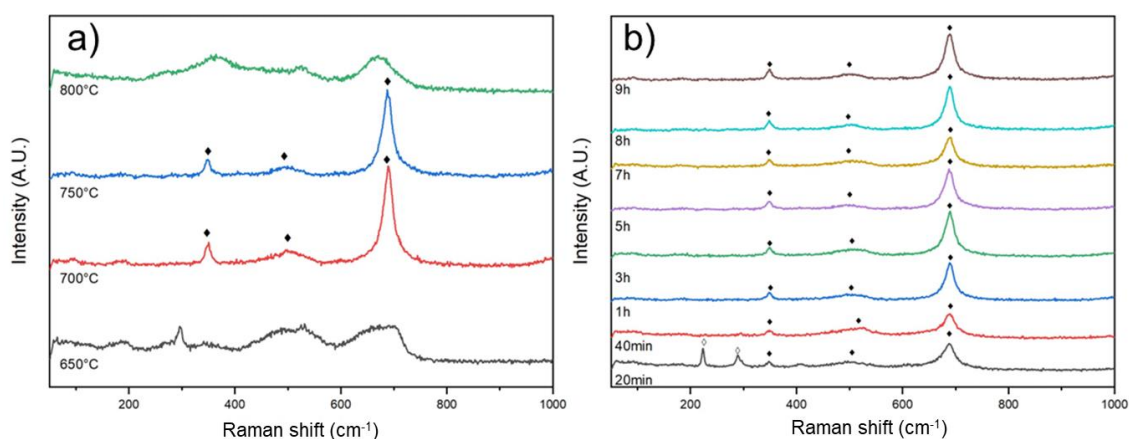


Figure 42. Integrated Raman spectroscopy of CFO-ACCL films deposited on quartz substrates for the investigation of a) annealing temperature and b) annealing duration, ('fingerprint' peaks of CuFeO_2 were marked as diamonds in both figures)

The influence of the temperature ramping rate and the cooling rate were also investigated, with the annealing temperature set at 750°C for 5 hours in a pure N_2 atmosphere. From the XRD patterns (**Figure 41 c**), the ramping rate and the cooling rate did not show a noticeable influence on the Delafossite phase formation, which will not be considered as the major factors to focus on in the later experiments.

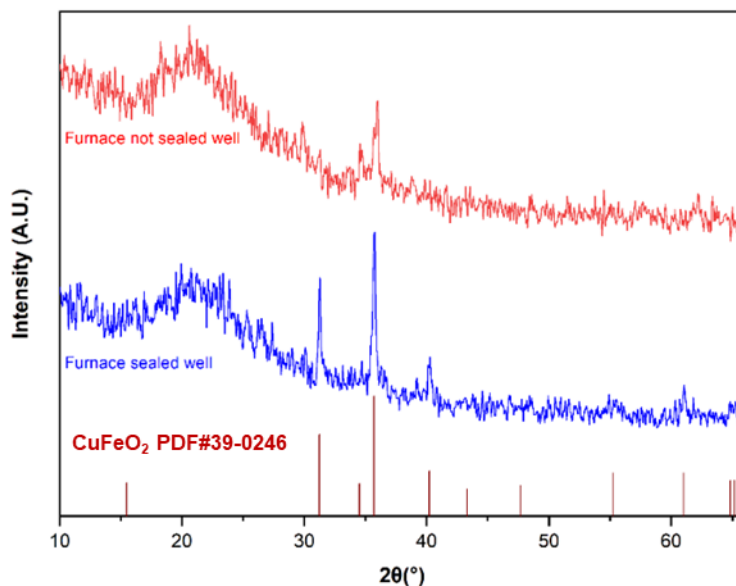


Figure 43. Integrated XRD patterns of Delafossite CuFeO_2 thin film under inert gas atmosphere and non-inert gas atmosphere

During these studies, an influence of the gas atmosphere was observed (**Figure 43**). When the films were annealed with N₂ mixed with a small amount of air, impurity phases appeared in the XRD patterns and the intensity of Delafossite CuFeO₂ peaks was significantly reduced.

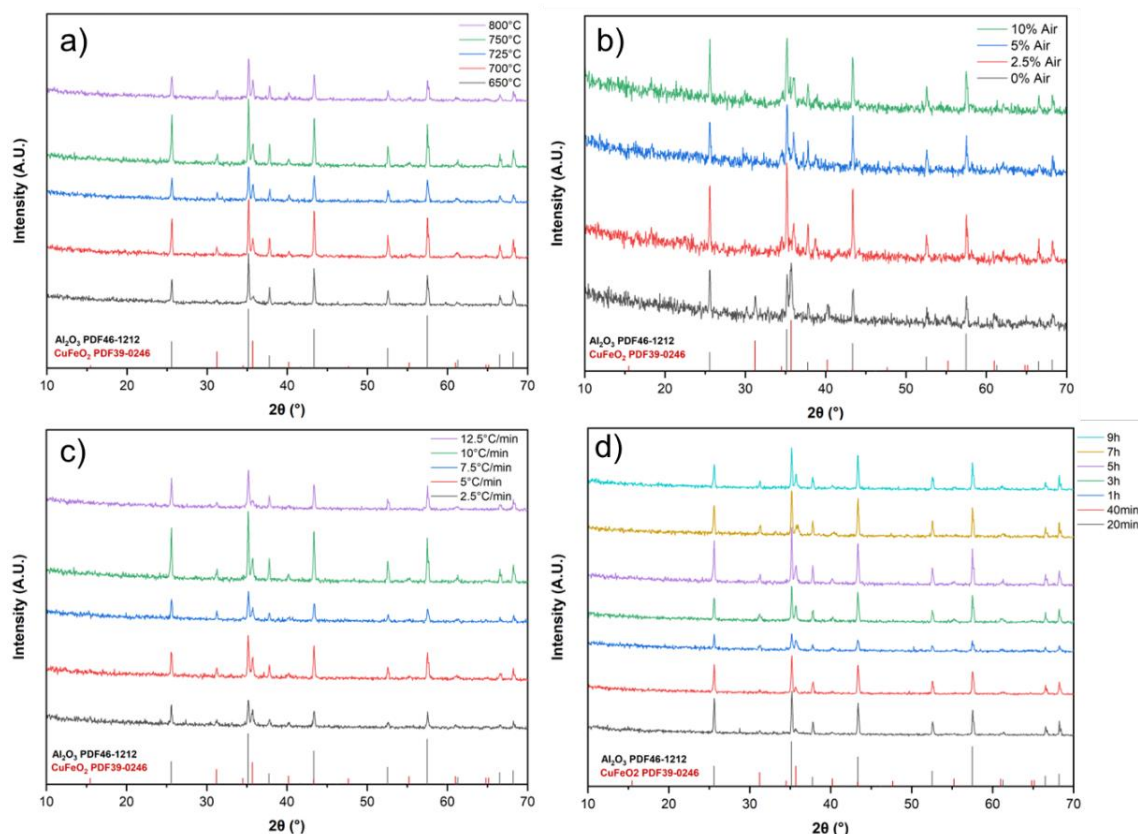


Figure 44. Integrated XRD patterns of CFO-ACCL films deposited on alumina substrate for the investigation on a) annealing temperature, b) annealing gas atmosphere, c) ramping rate, and d) annealing duration

When depositing CuFeO₂ thin films on alumina substrates, the investigations on annealing temperature (**Figure 44 a**), annealing time (**Figure 44 d**), and the temperature ramp rate (**Figure 44 c**) were repeated with the same deposition conditions used on quartz substrates. In contrast, the investigation of the gas atmosphere was systematically developed (**Figure 44 b**).

According to **Figure 41 a**), the Delafossite phase in the CFO-ACCL deposited on the quartz substrate decomposed at 800°C. In **Figure 44 a**), a clear and pure

Delafossite phase was observed in the CFO-ACCL films deposited on the alumina substrates at 800°C, and the decomposition hadn't started (or observed) yet. It is indicated that different substrates may have an effect on the film's thermal stability, and the Delafossite phase in the CFO-ACCL film deposited on the alumina substrate showed a better thermal stability compared to CFO-ACCL film deposited on quartz substrate.

The temperature ramp rate was tested from 2.5°C/min to 12.5°C/min. There was no noticeable difference in the formation of the Delafossite phase with lower rates. However, with a ramping rate of 12.5°C/min, the intensities of Delafossite CuFeO_2 peaks appeared to be decreased. The annealing time of CuFeO_2 thin films on Al_2O_3 substrates had the same trend as those on quartz substrates, where the Delafossite CuFeO_2 peak intensities grow before 1 h and remain at that level with increasing duration.

CFO-ACCL films deposited on AGSS for gas sensing measurement were all annealed at 750°C, with a ramping rate of 10°C/min in the inert N_2 gas atmosphere for 5 hours.

With previous experience with post-annealing treatment, CFO-ACCL films deposited on ITO-quartz substrate were also annealed at 750°C, with a ramping rate of 10°C/min in the inert N_2 gas atmosphere for 5 hours. Pure Delafossite phase was obtained and confirmed by XRD analysis.

Herein **Figure 45**, the XRD of ITO-quartz substrates was measured from substrates annealed at 750°C for 5 hours in an N_2 atmosphere, and its conductivity was measured after this high-temperature annealing to ensure no significant degradation of the ITO coating. A two-point resistance measurement showed the conductivity increased from $\sim 6\ \Omega$ to $\sim 13\ \Omega$, which indicated the performance as a conductive and transparent substrate for photoelectrochemical measurements was maintained after annealing.

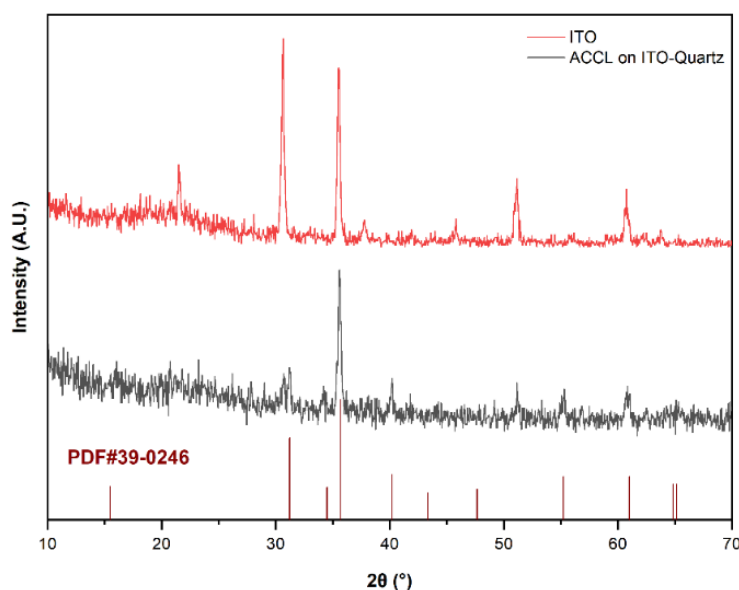


Figure 45. Integrated XRD patterns of ITO-quartz and CFO-ACCL thin films deposited on ITO-quartz substrate

3.3.1.3 Investigation of film morphology of CuFeO₂-ACCL films deposited on the different substrates

In **Chapter 3**, films deposited on different substrates were all synthesized with the optimal recipe (shown in **Table 12**).

Table 12. A Summary of optimal deposition and post-annealing conditions for CFO-ACCL films deposited on different substrates

Cu Precursor	Fe Precursor	Solvent	Substrate	Deposition Conditions	Annealing conditions
0.15 mmol [Cu(acac) ₂]	0.125 mmol [FeCl ₂ •4H ₂ O]	30ml Methanol	Quartz	420°C, 1400 sccm, N ₂	750°C, 10/min ramping, 5h, N ₂
0.14 mmol [Cu(acac) ₂]	0.13 mmol [FeCl ₂ •4H ₂ O]	30ml Methanol	Alumina (AGSS)	450°C, 1400 sccm, N ₂	750°C, 10/min ramping, 5h, N ₂
0.15 mmol [Cu(acac) ₂]	0.13 mmol [FeCl ₂ •4H ₂ O]	30ml Methanol	ITO-Quartz	450°C, 1400 sccm, N ₂	750°C, 10/min ramping, 5h, N ₂

The morphology of CFO-ACCL films deposited on different substrates was characterized by SEM, as shown in **Figure 46** and **Figure 47**. From SEM images, thin films were composed of small hexagonal particles with a relatively small size (~100-150 nm) uniformly distributed across the substrate. Hexagonal particles did not stack with each other in the same direction or plane but overlapped each other with a small area, resulting in a certain degree of porosity.

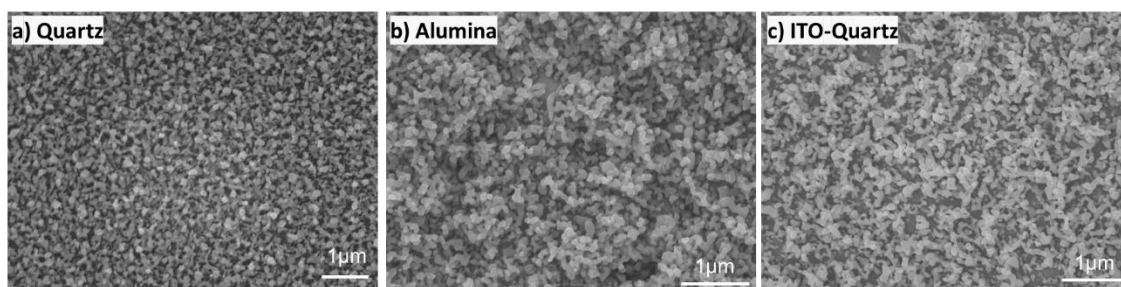


Figure 46. SEM images of CFO-ACCL films deposited on a) quartz, b) alumina, and c) ITO-quartz substrate

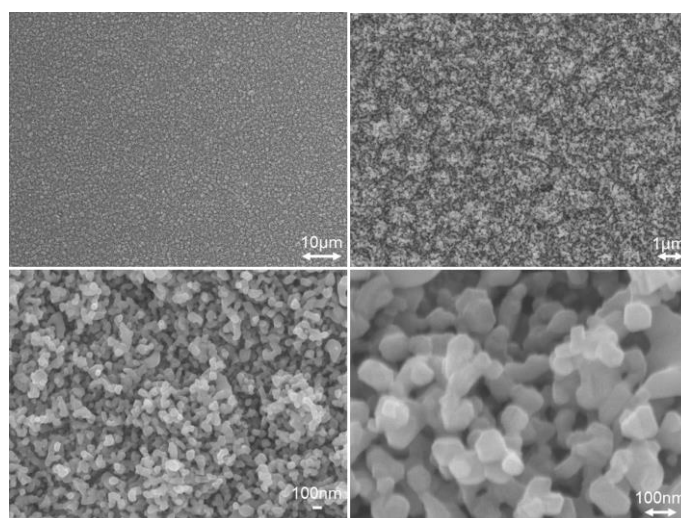


Figure 47. SEM images of CFO-ACCL films deposited on alumina substrate with different magnifications

3.3.2 Investigation of the optimal deposition and annealing conditions of CFO-ACAC film

3.3.2.1 Adjusting Cu/Fe elemental composition in the as-deposited film

To deposit CFO-ACAC film, $[\text{Cu}(\text{acac})_2]$ and $[\text{Fe}(\text{acac})_3]$ were used as the Cu/Fe precursors, and methanol was used as the solvent. Quartz substrates were used to investigate the optimal deposition and annealing conditions initially. The temperature was investigated initially, where 0.15 mmol $[\text{Cu}(\text{acac})_2]$ and $[\text{Fe}(\text{acac})_3]$ were used, and the flow rate was controlled at 1400 sccm.

From EDX results, when the exact molar amounts of Cu and Fe precursors were used, Cu was deposited with a higher atomic percentage than Fe. The atomic percentage of Cu was even higher with increasing temperature, which coincides

with the previous observation for CFO-ACCL films. Among five temperatures, it was found that films deposited at 325°C (**Figure 48 c**)-350°C (**Figure 48 b**) had a Cu/Fe ratio close to 1:1 ratio. However, from the visual appearance of the films, the one deposited at 325°C had a higher degree of uniformity (**Figure 48 a**).

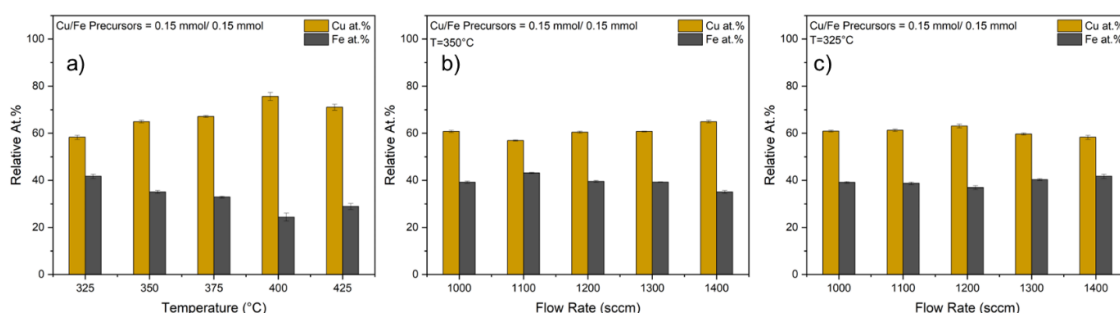


Figure 48. Cu/Fe relative atomic ratios obtained from EDX analysis of CFO-ACAC films deposited on quartz substrates: a) deposited at five different temperatures with Cu/Fe precursor ratio of fixed 0.15 mmol/ 0.15 mmol; b) deposited with five different gas flow rate ranging from 1000 sccm to 1400 sccm, Cu/Fe precursors of 0.15 mmol/ 0.15 mmol, deposition temperature of 350°C; c) deposited with five different gas flow rate ranging from 1000 sccm to 1400 sccm, Cu/Fe precursors of 0.15 mmol/ 0.15 mmol, deposition temperature of 325°

The optimisation of the flow rate was investigated at both 325°C and 350°C. The relative ratio of Cu and Fe between the two temperatures had a ~5% difference. However, it was determined that the change in flow rate did not play an important role in adjusting the Cu/Fe relative atomic ratio (**Figure 49**). There was no significant difference in the uniformity of the films at 325°C and 350°C except for the overall relative thickness. Ultimately, 1000 sccm was chosen for further investigation after visual inspection because the film was thicker and had a better appearance (**Figure 49 b**).



Figure 49. Digital photos of CFO-ACAC films: (Left) deposited at five different temperatures ranging from 325°C to 425°C, with gas flow rate of 1000 sccm to 1400 sccm and Cu/Fe precursor ratio of 0.15 mmol/0.15 mmol; (Right) deposited at 325°C with five different flow rates ranging from 1000 sccm to 1400 sccm, Cu/Fe precursor ratio of 0.15 mmol/0.15 mmol

To obtain the film with a close Cu/Fe 1:1 relative atomic ratio, the amount of Cu/Fe precursors was adjusted, where the amount of Fe precursor was fixed at 0.15 mmol, and the amount of Cu precursor was adjusted (**Table 13**). Temperature and gas flow rates were also optimised.

In the end, the goal of a close 1:1 Fe/Cu relatively atomic ratio deposited on the film was obtained when using 0.085-0.095 mmol [Cu(acac)₂] and 0.15 mmol [Fe(acac)₃] in 30 ml methanol, deposited at 320°C with a gas flow rate of 1000 sccm on the quartz substrate. 0.9 mmol [Cu(acac)₂] was used in further investigations.

Table 13. Cu/Fe relative atomic ratios obtained from EDX analysis of CFO-ACAC films deposited on quartz substrates where deposition temperature, gas flow rate and the amount of Cu/Fe precursors are all variables

Sample	n- [Cu(acac) ₂]	n- [Fe(acac) ₃]	Temperature	Substrate	Low Rate	EDX Relative Cu/Fe at. %
ACAC-10	0.075 mmol	0.15 mmol	350°C	Quartz	1400 sccm	56.44/43.56 ± 0.3
ACAC-11	0.075 mmol	0.15 mmol	325°C	Quartz	1400 sccm	53.03/46.97 ± 0.6
ACAC-15	0.075 mmol	0.15 mmol	325°C	Quartz	1000 sccm	45.12/54.88 ± 0.5
ACAC-16	0.075 mmol	0.15 mmol	325°C	Quartz	1100 sccm	43.89/56.11 ± 0.5
ACAC-17	0.075 mmol	0.15 mmol	325°C	Quartz	1200 sccm	46.19/53.81 ± 0.2
ACAC-18	0.075 mmol	0.15 mmol	325°C	Quartz	1300 sccm	45.68/54.32 ± 0.2
ACAC-19	0.075 mmol	0.15 mmol	325°C	Quartz	1400 sccm	46.19/53.82 ± 0.2
ACAC-20	0.07 mmol	0.15 mmol	325°C	Quartz	1400 sccm	40.88/59.12 ± 0.4
ACAC-21	0.07 mmol	0.15 mmol	325°C	Quartz	1300 sccm	40.85/59.15
ACAC-22	0.07 mmol	0.15 mmol	325°C	Quartz	1200 sccm	40.69/59.31
ACAC-23	0.07 mmol	0.15 mmol	325°C	Quartz	1100 sccm	42.09/57.91
ACAC-24	0.07 mmol	0.15 mmol	325°C	Quartz	1000 sccm	42.28/57.72
ACAC-29	0.08 mmol	0.15 mmol	320°C	Quartz	1000 sccm	47.13/52.87 ± 0.7
ACAC-30	0.078 mmol	0.15 mmol	320°C	Quartz	1000 sccm	44.71/55.29 ± 0.3
ACAC-31	0.075 mmol	0.15 mmol	320°C	Quartz	1000 sccm	42.36/57.64 ± 0.3
ACAC-32	0.072 mmol	0.15 mmol	320°C	Quartz	1000 sccm	45.48/54.52 ± 2
ACAC-33	0.07 mmol	0.15 mmol	320°C	Quartz	1000 sccm	45.89/54.11 ± 0.1
ACAC-34 (optimal)	0.085 mmol	0.15 mmol	320°C	Quartz	1000 sccm	50.10/49.90 ± 0.3
ACAC-35 (optimal)	0.09 mmol	0.15 mmol	320°C	Quartz	1000 sccm	50.59/49.31 ± 1
ACAC-36 (optimal)	0.095 mmol	0.15 mmol	320°C	Quartz	1000 sccm	49.53/50.47 ± 1
ACAC-37	0.10 mmol	0.15 mmol	320°C	Quartz	1000 sccm	52.82/47.18 ± 1
ACAC-38	0.11 mmol	0.15 mmol	320°C	Quartz	1000 sccm	52.00/48.00 ± 0.6
ACAC-39	0.12 mmol	0.15 mmol	320°C	Quartz	1000 sccm	55.80/44.20 ± 0.4

The optimal deposition conditions of CFO-ACAC films on alumina (**Table 14**) and ITO-quartz (**Table 15**) substrates were adjusted based on previous deposition experience. The temperatures, the N₂ flow rate and the amount of [Fe(acac)₃] were fixed. The adjustment was only applied to the amount of [Cu(acac)₂]. In the end, 0.10 mmol [Cu(acac)₂], and 0.15 mmol [Fe(acac)₃] in 30 ml methanol were used to synthesize desired CFO-ACAC thin films on alumina and ITO-quartz substrates at 320°C with N₂ gas flow rate of 1000 sccm.

Table 14. Cu/Fe relative atomic ratios obtained from EDX analysis of CFO-ACAC films deposited on alumina substrate at 320°C with gas flow rate of 1000 sccm, the amount of Cu/Fe precursors varies from 0.08 mmol/ 0.15 mmol to 0.13 mmol/ 0.15 mmol

Sample	n-[Cu(acac) ₂]	n-[Fe(acac) ₃]	Temperature	Substrate	Flow Rate	EDX Relative Cu/Fe at. %
ACAC-75	0.08 mmol	0.15 mmol	320°C	Alumina	1000 sccm	44.02/55.98 ± 0.2
ACAC-76	0.09 mmol	0.15 mmol	320°C	Alumina	1000 sccm	46.89/53.11 ± 0.2
ACAC-77 (optimal)	0.10 mmol	0.15 mmol	320°C	Alumina	1000 sccm	49.71/50.29 ± 0.3
ACAC-78	0.11 mmol	0.15 mmol	320°C	Alumina	1000 sccm	50.73/49.27 ± 0.2
ACAC-79	0.12 mmol	0.15 mmol	320°C	Alumina	1000 sccm	52.26/47.74 ± 0.2
ACAC-80	0.13 mmol	0.15 mmol	320°C	Alumina	1000 sccm	52.72/47.28 ± 0.4

Table 15. Cu/Fe relative atomic ratios obtained from EDX analysis of CFO-ACAC films deposited on quartz substrates at 320°C with a gas flow rate of 1000 sccm, the amount of Cu/Fe precursors varies from 0.09 mmol/ 0.15 mmol to 0.15 mmol/ 0.15 mmol

Sample	n-[Cu(acac) ₂]	n-[Fe(acac) ₃]	Temperature	Substrate	Flow Rate	EDX Relative Cu/Fe at. %
ACAC-68	0.09 mmol	0.15 mmol	320°C	ITO-Quartz	1000 sccm	47.54/52.46 ± 0.1
ACAC-69 (optimal)	0.10 mmol	0.15 mmol	320°C	ITO-Quartz	1000 sccm	49.30/50.70 ± 0.1
ACAC-70	0.11 mmol	0.15 mmol	320°C	ITO-Quartz	1000 sccm	50.98/49.01 ± 0.1
ACAC-71	0.12 mmol	0.15 mmol	320°C	ITO-Quartz	1000 sccm	49.89/50.11 ± 0.3
ACAC-72	0.13 mmol	0.15 mmol	320°C	ITO-Quartz	1000 sccm	51.17/48.83 ± 0.2
ACAC-73	0.14 mmol	0.15 mmol	320°C	ITO-Quartz	1000 sccm	54.90/45.09 ± 0.3
ACAC-74	0.15 mmol	0.15 mmol	320°C	ITO-Quartz	1000 sccm	55.80/44.20 ± 0.2

3.3.2.2 Investigation of the optimal post-annealing treatment conditions of CuFeO₂-ACAC film

Annealing temperature and duration were confirmed as critical factors in forming Delafossite CuFeO₂ thin films with high purity. Different annealing temperatures and durations were explored using the same procedures as CFO-ACCL films.

According to the XRD analysis of annealing temperatures (**Figure 50 a**), the pure Delafossite phase showed up from 700°C, which is the same as for the CFO-ACCL films. In CFO-ACAC films, the Delafossite phase appeared 30 minutes after annealing to compare non-annealed samples (**Figure 50 b**). Consequently, the annealing conditions were set the same as CFO-ACCL films, which were annealed at 750°C for 5 hours.

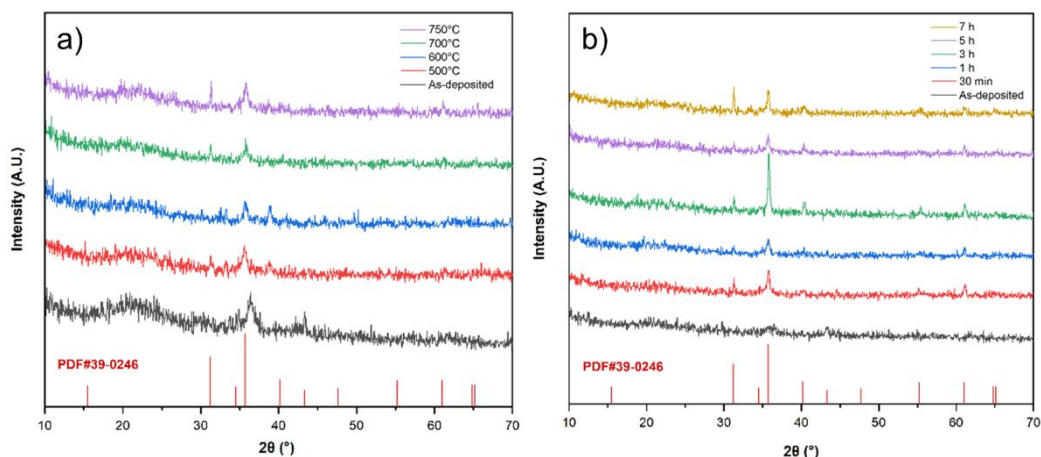


Figure 50. Integrated XRD patterns of CFO-ACAC films annealed a) at different temperatures ranging from as-deposited to 750°C for 5h; b) for the different duration ranging from non-annealing to 7h at 750°C

The optimal post-annealing treatment conditions on the quartz substrate were applied on alumina and ITO-quartz substrates. XRD patterns confirmed the formation of the Delafossite CuFeO_2 phase (**Figure 51**). Raman spectroscopy was conducted for the CFO-ACAC deposited on ITO-quartz substrates (**Figure 52**). The fingerprints of the ITO-quartz substrate were performed in the same range of Delafossite CuFeO_2 . The purity of the Delafossite phase was confirmed since no CuO or Fe_2O_3 fingerprints showed up.

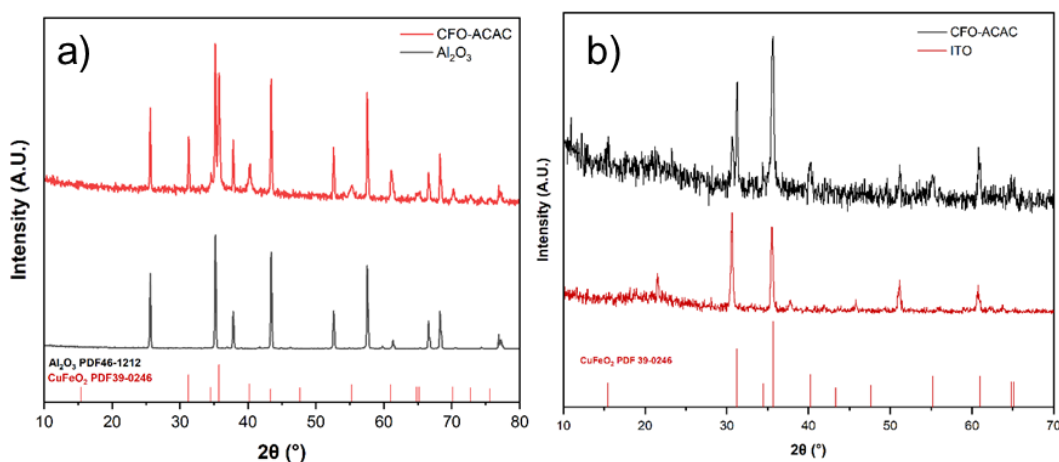


Figure 51. Integrated XRD patterns of CFO-ACAC film deposited on a) alumina and b) ITO-quartz substrate

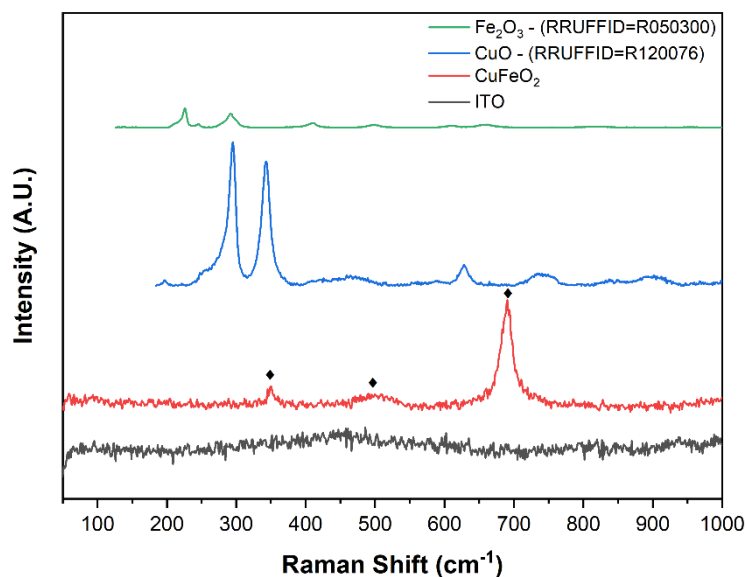


Figure 52. Integrated Raman spectroscopy of CFO-ACAC film deposited on ITO-quartz (CuFeO_2 'fingerprint' peaks are marked as diamond); CuO in RUUFFTM database and Fe_2O_3 in RUUFFTM database

3.3.2.3 Investigation of film morphology of CuFeO_2 -ACAC films deposited on the different substrates

The morphology of CFO-ACAC films deposited on quartz, alumina and ITO-quartz substrates was characterized by SEM in the same magnification ($\times 15,000$). Compared to the CFO-ACCL films (**Figure 46**), the overall particle size of the CFO-ACAC films was relatively larger (~ 200 nm) regardless of the substrate (**Figure 53**).

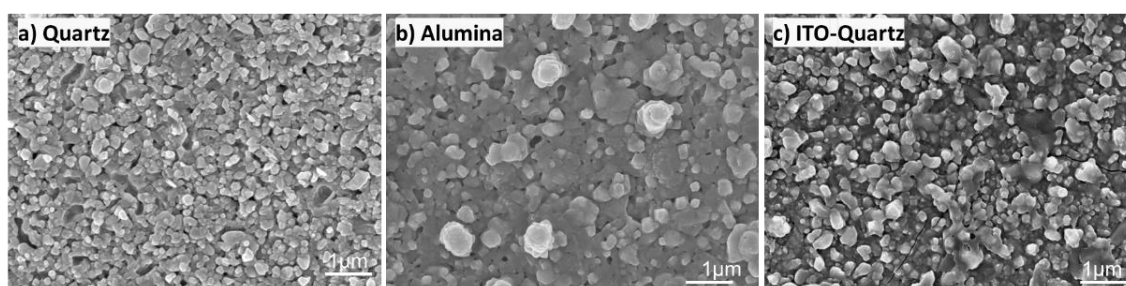


Figure 53. SEM images of CFO-ACAC films deposited on a) Quartz, b) Alumina, and c) ITO-quartz substrate

3.3.3 Investigation of the optimal conditions of depositing CFO-CN film

3.3.3.1 Adjusting Cu/Fe elemental composition in the as-deposited film

To deposit CFO-CN film, $[\text{Cu}(\text{acac})_2]$ and $[\text{Fe}(\text{acac})_3]$ were used as the Cu/Fe precursors and acetonitrile was used as the solvent. Similar to the investigation for CFO-ACAC, quartz substrates were initially used to investigate the optimal deposition and annealing conditions. The temperature was investigated first, where 0.075 mmol $[\text{Cu}(\text{acac})_2]$ and 0.075 mmol $[\text{Fe}(\text{acac})_3]$ in 15 ml acetonitrile were deposited at different temperatures, with the N_2 flow rate controlled at 1000 sccm (**Table 16**). EDX analysis showed that Cu was deposited with a higher atomic percentage than Fe, and hence, the amount of Cu precursor needed to be reduced.

Table 16. Cu/Fe relative atomic ratios obtained from EDX analysis of CFO-CN films deposited on quartz substrates at various temperatures (275°C to 400°C) with a gas flow rate of 1000 sccm and a Cu/Fe precursor ratio of 0.075 mmol/0.075 mmol

Sample	n- $[\text{Cu}(\text{acac})_2]$	n- $[\text{Fe}(\text{acac})_3]$	Temperature	Substrate	Flow Rate	EDX Relative Cu/Fe at. %
CN-12	0.075 mmol	0.075 mmol	400°C	Quartz	1000 sccm	64.92/35.08 ± 4
CN-13	0.075 mmol	0.075 mmol	375°C	Quartz	1000 sccm	63.85/36.15 ± 2
CN-14	0.075 mmol	0.075 mmol	350°C	Quartz	1000 sccm	56.90/43.10 ± 0.2
CN-15	0.075 mmol	0.075 mmol	325°C	Quartz	1000 sccm	59.08/40.92 ± 0.7
CN-16	0.075 mmol	0.075 mmol	300°C	Quartz	1000 sccm	55.66/44.34 ± 0.3
CN-17	0.075 mmol	0.075 mmol	275°C	Quartz	1000 sccm	45.05/54.95 ± 1

Table 17. Cu/Fe relative atomic ratios obtained from EDX analysis of CFO-CN films deposited on quartz substrates at various temperatures (275°C to 400°C) with a gas flow rate of 1000 sccm and a Cu/Fe precursor ratio of 0.09 mmol/0.075 mmol

Sample	n- $[\text{Cu}(\text{acac})_2]$	n- $[\text{Fe}(\text{acac})_3]$	Temperature	Substrate	Low Rate	EDX Relative Cu/Fe at. %
CN-2	0.09 mmol	0.15 mmol	300°C	Quartz	1000 sccm	41.12/58.88 ± 3
CN-3	0.09 mmol	0.15 mmol	325°C	Quartz	1000 sccm	57.94/42.06 ± 1
CN-4	0.09 mmol	0.15 mmol	350°C	Quartz	1000 sccm	49.51/50.49 ± 0.7
CN-5	0.09 mmol	0.15 mmol	375°C	Quartz	1000 sccm	49.14/50.86 ± 0.8
CN-6	0.09 mmol	0.15 mmol	400°C	Quartz	1000 sccm	59.44/40.56 ± 2
CN-7	0.09 mmol	0.15 mmol	275°C	Quartz	1000 sccm	23.51/76.49 ± 2

As shown in **Table 16**, when the Cu and Fe precursors were present in equal amounts, the Cu and Fe tended to have a 1:1 relative atomic ratio at 275°C to 300°C. However, in this temperature range, the film was relatively thin because both Cu and Fe tend to be deposited at temperatures ranging from 300°C to 400°C, during which, as the temperature increases, more Cu or Fe can be deposited on the film (**Figure 54**).

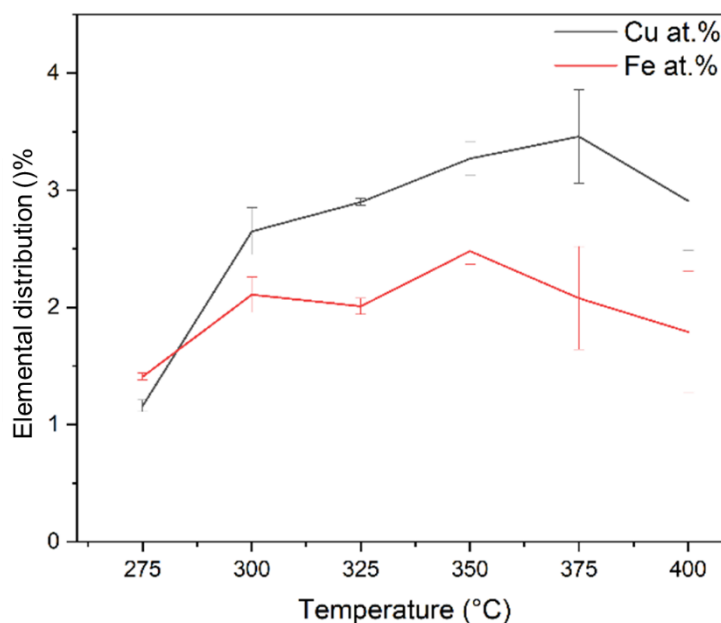


Figure 54. Illustration of Cu/Fe elemental distribution in the as-deposited thin film obtained from EDX analysis of CFO-CN films deposited on quartz substrates at various temperatures (275°C to 400°C) with a gas flow rate of 1000 sccm and a Cu/Fe precursor ratio of 0.075 mmol/0.075 mmol

Since the only difference between CFO-ACAC and CFO-CN film is solvent (from 30 ml methanol to 30 ml acetonitrile), the optimal amount of Cu/Fe precursors used in CFO-ACAC films on the quartz substrates were tried subsequently, with the optimal temperature range shifted to 350-375°C (**Table 18**).

Along with the results in **Table 17**, the amount of Cu/Fe precursors was fine-tuned in **Table 18**. Ultimately, the best Cu/Fe elemental distribution on the quartz substrates was achieved when 0.10 mmol [Cu(acac)₂] and 0.15 mmol [Fe(acac)₃] were used in the deposition.

Table 18. Relative Cu/Fe atomic ratio from EDX analysis of CFO-CN films deposited on quartz substrates at 350°C with gas flow rate of 1000 sccm, the amount of Cu/Fe precursors varies from 0.08 mmol/ 0.15 mmol to 0.10 mmol/ 0.15 mmol

Sample	n-[Cu(acac) ₂]	n-[Fe(acac) ₃]	Temperature	Substrate	Low Rate	EDX Relative Cu/Fe at. %
CN-18	0.08 mmol	0.15 mmol	350°C	Quartz	1000 sccm	40.52/59.48 ± 0.4
CN-19	0.085 mmol	0.15 mmol	350°C	Quartz	1000 sccm	44.63/55.37 ± 1
CN-20	0.09 mmol	0.15 mmol	350°C	Quartz	1000 sccm	46.78/53.22 ± 0.7
CN-21	0.095 mmol	0.15 mmol	350°C	Quartz	1000 sccm	51.51/48.49 ± 1
CN-22	0.10 mmol	0.15 mmol	350°C	Quartz	1000 sccm	49.34/50.66 ± 1

Table 19. Relative Cu/Fe atomic ratio from EDX analysis of CFO-CN films deposited on alumina substrates at 350°C with gas flow rate of 1000 sccm, the amount of Cu/Fe precursors varies from 0.10 mmol/ 0.15 mmol to 0.15 mmol/ 0.15 mmol

Sample	n-[Cu(acac) ₂]	n-[Fe(acac) ₃]	Temperature	Substrate	Flow Rate	EDX Relative Cu/Fe at. %
CN-49	0.10 mmol	0.15 mmol	350°C	Alumina	1000 sccm	48.05/51.95 ± 0.4
CN-50 (optimal)	0.11 mmol	0.15 mmol	350°C	Alumina	1000 sccm	50.00/50.00 ± 0.8
CN-51 (optimal)	0.12 mmol	0.15 mmol	350°C	Alumina	1000 sccm	48.28/51.72 ± 0.9
CN-52 (optimal)	0.13 mmol	0.15 mmol	350°C	Alumina	1000 sccm	50.36/49.64 ± 0.5
CN-53	0.14 mmol	0.15 mmol	350°C	Alumina	1000 sccm	52.26/47.74 ± 1
CN-54	0.15 mmol	0.15 mmol	350°C	Alumina	1000 sccm	54.97/45.03 ± 2

Table 20. Relative Cu/Fe atomic ratio from EDX analysis of CFO-CN films deposited on ITO-quartz substrates at 350°C with gas flow rate of 1000 sccm, the amount of Cu/Fe precursors varies from 0.08 mmol/ 0.15 mmol to 0.13 mmol/ 0.15 mmol

Sample	n-[Cu(acac) ₂]	n-[Fe(acac) ₃]	Temperature	Substrate	Low Rate	EDX Relative Cu/Fe at. %
CN-23	0.08 mmol	0.15 mmol	350°C	ITO-Quartz	1000 sccm	40.41/59.59 ± 0.4
CN-24	0.085 mmol	0.15 mmol	350°C	ITO-Quartz	1000 sccm	46.45/53.55 ± 0.2
CN-25	0.09 mmol	0.15 mmol	350°C	ITO-Quartz	1000 sccm	44.48/55.52 ± 0.5
CN-26	0.095 mmol	0.15 mmol	350°C	ITO-Quartz	1000 sccm	43.29/56.71 ± 0.4
CN-27	0.10 mmol	0.15 mmol	350°C	ITO-Quartz	1000 sccm	43.55/56.45 ± 0.3
CN-28	0.105 mmol	0.15 mmol	350°C	ITO-Quartz	1000 sccm	47.64/52.36 ± 0.9
CN-29	0.11 mmol	0.15 mmol	350°C	ITO-Quartz	1000 sccm	54.97/45.03 ± 0.3
CN-30	0.115 mmol	0.15 mmol	350°C	ITO-Quartz	1000 sccm	52.85/47.15 ± 0.4
CN-31	0.12 mmol	0.15 mmol	350°C	ITO-Quartz	1000 sccm	47.53/52.47 ± 0.4
CN-32	0.125 mmol	0.15 mmol	350°C	ITO-Quartz	1000 sccm	47.34/52.66 ± 0.2
CN-33 (optimal)	0.13 mmol	0.15 mmol	350°C	ITO-Quartz	1000 sccm	49.87/50.13 ± 0.4

CFO-CN films deposited on alumina and ITO-quartz substrates were further adjusted by changing the amount of $[\text{Cu}(\text{acac})_2]$ used in the deposition. **Table 19** and **Table 20** show that the best relative Cu/Fe atomic ratio was obtained when using 0.11-0.13 mmol $[\text{Cu}(\text{acac})_2]$ for the alumina substrates and ~ 0.13 mmol $[\text{Cu}(\text{acac})_2]$ for ITO-quartz substrates. In the end, 0.13 mmol $[\text{Cu}(\text{acac})_2]$ was used for CFO-CN films deposited on alumina and ITO-quartz substrates in the later experiments in this project.

3.3.3.2 Investigation of the optimal annealing conditions of CuFeO_2 -CN film

CFO-CN films on the quartz substrate were annealed at different temperatures from 550°C to 800°C for 5 hours. The pure Delafossite CuFeO_2 phase appeared at 700°C and remained the same until 750°C , showing consistency with the CFO-ACCL and CFO-ACAC films (**Figure 55**).

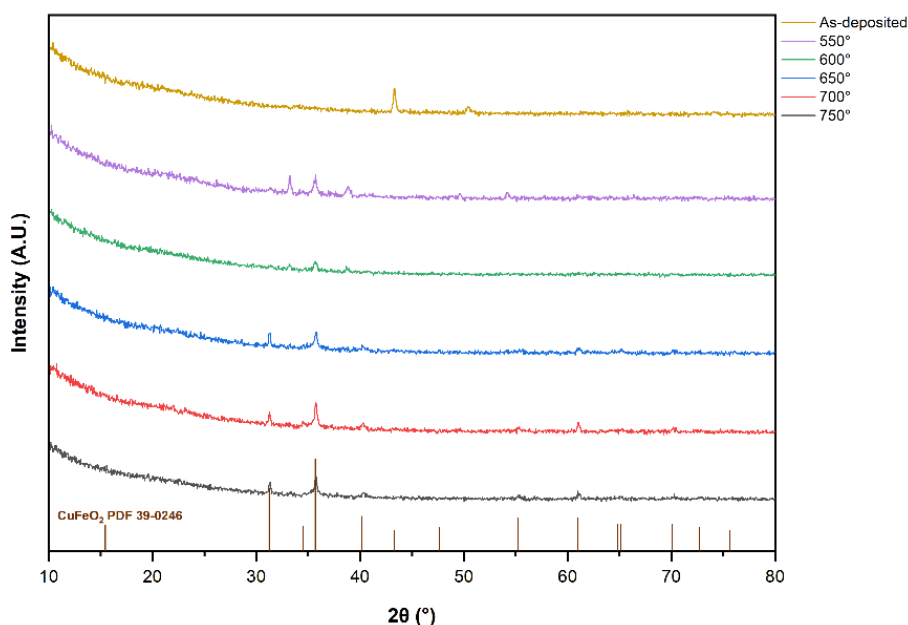


Figure 55. Integrated XRD patterns of CFO-CN films deposited on the quartz substrate with optimal conditions and annealed at different temperatures in N_2

CFO-CN films deposited on alumina and ITO-quartz substrates were analysed by XRD and confirmed to be pure Delafossite phase under the optimal annealing conditions at 750°C for 5h under N_2 , as shown in **Figure 56**.

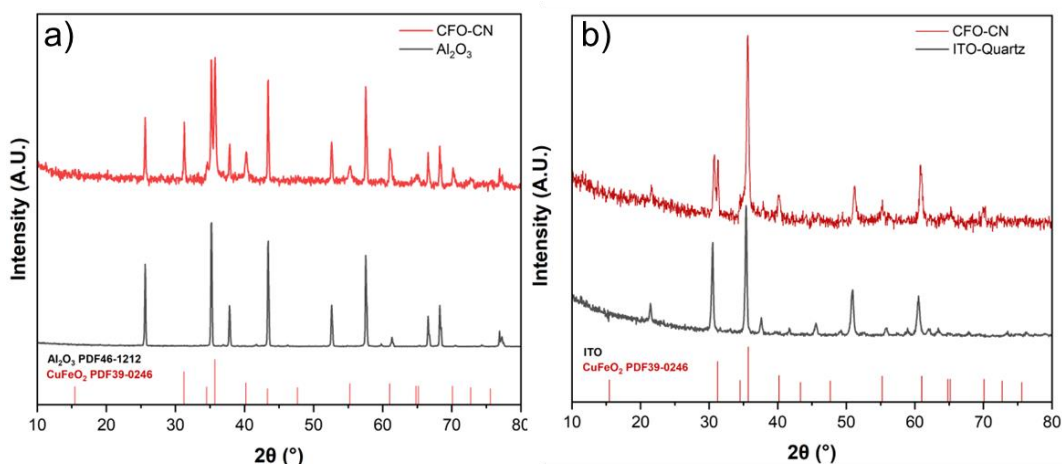


Figure 56. Integrated XRD patterns of CFO-CN films deposited with optimal conditions on a) Alumina and b) ITO-quartz substrate and annealed at 750°C in N₂ for 5h

3.3.3.3 Investigation of film morphology of CuFeO₂-CN films deposited on the different substrates

Unlike CFO-ACCL and CFO-ACAC films, CFO-CN films on different substrates synthesized and annealed using the same methods showed different morphologies (**Figure 57**). On the quartz substrate, the film morphology can be described as ‘microscale network’ composed of hexagonal particles of ~250 nm. On the alumina substrate, CFO-CN films formed by similar sizes of particles showed a hollow morphology. On ITO-quartz substrate, hexagonal particles ranging from ~200 nm to ~500 nm were observed and stacked layer by layer to form the film composed of nanosheets.

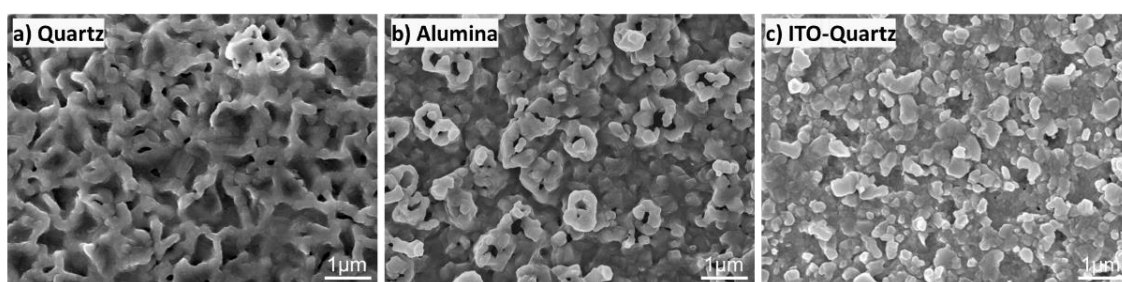


Figure 57. SEM images of CFO-CN films deposited with optimal conditions on a) Quartz, b) Alumina, and c) ITO-quartz substrate

Noticeably, CFO-CN film phase transition and morphological changes were also observed in films deposited on quartz substrates annealed at different

temperatures (**Figure 58**). At 650°C, tiny particles can be seen from the SEM images, during which the Delafossite CuFeO_2 was being formed. At 700°C, Delafossite nanowebbs were shaped and then extended in 2D at 750°C. When the temperature was raised to 800°C, the 2D nanoweb structure began to ‘dissolve’ into tiny particles, indicating that the Delafossite CuFeO_2 was being decomposed into copper and iron metal oxides.

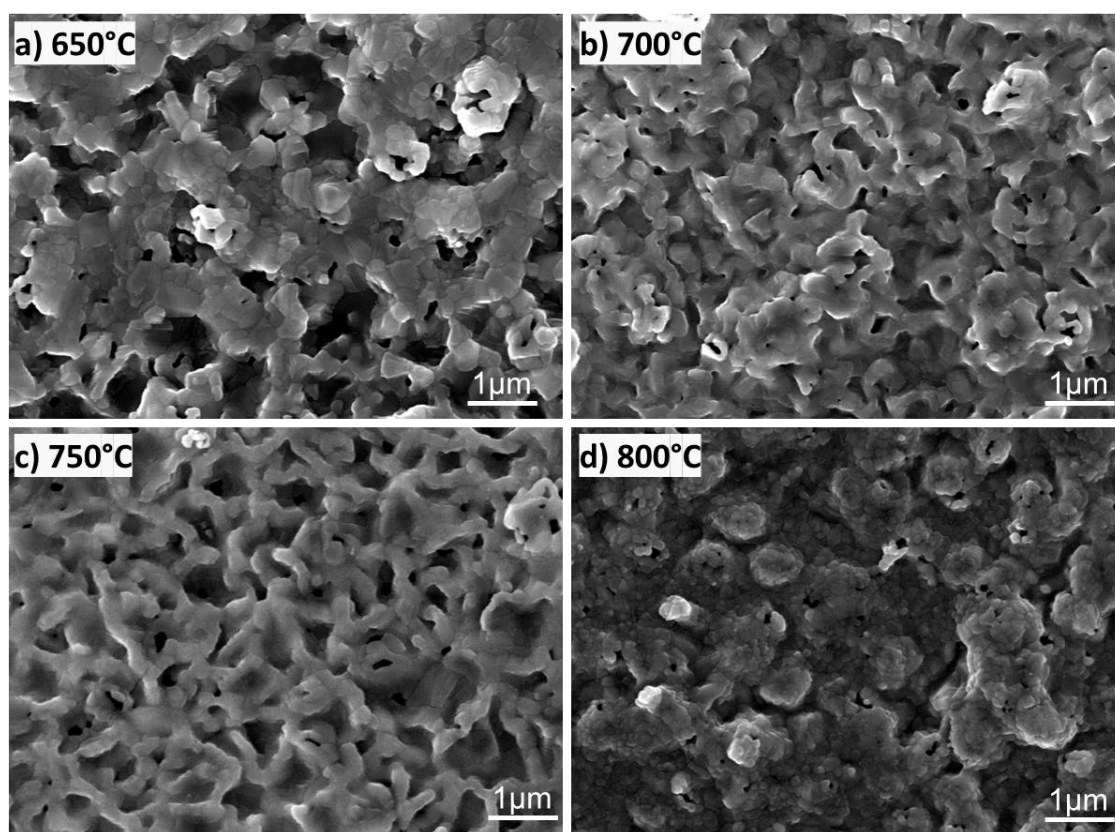


Figure 58. SEM images of CFO-CN deposited on quartz substrate with optimal conditions and annealed at a) 650°C, b) 700°C, c) 750°C, d) 800°C for 5h in the N_2 atmosphere

3.4 Summary

As depicted in **Figure 59**, achieving a high-purity, single-phase CuFeO_2 thin film is challenging due to the simultaneous deposition of three elements with a strict ratio. The phase composition can spontaneously change with deposition temperature, precursors, solvent, substrate, carrier gas, and interactions with other elements further complicate the process. This chapter described how Delafossite CuFeO_2

thin films were successfully and precisely synthesized via aerosol-assisted chemical vapour deposition and the post-annealing treatments on different substrates.

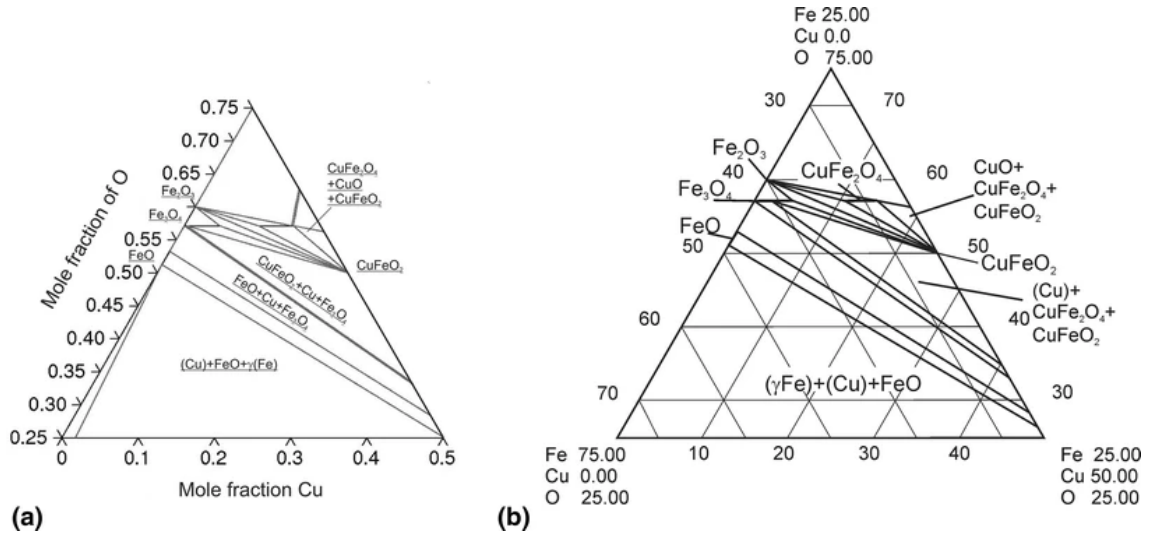


Figure 59. Thermodynamic study on Cu-Fe-O system, isothermal section at 1200K (total pressure 1 atm): (a) calculated and (b) experimental equilibrium²⁹⁷

AACVD has been found to be a simple and valuable method to deposit multi-metal oxide films with well-controlled stoichiometry, pure crystal phase, and tuneable morphology by varying the starting chemicals, solvents, substrates, deposition or annealing factors. Consequently, three groups of starting chemicals were used, and the optimal deposition conditions were summarized for films on different substrates (**Table 21**). Combined with the film thickness control method that will be introduced later in **Chapter 5**, the research in this chapter is able to provide comprehensive guidance for the study of CuFeO_2 film deposition.

CuFeO_2 thin films deposited on quartz offer a cost-effective means to explore their electronic and optical properties, such as conductivity and band gap. Alumina is a commonly used substrate material for gas-sensing materials. In practice, the size of the alumina gas sensor substrate (AGGS) is fairly small (2*2 mm). Hence, CuFeO_2 thin films deposited on alumina serve as suitable alternatives for investigating the properties of gas-sensing films on such substrates. On the other

hand, ITO-quartz substrates are conductive, transparent, and thermally stable substrate for the investigation of CuFeO₂ thin films being used as photocathode.

Table 21. A summary of optimal deposition and post-annealing conditions for CuFeO₂ film deposition on different substrates

Cu Precursor	Fe Precursor	Solvent	Substrate	Deposition Conditions	Annealing conditions
0.15 mmol [Cu(acac) ₂]	0.125 mmol [FeCl ₂ •4H ₂ O]	30ml Methanol	Quartz	420°C, 1400 sccm, N ₂	750°C, 10/min ramping, 5h, N ₂
0.14 mmol [Cu(acac) ₂]	0.13 mmol [FeCl ₂ •4H ₂ O]	30ml Methanol	Alumina (AGSS)	450°C, 1400 sccm, N ₂	750°C, 10/min ramping, 5h, N ₂
0.15 mmol [Cu(acac) ₂]	0.13 mmol [FeCl ₂ •4H ₂ O]	30ml Methanol	ITO-Quartz	450°C, 1400 sccm, N ₂	750°C, 10/min ramping, 5h, N ₂
0.09 mmol [Cu(acac) ₂]	0.15 mmol [Fe(acac) ₃]	30ml Methanol	Quartz	320°C, 1000 sccm, N ₂	750°C, 10/min ramping, 5h, N ₂
0.10 mmol [Cu(acac) ₂]	0.15 mmol [Fe(acac) ₃]	30ml Methanol	Alumina (AGSS)	320°C, 1000 sccm, N ₂	750°C, 10/min ramping, 5h, N ₂
0.10 mmol [Cu(acac) ₂]	0.15 mmol [Fe(acac) ₃]	30ml Methanol	ITO-Quartz	320°C, 1000 sccm, N ₂	750°C, 10/min ramping, 5h, N ₂
0.09 mmol [Cu(acac) ₂]	0.15 mmol [Fe(acac) ₃]	30ml Acetonitrile	Quartz	350°C, 1000 sccm, N ₂	750°C, 10/min ramping, 5h, N ₂
0.13 mmol [Cu(acac) ₂]	0.15 mmol [Fe(acac) ₃]	30ml Acetonitrile	Alumina (AGSS)	350°C, 1000 sccm, N ₂	750°C, 10/min ramping, 5h, N ₂
0.13 mmol [Cu(acac) ₂]	0.15 mmol [Fe(acac) ₃]	30ml Acetonitrile	ITO-Quartz	350°C, 1000 sccm, N ₂	750°C, 10/min ramping, 5h, N ₂

3.5 Appendix

AACVD deposition details for the CFO films on different substrates are summarized and listed in the appendix. The relative atomic ratio of as-deposited Cu/Fe was obtained from EDX analysis.

Table 22. Relative Cu/Fe atomic ratio from EDX analysis of CFO-ACCL films deposited on glass substrates with gas flow rate of 1400 sccm; deposition temperature and the amount of Cu/Fe precursors are variables

Sample	n- [Cu(acac) ₂]	n- [FeCl ₂ •4H ₂ O]	Temperature	Substrate	Flow Rate	EDX Relative Cu/Fe at. %
ACCL-2	0.13 mmol	0.196 mmol	350°C	Glass	1400 sccm	5.93/94.07 ± 0.6
ACCL-14	0.13 mmol	0.196 mmol	375°C	Glass	1400 sccm	5.76/94.24 ± 1
ACCL-7	0.13 mmol	0.196 mmol	400°C	Glass	1400 sccm	30.80/69.20 ± 3
ACCL-20	0.13 mmol	0.196 mmol	425°C	Glass	1400 sccm	26.72/73.28 ± 4
ACCL-21	0.13 mmol	0.196 mmol	450°C	Glass	1400 sccm	39.28/60.72 ± 4

Sample	n- [Cu(acac) ₂]	n- [FeCl ₂ •4H ₂ O]	Temperature	Substrate	Flow Rate	EDX Relative Cu/Fe at. %
ACCL-8	0.13 mmol	0.065 mmol	350°C	Glass	1400 sccm	61.37/38.63 ± 0.6
ACCL-11	0.13 mmol	0.065 mmol	375°C	Glass	1400 sccm	62.85/37.15 ± 0.8
ACCL-12	0.13 mmol	0.065 mmol	400°C	Glass	1400 sccm	67.14/32.86 ± 2
ACCL-22	0.13 mmol	0.065 mmol	425°C	Glass	1400 sccm	74.27/25.73 ± 0.6
ACCL-23	0.13 mmol	0.065 mmol	450°C	Glass	1400 sccm	78.56/21.44 ± 0.4
ACCL-15	0.13 mmol	0.13 mmol	350°C	Glass	1400 sccm	17.99/82.01 ± 1
ACCL-30	0.13 mmol	0.13 mmol	375°C	Glass	1400 sccm	22.59/77.41 ± 0.4
ACCL-31	0.13 mmol	0.13 mmol	400°C	Glass	1400 sccm	27.82/72.18 ± 2
ACCL-32	0.13 mmol	0.13 mmol	425°C	Glass	1400 sccm	41.32/58.68 ± 2
ACCL-33	0.13 mmol	0.13 mmol	450°C	Glass	1400 sccm	46.82/53.18 ± 0.9
ACCL-29	0.13 mmol	0.145 mmol	350°C	Glass	1400 sccm	10.97/89.03 ± 0.1
ACCL-16	0.13 mmol	0.145 mmol	375°C	Glass	1400 sccm	20.76/79.24 ± 0.8
ACCL-17	0.13 mmol	0.145 mmol	400°C	Glass	1400 sccm	34.20/65.80 ± 1
ACCL-18	0.13 mmol	0.145 mmol	425°C	Glass	1400 sccm	40.16/59.84 ± 3
ACCL-19	0.13 mmol	0.145 mmol	450°C	Glass	1400 sccm	29.18/70.82 ± 2
ACCL-34	0.145 mmol	0.13 mmol	350°C	Glass	1400 sccm	41.76/58.24 ± 2
ACCL-35	0.145 mmol	0.13 mmol	375°C	Glass	1400 sccm	34.22/65.78 ± 0.7
ACCL-36	0.145 mmol	0.13 mmol	400°C	Glass	1400 sccm	46.68/53.32 ± 2
ACCL-37	0.145 mmol	0.13 mmol	425°C	Glass	1400 sccm	52.16/47.84 ± 3
ACCL-38	0.145 mmol	0.13 mmol	450°C	Glass	1400 sccm	62.75/37.25 ± 4
ACCL-24	0.117 mmol	0.208 mmol	350°C	Glass	1400 sccm	7.26/92.74 ± 0.7
ACCL-25	0.117 mmol	0.208 mmol	375°C	Glass	1400 sccm	6.78/93.22 ± 0.8
ACCL-26	0.117 mmol	0.208 mmol	400°C	Glass	1400 sccm	14.44/85.6 ± 2
ACCL-27	0.117 mmol	0.208 mmol	425°C	Glass	1400 sccm	27.62/72.38 ± 3
ACCL-28	0.117 mmol	0.208 mmol	450°C	Glass	1400 sccm	33.31/66.69 ± 3
ACCL-44	0.15 mmol	0.13 mmol	350°C	Glass	1400 sccm	35.72/64.28 ± 0.3
ACCL-40	0.15 mmol	0.13 mmol	375°C	Glass	1400 sccm	40.08/59.92 ± 0.7
ACCL-41	0.15 mmol	0.13 mmol	400°C	Glass	1400 sccm	46.88/53.12 ± 1
ACCL-42	0.15 mmol	0.13 mmol	425°C	Glass	1400 sccm	59.69/40.31 ± 2
ACCL-43	0.15 mmol	0.13 mmol	450°C	Glass	1400 sccm	62.22/37.78 ± 3

Table 23. Relative Cu/Fe atomic ratio from EDX analysis of CFO-ACCL films deposited on quartz substrates with gas flow rate of 1400 sccm; deposition temperature and the amount of Cu/Fe precursors are variables

Sample	n- [Cu(acac) ₂]	n- [FeCl ₂ •4H ₂ O]	Temperature	Substrate	Flow Rate	EDX Relative Cu/Fe at. %
ACCL-47	0.15 mmol	0.13 mmol	350°C	Quartz	1400 sccm	19.73/80.27 ± 6
ACCL-48	0.15 mmol	0.13 mmol	375°C	Quartz	1400 sccm	41.72/58.28 ± 1
ACCL-49	0.15 mmol	0.13 mmol	400°C	Quartz	1400 sccm	49.95/50.05 ± 1
ACCL-50	0.15 mmol	0.13 mmol	425°C	Quartz	1400 sccm	54.01/45.99 ± 2
ACCL-51	0.15 mmol	0.13 mmol	450°C	Quartz	1400 sccm	67.50/32.50 ± 3
ACCL-62	0.145 mmol	0.13 mmol	350°C	Quartz	1400 sccm	11.64/88.36 ± 3
ACCL-63	0.145 mmol	0.13 mmol	375°C	Quartz	1400 sccm	31.14/68.86 ± 2
ACCL-64	0.145 mmol	0.13 mmol	400°C	Quartz	1400 sccm	43.52/56.48 ± 2
ACCL-52	0.145 mmol	0.13 mmol	425°C	Quartz	1400 sccm	51.60/48.40 ± 2
ACCL-60	0.145 mmol	0.13 mmol	450°C	Quartz	1400 sccm	47.78/52.22 ± 2
ACCL-65	0.13 mmol	0.13 mmol	350°C	Quartz	1400 sccm	6.63/93.37 ± 5
ACCL-66	0.13 mmol	0.13 mmol	375°C	Quartz	1400 sccm	18.51/81.49 ± 2
ACCL-67	0.13 mmol	0.13 mmol	400°C	Quartz	1400 sccm	35.59/64.41 ± 1
ACCL-68	0.13 mmol	0.13 mmol	425°C	Quartz	1400 sccm	41.73/58.27 ± 2
ACCL-59	0.13 mmol	0.13 mmol	450°C	Quartz	1400 sccm	47.80/52.20 ± 2

Table 24. Relative Cu/Fe atomic ratio from EDX analysis of CFO-ACCL films deposited on quartz substrates at 420°C with the amount of Cu/Fe precursors of 0.15 mmol/ 0.125 mmol; gas flow rate varies from 700 sccm to 1400 sccm

Sample	n- [Cu(acac) ₂]	n- [FeCl ₂ •4H ₂ O]	Temperature	Substrate	Flow Rate	EDX Relative Cu/Fe at. %
ACCL-101	0.15 mmol	0.125 mmol	420°C	Quartz	700 sccm	56.02/43.98± 0.7
ACCL-102	0.15 mmol	0.125 mmol	420°C	Quartz	800 sccm	55.62/44.38 ± 0.6
ACCL-103	0.15 mmol	0.125 mmol	420°C	Quartz	900 sccm	52.61/47.39 ± 1
ACCL-104	0.15 mmol	0.125 mmol	420°C	Quartz	1000 sccm	50.58/49.42 ± 0.6
ACCL-105	0.15 mmol	0.125 mmol	420°C	Quartz	1100 sccm	47.64/52.36 ± 1
ACCL-106	0.15 mmol	0.125 mmol	420°C	Quartz	1200 sccm	50.94/49.06 ± 1
ACCL-107	0.15 mmol	0.125 mmol	420°C	Quartz	1300 sccm	54.04/45.96 ± 0.5
ACCL-108	0.15 mmol	0.125 mmol	420°C	Quartz	1400 sccm	54.82/45.18 ± 0.3

Table 25. Relative Cu/Fe atomic ratio from EDX analysis of CFO-ACCL films deposited on alumina substrates where gas flow rate, deposition temperature and the amount of Cu/Fe precursors are all variables

Sample	n- [Cu(acac) ₂]	n- [FeCl ₂ •4H ₂ O]	Temperature	Substrate	Flow Rate	EDX Relative Cu/Fe at. %
ACCL-170	0.15 mmol	0.125 mmol	420°C	Alumina	1400 sccm	59.18/40.82 ± 1
ACCL-171	0.15 mmol	0.125 mmol	420°C	Alumina	1300 sccm	55.72/44.28 ± 1
ACCL-172	0.15 mmol	0.125 mmol	420°C	Alumina	1200 sccm	58.37/41.63 ± 2
ACCL-173	0.15 mmol	0.125 mmol	420°C	Alumina	1100 sccm	56.14/43.86 ± 1
ACCL-174	0.15 mmol	0.125 mmol	420°C	Alumina	1000 sccm	60.91/39.09 ± 1
ACCL-206	0.15 mmol	0.13 mmol	420°C	Alumina	1400 sccm	65.24/34.76 ± 3
ACCL-193	0.15 mmol	0.13 mmol	420°C	Alumina	1300 sccm	58.63/41.37 ± 1
ACCL-203	0.15 mmol	0.13 mmol	420°C	Alumina	1200 sccm	60.27/39.73 ± 2
ACCL-204	0.15 mmol	0.13 mmol	420°C	Alumina	1100 sccm	61.11/38.89 ± 1
ACCL-205	0.15 mmol	0.13 mmol	420°C	Alumina	1000 sccm	58.73/41.27 ± 2
ACCL-213	0.15 mmol	0.13 mmol	400°C	Alumina	1400 sccm	62.30/37.70 ± 1
ACCL-214	0.15 mmol	0.13 mmol	410°C	Alumina	1400 sccm	59.59/40.41 ± 1
ACCL-215	0.15 mmol	0.13 mmol	420°C	Alumina	1400 sccm	51.52/48.48 ± 0.7
ACCL-216	0.15 mmol	0.13 mmol	430°C	Alumina	1400 sccm	57.42/42.58 ± 0.8
ACCL-217	0.15 mmol	0.13 mmol	440°C	Alumina	1400 sccm	57.49/42.51 ± 0.6
ACCL-218	0.15 mmol	0.13 mmol	450°C	Alumina	1400 sccm	55.06/44.94 ± 0.7

Table 26. Relative Cu/Fe atomic ratio from EDX analysis of CFO-ACAC films deposited on quartz substrates with gas flow rate of 1400 sccm and the amount of Cu/Fe precursors of 0.15 mmol/0.15 mmol; while the deposition temperature varies from 325°C to 425 °C

Sample	n- [Cu(acac) ₂]	n- [Fe(acac) ₃]	Temperature	Substrate	Flow Rate	EDX Relative Cu/Fe at. %
ACAC-0	0.15 mmol	0.15 mmol	325°C	Quartz	1400 sccm	58.28/41.72 ± 0.9
ACAC-1	0.15 mmol	0.15 mmol	350°C	Quartz	1400 sccm	64.92/35.08 ± 0.6
ACAC-2	0.15 mmol	0.15 mmol	375°C	Quartz	1400 sccm	67.12/32.88 ± 0.4
ACAC-3	0.15 mmol	0.15 mmol	400°C	Quartz	1400 sccm	75.61/24.39 ± 2
ACAC-4	0.15 mmol	0.15 mmol	425°C	Quartz	1400 sccm	71.09/28.91 ± 1

Table 27. Relative Cu/Fe atomic ratio from EDX analysis of CFO-ACAC films deposited on quartz substrates at 350°C with the amount of Cu/Fe precursors of 0.15 mmol/ 0.15 mmol; gas flow rate varies from 1000 sccm to 1400 sccm

Sample	n- [Cu(acac) ₂]	n- [Fe(acac) ₃]	Temperature	Substrate	Flow Rate	EDX Relative Cu/Fe at. %
ACAC-5	0.15 mmol	0.15 mmol	350°C	Quartz	1000 sccm	60.79/39.21 ± 0.4
ACAC-6	0.15 mmol	0.15 mmol	350°C	Quartz	1100 sccm	56.90/43.10 ± 0.2
ACAC-7	0.15 mmol	0.15 mmol	350°C	Quartz	1200 sccm	60.43/39.56 ± 0.5
ACAC-8	0.15 mmol	0.15 mmol	350°C	Quartz	1300 sccm	60.74/39.26 ± 0.1
ACAC-1	0.15 mmol	0.15 mmol	350°C	Quartz	1400 sccm	64.92/35.08 ± 0.5

Table 28. Relative Cu/Fe atomic ratio from EDX analysis of CFO-ACAC films deposited on quartz substrates at 325°C with the amount of Cu/Fe precursors of 0.15 mmol/ 0.15 mmol; gas flow rate varies from 1000 sccm to 1400 sccm

Sample	n- [Cu(acac) ₂]	n- [Fe(acac) ₃]	Temperature	Substrate	Flow Rate	EDX Relative Cu/Fe at. %
ACAC-9	0.15 mmol	0.15 mmol	325°C	Quartz	1000 sccm	60.88/39.12 ± 0.4
ACAC-12	0.15 mmol	0.15 mmol	325°C	Quartz	1100 sccm	61.26/38.74 ± 0.5
ACAC-13	0.15 mmol	0.15 mmol	325°C	Quartz	1200 sccm	63.08/36.92 ± 0.8
ACAC-14	0.15 mmol	0.15 mmol	325°C	Quartz	1300 sccm	59.67/40.33 ± 0.4
ACAC-0	0.15 mmol	0.15 mmol	325°C	Quartz	1400 sccm	58.28/41.72 ± 0.9

Table 29. Investigation on the annealing temperature of CFO-ACAC deposited on quartz substrate in N₂ with a fixed duration of 5h and ramping rate of 10°C/min

Sample	Temperature	Duration	Gas Atmosphere	Ramping Rate	Substrate
ACAC-11-2	500°C	5h	N ₂	10°C/min	Quartz
ACAC-11-3	600°C	5h	N ₂	10°C/min	Quartz
ACAC-11-4	700°C	5h	N ₂	10°C/min	Quartz
ACAC-11-1	750°C	5h	N ₂	10°C/min	Quartz

Table 30. Investigation on the annealing duration of CFO-ACAC deposited on quartz substrate in N₂ at 750°C with a fixed ramping rate of 10°C/min

Sample	Temperature	Duration	Gas Atmosphere	Ramping Rate	Substrate
ACAC-35-1	750°C	30 min	N ₂	10°C/min	Quartz
ACAC-35-2	750°C	1h	N ₂	10°C/min	Quartz
ACAC-35-3	750°C	3h	N ₂	10°C/min	Quartz
ACAC-35-4	750°C	5h	N ₂	10°C/min	Quartz
ACAC-35-5	750°C	7h	N ₂	10°C/min	Quartz
ACAC-35-6	/	/	/	/	Quartz

Chapter 4. Gas sensing performance of Delafossite CuFeO_2 gas sensor with various morphologies

4.1 Introduction

In the last Chapter, Delafossite CuFeO_2 thin films were successfully deposited on different substrates using different precursors and solvents.

In this Chapter, the gas-sensing performance of Delafossite CuFeO_2 thin films deposited on Al_2O_3 substrates was measured in which many factors were evaluated, including the operating temperature, humidity and different gas environments. The influence of film morphology is discussed, and the gas-sensing mechanism is reviewed.

4.2 Experiment

The semiconducting metal oxide sensor response is greatly influenced by operating temperatures and gas concentration⁵⁹. Here, gas sensor response for the same material with different morphologies was measured simultaneously under identical experiment conditions⁹⁷.

CFO-ACCL, CFO-ACAC and CFO-CN films deposited on AGSS were evaluated as an effective p-type gas sensor material. Films deposited following the recipes shown in the **Table 21**.

4.2.1 Investigation of the CuFeO_2 gas sensors in response to oxidizing gas

Oxygen gas was considered to analyse the response, sensitivity and recovery speed of CuFeO_2 gas sensors towards oxidizing gas. N_2 (BOC), compressed air (BOC) and 2000 ppm oxygen (BOC) were used to adjust the concentration of oxygen. Different temperatures were applied during the change of oxygen concentrations (**Table 31** and **Table 32**). Before the gas-sensing measurements,

CuFeO₂ sensors were heated up under pure N₂ at 300°C to be aged and stabilized. Pure and dry N₂ was used as the background gas, the input of which started for at least 1h before each test to restore the sensors to the default state. Analysing of each group of mixed gas lasted for 5 minutes, and the relaxation time was 15 minutes.

Table 31. Variation of oxygen concentrations from 10,000 ppm to 200,000 sccm during gas sensing tests at operating temperatures ranging from 150°C to 300°C

N ₂ (vol.%)	Air (vol.%)	O ₂ (vol.%)	O ₂ (ppm)
95%	5%	1	10,000
75%	25%	5	50,000
50%	50%	10	100,000
0%	100%	20	200,000
T=300°C, 250°C, 200°C, 150°C			

Table 32. Variation of low oxygen concentrations from 0 sccm to 2,000 sccm during gas sensing tests at operating temperatures ranging from 150°C to 300°

N ₂ (vol.%)	2000 ppm O ₂ /N ₂ (vol.%)	O ₂ (vol.%)	O ₂ (ppm)
100%	0%	0	0
95%	5%	0.01	100
87.5%	12.5%	0.025	250
75%	25%	0.05	500
50%	50%	0.1	1,000
0%	100%	0.2	2,000
T=300°C, 250°C, 200°C, 150°C			

4.2.2 Investigation of humidity effect of CuFeO₂ sensors

Water vapour is an inevitable constitution to be considered by all the gas sensing measurements. Here, the sensor response to humidity was measured in a background of pure N₂ to exclude interference from O₂. N₂ gas was split into two gas lines from the cylinder. The first line was connected with a "cold trap" filled with dry ice and acetone (-78°C) to generate a dry gas stream, and the other line was connected to a flask and bubbled through deionized water to generate a humid gas stream. The two gas lines were mixed by a three-head adaptor before purging to the gas sensing analyser. The humidity was monitored by the humidity sensor at the gas outlet and was controlled by the ratio of N₂ bubbled through the

deionized water and dry N₂. Before each test, N₂ flowed for 1.5 hours to restore the sensors to the default state, as it took longer to recover to the initial baseline response after exposure to humidity. The analysing time of each group of mixed gas lasted for 30 minutes, and the relaxation time was 30 minutes. The output voltage of the Honeywell humidity sensor was set as shown in the **Table 33**.

Table 33. The output voltage of the Honeywell humidity sensor and the corresponding relative humidity

V_{dc}	Relative humidity (R.H.)
0.743	0%
1.047	10%
1.351	20%
1.959	40%
2.567	60%

4.2.3 Investigation of the activation energy of CuFeO₂ sensors

The resistivity of all CuFeO₂ gas sensors under dry N₂ or dry air was recorded for 15 min at each temperature and calculated based on the average value. The activation energies of the CuFeO₂ gas sensor were calculated, plotted and evaluated under dry N₂ and dry air atmospheres in the temperature range of 150°C to 300°C at intervals of 50°C in accordance with the Arrhenius relationship.

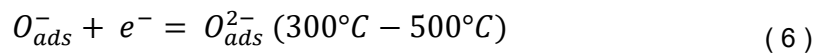
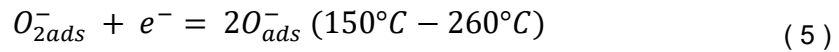
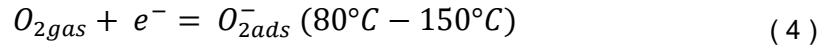
4.3 Results and discussion

4.3.1 The activation energy of CFO films towards dry air and dry N₂

The gas sensing mechanism is determined by the surface phenomenon, which is fundamentally a surface-related issue resulting in a change in sensor resistance that is highly related to the adsorption or depletion processes of target gases²⁹⁸. The whole process can be summarized into: oxygen adsorption on the sensitive layer structure, charge carriers transfer from material to oxygen, analyte gas adsorption, chemical reaction, charge carriers transfer to the semiconductor, and desorption of the products. The oxygen adsorption includes both physical and chemical process and plays the main role in sensing mechanism due to the high

affinity to the electron. Besides oxygen, water molecules and hydroxide groups can also be absorbed on the semiconducting metal oxide material's surface.

Depending on the temperature^{299,300}, oxygen species can be generated as the form of O_2^- , O^- and O^{2-} :



The adsorbed oxygen species trap electrons and form a depletion layer, which causes changes in the electrical conductivity of the sensing layers²⁹⁸.

Since the detection of a specific gas partially depends on the thermodynamic of gas absorption on the surface of semiconductor materials, the gas sensing performance is highly related to the operating temperature. For a given sensor, the highest response for a specific gas is obtained at a specific temperature, where the equilibrium is reached between the adsorption and desorption rate²⁹⁸. Therefore, the fast adsorption-desorption cycle of chemisorbed oxygen on the surface is highly desirable in excellent gas sensors.

Furthermore, the activation energy required for the reaction occurring during detection is reached at the optimal temperature. Depending on gas sensing conditions, adjusting the sensor's operating temperature can be a common method to improve gas sensing performance²⁹⁸. Therefore, understanding the activation energy required by various gases is crucial to understand the use of $CuFeO_2$ as a p-type gas-sensing material.

The relationship between the electrical resistance of semiconducting gas sensors and the ambient temperature can be described as follows³⁰¹:

$$R = R_0 e^{\left(-\frac{E_a}{k_B T}\right)} \quad (7)$$

Where R is the resistance of the sensor after contacting the analyte gas, R_0 is the resistance before contacting the analyte gas, k_B is the Boltzmann constant, E_a is the activation energy, and T is the ambient temperature in Kelvin. Therefore, we conducted the resistance test for three CFO sensors at different temperatures in dry N_2 and dry Air atmospheres.

The Arrhenius plots (**Figure 60**) showed that the activation energy of conductance of the three CFO films is very close. However, a slight difference exists, either in dry air or N_2 atmosphere, such as ACAC has the lowest activation energy in all three environments.

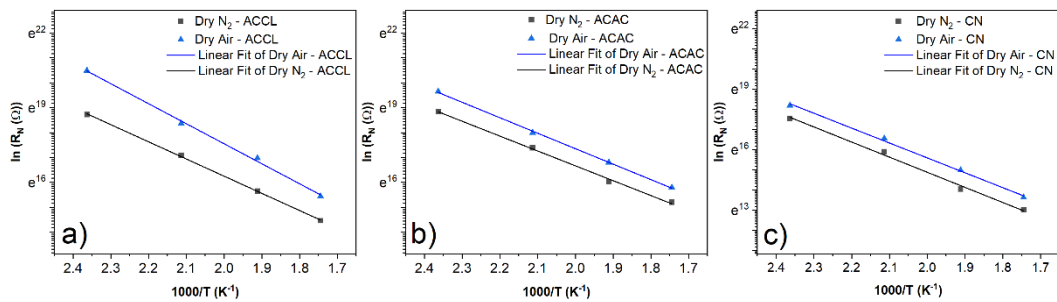


Figure 60. Arrhenius plots of a) CFO-ACCL, b) CFO-ACAC, and c) CFO-CN films in dry N_2 and dry air gas atmosphere

Table 34. Activation energy of CFO-ACCL, CFO-ACAC and CFO-CN films calculated from Arrhenius plots in dry air and dry N_2 atmosphere

	Slope	r	Ea (kJ/mol)	Ea (eV)
ACCL-Dry Air	7.80259	0.99879	65	0.67
ACAC-Dry Air	6.44491	0.99955	54	0.56
CN-Dry Air	7.12946	0.99903	59	0.61
ACCL-Dry N_2	6.69753	0.99892	56	0.58
ACAC- Dry N_2	5.89246	0.9992	49	0.51
CN- Dry N_2	7.2904	0.99494	61	0.63

The activation energies have been calculated and summarized in **Table 34**, where three CFO sensors showed slight energy differences when testing the same analyte gas. Overall, more energy is needed to overcome the energy barrier in dried air (oxygen atmosphere) than in dry N_2 atmosphere, i.e. the presence of oxygen increases the barrier to conduction. Also, in CFO-ACAC, this energy barrier

is relatively smaller than the other samples in both air and N₂, which might be from the its morphology that the grain size is neither too small nor too large, which means the conductance may not be fully controlled by charges on the grain surface, nor be limited by the Schottky barrier at grain boundaries ⁵⁸, compared with the CFO-ACCL and CFO-CN (**Figure 61**) .

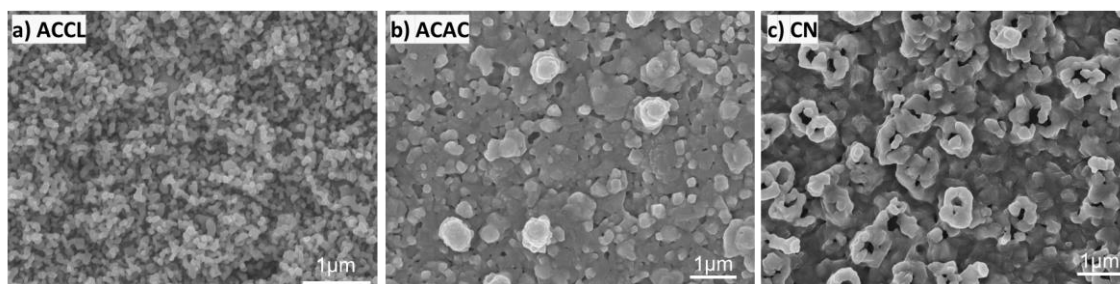


Figure 61. SEM images of a) CFO-ACCL, b) CFO-ACAC, and c) CFO-CN films deposited on alumina substrates

4.3.2 The gas sensing performance of CFO films towards oxidizing analyte gas

Oxygen and N₂ gas were first applied to understand the response of CFO films towards oxygen (**Figure 62**), which can not only provide us with CFO film's gas sensing ability towards oxidizing gas but also illustrate the fundamental defect chemistry at the surface of the material. The operating temperature was varied from 150°C (below which temperature the resistance became challenging to measure, **Figure 62 c), e), g)** to 300°C at intervals of 50°C. Above 300°C, after heating in an oxygen-containing atmosphere, the oxygen state on the surface of Delafossite CuFeO₂ might be changed (which had been indicated by the PEC thermal stability of Delafossite CFO films, which is presented in **Section 6.3.2**). Hence, the sensors were not tested above this temperature. The volume percentage of oxygen and nitrogen gas was altered to evaluate and compare the sensitivity of different sensors (**Figure 62**).

As shown in **Figure 62 a)**, CFO-ACCL showed the expected 'p-type response' towards oxygen (resistance decreases), while CFO-ACAC and CFO-CN

unexpectedly showed 'n-type responses'. It can be seen that at 150°C, the sensitivity was relatively poor compare with the sensitivities at 200°C, 250°C and 300°C (**Figure 62 d), f), h)**). Specifically, the response in **Figure 62 f)** at 150°C was relatively high due to the noisy background, since the results are calculated from the average number. As the operating temperature increased, all three CFO sensors showed better sensitivity.

Moreover, with the increased operating temperature, gas sensors took less time to respond towards the analyte gas (**Figure 62 g)**). Also, they had a faster speed (better performance) in recovering to the initial resistance when the analyte gas was switched off (**Figure 62 g)**). This phenomenon suggests that the surface oxygen species have an impact on the kinetics of the gas-sensing reactions, and the forward reaction speed is faster than the recovery reaction because it is easier and faster to heal the oxygen vacancy than generate it. As the temperature increases, this healing-generating process is easier due to the increased energy used to break the metal-oxygen bonds.

Here, the volume percentage of O₂ in the analyte gas was up to ~20% (the same setting as the compressed air). To continue investigating the sensitivity of CFO gas sensors, three CFO gas sensors were tested to lower concentrations of oxygen (2000 ppm O₂ mixed with dry N₂) at different temperatures.

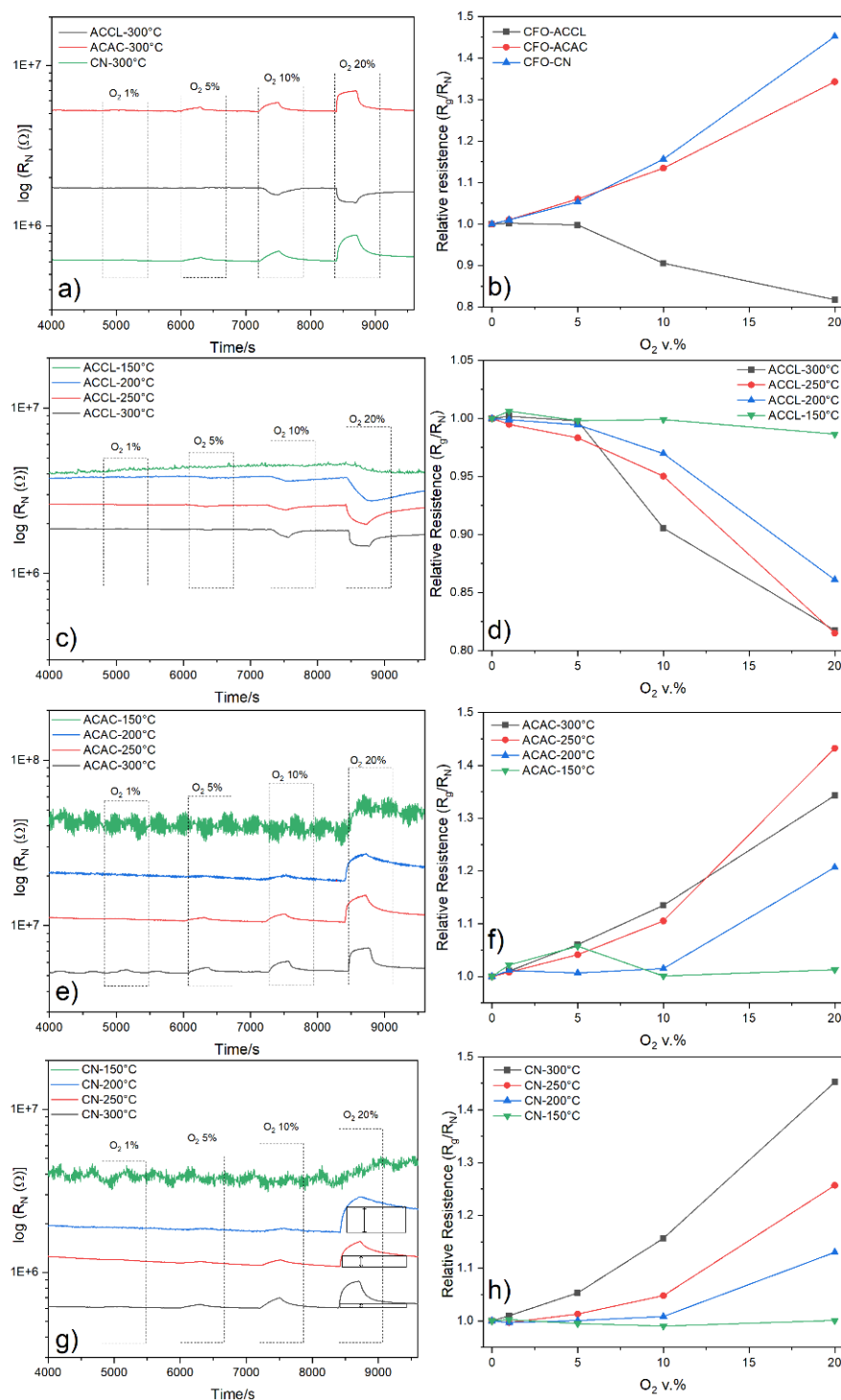


Figure 62. a) Gas-sensing response of three CFO films towards different concentrations of oxygen at 300°C, b) sensitivity of three CFO films towards different concentrations of oxygen at 300°C, c) gas-sensing response of CFO-ACCL film towards different concentrations of oxygen from 150°C to 300°C; d) sensitivity of CFO-ACCL film towards different concentrations of oxygen from 150°C to 300°C, e) gas-sensing response of CFO-ACAC film towards different concentrations of oxygen from 150°C to 300°C; f) the sensitivity of CFO-ACAC film towards different concentrations of oxygen from 150°C to 300°C, g) gas-sensing response of CFO-CN film

towards different concentrations of oxygen from 150°C to 300°C, and the comparison of the response rate and recovery rate when the oxygen volume is 20%; h) sensitivity of CFO-CN film towards different concentrations of oxygen from 150°C to 300°C

4.3.3 Sensitivity of CFO gas sensors towards oxidized analyte gas with low concentrations

To further investigate the sensitivity of CFO gas sensors, three CFO gas sensors were tested under 2000 ppm O₂ mixed with dry N₂ at different temperatures.

The resistance of each CFO gas sensor remains similar, showing a trend of $R_{ACAC} > R_{ACCL} > R_{CN}$. This trend can be illustrated by the influence of the film's morphology (as shown in **Figure 61**), in which the differences in grain boundaries and grain size can reflect on the gas sensing performance.

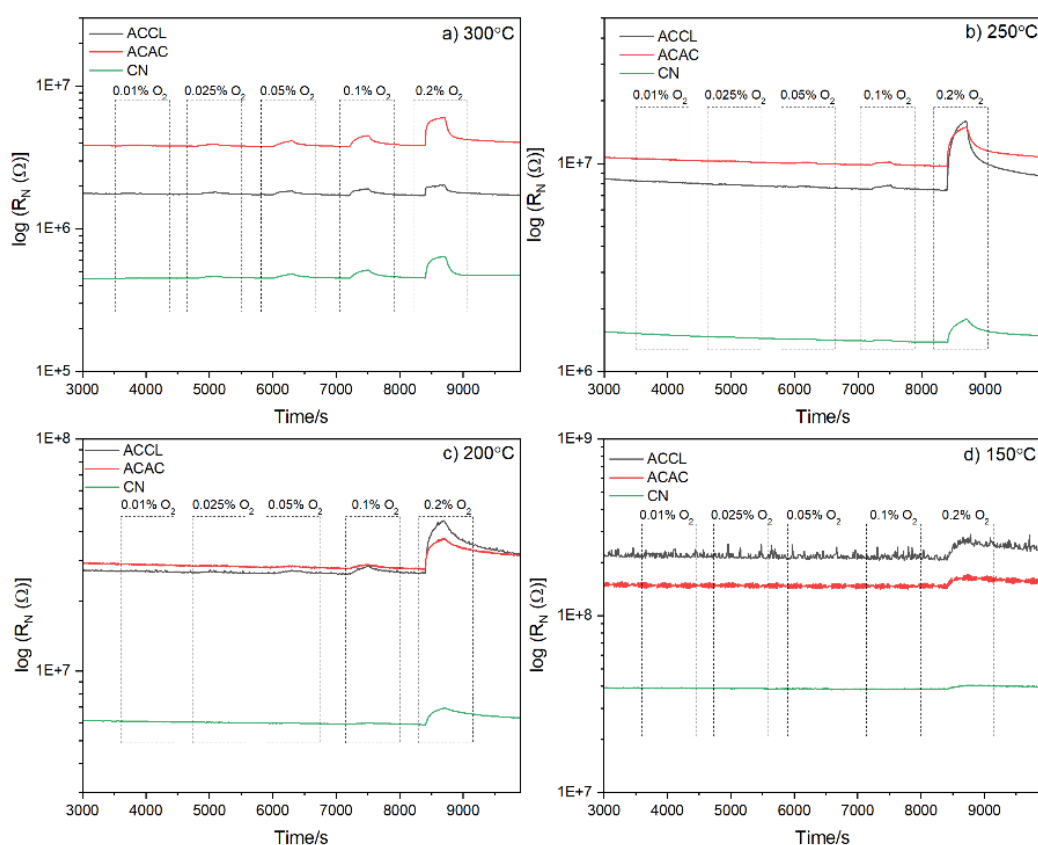


Figure 63. Gas sensing response of three CFO films towards low concentrations of oxygen gas at different temperatures ranging from 150°C to 300°C

Still, at 300°C, all three CFO sensors demonstrated the best performance compared to measurements taken at 150°C, 200°C, and 250°C. The sensors exhibited high sensitivity, rapid recovery speed, and a significant recovery degree at this temperature, indicating a convincingly high degree of repeatability. In **Figure 63 a)**, CFO gas sensors responded to O₂ from 100 ppm, suggesting a reasonable sensitivity, while the commercial O₂ gas sensor can guarantee an accuracy of ± 0.1 ppb (for example, Orbisphere GA2800 ATEX electrochemical oxygen sensor).

However, unlike previous tests, all the CFO gas sensors showed n-type gas sensing properties, while CFO-ACCL previously showed a p-type response to higher oxygen concentrations. An n-type to p-type transition in CFO-ACCL film was observed as the concentration of the oxygen was increased. However, the low-concentration analyte oxygen environment was tested after the high concentration.

Note that semiconductor oxides based gas sensors were classified upon the sign of the resistance change. If being exposed to reducing gases such as H₂O, CO, EtOH and the resistance increases, the material is classified as “n”-type while if resistance decreases, the material is classified as “p”-type. This classification corresponds to the surface conductivity of the oxides which is determined by the nature of the major charge carriers at the surface, i.e. holes or electrons³⁰². The changing the behaviours of the oxides from either n-to-p or p-to-n have been recorded in single materials such as SnO₂^{303–305}, In₂O₃³⁰⁶ and Fe₂O₃^{307,308}, or mixtures of n- and p-type oxides³⁰⁹, which relates to the dominating contribution of one of the material in the overall conductivity.

The explanation of the switching from one type to the other was summarized into 1) different kind of surface reactions in different conditions such as humidity, temperature, composition, etc ³⁰⁶or 2) the change of surface type of conduction induced by either special ambient conditions such as pure oxygen treatment³⁰⁵ or additives³⁰⁴ and the detailed phase transformation is discussed in **Chapter 6**).

The low-temperature annealing under N₂ could not convert the CuFe₂O₄ phase back to CuFeO₂ due to insufficient energy, and therefore, the film exhibited an n-type character. Another possibility is that the Delafossite phase was decomposed, and the CuO, Fe₂O₃ phase and amorphous phase appeared, which leads to a n-type character.

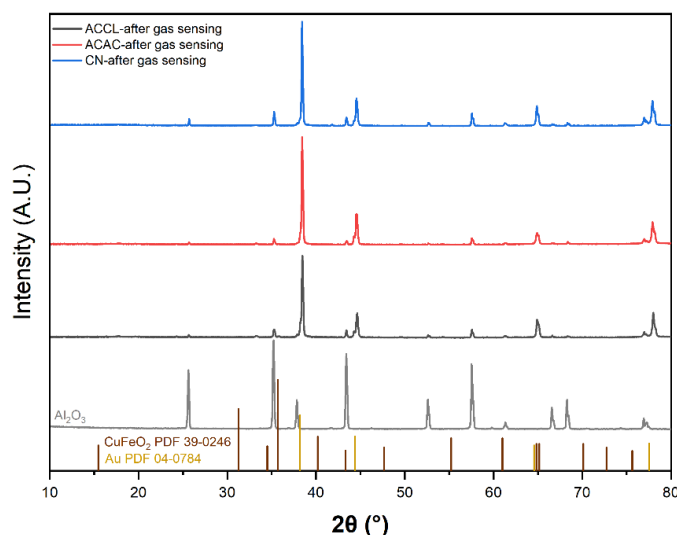


Figure 64. Integrated microfocus XRD patterns of three CFO films after gas sensing tests

Microfocus XRD has a much smaller X-ray beam size compared with conventional XRD which allows for the analysis of very small or localized areas of a sample, down to the micrometre. As we mentioned previously, CuFeO₂ gas sensors were deposited on AGGS for the measurement of gas sensing performance. Therefore, to conduct XRD analysis on CuFeO₂ thin films after being measured for gas-sensing tests, microfocus XRD was applied.

Microfocus XRD patterns of three CFO gas sensors was conducted after all the gas sensing tests (**Figure 64**). According to Microfocus XRD's results, peaks from the Al₂O₃ substrate and Au electrode can be clearly observed. In contrast, Delafossite CuFeO₂, CuO, and CuFe₂O₄ peaks were not found. It is hard to conclude with concrete evidence, but it is likely to be the second assumption that the Delafossite phase decomposed during ageing and testing.

The temperature has a more significant impact on gas sensors' sensitivity at lower oxygen concentrations. At 250°C, CFO-ACAC and CFO-CN showed a similar response, but the response can only be seen from 500 ppm. When the oxygen concentration was 2000 ppm, the recovery rate and the recovery degree at 250°C significantly reduced. However, CFO-ACCL showed a significant increase in the response at 250°C when O₂ concentration was at 2000 ppm, where the sensitivity was larger than CFO-ACCL and CFO-CN and much larger than itself at 300°C.

Moreover, the CFO-ACCL gas sensor's resistance increased to the same degree as CFO-ACAC when the temperature decreased to 200°C, still showing a better sensitivity than CFO-ACCL and CFO-CN gas sensors. According to the activation energy test results in **Section 4.3.1**, the smaller energy barrier observed for ACAC films illustrates why there is a swapover of baseline resistance between different samples as a function of temperature.

At 150°C, all three CFO gas sensors only showed a response towards the oxygen with a concentration of 2000 ppm. Here, the response speed was much slower than the higher temperatures. They can hardly be recovered to the initial resistance due to insufficient energy to heal surface oxygen vacancies, which requires breaking the O=O molecular bond after one end interacts with the vacancy.

4.3.4 The gas sensing performance of CFO gas sensors towards humidity resistance

Water molecules increases the conductivity of n-type semiconductors and decreases the conductivity of p-type semiconductors, which can be explained as the donation of electrons from the chemically absorbed water molecules to the semiconducting metal oxide's surface. An alternative explanation suggested that the water molecules replace the previously adsorbed and ionized oxygen (O⁻, O²⁻, etc) and consequently discharge the electrons from the ionized oxygen³¹⁰.

The performance of three CFO gas sensors in the presence of variable humidity in the analyte gas was evaluated to compare CFO films' sensitivity towards humidity. In the O₂-sensing tests, ACCL provided a p-type response (**Figure 62**), while in the humidity-sensing tests, ACCL provided an n-type response. The ACAC sensors showed an n-type response in both environments, but ACAC showed a higher response towards oxygen than towards humidity. In contrast, the CFO-CN sensor showed better sensitivity in the humidity test.

Besides the response towards oxidized analyte gas, CFO gas sensors tested the response towards humidity. **Figure 65 a)** shows how CFO gas sensors' resistance changed towards the different humidity at 300°C. The CFO-CN sensor showed greater sensitivity towards H₂O than CFO-ACAC CFO-ACCL, with all three CFO sensors presenting an 'n-type response' to water.

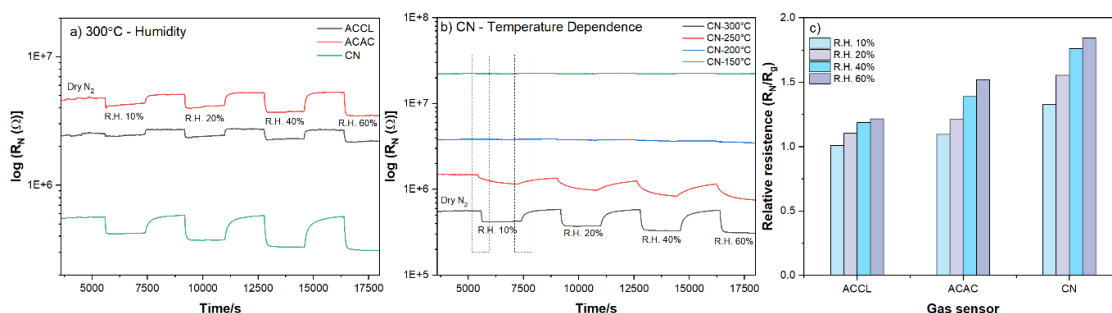


Figure 65. a) Gas-sensing response of three CFO gas sensing films towards different relative humidity at 300°C; b) gas-sensing response of the CFO-CN film towards different relative humidity at different temperatures ranging from 150°C to 300°C; and c) the comparison of three CFO films' response towards different relative humidity

As the temperature decreases, the humidity response changes and significantly influences the recovery and response speed (**Figure 65 b**). The same trend was shown by CFO-ACCL and CFO-ACAC gas sensors. The decreased degree of sensitivity of CFO-ACCL and CFO-ACAC were slightly smaller than CFO-CN sensors and were summarized in **Figure 65 c**).

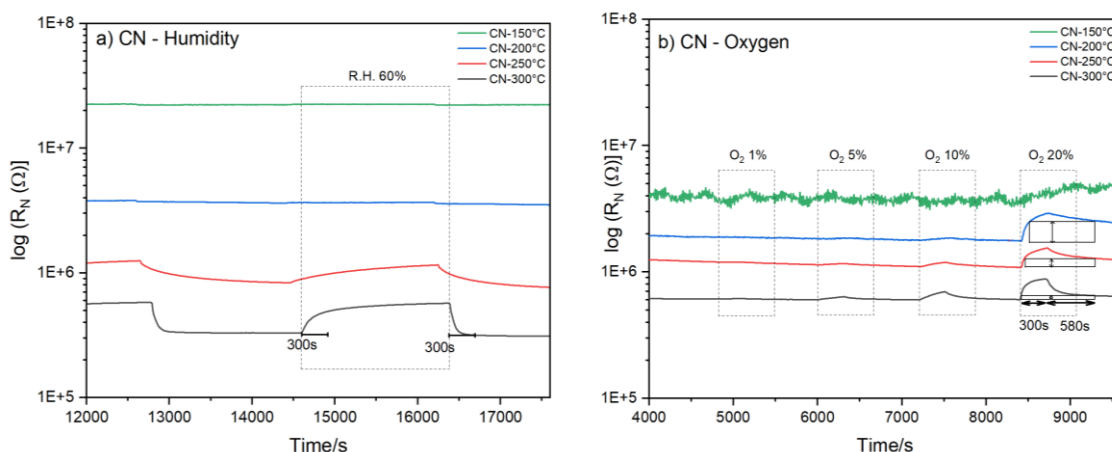


Figure 66. Comparison of the gas-sensing response and recovery rate of CFO-CN films towards (Left) humidity (R.H. = 60%) and (Right) different concentrations of oxygen at different temperatures ranging from 150°C to 300°C

The response to O₂ with temperature for CFO-CN with the response to H₂O with temperature was compared in **Figure 66**. A 1% O₂ atmosphere (10,000 ppm O₂) has an approximately similar ‘active species’ concentration to H₂O at 60% relative humidity (~ 17,000 ppm H₂O), providing a relatable benchmark for understanding the sensitivity of CFO films to humidity levels. Notably, the response rate and recovery rate are much faster in a 60% RH environment than in 1% O₂ environment. It was only when a 20% O₂ environment (200,000 ppm O₂) was employed for testing that similar results were achieved. This suggests quite different chemistry reaction observed when CFO films interacts with humidity and O₂ compared to interactions to H₂O. It highlights that p-type CuFeO₂ gas sensors are more sensitive towards humidity than oxidizing gas.

4.4 Summary

There are few studies focusing on the gas sensing performance of CuFeO₂, apart from it being measured as an alcohol¹²³ sensor and for oxygen detection³¹¹.

This chapter addresses the gap in research regarding the application of CuFeO₂ as a gas sensor, particularly in environments containing N₂, O₂, and humidity, while the analysis of the activation energy of N₂ and O₂ was also conducted. Furthermore,

it investigates how variations in film morphology affect gas sensing performance, providing valuable insights for improving the gas sensing performance of p-type CuFeO_2 thin film in the future.

In summary, the gas sensing measurements, three CFO gas sensors responded to the analyte O_2 gas at different concentrations at different temperatures. The gas sensing sensitivity showed temperature dependence, whereas gas sensors have higher sensitivity in the oxygen and humidity tests.

ACCL gas sensor showed p-type behaviour at the beginning, in the different analyte gases where oxygen/nitrogen proportion changes from 1% to 20%. However, the CFO-ACCL gas sensor consistently behaved as an n-type gas sensor in further low concentrations of oxygen and humidity tests. CFO-ACAC and CFO-CN sensors presented n-type properties from the beginning to the end for all the tests. This result shows the similarity to Patsch et al., who reported the p-n type gas sensing behaviour transition in Delafossite CuFeO_2 inorganic nanowires, in which the CuFeO_2 nanowires were used to detect oxygen target gas at 200°C and 500°C and showed p-type and n-type gas sensing behaviours respectively¹²⁸. Their research indicated that the p-n behaviour transitioned from low temperature to high temperature, but the phase composite at 500°C was not confirmed. Therefore, whether it is CuFeO_2 or the converted CuFe_2O_4 phase that showed the n-type behaviour remains unclear.

In this research, gas sensors with n-type behaviours were tested under micro-focused XRD. The results indicated that the Delafossite phase was decomposed under constant heating while being exposed to oxygen and humid environments, therefore leading to this p-to-n transition.

Combined with the annealing stability results from **Chapter 6**, it is speculated that after extended gas sensing tests under at least a partial O_2 atmosphere, the CuFeO_2 phase in all three CFO sensors was decomposed. N-type CuFe_2O_4 phase

might be formed gradually and, therefore, was shown as an n-p convert in the CFO-ACCL gas sensor and the stable n-type performance in CFO-ACAC and CFO-CN sensors. Low-temperature annealing under N₂ could not convert the CuFe₂O₄ phase back to CuFeO₂ due to insufficient energy to overcome the barrier. Therefore, gas sensors were not utterly relaxed to the original testing point.

In further investigation, it would be worth trying to anneal the gas sensors at 750°C and relax them under dry N₂ after each test to see if the gas-sensing performance is reversible, which will provide insights in the reusability and lifetime of CuFeO₂ gas sensor.

Chapter 5. Synthesis, Morphology Modification and Photoactivity of p-type Delafossite CuFeO_2 Thin Film

5.1 Introduction

In the previous chapter, CFO-ACCL, ACAC, and CN films were successfully deposited on various substrates using AACVD and a post-deposition treatment. Specifically, gas sensor tests were conducted on films deposited on alumina substrate and AGSS, revealing variations in gas sensing ability among the three CFO films.

It is worth noting that film morphology undergoes changes based on different precursors, solvents, and substrates employed. Therefore, if a comprehensive understanding of the influence factors on film morphology could be achieved, it should be possible to optimize and enhance the performance of CFO films in diverse applications.

In this chapter, our main objective was to deposit the three types of CFO films onto ITO-quartz substrates, with a specific focus on their application as photocathode materials to facilitate photocurrent generation and water-splitting reactions. Some CFO films were deposited on quartz substrates for characterization, where ITO interference was excluded. Notably, a correlation was observed between the film thickness and the quantities of precursor and solvent utilized during AACVD. This correlation allowed us to adjust the film thickness, accordingly, enabling further investigation into the impact of thickness on the film's photo-performance.

To evaluate the photocathodic activity of the three types of CFO films, LSV tests with chopped light were performed, allowing a comparison between background current and photocurrents to elucidate the films' photo performance.

To further deepen our understanding of the impact of film morphology and thickness on the material's photocathodic reactivity and explain the charge carrier's transporting mechanism, TAS experiments were conducted, providing additional support and insights.

5.2 Experiment

5.2.1 Deposition of Delafossite CuFeO_2 with well-controlled morphology

Delafossite CuFeO_2 thin films were synthesized by aerosol-assisted chemical vapour deposition (AACVD) with the post-deposition treatment in the tube furnace (**Figure 67**). All the films for photoelectrochemical (PEC) measurement were deposited on conductive ITO-quartz substrates (6-8 Ω , 2×2 cm, South China Science & Technology Company Limited). The substrate was cut into four pieces for the reproducibility test, and a 0.5×2 cm square was left uncoated to ensure the electrical connection could be made to the CFO films.

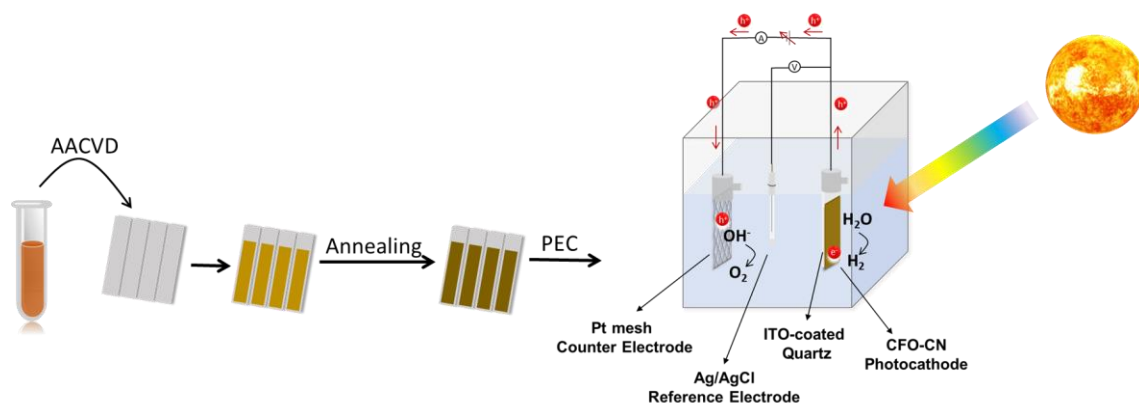


Figure 67. Schematic of CFO films being deposited via AACVD, being annealed and then being used as photocathode

5.2.1.1 From $[\text{Cu}(\text{acac})_2]$, $[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]$ and 30 cm^3 methanol (CFO-ACCL)

In this chapter, standard CFO-ACCL thin film was deposited as follow: $[\text{Cu}(\text{acac})_2]$ (0.15 mmol) and $[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]$ (0.13 mmol) were added into methanol (30 cm^3) and then sonicated at room temperature until dissolved completely. The mixed precursors were aerosolised with the aerosol transferred by N_2 gas (flow rate of

1400 sccm, oxygen-free nitrogen, BOC) to the reaction chamber. The reaction temperature was 450°C, and a yellow-brownish film was obtained from the CVD reaction. After being annealed in the N₂ atmosphere at 750°C for 5 hours, Delafossite CuFeO₂ was obtained.

5.2.1.2 From [Cu(acac)₂], [Fe(acac)₃] and 30 cm³ methanol (CFO-ACAC)

In this chapter, standard CFO-ACAC thin film was deposited as follow: [Cu(acac)₂] (0.10 mmol) and [Fe(acac)₃] (0.15 mmol) were added into methanol (30 cm³) and then sonicated at room temperature until dissolved completely. The mixed precursors were aerosolised and then passed into the reaction chamber by N₂ (flow rate of 1000 sccm, oxygen-free nitrogen, BOC). The reaction temperature was 320°C, and a dark-bluish film was obtained. After being annealed in an N₂ atmosphere at 750°C for 5 hours, Delafossite CuFeO₂ was formed.

5.2.1.3 From [Cu(acac)₂], [Fe(acac)₃] and 30 cm³ acetonitrile (CFO-CN)

In this chapter, standard CFO-CN thin film was deposited as follow: [Cu(acac)₂] (0.13 mmol) and [Fe(acac)₃] (0.15 mmol) were added into acetonitrile (30 cm³) and then sonicated at room temperature until dissolved completely. The N₂ flow rate was 1000 sccm to transfer the aerosol from mixed precursors to the reactor. The reaction temperature was 350°C, and a deep greyish film was obtained. The film was annealed at 750°C for 5 hours, and the Delafossite CuFeO₂ phase was achieved.

5.2.2 Deposition of Delafossite CuFeO_2 with finely adjusted thickness

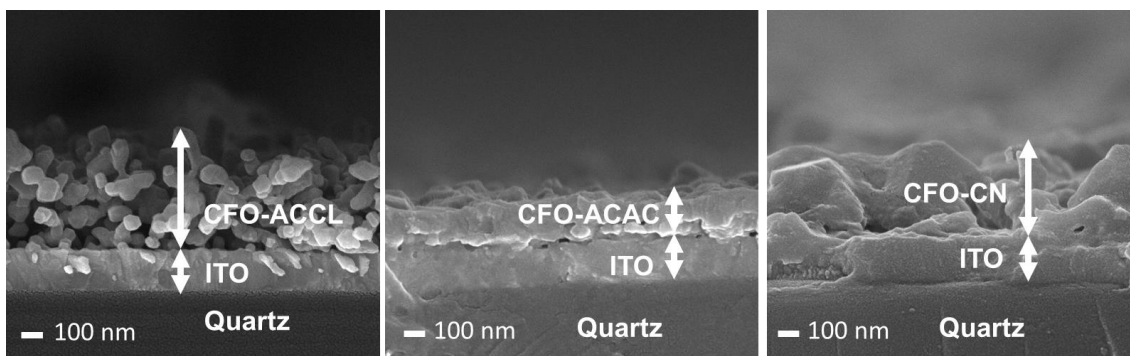


Figure 68. SEM images showing accurate measurement of film thickness of CFO-ACCL, CFO-ACAC, and CFO-CN deposited on ITO-quartz substrate

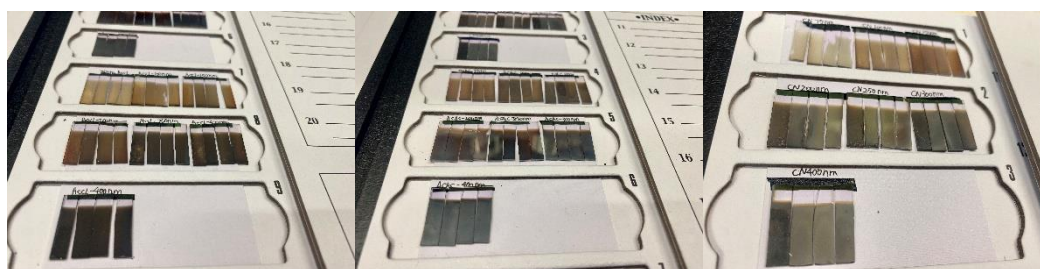


Figure 69. Digital photos of three types of CFO photocathode deposited on ITO-quartz substrate with different thicknesses

As discussed in **Section 5.2**, Cu/Fe precursors with 30 cm^3 solvent are regarded as a standard precursor solution volume for three CFO films. By depositing films with 7.5 ml, 15 ml, 22.5 ml and 30 ml standard precursor-solvent solutions and analysing the films' cross-section from SEM (**Figure 68**), an approximately linear correlation between the films' thickness (**Figure 69**) and volume of precursor-solvent solution was plotted (**Figure 70**); more than 10 positions were selected during the cross-section measurement, and the average results were chosen for the plot to ensure accuracy. In this way, the thickness of three CFO films was subsequently fine-adjusted.

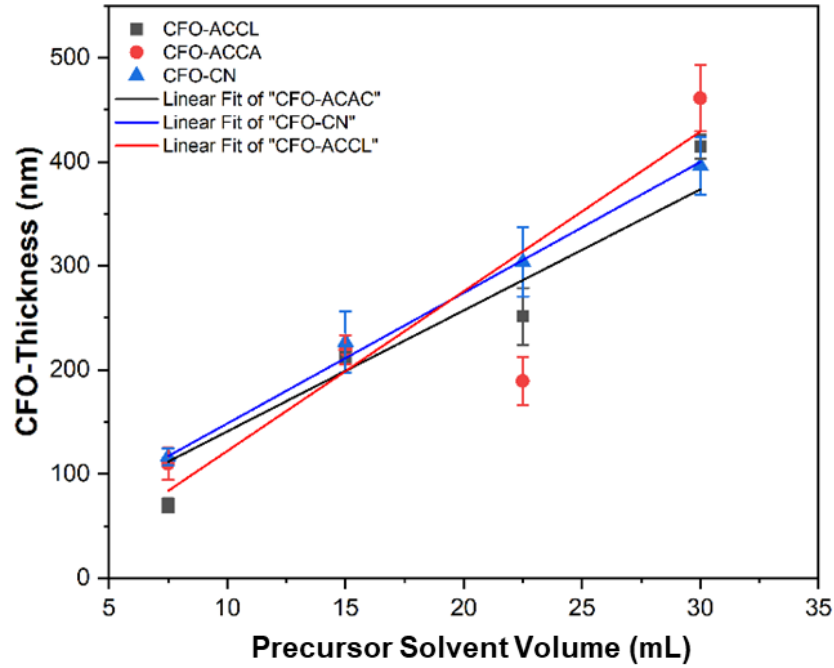


Figure 70. Correlation of film thickness and the precursor-solvent volume in three CFO films

The linear plot of three CFO film thicknesses can be summarized as follows:

$$\text{ACCL thickness (nm)} = 460.5 \times V_{\text{precursor solution}} \% \times 30 \text{ ml} - 31.3 \quad (8)$$

$$\text{ACCA thickness (nm)} = 450.5 \times V_{\text{precursor solution}} \% \times 30 \text{ ml} - 38.3 \quad (9)$$

$$\text{CN thickness (nm)} = 354.1 \times V_{\text{precursor solution}} \% \times 30 \text{ ml} + 42 \quad (10)$$

5.2.3 Investigation of the PEC measurement conditions

5.2.3.1 pH effect

In the literature ^{113,131,134,135,144,145}, NaOH is widely used as the electrolyte in the PEC measurement for the CuFeO₂ electrode. Reflecting on the previous work, the pH effect was investigated in this section to understand what the optimum PEC measurement conditions were. Here, a buffer solution was initially considered to investigate the pH effect. 0.1 M potassium phosphate buffer solution was synthesized using KH₂PO₄ and K₂HPO₄. Buffer solutions with pH=6, 7, and 8 were chosen to be tested on CFO-ACCL films (**Table 35**).

Table 35. Volume of 1M K₂HPO₄ and 1M KH₂PO₄ solution used to synthesize buffer solution with pH = 6, 7 and 8

Desired pH	The volume of 1M K ₂ HPO ₄ (ml)	The volume of 1M KH ₂ PO ₄ (ml)
6.0	13.2	86.8
7.0	1.5	38.5
8.0	94.0	6.0

5.2.3.2 Selection of the electrolyte

The investigation of the pH effect suggested several electrolytes that could be used to measure CuFeO₂'s photoelectric properties. NaOH, Na₂SO₄, NaHCO₃, and HCl solutions were prepared in the lab, and the LSV of the CuFeO₂ photocathodes was performed as a comparison using deionized water as the background.

During PEC measurements, 10% 0.1 M Na₂S₂O₈ was applied as the electron scavenger in some testing environments to slow down the electron-hole recombination rate and reflect the CFO film's photoelectrochemical potential.

5.2.3.3 Gas atmosphere

In this section, 1M NaOH was used as the electrolyte. The effect of the electrolyte's gas ambient on the CuFeO₂'s photo-performance was explored. 100 sccm O₂ or 100 sccm N₂ gas was purged into the PEC cell for more than 20 minutes before conducting each PEC measurement. As a comparison, a PEC cell without purging any gas will be regarded as an "Air atmosphere".

5.3 Result and discussion

5.3.1 Characterization of three CFO films

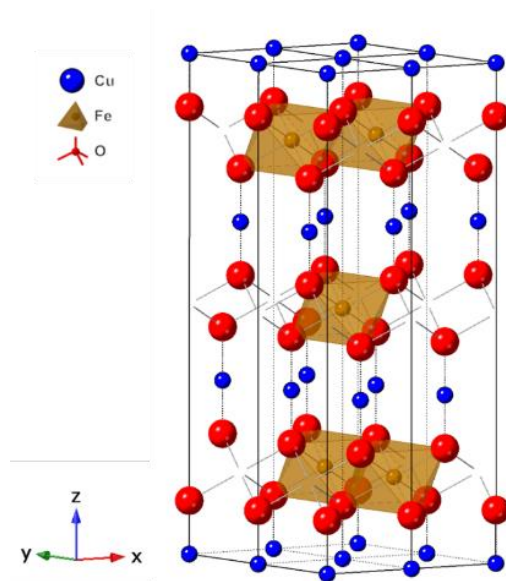


Figure 71. Crystal structure of Delafossite 3R-CuFeO₂

The crystal structure (**Figure 71**) of three CFO films has been structurally characterized by X-ray diffraction after annealing. The ITO peaks can be found by comparing the peaks with pure ITO-quartz substrate. No additional peaks were found, such as CuFe₂O₄, CuO (from the intermediate phase), and Fe₂O₃ (from the starting metal oxides).

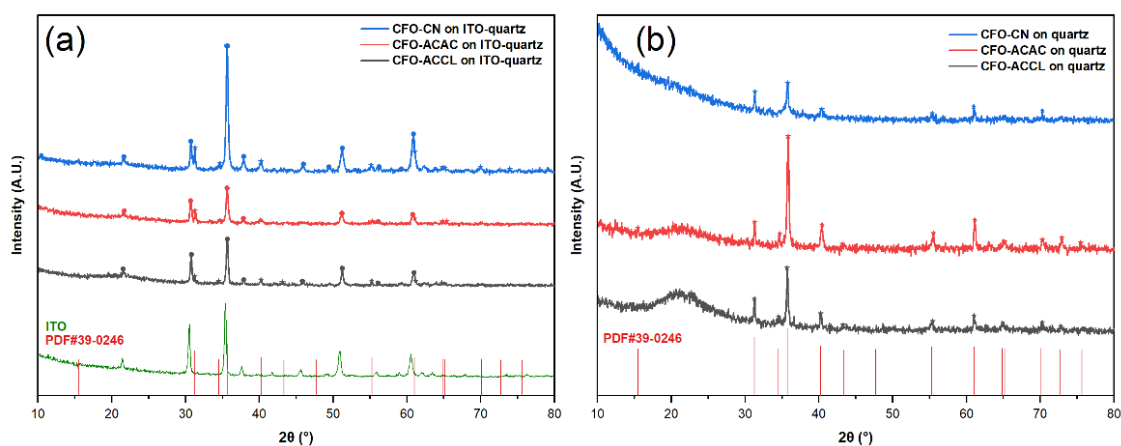


Figure 72. Integrated XRD patterns of CFO-ACCL, CFO-ACAC and CFO-CN films on a) ITO-quartz and b) quartz substrate

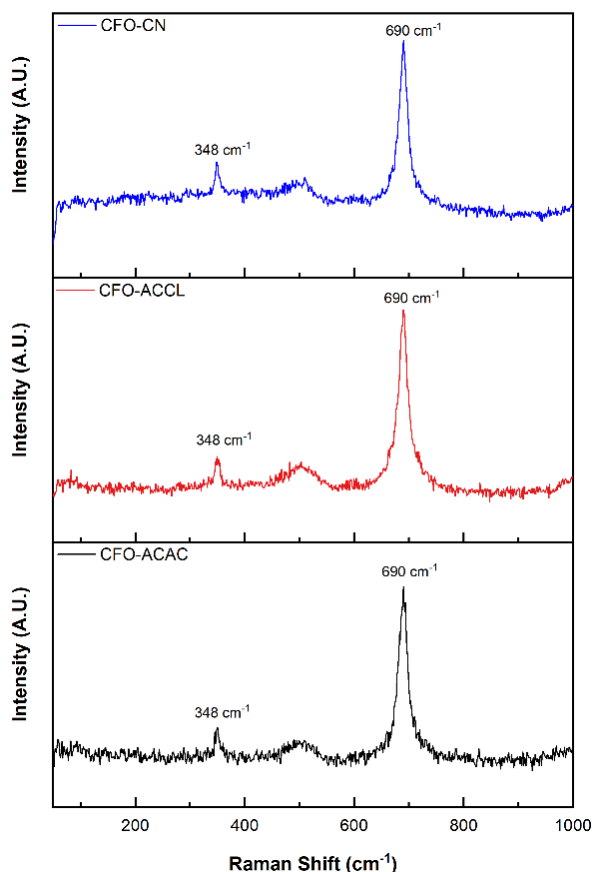


Figure 73. Integrated Raman spectroscopy of CFO-ACCL, CFO-ACAC and CFO-CN films deposited on ITO-quartz

Raman spectroscopy also confirmed the Delafossite CuFeO_2 phase via two relatively sharp characteristic peaks at ~ 348 and $\sim 688 \text{ cm}^{-1}$ ¹¹³. Here, a referenced Raman spectrum of Delafossite CuFeO_2 from the RRUFF database³⁶ showed the fingerprint location of peaks at $\sim 348 \text{ cm}^{-1}$, $\sim 500 \text{ cm}^{-1}$, and $\sim 690 \text{ cm}^{-1}$ (**Figure 73**).

Delafossite-type structures are characterised by the rhombohedral symmetry of the space group C_{3v} ⁶ and the point group C_{3v} , and these vibrations can be described by the reducible representation by $1A_{1g} + 3A_{2u} + 1E_g + 3E_u$ ²²³.

The A symmetry illustrates the vibrations perpendicular to the c-axis (octahedral structure). The inversion centre located Cu atom, which leads to a result that only even modes (sub-index g, A_{1g} and E_g) are Raman active^{294–296}. While the other odd vibration mode (A_{2u} and E_u) have only acoustic vibrations, which is invisible in the

Raman spectroscopy. Therefore, the peak located at 348 cm^{-1} can be allocated to E_g vibration and peak located at 690 cm^{-1} to A_{1g} vibration mode. The peak located at 500 cm^{-1} can be related to a surface plasmonic resonance of the material mixture²²³.

Energy Dispersive X-ray spectroscopy (EDX) analysed the as-deposited CFO films to determine the element ratios. Five points were randomly selected for each film (**Figure 74**). Therefore, the average relative ratio of Cu/Fe deposited in the CFO films was calculated alongside the standard deviation and standard error, indicating that the atomic ratio of Cu and Fe deposited on the film is the same in all cases (**Table 36**).

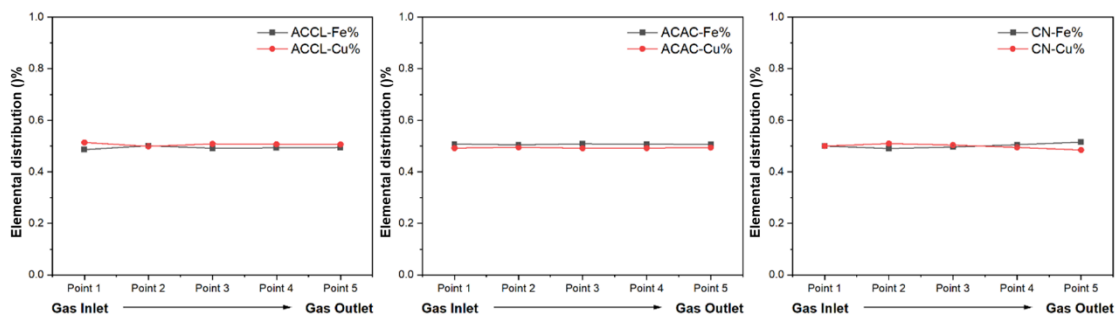


Figure 74. Diagrams of Cu/Fe relative atomic ratios obtained from five points in the EDX analysis for as-deposited a) CFO-ACCL; b) CFO-ACAC; c) CFO-CN films under optimal deposition conditions

Table 36. EDX analysis results of Cu/Fe relative atomic ratios obtained from five points in three types of as-deposited CFO films under optimal deposition conditions

CFO on ITO-quartz	Mean - Cu (at. %)	Mean - Fe (at. %)	Standard Deviation - Cu (at. %)	Standard Deviation - Fe (at. %)	Standard error - Cu (at. %)	Standard error - Fe (at. %)
CFO-ACCL	50.68	49.32	0.5	0.5	0.2	0.2
CFO-ACAC	49.30	50.70	0.2	0.2	0.1	0.1
CFO-CN	49.87	50.13	0.9	0.9	0.4	0.4

Figure 75 presents the X-ray photoelectron emission peaks of Cu 2p, Fe 2p, and O 1s for sample CFO thin films deposited on ITO-coated quartz substrates. The doublet peaks of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of Delafossite CuFeO_2 dominate the deconvoluted Cu 2p spectrum in all three films, located at $\sim 933.0\text{ eV}$ and ~ 953.0

eV with a peak splitting difference of ~ 20 eV, indicating a Cu(I) oxidation state³¹². At the same time, the satellite peaks (~ 941.5 eV) and Cu 2p_{3/2} and Cu 2p_{1/2} peaks (~ 933.0 eV and ~ 953.0 eV) from divalent oxidation state (Cu²⁺) can still be observed but are of low intensity¹³⁵. The doublet peaks of Fe 2p_{3/2} and Fe 2p_{1/2} were found at ~ 711.0 eV and ~ 724.0 eV with the binding energy separation of ~ 11.3 eV, indicating Fe (III)¹³¹. An In 2p_{1/2} peak was observed in the Fe 2p high-resolution scan window at ~ 703 eV³¹². The satellite peaks at ~ 718.0 eV and ~ 732.5 eV, further confirm the assignment of Fe (III).

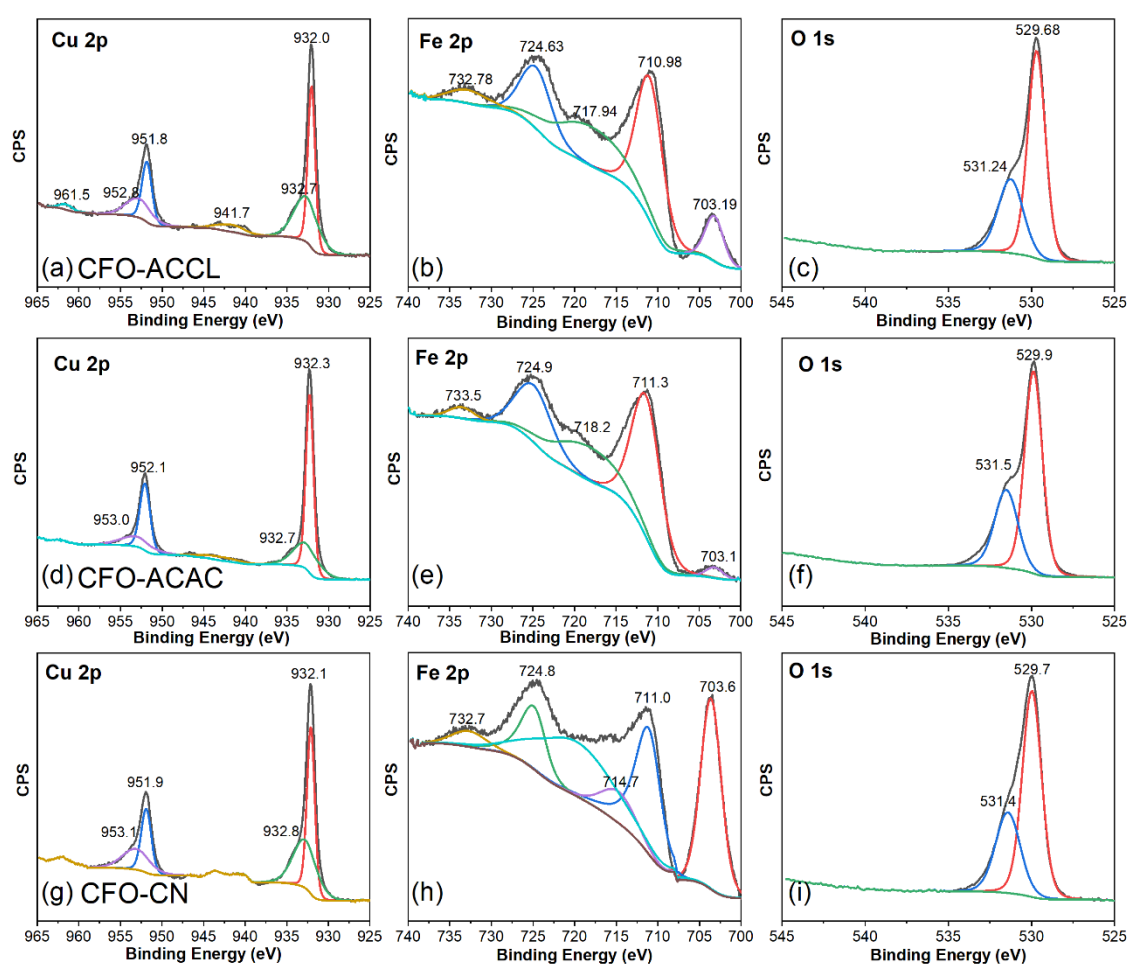


Figure 75. XPS of Cu 2p, Fe 2p, and O 1s peaks of CFO-ACCL, CFO-ACAC and CFO-CN films deposited on ITO-quartz substrate

According to the literature¹³⁰, in the deconvoluted O 1s spectrum, the lattice oxygen (metal-oxygen chemical bond in the Delafossite structure) and the surface

oxygen (i.e., adsorbed oxygen) are assigned at ~529.5 eV and ~531.6 eV respectively.

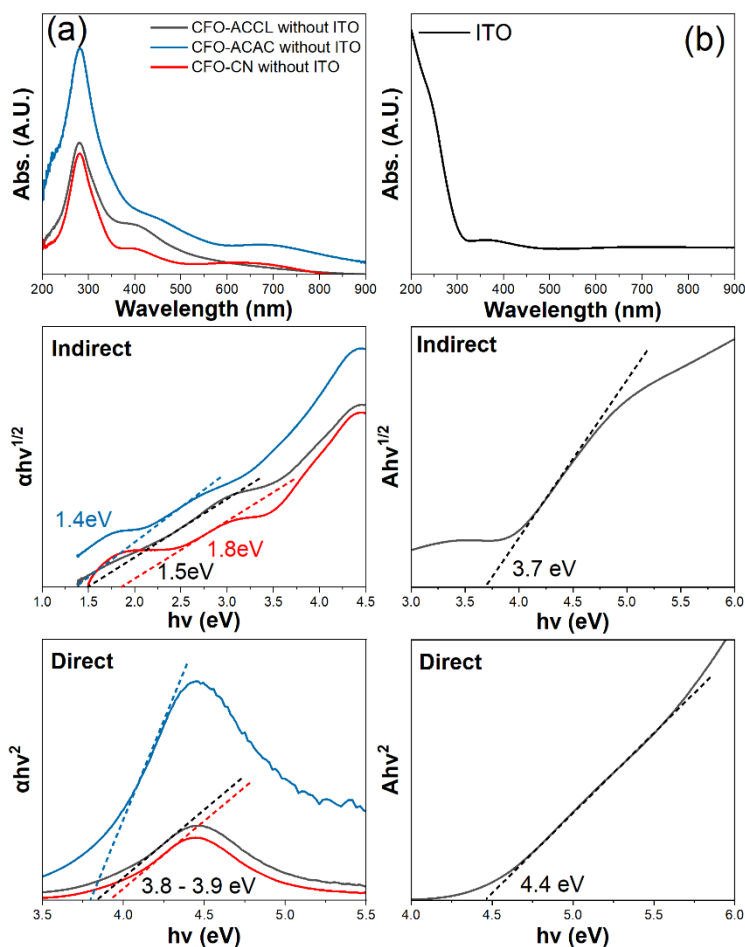


Figure 76. UV-vis absorption spectroscopy and Tauc plot for indirect band gap and direct band gap of a) three types of CFO-ACCL, CFO-ACAC and CFO-CN films without ITO-quartz as background; b) ITO-quartz substrate

In the UV-vis spectroscopy of CFO-ACCL, CFO-ACAC, and CFO-CN films, two to three absorption peaks were apparent in all samples, including one at ~1.5 eV and another at ~2.5 eV, consistent with results from previous research^{113,140}. Using ITO-coated quartz as a blank for the background, a strong absorption peak was observed for the CFO films at ~280 nm in the UV-absorption spectrum (**Figure 76 a**)), which can be found in many cuprous Delafossites. This strong and narrow absorption peak was observed at ~3.7-4.5 eV in the Tauc plot (**Figure 76 a**)) can

be confidently assigned as a Cu 3d + O 2p → Cu 4s excitation peak, enabled by the linear O-Cu-O structure ¹¹³.

Three broad peaks between 1.5 eV and 3.8 eV seems to comprise several overlapping peaks from energy-loss features. These energy-loss features match well with the absorption edges of CuFeO₂ at ~390nm, ~450 nm and ~675 nm and are raised from charge transfers such as Fe t_{2g} to 3_g d-d excitations, which only changes the local electronic configuration but not contribute to conducting charge carriers that are required for PEC use, and Cu-to-Fe metal-to-metal charge transfer, which is responsible for the adsorption of CuFeO₂ since the valence band edge mainly consisted of Cu 3d states.

CFO-ACCL, CFO-ACAC, and CFO-CN films deposited on quartz (not ITO-quartz) substrates were used for the Hall effect measurement to ensure a non-conductive substrate. Film thickness was determined by measuring the cross-section of the film using SEM. The positive Hall coefficient confirms the p-type conductivity of three different CFO films. **Table 37** presents the film conductivity, average film carrier mobility and sheet concentration. CFO-CN has the highest conductivity, relatively high charge carrier mobility, and a large sheet concentration among the three CFO films.

Table 37. Hall effect measurement of CFO-ACCL, CFO-ACAC and CFO-CN films deposited on the quartz substrate

Film	Thickness (nm)	Hall co-efficient	Conductivity (S/cm)	Mobility (cm ² /Vs)	Sheet Concentration (/cm ²)
CFO-ACCL	170	+1.8 × 10 ⁷	2.8 × 10 ⁻⁵	4.4 × 10 ²	9.9 × 10 ⁶
CFO-ACAC	430	+ 6.7 × 10 ⁷	2.1 × 10 ⁻⁵	1.3 × 10 ³	8.4 × 10 ⁶
CFO-CN	400	+5.8 × 10 ⁷	3.3 × 10 ⁻⁴	7.7 × 10 ³	2.6 × 10 ⁷

Compared with electrical properties in previous studies (**Table 38**), the charge carrier's mobility of three CFO films is relatively high, with CFO-CN having the highest charge carrier mobility. However, the conductivity performance and the

sheet concentration were low (room temperature measurement), though all three sets of CFO films in our research showed a similar magnitude of values.

Table 38. Summary of electrical properties of Delafossite CuFeO₂ in recent research

Charge carrier mobility (cm ² V ⁻¹ s ⁻¹)	Conductivity (S•cm ⁻¹)	Carrier concentration (cm ⁻³)	Thickness (nm)	Reference
0.2	N/A	N/A	N/A	131
N/A	0.67±0.02	(2.56±1.24) ×10 ¹⁸	80	225
0.7	0.358	5.34 × 10 ¹⁸	90	109
N/A	3	N/A	N/A	123
N/A	N/A	N/A	45±3 or 41±3	226
7.95 × 10 ¹⁹	N/A	N/A	N/A	136
34 to 8.8	N/A	N/A	N/A	115
N/A	0.001	N/A	30	112

5.3.2 Investigation of morphology and thickness for three CFO films

The film morphology dramatically changed with the adjustment of precursors and solvent, as observed via scanning electron microscopy (SEM) (**Figure 77**), and mainly reflected in the particle size (**Table 39**). In CFO-ACCL film, the particle size is relatively small (~60-140 nm), and particles are well distributed on the substrate. In the CFO-ACAC film, the particle size is similar (~90-170 nm) to the CFO-ACCL. However, the particles tend to bond tightly, forming a flat surface. Regardless of the thickness variation, the particle size of the CFO-CN film is much larger than that of CFO-ACCL and CFO-ACAC. In short, particle size increases with the sequence: CFO-ACCL =< CFO-ACAC < CFO-CN. When the thickness is controlled at ~300 nm, the grain size of ACCL, ACAC and CN films is ~130 nm, ~140 nm and ~380 nm, respectively.

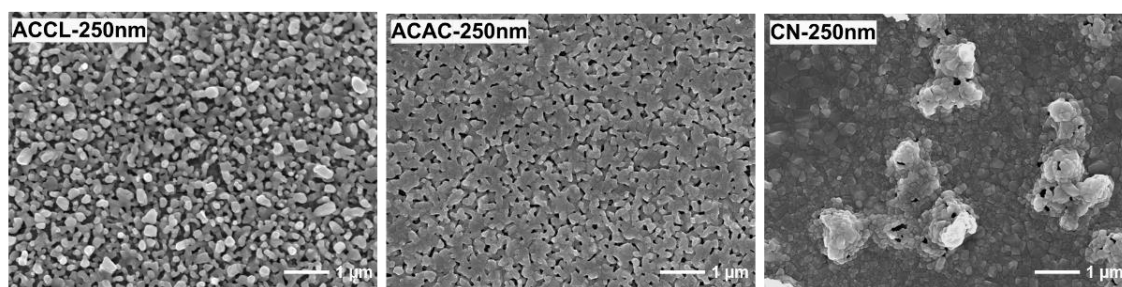


Figure 77. SEM images of ~250nm CFO-ACCL, CFO-ACAC and CFO-CN films showing different morphologies

The films' growth can be summarised by analysing the films with thickness varying from 75 nm to 400 nm under 'top-down' SEM (**Figure 78, Table 39**). All three CFO films exhibited a distinct "layer-by-layer" growth pattern. More specifically, the deposition process favoured the formation of subsequent layers once the preceding layer had been fully developed. This observation indicates a sequential growth mechanism where the film's growth initiates with the first layer and proceeds systematically to subsequent layers.

Particle size was estimated using SEM images (**Figure 78**). A diagonal line in each SEM images was drawn, the lengths of all particles on the line were measured, and then used to calculate the average based on the numbers of particles measured.

In the CFO-ACCL films, particles were smaller (61-62 nm) than in ACAC (88-91 nm) and CN (77-176 nm) films at a thickness equal to or less than 100 nm. The apparent particle size grew as the thickness increased for CFO-ACCL, but smaller particles were observed again when the thickness reached 300 nm. In CFO-ACAC and CFO-CN films, the particle size tended to increase with the film thickness increase. The particles in CFO-ACAC films increased in size at a relatively small but constant rate with increasing film thickness (from 91 nm to 170 nm), while the particle size in CFO-CN films increased rapidly from 77 nm to 517 nm. This suggests that for CFO-CN, after forming the first layer of the thin film with relatively small particles, larger particles tended to grow to form another layer.

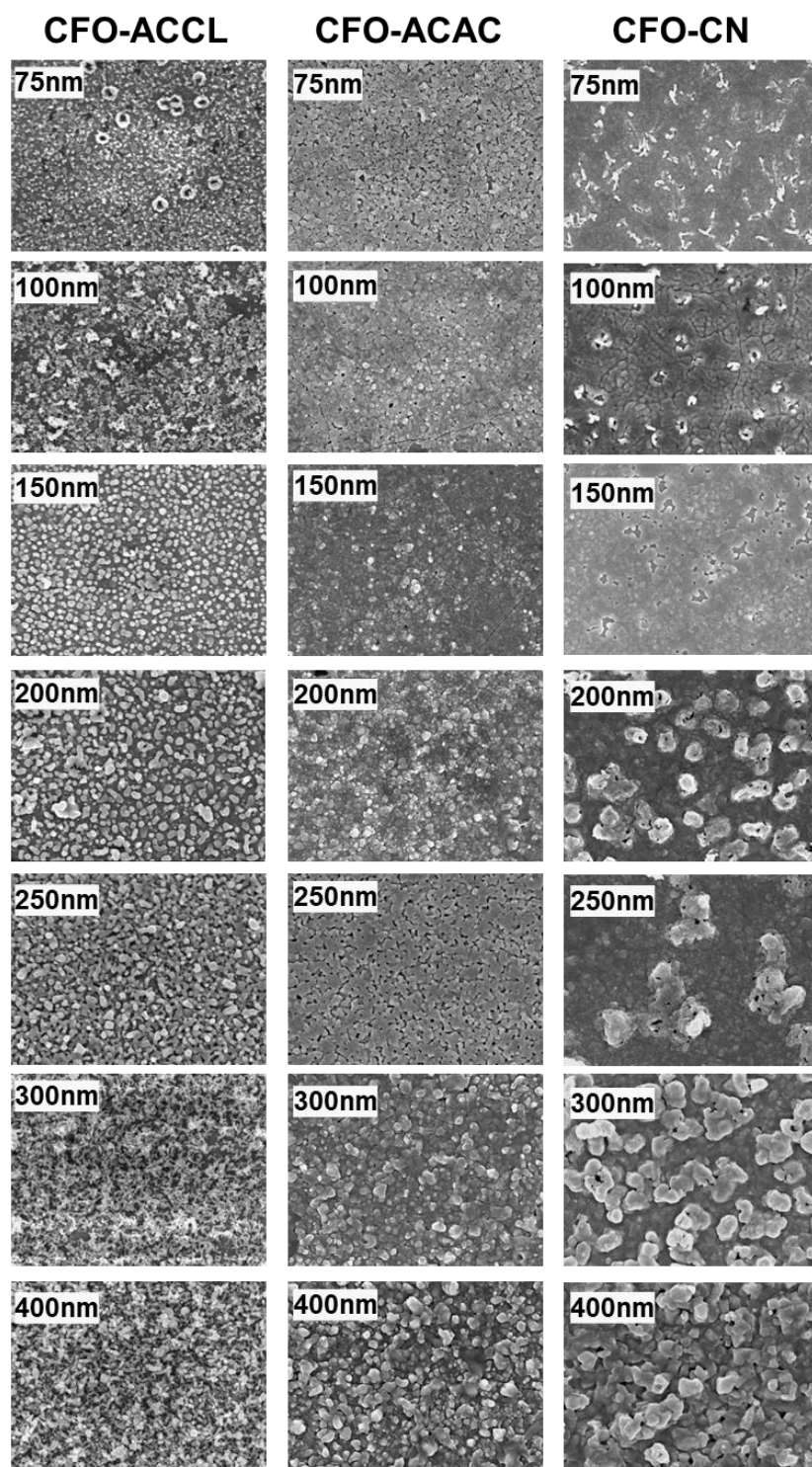


Figure 78. SEM images of CFO-ACCL, ACO-ACAC and CFO-CN films with thicknesses ranging from 75 nm to 400 nm

From SEM, the CFO-ACCL film consists of relatively small particles when the thickness is 75 nm (61 ± 2 nm), 100 nm (62 ± 2 nm), 300 nm (140 ± 10 nm) and 400

nm (136 ± 9 nm). The average surface roughness of these films was measured from AFM analysis (**Figure 79**).

Table 39. The particle size of CFO-ACCL, CFO-ACAC and CFO-CN films with different thickness

Film/Thickness	75 nm	100 nm	150 nm	200 nm	250 nm	300 nm	400 nm
ACCL	61 ± 2	62 ± 2	127 ± 9	148 ± 12	194 ± 21	140 ± 10	136 ± 9
ACAC	91 ± 9	88 ± 6	97 ± 9	106 ± 5	135 ± 10	166 ± 18	170 ± 14
CN	77 ± 7	176 ± 18	208 ± 27	190 ± 22	194 ± 19	378 ± 34	517 ± 23

In AFM, the CFO-ACCL roughness was relatively large compared with ACAC and CN films with the same thickness (**Table 41**). In contrast to the CFO-ACCL film, the CFO-ACAC film had a relatively constant particle size as the film thickness increased, with roughness around 32 nm when thickness changes from 200 nm to 400 nm. In the CFO-CN film, the particle size changed significantly as the thickness increased, although not as much as the rate of increase for CFO-ACCL.

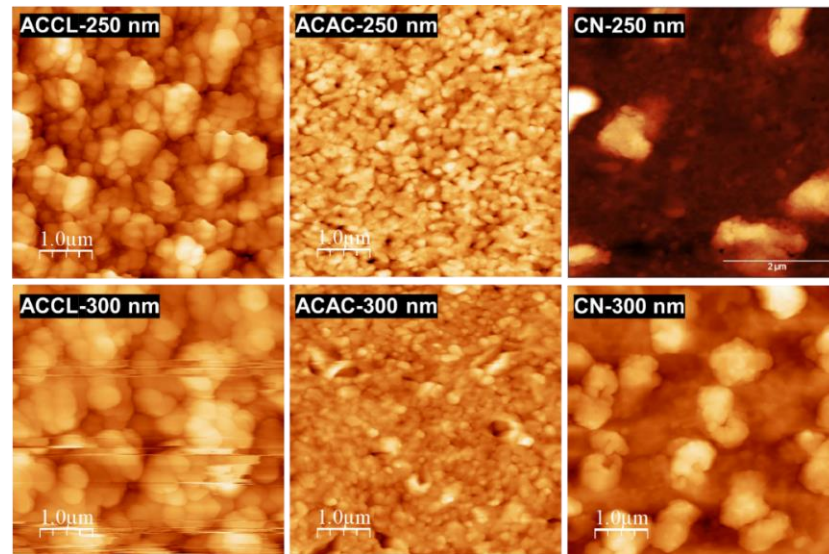


Figure 79. AFM images CFO-ACCL, CFO-ACAC and CFO-CN films of 250 nm and 300 nm

The average R.M.S. roughness slightly increased with thickness, with a rate of increase that was greater than all the ACAC and ACCL films with a thickness of no more than 250 nm.

Three CFO films for EP were deposited on Si substrates using conditions that produced a 75 nm-thick film on ITO-quartz. SEM images were taken to confirm

that these film had a morphology that was consistent with the films on ITO-quartz, despite some of the thickness values determined via EP being divergent from the target thickness.

From EP, the specific surface area of three CFO films has been obtained by measuring the multilayer toluene adsorption at the surfaces with gradually increasing relative pressures and fitting with BET theory. The results are summarised in **Table 40**.

Overall, these films with different thicknesses showed differing degrees of porosity and surface roughness in all three CFO films shown in **Table 40** and **Table 41**.

Table 40. Summary of surface areas of CFO-ACCL, CFO-ACAC and CFO-CN films measured from EP analysis

Film	Thickness	Surface area	BET Fitting R ²
CFO-ACCL	180 nm	4.7 m ² /cm ³	0.983
CFO-ACAC	97 nm	11.2 m ² /cm ³	0.972
CFO-CN	110 nm	7.3 m ² /cm ³	0.995

In summary, by adjusting AACVD deposition conditions, we successfully adjusted the morphology of CFO films, and the results from EP, SEM and AFM can be summarized below.

Table 41. Summary of AFM results from CFO-ACCL, CFO-ACAC and CFO-CN films

	Average R.M.S. Roughness - 75 nm	Average R.M.S. Roughness - 200 nm	Average R.M.S. Roughness - 250 nm	Average R.M.S. Roughness - 300 nm
ACCL	61±2 nm	/	100±3 nm	160±9 nm
ACAC	/	32 ±0.8 nm	30±3 nm	34±2 nm
CN	/	/	110±10 nm	130±7 nm

CFO-ACCL had similar samples tested using EP and AFM, i.e. film with a thickness of 180 nm for EP and film with a thickness of 250 nm for AFM, where in this range, the particle size is ~150-200 nm from SEM results, the roughness is ~100 nm, and the surface area is 4.7 m²/cm².

The CFO-CN exhibits consistent particle sizes from 100 nm to 250 nm thick as determined by SEM (~175-195 nm). Its grain size (~195 nm), as well as roughness (100-110 nm), closely mirrors that of CFO-ACCL when at a thickness of 250 nm, but with CFO-CN having a relatively larger surface area (7.3 m²/cm²) compared to CFO-ACCL (4.7 m²/cm²).

Films of CFO-ACCL and CFO-CN that are of the same thickness (250 nm) may be expected to have similar morphologies or structures. However, while our AFM and SEM data reveal some similarities between the films, we have observed that their morphologies are not identical and that the film morphology is indeed dependent on deposition conditions.

CFO-ACAC has a relatively constant particle size, as deduced from SEM measurements across the thickness range of 75-250 nm (particle size increases from ~90 nm to ~135 nm), which suggests the EP and AFM data can be compared directly, particularly since the roughness data from AFM is similarly 'flat' in profile (consistently ~30 nm). We observe that CFO-ACAC has significantly smaller particles than either CFO-ACCL or CFO-CN, lower roughness but also significantly higher surface area than either of the previous two, so CFO-ACCL and CFO-CN seem morphologically related whilst CFO-ACAC appears to be distinctly morphologically different.

5.3.3 Investigation of the optimal photoelectrochemical measurement environment of three CFO films

5.3.3.1 pH environment

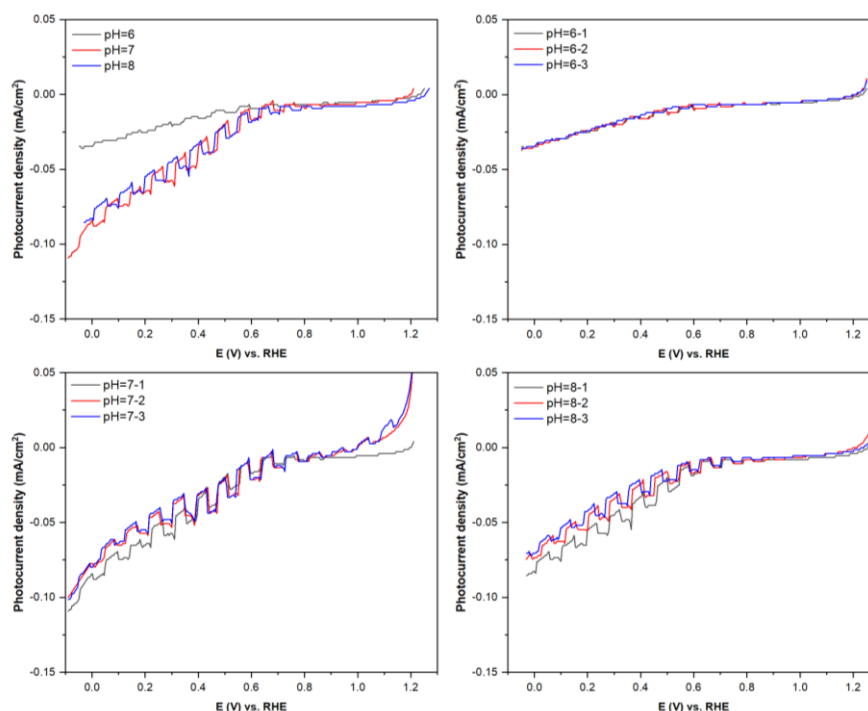


Figure 80. pH effect measured using buffer solutions on the photoelectrochemical performance in the CFO-ACCL films, LSV measurements were conducted three times to investigate the stability of the material in each environment with different pH

The pH effect was investigated in the beginning from CFO-ACCL films, and K_2HPO_4/KH_2PO_4 buffer solution was chosen to adjust the pH at 6, 7 and 8 (**Figure 80**).

From the LSV chopped measurement, it can be seen that the photocurrent density of $CuFeO_2$ films obtained in neutral or alkaline electrolytes are obviously higher than its in the acidic solution. Additionally, photocurrent densities of the film measured in the electrolyte with pH at 6 were gradually decreasing in three tests, indicating the film was gradually dissolved and being inactive. The performance in neutral and alkaline electrolytes also showed a good degree of stability. All three scans gave approximately the same photocurrent density.

5.3.3.2 Electrolyte selection

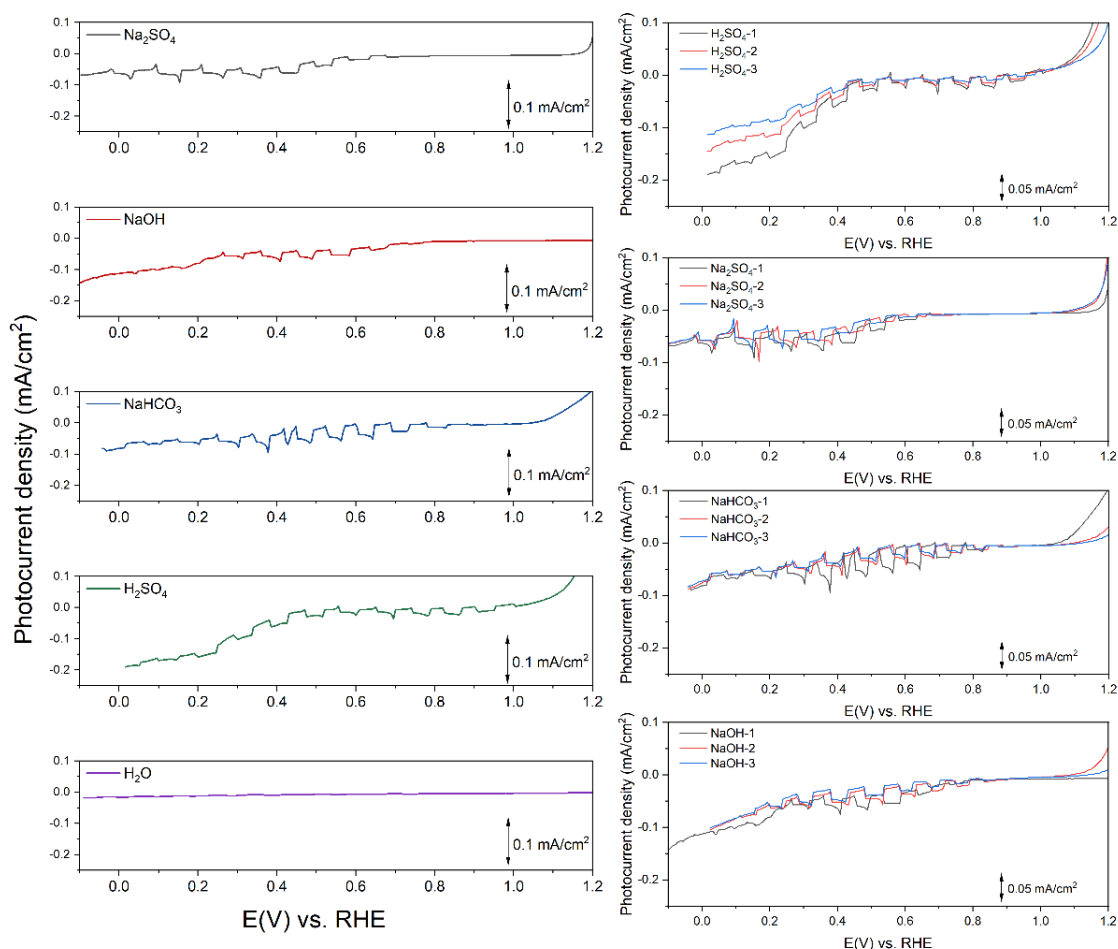


Figure 81. Comparison of single LSV scan (Lest) and three LSV scans for five electrolytes in the PEC measurement for CFO-ACCL electrode

As a result of the investigation on pH effect, 1M NaOH, 1M NaHCO₃, 0.5 M Na₂SO₄, and 0.5 M H₂SO₄ were chosen as the electrolytes to compare the PEC performance with deionized water (**Figure 81**). Five single LSV scans were conducted to assess the performance of the CFO-ACCL film in five different electrolytes, followed by three additional scans to evaluate the stability. If significant discrepancies between scans are observed, it may indicate electrolyte reacted with the CFO-ACCL photoelectrode, rendering the electrolyte unsuitable for use.

As we can see, photocurrent density in 0.5 M H₂SO₄ significantly decreased in the second and third scan, though the first scan showed the same amount of photocurrent density as the other electrolytes. Therefore H₂SO₄ was excluded. 1M NaOH and 0.5 M Na₂SO₄ showed the same degree of photocurrent density and stability, while 1M NaHCO₃ showed a better PEC performance among the selected electrolytes. However, HCO₃⁻ can quickly receive the electron and work as an electron acceptor. Using HCO₃⁻ as the electrolyte seems to have some “fake” benefits and is not comparable with electrolytes without adding electron scavengers, which will boost PEC performance of the film as electrons will be removed with ‘external’ help and the recombination rate will be slowed down. Therefore, NaHCO₃ was excluded in this thesis. 1 M NaOH and 0.5 M Na₂SO₄ were suitable electrolytes for CuFeO₂ photocathode research. Considering the ease to compare the PEC performance with literatures, 1M NaOH was chosen as the primary electrolyte because the results can be easily compared with peer work.

5.3.3.3 Gas environment

In this section, CFO-ACCL, CFO-ACAC and CFO-CN films were all examined under an O₂-saturated, N₂-saturated atmosphere and compared with the air environment (**Figure 82**).

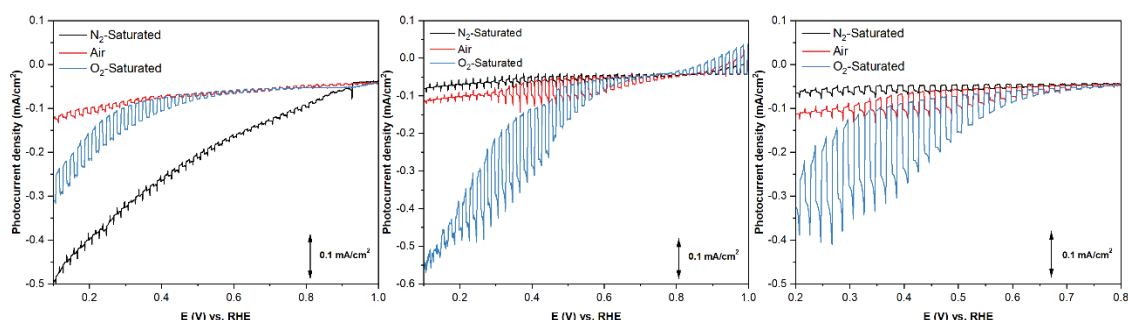


Figure 82. Integrated chopped LSVs of a) CFO-ACCL, b) CFO-ACAC, c) CFO-CN films of 150 nm measured in 1M NaOH electrolyte under different gas atmospheres

The higher photocurrent density was observed in all three cases when the measurement conducted under the O₂-saturated electrolyte. Contrarily, in the N₂-

saturated electrolyte, the photogenerated current is suppressed, indicating that O₂ plays a vital role in consuming electrons trapped in the surface and separating charge carriers and slowing down the recombination.

CFO-CN films performed the best in all the gas atmospheres compared with CFO-ACCL and CFO-CN films.

5.3.3.4 Sacrificial agent

Sacrificial agents act as electron donors or hole scavengers, effectively mitigating the recombination of photoexcited charge carriers. When investigating a particular material employed as a photocathode or photoanode, incorporating sacrificial agents into the electrolyte can concentrate electrons or holes within the respective half-reaction. This serves to diminish the impact of rapid charge carrier recombination, thereby unlocking the material's latent photoactivity potential.

To further investigate the effect of O₂, we compared the O₂-saturated electrolyte with electrolyte with different concentrations of 0.1 M Na₂S₂O₈ electron scavenger (**Figure 83**). In the O₂-saturated electrolyte, the photogenerated current density (0.18 mA/cm²) was similar to the test in 1M NaOH electrolyte with 10 vol.% 0.1 M Na₂S₂O₈ (0.21 mA/cm²). When combining these two conditions together, the photocurrent density was additive and reached 0.39 mA/cm². Presumably, O₂ can be adsorbed on the surface of the CuFeO₂ film as a surface trap for electrons, forming oxygen species such as O₂⁻, O₂²⁻, O⁻³¹³⁻³¹⁶, similar to electron scavengers.

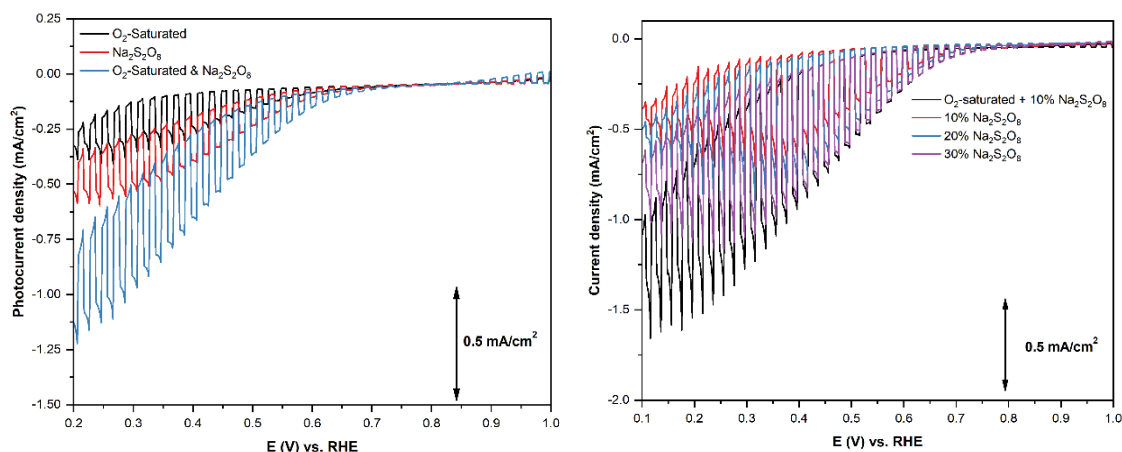


Figure 83. Chopped LSV scans of a) CFO-CN films measured in O₂-saturated 1M NaOH, 1M NaOH with 10 vol.% 0.1 M Na₂S₂O₈, and O₂-saturated 1MOH with 10 vol.% 0.1 M Na₂S₂O₈, b) CFO-CN films measured in O₂-saturated 1MOH with 10 vol.% 0.1 M Na₂S₂O₈, 1M NaOH with 10 vol.% 0.1 M Na₂S₂O₈, 1M NaOH with 20 vol.% 0.1 M Na₂S₂O₈, and 1M NaOH with 30 vol.% 0.1 M Na₂S₂O₈

When changing the concentration of 0.1 M Na₂S₂O₈ in the electrolyte, a noticeable rise was shown in photocurrent density. Photocurrent density archived the same degree when using 1M NaOH with 30 vol.% 0.1 M Na₂S₂O₈ and O₂-saturated 1M NaOH as electrolyte.

5.3.4 Investigation of the photoelectrochemical performance of CFO films

PEC performance of CFO-ACCL, CFO-ACAC and CFO-CN films with different thicknesses was evaluated in 1M NaOH electrolyte with 10 vol.% 0.1 M Na₂S₂O₈ (Figure 84).

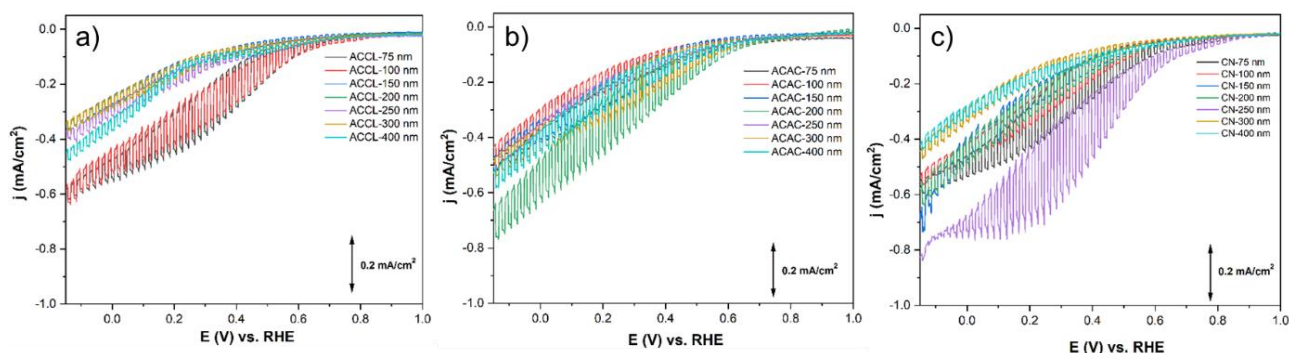


Figure 84. Chopped LSV of a) CFO-ACCL, b) CFO-ACAC and c) CFO-CN films with thicknesses ranging from 75 nm to 400 nm; Electrolyte: 1M NaOH with 10% 0.1 M Na₂S₂O₈

Among CFO-ACCL, CFO-ACAC and CFO-CN films, CFO-CN (~250 nm) showed the best performance and reached $\sim 240 \mu\text{A}/\text{cm}^2$ at 0.4 V vs RHE (**Figure 33**), which aligns with previous research results in **Table 3**.

Film morphology and thickness played a vital role in the films' photoactivity. As the thickness changed (**Figure 84**), the photocurrent density varied significantly in all three types of CFO films.

The Incident Photo to Charge Carrier Efficiency (IPCE) of CFO-ACCL, CFO-ACAC, and CFO-CN films were compared using the film that exhibits the highest photocurrent within each respective groups (75 nm CFO-ACCL, 200 nm CFO-ACAC, and 250 nm CFO-CN). **Figure 85** demonstrated a clear efficiency trend that the IPCE of CFO-CN (250 nm) > CFO-ACAC (200 nm) > CFO-ACCL (75 nm).

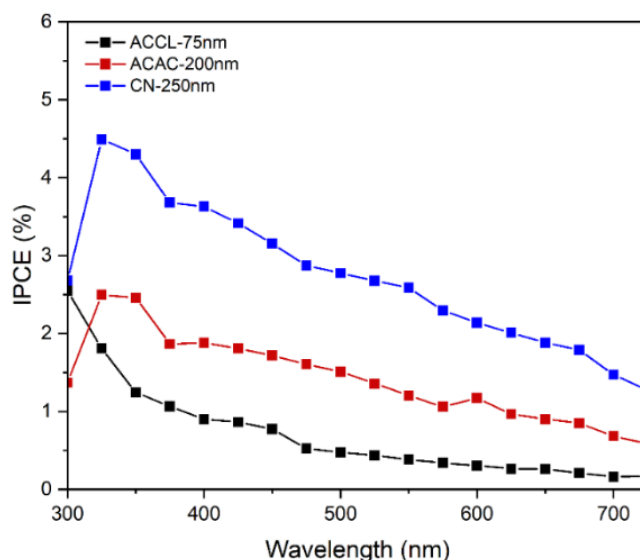


Figure 85. IPCE of 75 nm CFO-ACCL, 200 nm CFO-ACAC, and 250 nm CFO-CN films in 1M NaOH with 10 vol.% 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$

The highest efficiency of 4.5% was attained in the CFO-CN film with a thickness of 250 nm, observed at an incident wavelength of 325 nm. As the wavelength increased (resulting in decreased photon energy), a corresponding decrease in IPCE was observed. The reason of which will be proposed and discussed in 5.3.5 in detail.

5.3.5 Investigation of photoelectrochemical mechanism on CFO-ACCL, CFO-ACAC, and CFO-CN films

5.3.5.1 Transient absorption spectroscopy (TAS) results

To understand the differences in the performance of the CFO films in terms of their photoinduced mechanisms and the charge recombination³¹⁷, femtosecond transient absorption (TA) spectra were recorded following 280 nm excitation in collaboration with Prof. Helen Fielding and Dr. Rhea Kumar in the Department of Chemistry, UCL. The pump wavelength was selected from UV results to ensure that photons of sufficient energy were used to excite each material above its peak efficiency according to IPCE spectra (**Figure 85**).

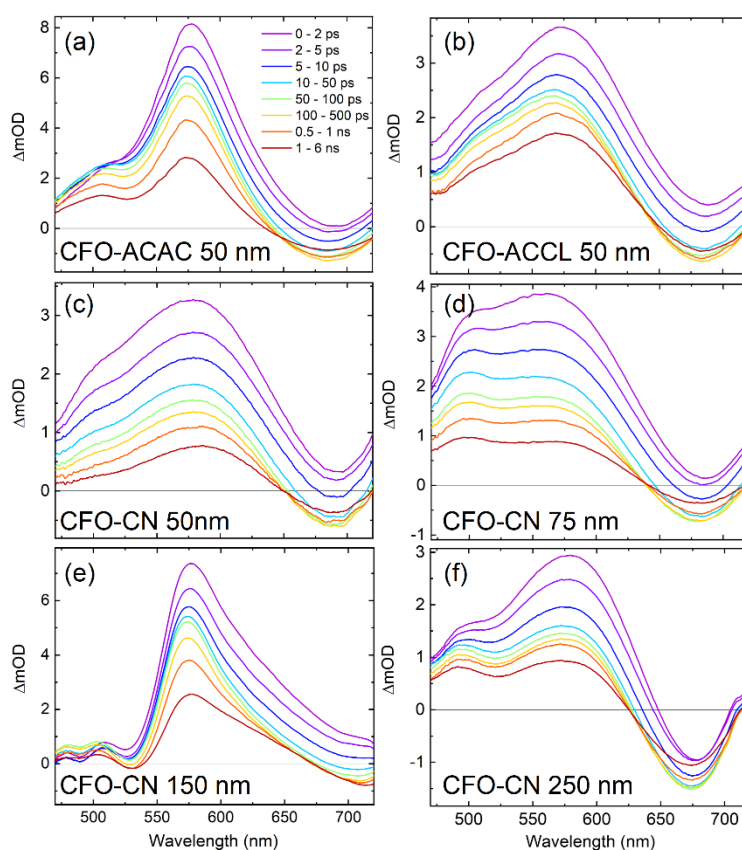


Figure 86. Transient absorption spectra in the visible probing region following 280 nm excitation (100 nJ) for (a-c) CFO-ACCL, CFO-ACAC, and CFO-CN films of 50 nm and (c-f) CFO-CN films of 75 nm, 150 nm and 250 nm

TA spectroscopy measurements were carried out on 50 nm CFO-ACCL, CFO-ACAC and CFO-CN films to examine the differences. Further experiments were also conducted on CFO-CN films of 75 nm, 150 nm and 250 nm thickness to probe the mechanisms responsible for the strong dependence of photoelectrochemical performance on film thickness. The measured spectra are presented in **Figure 83**.

All spectra contain a solid positive, excited state absorption (ESA) feature centred at 560-575 nm that has been previously assigned in the literature to the intra-band transition where the photoexcited electron transfer from O 2p $\rightarrow$ Fe 3d^{1,318,319}. This feature is formed instantaneously with the pump pulse and subsequently decays over the 6 ns timescale of the measurement. The spectra also all contain a negative feature in the red edge of the probing region, which appears to grow on a slower timescale than the ESA. In CFO-CN films, a distinct negative contribution is observed before 525 nm when the thickness is $\sim$ 150 nm. However, the underlying cause of this phenomenon remains unclear, but it might be due to the overlapping positive and negative feature which “artificially” alters the kinetics.

Prior TA measurements on CuFeO₂ films conducted by Fugate and co-workers detected a negative feature, which they assigned to stimulated emission (SE) as a result of hole thermalisation (**Figure 8**)³¹⁸. Our observations are consistent with theirs, therefore, we also assign the negative feature in these spectra to SE due to hole thermalisation.

The kinetic traces for the evolution of the distinct Gaussians are shown in **Figure 87** together with exponential fits to the data. In all spectra, the decay of the ESA was fit to a three-component exponential, which has been previously assigned to the recombination of electrons and holes¹⁴⁴. The SE feature was fit to a biexponential curve in each case, of which the growth and decay represent hole thermalisation (since in the hole thermalization electrons from Cu 3d backfilled the

vacancies in O 2p and generated a negative feature, shown in **Figure 8**) and charge separation, respectively.

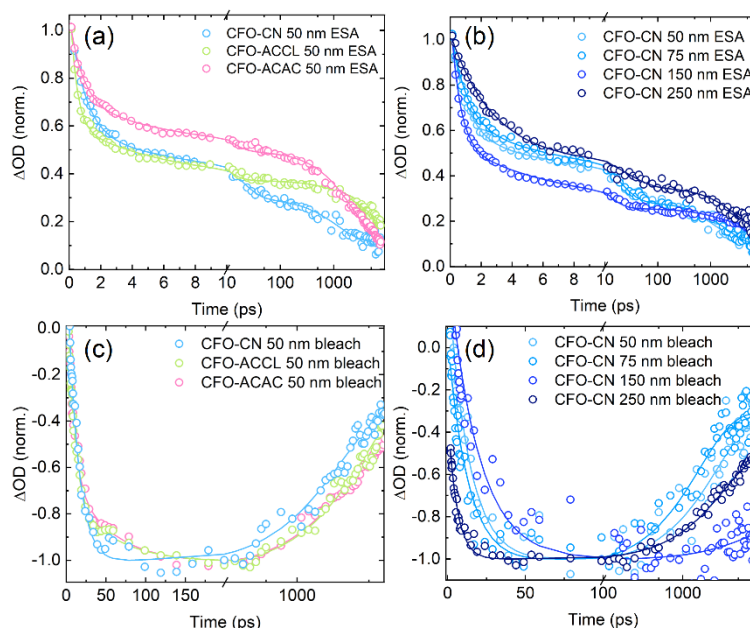


Figure 87. Normalised kinetics extracted from deconvolution of two principal spectral features: (a, b) the ESA peak and (c, d) the SE peak for (a, c) the three different CFO films of 50 nm and (b, d) four different thicknesses of CFO-CN films

Firstly, interpreting the excited charge carrier dynamics in the three different CFO films (**Figure 87 a**), all photoexcited electrons decay to a relatively low population within the 6 ns timescale of the measurement. The decay of charge carriers comprise geminate recombination of electrons and holes and, non-geminate recombination of electrons and holes.

Here, geminate recombination³²⁰ refers to the process where an electron and a hole, which are initially created as a result of light absorption or other excitation mechanisms, recombine with each other before they can contribute to any useful processes such as charge transport or chemical reactions. In other words, the electron and hole recombine with each other before they have a chance to encounter any other charge carriers. Non-geminate recombination, on the other hand, involves the recombination of an electron or a hole with a charge carrier of opposite polarity that was not initially paired with it. This can occur when an

electron or hole encounters another charge carrier of opposite polarity before recombining with its initially paired carrier. In another word, non-geminate recombination occurs after hole thermalization process and it can be indicated by a slower ESA decay.

Table 42. Summary of time constants associated with the exponential fit to the ESA decay in 50 nm CFO-ACCL, 50 nm CFO-ACAC and four different thicknesses of CFO-CN films studied by TA spectroscopy

Sample	IPCE% ($\lambda = 300$ nm)	Exp decay τ_1 / ps (weight)	Exp decay τ_2 / ps (weight)	Exp decay τ_3 / ns (weight)
ACCL 50 nm	/	0.41 $\pm$ 0.03 (55 %)	6.1 $\pm$ 0.49 (24 %)	4 $\pm$ 0.7 (21 %)
ACAC 50 nm	/	0.82 $\pm$ 0.1 (37 %)	7.2 $\pm$ 0.92 (23 %)	2 $\pm$ 0.1 (40 %)
CN 50 nm	/	1.00 $\pm$ 0.08 (53 %)	14.9 $\pm$ 1.8 (28 %)	1 $\pm$ 0.1 (19 %)
CN 75 nm	0.50	1.08 $\pm$ 0.09 (46 %)	15.0 $\pm$ 1.4 (34 %)	2 $\pm$ 0.2 (20 %)
CN 150 nm	0.14	0.59 $\pm$ 0.03 (61 %)	7.4 $\pm$ 0.4 (30 %)	2 $\pm$ 0.3 (9 %)
CN 250 nm	2.68	2.64 $\pm$ 0.21 (59 %)	28.7 $\pm$ 7.2 (17 %)	3 $\pm$ 0.7 (24 %)

The lifetimes of the three exponential components used to fit the data are summarised in **Table 42** alongside their weights of contribution to the overall exponential curve. All three CFO films of 50 nm thickness (**Figure 87 a**)) contain a sub-picosecond ultrafast component of ESA decay, a component of a few picoseconds and a nanosecond component. The geminate recombination process is likely to dominate the ultrafast decay, where this appears to have a stronger contribution for CFO-CN and CFO-ACCL films in which the exponential weights reveal that this constitutes more than 50% of the exponential decay. This is in contrast to CFO-ACAC, where the sub-picosecond component contributes only 37% of the decay. Furthermore, the sub-picosecond decay process is much faster in CFO-ACCL films than CFO-ACAC and CFO-CN, with a rate of recombination that is double that of CFO-ACAC and approximately 2.5 times faster than CFO-CN. The combination of the highest rate of ultrafast recombination and the strongest

contribution of this sub-picosecond recombination, therefore, rationalises the poor performance of CFO-ACCL films compared to the other two films, as observed in IPCE measurements (**Figure 85**).

Comparison of the ESA evolution in CFO-CN films of different thicknesses reveals further variation in behaviour (**Figure 87 b**). Both picosecond decay components in 50 nm and 75 nm films are consistent with one another but are much faster in 150 nm films and much slower in 250 nm films. This indicates that the rapid recombination of charge carriers in 150 nm films is responsible for its poor performance (IPCE($\lambda=300$ nm) = 0.14%) compared to other thicknesses. Likewise, the enhanced performance of 250 nm films (IPCE ($\lambda =300$ nm) = 2.68%) can be justified by its much slower timescale of charge carrier recombination.

Further differences can be observed in comparing the temporal evolution of the SE feature in the three different CFO morphologies (**Figure 87 c**). The time constants associated with the exponential fits to the kinetic data of SE evolution are summarised in **Table 43**.

Table 43. Summary of time constants associated with the exponential fit to the evolution of the negative SE feature in 50 nm CFO-ACCL, 50 nm CFO-ACAC and four different thicknesses of CFO-CN films studied by TA spectroscopy

Sample	Exp rise τ / ps	Exp decay τ / ns	Sample	Exp rise τ / ps	Exp decay τ / ns
ACCL 50 nm	22 $\pm$ 1.1 (60%)	4 $\pm$ 0.2 (40 %)	CN 75 nm	13.2 $\pm$ 0.7 (60 %)	2 $\pm$ 0.2 (50 %)
ACAC 50 nm	27 $\pm$ 1.3(38%)	3 $\pm$ 0.2 (62 %)	CN 150 nm	19 $\pm$ 1.7 (89 %)	7 $\pm$ 2 (11 %)
CN 50 nm	13.4 $\pm$ 1.6 (65%)	3 $\pm$ 0.6 (35 %)	CN 250 nm	5.9 $\pm$ 0.3 (44 %)	3 $\pm$ 0.3 (55 %)

The growth of this feature, representing the occurrence of hole thermalisation to the band edge, is much faster in CFO-CN films than CFO-ACCL and CFO-ACAC films, being 13 ps compared with 22 ps (CFO-ACCL) and 27 ps (CFO-ACAC). Since in the hole thermalisation process (**Figure 8**), photoexcited electrons and holes are located in Fe 3d and Cu 3d, respectively, with no direct covalent bonding, the electron-hole recombination is suppressed. The decay of the SE feature then

represents the process of charge separation, which competes against charge recombination to promote film performance. The onset of this SE decay (the tuning point of the kinetic trace in **Figure 87 c)**) occurs at 60 ps in CFO-CN films compared to 200 ps in CFO-ACCL and CFO-ACAC, meaning that charge separation is more competitive against than charge recombination in CFO-CN films compared to CFO-ACCL and CFO-ACAC, further rationalising its enhanced photoelectrochemical performance.

The most dramatic discrepancies can be observed when comparing the SE dynamics for different thicknesses of CFO-CN films (**Figure 87 d)**). With an analogous trend to that observed in the recombination dynamics, the rate of hole thermalisation is consistent for 50 nm and 75 nm films, at 13 ps, but superior in 250 nm films and poorer in 150 nm films, with timescales of 6 ps and 19 ps, respectively. As the rapid hole thermalisation facilitates charge separation, this trend further explains the worse performance of 150 nm CFO-CN films ($\text{IPCE}(\lambda=300\text{ nm})=0.14\%$) compared to the others and the significantly enhanced performance of 250 nm films ($\text{IPCE}(\lambda=300\text{ nm})=2.68\%$). Owing to the fast hole thermalisation, the onset of the charge separation process (manifesting as the decay of the SE feature) occurs much earlier in 250 nm films, at 25 ps, compared to 75 ps in 50 nm and 75 nm films. Due to the slow rate of hole thermalisation in 150 nm films, the decay of SE does not begin until 300 ps, and even still, its rate is far slower than in the other films, with a timescale of 7 ns compared to 2-3 ns. This, therefore, indicates that the poor performance of 150 nm films arises due to a combination of rapid carrier recombination on an ultrafast timescale and a less competitive rate of hole thermalisation on the picosecond timescale, which subsequently depletes the rate of charge carrier separation.

Moreover, the negative feature denoting hole thermalisation and, therefore, representing a mechanism for the facilitation of charge separation is much more

pronounced in the 250 nm CFO-CN film TA spectrum than in all the others in the series. The relative amplitudes of the non-normalised transient features were compared in a ratio of SE: ESA to arrive at a quantified metric of the relative population of thermalised holes compared to the total population of photoexcited electrons. The resultant ratios are presented in **Table 44**.

Table 44. Summary of ratios of amplitudes of SE: ESA features 50 nm CFO-ACCL, 50 nm CFO-ACAC and four different thicknesses of CFO-CN films in TA spectra.

Sample	Ratio	Sample	Ratio
ACCL 50 nm	0.15	CN 75 nm	0.19
ACAC 50 nm	0.11	CN 150 nm	0.21
CN 50 nm	0.18	CN 250 nm	0.40

TAS data is corrected for the thickness for absorbance at the excitation wavelength with amplitude ratios shown in **Table 44**. 250 nm CFO-CN film shows a ratio that is double that of the other films, which are otherwise comparable, again justifying its enhanced photoelectrochemical performance. These results, therefore, indicates that due to the rapid rate of hole thermalisation in 250 nm CFO-CN films, this process is much more significant in the competition against recombination. Thus, a greater population of hole thermalisation is observed than in the other films.

5.3.5.2 Photoelectrochemical mechanism discussion from TAS results

In order to understand the difference in PEC performance among three CFO films, two aspects need to be considered: 1) surface reaction and 2) charge carriers separation and recombination. The surface reaction efficiency^{321,322,323} can be explained by the kinetics of the photochemical reaction, which is represented as a quasi-first-order reaction. The surface reaction efficiency, r , is given by:

$$r = \frac{k_{abs}k_{r1}C_1}{1 + \sum k_{ri}C_i} \quad (9)$$

In which k_{abs} is the rate constant and is determined by the properties of the photoelectrode materials and the reaction conditions, C_1 is the concentration of

organics formed between electrolyte and photoelectrode, and $\sum k_{ri}C_i$ is the contributions of the i components in the system. k_{r1} is the constant rate of the following reaction (**Equation 10**) under solar irradiation.



When the light intensity is low,

$$k_{abs} = \alpha a_c k_1 \quad (11)$$

While at high intensity:

$$k_{abs} = \alpha a_s k_{OH} \frac{k_1 a_c I}{K_1 v_p} \quad (12)$$

Where α is a constant, a_c is the surface area of the photoelectrode, k_1 is the rate constant associated with the formation of the electron/hole pairs, I is the intensity of the light, k_{OH} is the reaction rate constant related to the hole trapping K_1 is the adsorption constant of the compound on the material surface, and v_p is the particle volume³²². Therefore, the material's surface area and particle size (particle volume), i.e. the material morphology, are key factors influencing the surface reaction rate.

On the other hand, the morphology of the material can also influence the charge carrier recombination and separation due to the effect of the grain boundary size or surface electron trap state density³²⁴.

The particle size in the CFO-ACCL-75 nm (61 ± 2 nm) and CFO-CN-75 nm (77 ± 7 nm) films is small, leading to a better PEC performance, which can be well-explained by the surface reaction rate due to the inverse relationship with v_p . Though CFO-ACCL-75 nm has a smaller grain size (61 ± 2 nm) than CFO-CN-75 nm (77 ± 7 nm) and hence would be expected to have a faster surface reaction rate,

the PEC performance reveals it might have a much faster charge carrier recombination rate, leading to a trade-off in its advantages in particle size.

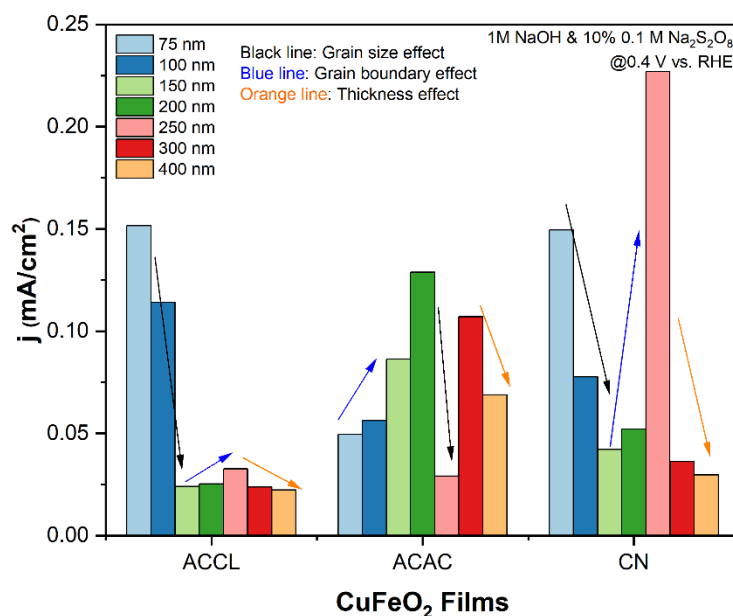


Figure 88. Photocurrent density change in CFO-ACCL, CFO-ACAC and CFO-CN films highlighting the dominant factors during different periods on PEC performance; Electrolyte: 1M NaOH with 10 vol.% 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$

When the thickness increases, the number of photons captured should theoretically increase proportionally, resulting in a significant improvement in the PEC performance. However, in our experiments, when the thickness increases from 75 nm to 100 nm, the photo performance of CFO-ACCL and CFO-CN decreases. This appears to be due to the grain size change in CFO-ACCL and CFO-CN film. Moreover, since the grain size of CFO-ACCL-100 nm (62 ± 2 nm) is smaller than CFO-CN-100 nm (176 ± 18 nm), CFO-CN showed a more significant drop in the photocurrent density than CFO-ACCL.

Though deposited from different Fe precursors and solvents during AACVD, CFO-ACCL and CFO-CN films have similar film morphologies and, therefore, similar trends in the PEC performance. In contrast, CFO-ACAC film has quite a distinct

morphology. As the thickness increases, the PEC performance change was also quite different from the other two types of CFO films.

Specifically, in the CFO-ACCL films, the most efficient thickness peaked at 75 nm (**Figure 88**). As the thickness increased to 150 nm, the photocurrent density dropped dramatically. From 150 nm, the photocurrent density very slightly increased to 250 nm, then decreased again as the film became thicker.

A similar trend in the PEC performance change was observed in CFO-CN films (**Figure 88**), likely due to the similarity in the film morphology. However, CFO-CN films generally performed better than the CFO-ACCL films and had a significantly higher photocurrent density peak at 250 nm.

As the thickness increases in CFO-ACCL and CFO-CN films (from 100 nm to 250 nm), large grains begin to appear (**Figure 78**). Essentially, large grain sizes (e.g. larger V_p) are expected to reduce the surface reaction rate (**Equation 12**). However, the PEC results reveal that a larger grain size appears to be preferred. In the TAS analysis, the ESA decay in the 250nm CFO-CN films is double ($\tau_1=2.64\pm0.21$) that of 50nm CFO-CN ($\tau_1=1.00\pm0.08$). This shows how the charge carriers' recombination rate in the films with larger grains was significantly decreased. It indicates that whilst large grain size reduces the surface reaction rate, it may also effectively enable carrier transport and charge separation, increasing the photocurrent density, as we observed from film thickness of 150 nm (0.042 mA/cm²) to 250 nm (0.227 mA/cm²). Compared with 50nm CFO-CN, the ESA feature in 50nm CFO-ACCL film decays at a rate ($\tau_1=0.41\pm0.03$) that is more than double that of 50nm CFO-CN ($\tau_1=1.00\pm0.08$), which indicates the initial charge carrier recombination rate in the thin CFO-ACCL is much larger than CFO-CN film.

Therefore, this results in a much smaller increase in the photocurrent density from 150 nm (0.024 mA/cm^2) to 250 nm (0.033 mA/cm^2) in CFO-ACCL.

In the CFO-ACCL films with thicknesses of 300 nm and 400 nm, the small photocurrent densities (0.024 mA/cm^2 and 0.022 mA/cm^2) may come from three aspects: 1) relatively small particle size ($\sim 140 \pm 10 \text{ nm}$ and $\sim 136 \pm 9 \text{ nm}$) - leading to negative grain boundary effect, 2) reduced light absorption and conversion - hindered by thick bulk, and 3) a relatively fast recombination rate due to the accumulation of defects on the surface.

In the 300 nm and 400 nm CFO-CN films, the photocurrent density was also limited by the reduced light absorption and conversion rate, but it may have a slower charge carrier recombination rate due to the much larger grain size and positive effect from the hopping mechanism of charge carrier transport, and therefore led to a better PEC performance.

Unlike both CFO-ACCL and CFO-CN films, CFO-ACAC film (**Figure 88**) exhibited a noticeably different trend of the photocurrent density with increased thicknesses. The photocurrent density increased consistently with increasing thickness from 75 nm rather than decreasing, reaching its first peak at 200 nm. In opposition to results found for CFO-ACCL and CFO-CN films, the photocurrent density for CFO-ACAC films experienced a sudden decline at a thickness of 250 nm but then quickly recovered and reached a second peak at 300 nm. As the thickness was further increased, the photocurrent exhibited a consistent downward trend.

According to the ellipsometry porosity analysis results, CFO-ACAC ($\sim 100 \text{ nm}$) has a relatively larger surface area than CFO-CN and CFO-ACAC, with similar thicknesses (**Table 39**). According to the surface reaction rate formula, a larger surface area (larger a_c) should have led to a better PEC performance. However, given that the CFO-CN has a slower charge carrier recombination (ESA decay $\tau_1 = 1.00 \pm 0.08$) rate than CFO-ACAC (ESA decay $\tau_1 = 0.82 \pm 0.1$) in the thin film

(Thickness = 50 nm), and it has a much bigger grain size (176 ± 18) at 100 nm, the PEC performance of CFO-CN turned out to be better than CFO-ACAC. This phenomenon also implies a trade-off in the particle size between surface reaction and charge carrier recombination. A significant difference in the particle size observed from the film surface can lead to a larger impact than a slight difference in the surface area in the film.

In the CFO-ACAC films, the grain size was pretty constant (~ 90 -170 nm). From 75 nm to 200 nm, as the grain size grows slowly (~ 90 -106 nm), more photocurrent density is generated (0.049 mA/cm^2 and 0.129 mA/cm^2), indicating the positive influence from the grain size effect of lowering the recombination rate outweighs the negative effects of the reduced surface reaction rate (increasing V_p). At 250 nm, though the particle size does not change tremendously, from SEM (**Figure 78**), the particles tend to bind with each other, forming a nano-web structure, which might be expected to alter the competition between the grain boundary effect and the particle size effect on surface reaction rate, leading to a significant reduction in the photocurrent density (from 0.129 mA/cm^2 to 0.029 mA/cm^2). At thickness of 300 nm and above, the nano-web structure is no longer observed. With larger particles, the PEC performance stabilised and then decreased at 400 nm with the influence of the thickness effect.

Small particle size enables a fast surface reaction rate, especially when the film is relatively thin (≤ 100 nm), during which the surface area does not significantly influence the photocurrent generation. When the particles grow larger (≥ 150 nm), there is competition between the surface reaction rate and grain boundary effect. There is also a trade-off between surface area and particle size. A larger grain size is preferred, enabling effective hole thermalisation and charge separation, which is demonstrated in TA spectra and associated kinetics. When the film thickness is greater than 300 nm, the effect of film thickness begins to dominate over the effect

of the surface reaction rate. The trade-off between the particle size and the film thickness indicates that the increased grain size does not enhance the charge carrier transport and charge separation enough to outweigh the performance loss due to film thickness, resulting in the reduction of the generated photocurrents as the film thickness grows.

5.4 Photoelectrochemical stability test of CFO thin films

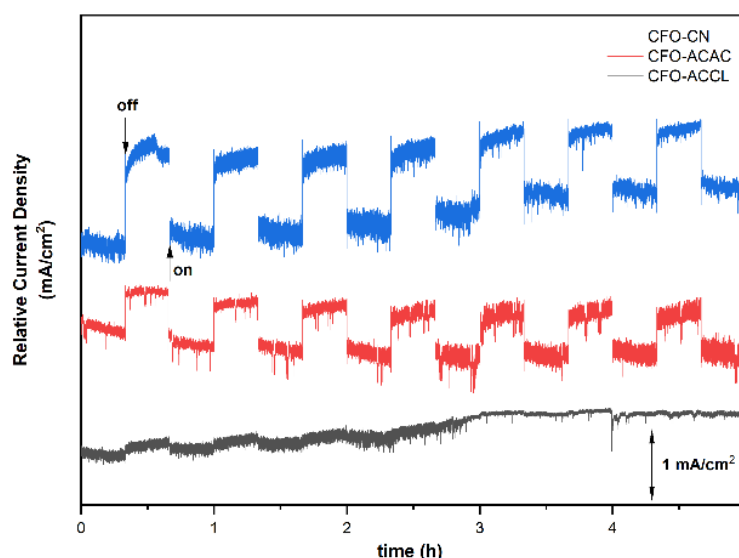


Figure 89. LSV stability test of CFO-ACCL, CFO-ACAC and CFO-CN films at 0.4 V vs RHE for 5 hours in 1M NaOH with 10 vol.% 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$

The stability test of CFO-ACCL, CFO-ACAC and CFO-CN films (300 nm) was conducted at 0.4 V vs RHE for five hours (**Figure 89**). Illumination was turned on and off every half an hour. The level of noise in terms of light on and off was compared over time. Among the three CFO films, CFO-CN showed the best stability. After five hours, it still generates constant photocurrents, albeit with a slightly reduced photocurrent density. The degree of the noisy background does not have obvious change. CFO-ACAC has moderate stability and the noise background significantly changed over time. CFO-ACCL is the least durable. After ~3 hours, it lost the photoactivity.

We compared the Cu 2p, Fe 2p, and O 1s spectrums before and after PEC measurements for the CFO-CN film (**Figure 90**). From the Cu 2p and Fe 2p XPS spectra, the element counts are systematically different but have the same trend and ratio, further indicating the stability of CFO-CN films. In the O 1s spectra, the relative peak area of surface oxygen increases, implying the oxygen-species accumulation on the film surface during the PEC measurement. This phenomenon confirms the oxygen effect in the testing environment. It shows us a promising way to improve the photo performance of CFO films in future work - decorate the surface with proactive oxygen species, and a desirable direction to study - to use in the abundant reactive oxygen species-environment.

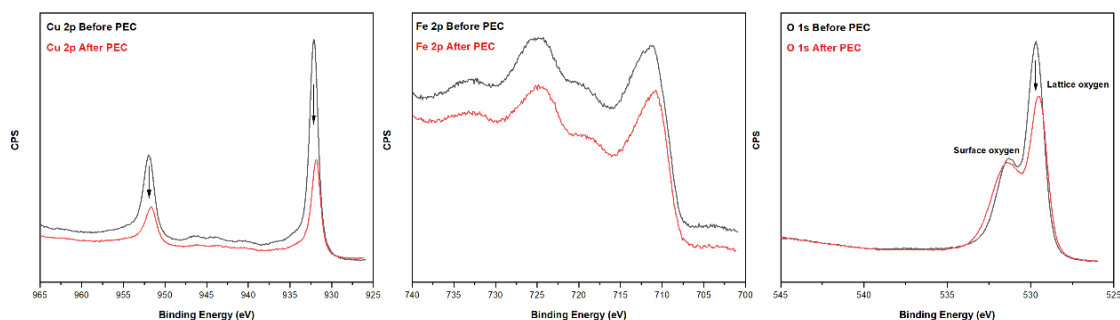


Figure 90. Comparison of XPS of Cu 2p, Fe 2p, and O 1s peaks of CFO-CN deposited on ITO-quartz substrate before and after PEC measurement in 1M NaOH with 10 vol.% 0.1 M Na₂S₂O₈

5.5 Summary

In conclusion, we successfully synthesized Delafossite CuFeO₂ thin films via aerosol-assisted chemical vapor deposition with well-controlled thickness and concisely adjusted morphology. No additional metal-oxide peaks in photoelectron spectra were found, indicating no crystalline impurities.

The photoelectrochemical test environment was investigated, in which experiments with different pH, electrolytes, gas environment pumped into the electrolyte, and necessity of electron scavenger were conducted, and the results were discussed.

This Chapter thoroughly investigated the impact of film morphology and thickness on PEC performance, offering insights not only for CuFeO₂ photocathodes but also for the development of other semiconducting metal oxides.

It is concluded that changing grain size and surface area impacts, significantly, the surface reaction rate but is not the only factor influencing the photoactivity of CuFeO₂. There is a competition between surface reaction and charge carrier separation, in which grain size can play a more critical and complicated role than the surface area on the grain boundary. The thickness effect dominates the PEC performance when the thickness is over 300 nm.

CFO-ACCL, CFO-ACAC and CFO-CN films all generated relatively high and stable photocurrent density in alkaline electrolytes and neutral environment while low and less stable photocurrent density in the acidic environment. 1M NaOH was then chosen as the electrolyte to facilitate the comparison to the results in the literature (**Table 3**). Note that CFO films perform even better in the NaHCO₃ electrolyte due to the electron removal ability from HCO₃⁻.

It is also found that O₂ plays a vital role in the electrolyte and seems to act as an electron scavenger. Apart from inputting saturated oxygen into electrolyte to boost the PEC performance, Na₂S₂O₈ was also found to be an effective sacrificial reagent to remove trapped electrons in the CFO surface, which significantly enhanced the photoactivity of CFO films and reveal its potential photoactivity.

So far, the best performance - the photocurrent density of ~240 μA/cm² in 1M NaOH with 10% 0.1 M Na₂S₂O₈ - was observed in the CFO-CN film with an optimal thickness of ~250 nm, which aligns with the results in the literature (**Table 3**). In a O₂-saturated 1M NaOH electrolyte with 10% 0.1 M Na₂S₂O₈, the performance can go even higher due to the increased concentration of electron scavengers.

In the CFO-ACCL films with thicknesses of 300 nm and 400 nm, the small photocurrent densities (0.024 mA/cm^2 and 0.022 mA/cm^2) may arise due to three aspects: 1) relatively small particle size ($\sim 140 \pm 10 \text{ nm}$ and $\sim 136 \pm 9 \text{ nm}$) - leading to negative grain boundary effect, 2) reduced light absorption and conversion - hindered by thick bulk, and 3) a relatively fast recombination rate due to the accumulation of defects on the surface¹⁴³. As a result of this study, TA spectroscopy confirmed this relationship between charge carrier recombination and film performance. The data also revealed the significance of hole thermalization and charge carrier separation in rationalizing the film performance.

In the 300 and 400 nm CFO-CN films, the photocurrent density was also limited by the reduced light absorption and conversion rate, but it may have a slower charge carrier recombination rate due to much larger grain size and positive effect from hopping mechanism of charge carrier transport^{131,143,144}, and therefore led to a better PEC performance. Further experimental investigations are expected to verify the influence of single or multiple factors listed above.

Due to the time and equipment limitations, not all CFO films thickness were investigated with TAS. In future studies, to comprehensively understand how thickness influences the hole thermalization process and subsequently enhance PEC performance in CFOs, films ranging from 50 nm to 400 nm in consistent thickness should all be investigated using TAS. Moreover, it is recommended to repeat the measurements using new batches of films deposited under the same conditions to mitigate bias and enhance the confidence in the results. Furthermore, it would be advantageous to deposit CuO and Fe_2O_3 using same precursors and procedures as CuFeO_2 . This would enable comparison and can provide deeper insights into the alteration of electronic dynamics.

Chapter 6. Thermal Stability and Thermal Treatments on Delafossite CuFeO₂ Photocathode

6.1 Introduction

In **Chapter 5**, the effect of thin film morphology and thickness on the photoelectrochemical performance of CFO films deposited from three precursor-solvent combinations via AACVD was investigated. Even though 250 nm CFO-CN films exhibited the best PEC performance, the low IPCE rate indicated a significant barrier for CFO photocathodes to be used for practical photoelectrochemical water splitting.

In this Chapter, to increase the photoactivity of the CFO films, various thermal treatments during the post-annealing process were developed according to previous research³²⁵. The objective of studying these post-annealing processes is to identify the optimal method for altering the defect status of the CFO film. This alteration aims to introduce oxygen interstitials, thereby enhancing the p-type electronic conductivity and promoting charge carrier diffusion. 250 nm CFO-CN film, annealed at 750°C for 5 hours under an inert N₂ atmosphere, was used as the standard CFO thin film used for modifications and to compare with the thermally modified CFO-CN films.

Related to this, the thermal stability of CFO films deposited on ITO-quartz substrate was also investigated and evaluated from PEC performance. The thermal stability test data, being aged and tested at different temperatures, further describes the phase composition and helps understand the possible changes when CFO films were used as gas sensing materials in **Chapter 4**.

Modified films were characterized for crystal structure, element composition, morphology, and surface conditions via EDX, XRD, XPS, UV-vis and SEM. Their

PEC properties were investigated by linear sweep voltammetry and chronoamperometry.

6.2 Experiment

The investigation of functional oxygens in the CFO lattice or on the film surface can be a way to improve its photoactivity, and recent research about increasing oxygen interstitials in CFO was reported. Mangier et al.³²⁵ investigated the effects of oxygen off-stoichiometry in $\text{CuFeO}_{2+\delta}$ prepared by solid-state reaction, where it was found that rapid temperature quenching can allow excessive oxygen in the Delafossite CuFeO_2 structure, but that a CuO co-phase was observed when the quenching temperature was over 480°C ³²⁵. The off-stoichiometry value δ is easily calculable and accurate for $T < 480^\circ\text{C}$ following the formula:

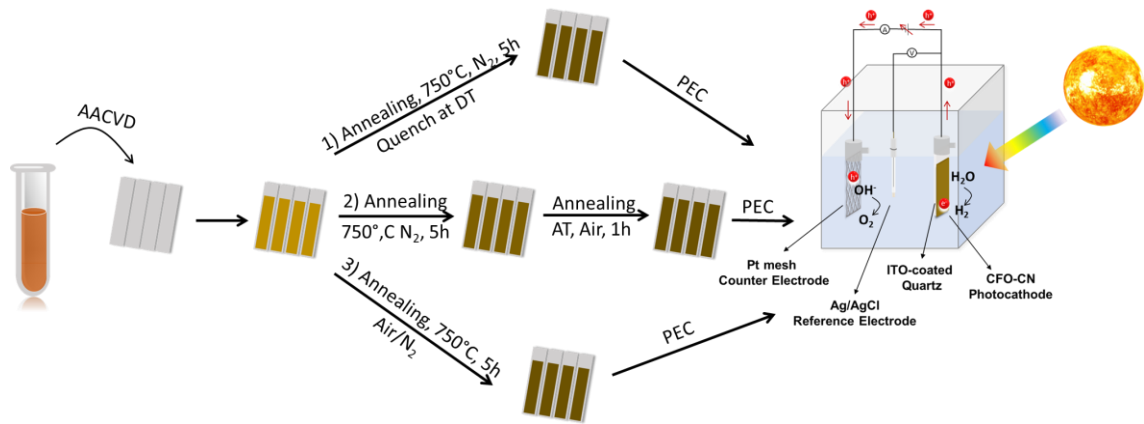
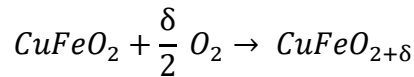


Figure 91. Schematic of three approaches to investigate the effect of oxygen in CFO-CN film's photoactivity

Therefore, CFO thin film experiments related to oxygen content were conducted in three approaches (**Figure 91**):

1) The standard CFO-CN film was deposited following the recipe from **Chapter 4** and cut into four pieces as discussed above. All the CFO-CN films were annealed at 750°C for 5h annealing under N_2 . Quench starts when the film was taken out of

the furnace into air at different temperatures (<100°C, 200°C, 300°C, 400°C and 450°C) where oxygen shall be inserted on the surface of the film. PEC measurement was used to analyse the photoelectrochemical change where 1M NaOH was used as the electrolyte, and no gas was purged into the testing cell before the measurement.

2) Standard CFO-CN films deposited under the same conditions via AACVD were cut into several pieces, annealed at 750°C, 5h annealing under N₂ and cooled down to room temperature. Each piece was annealed in the air in the chamber furnace at different temperatures (200°C, 250°C, 300°C, 350°C and 400°C) for 1 hour. PEC performance of each piece was measured in 1M NaOH electrolyte with 10% 0.1 M Na₂S₂O₈ to compare with the standard CFO-CN film. No gas was purged into the testing cell before the measurement.

Moreover, it is also a way to evaluate the thermal stability of the CFO-CN films in the air atmosphere. Due to the lack of techniques for testing the thermal stability of small CFO gas sensors (in **Chapter 3**), the thermal stability results obtained from PEC measurements are meaningful and instructive for setting the operating temperature of CFO sensors.

3) In **Chapter 3**, different gas atmospheres (different ratio between N₂ and Air used for annealing gas) was investigated in the post-annealing treatment. A small percentage of O₂ (2.5 vol.% air * 20% = 0.5 vol.% O₂) in the N₂ inert atmosphere can trigger the phase transition from Delafossite CuFeO₂ to CuFe₂O₄ and CuO. It was also worth exploring if a small amount of O₂ in the post-annealing treatment made a big difference to the CFO film's PEC performance. Herein, standard CFO-CN films were compared with CFO-CN films deposited under the same AACVD conditions and annealed under four different gas atmospheres (N₂/Air = 195 sccm/ 5 sccm (0.5% vol. O₂, 5,000 ppm), 190 sccm/10 sccm (1% vol. O₂, 10,000 ppm), 185 sccm/15 sccm (1.5% vol. O₂, 15,000 ppm) and 180 sccm/ 20 sccm (2% vol.

O₂, 20,000 ppm)) at 750°C for 5 hours. Linear sweep voltammetry tests were conducted in 1M NaOH to evaluate the photoactivity of the mixed phase with excessive oxygen.

6.3 Results and discussion

6.3.1 Characterization and the PEC performance of CFO-CN films quenched at different temperatures during annealing

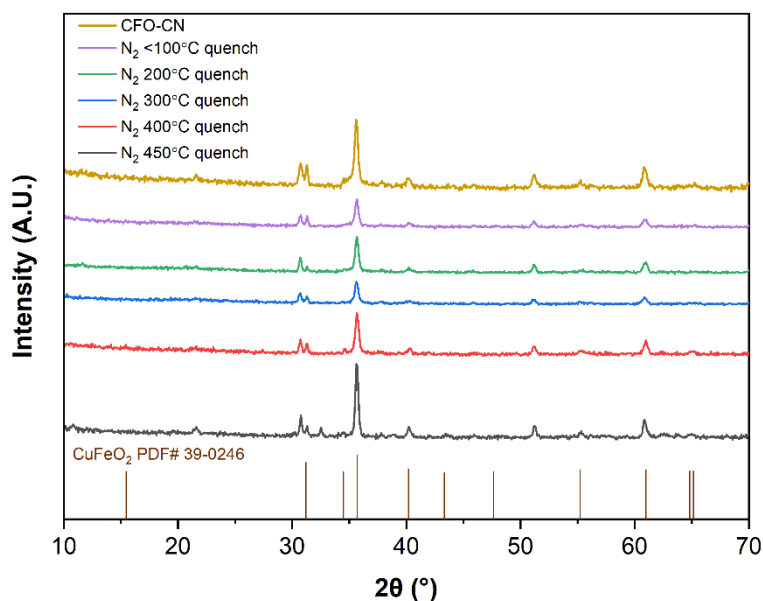


Figure 92. Integrated XRD patterns of CFO-CN films being annealed under same conditions (750°C, 5h, in N₂ atmosphere) and quenched at different temperatures

XRD was used to monitor and analyse the crystal structure transition in terms of oxygen insertion. In **Figure 92**, XRD patterns show the crystal structure of CFO-CN films annealed under the same conditions with different quenching temperatures from 450 °C to natural cooling below 100 °C. From XRD patterns, the lattice parameters do not have a noticeable change, keeping at the same value as $a=3.035$ Å and $c=17.166$ Å.

For the XPS analysis, when all peaks were normalized according to the minimum and maximum values, there were no apparent changes in the peak position or peak intensity in the Cu 2p and Fe 2p peaks, indicating there is no significant

composition change at the surface of the film after quenching at different temperatures. The valence states of Cu and Fe are still dominant by Cu^+ and Fe^{3+} . However, in the Cu 2p peaks, a shoulder nearby ~ 933 eV was noticed. The changes on the should indicate the changes of Cu(II), which reflects the degree of oxygen insertion onto the film surface. According to the Cu 2p spectra in **Figure 93 a)**, CFO-CN films quenched at 200°C should have more oxygen interstitials, while at 400°C , more Cu(II) appeared, which indicated more oxygen was inserted or absorbed onto the film's surface.

In the O 1s peaks, the position of lattice oxygen (~ 529.5 eV) and surface oxygen (~ 531.6 eV) remained the same except for the film quenched at 200°C , where the surface oxygen has a slight chemical shift, implying the valence change of surface oxygen from O^- to O^{2-} . The increased peak area and the intensity also indicate the excessive oxygen on the thin film surface. However, since the Cu and Fe states do not have any significant change, the binding energy shift of the oxygen might be derived from extrinsic oxygen absorbed on the surface rather than oxygen intercalation in the Delafossite structure.

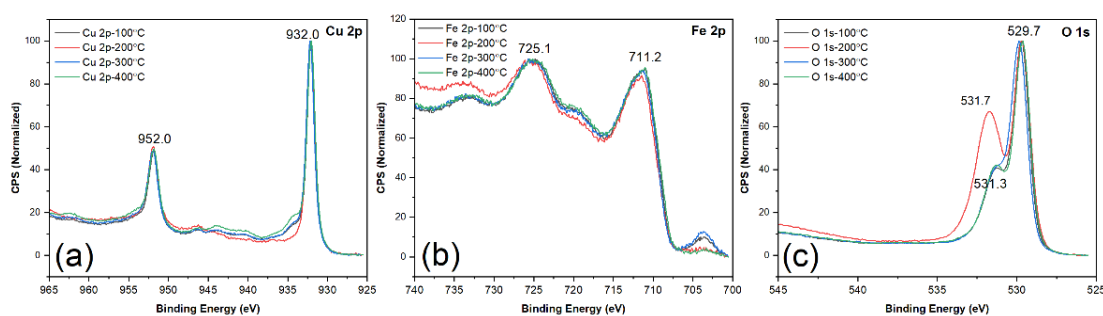


Figure 93. Comparison of XPS of Cu 2p, Fe 2p, and O 1s peaks of CFO-CN films annealed at 750°C for 5h in N_2 but quenched at different temperatures

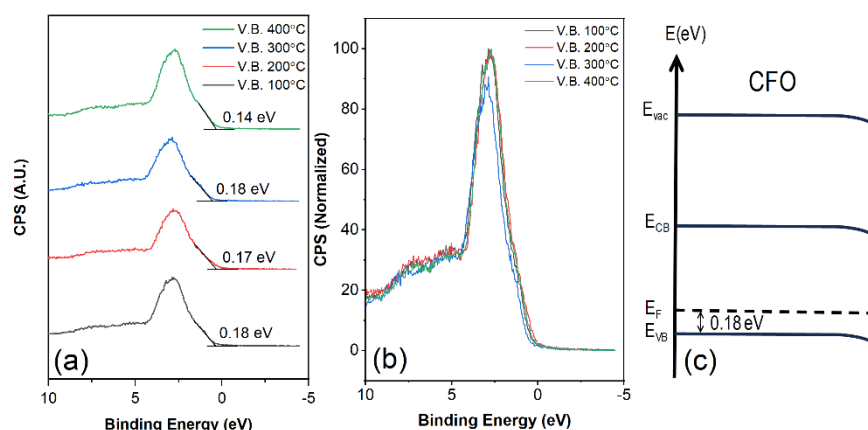


Figure 94. (a) Individual and (b) integrated valence band spectra of CFO-CN films annealed at 750°C for 5h in N₂ but quenched at different temperatures, (c) band diagram of CFO-CN film showing the difference between valence band and Fermi level measured from XPS

The valence band spectra (**Figure 94**) showed the energy gap between the Fermi level and the valence band edge. As the quenching temperature increases, this energy gap slightly decreases. This phenomenon indicates that the involvement of surface oxygen slightly shifts the Fermi level towards the valence band.

As it can be seen in **Figure 93**, CFO films quenched at 200°C exhibited the excess of surface oxygen which indicates a higher concentration of oxygen interstitials compared to films quenched at other temperatures. Therefore it is expected to show the most significant enhancement during PEC measurement. By contrast, the PEC measurement results illustrated a different story.

In films quenched at temperatures over 200°C, the PEC data showed a significant decrease in the photocurrent density and stability. The result suggests that the surface oxygen generated during quenching did not effectively functionalize on the improvement of photocatalytic performance, which indicates that the desired electron-trapping layer might not be formed. It is possible that a small amount of the oxygen was physically absorbed on the surface, which accounts for the changes in the O 1s and Cu 2p spectra. However, since it cannot be reused and

reversed, the physisorbed oxygen was consumed too swiftly to be observed in the plots.

Though, in theory, high-temperature quenching can embed oxygen into the CFO-CN film, it negatively affects the stable Delafossite structure, resulting in a higher current generation in the dark background conditions, as shown in **Figure 95**. The photocurrent density generated at 0.4 V vs RHE in the different CFO films have been summarised in **Table 45**.

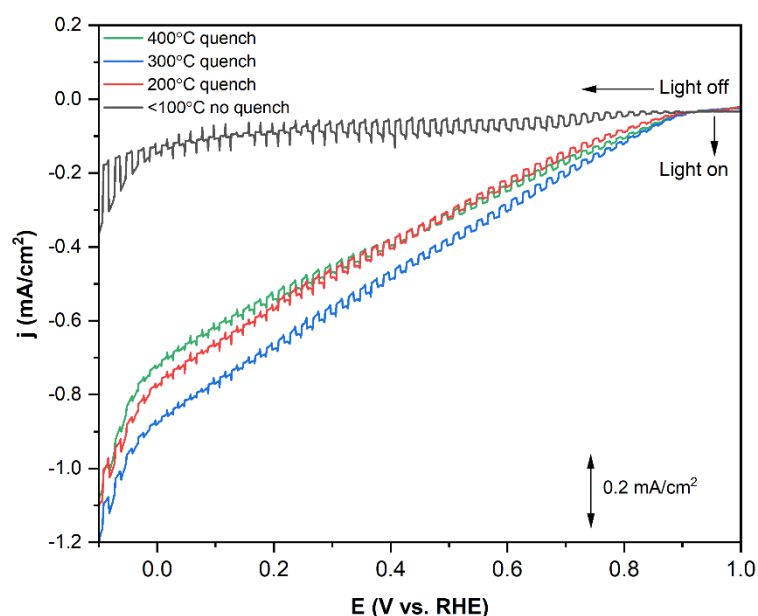


Figure 95. Chopped LSV of CFO-CN films quenched after annealing at different temperatures (1M NaOH, A=0.75cm²)

Table 45. Summary of the photocurrent density obtained at 0.4 V vs RHE in 1M NaOH of CFO-CN films quenched at different temperatures

Quench Temperature	j (mA/cm ²)	Enhancement (%)
<100°C	0.065	/
200°C	0.033	-49.23
300°C	0.023	-64.62
400°C	0.028	-56.92

6.3.2 Thermal stability of CFO-CN films being annealed in the air for 1 hour at different temperatures

In the previous section, quenching at various temperatures had a minimal effect on surface oxygen levels. Though when quenching was performed at 200°C, there was a noticeable alteration in the oxygen peak within the O 1s and Cu 2p spectrum, the PEC activity did not exhibit a significant enhancement.

Therefore, a new method, 1-hour post-annealing treatment in air, was investigated to see if it is possible to introduce oxygen into Delafossite CuFeO_2 thin film by annealing in air at various temperatures. This is also helpful to understand the thermal stability of the CFO-CN film.

The integrated XRD pattern later confirms the stability of the Delafossite crystals' composition, indicating that no additional phases were formed during the short air annealing process (**Figure 96**). Despite variations in the post-air-annealing temperature, all other conditions remained constant, resulting in comparable peak intensities within an acceptable range.

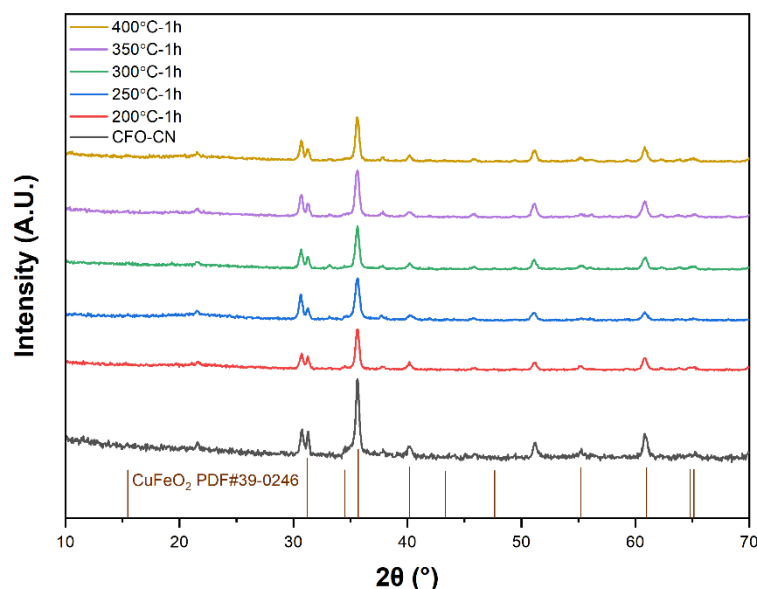


Figure 96. Integrated XRD patterns of CFO-CN films being annealed in air at different temperatures for 1h

XPS spectroscopy of films annealed in the air atmosphere for 1 hour are similar to the ones being quenched at different temperatures, and a similar result was observed in the different pieces in the Cu 2p and Fe 2p spectroscopy (**Figure 97**).

In O 1s spectroscopy, a prominent surface oxygen peak was observed with a similar binding energy (531.4 eV). In comparison, the lattice oxygen peak remained at the same intensity peaked at 529.5 eV. The peak observed at ~535.9 eV in O 1s spectroscopy is inferred to H₂O (g) absorbed on the surface³²⁶ as the water absorption on Cu shifts between ~535-536 eV reported in past research³²⁷.

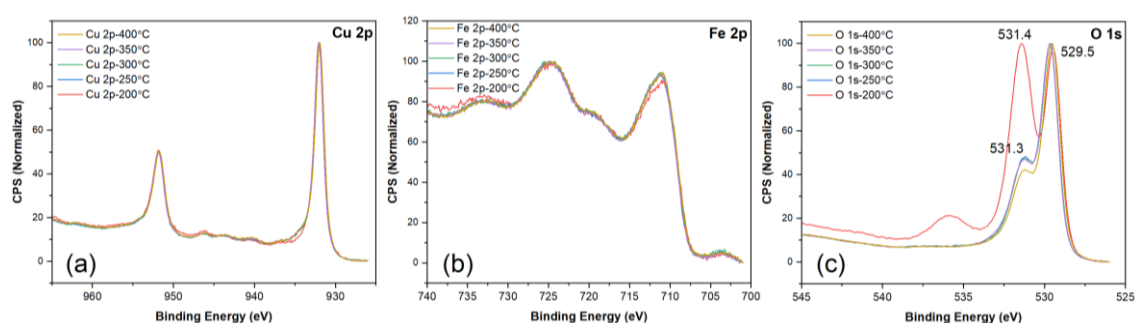


Figure 97. Comparison of XPS of a) Cu 2p; b) Fe 2p; c) O 1s peaks of CFO-CN films annealed at different temperatures for 1h

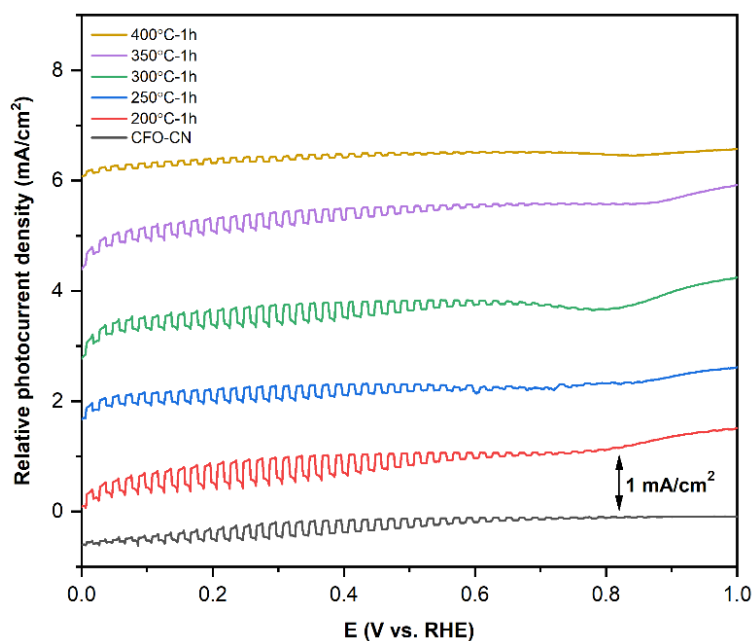


Figure 98. Chopped LSV of CFO-CN films being annealed in air at different temperatures for 1h (1M NaOH + 10% 0.1 M Na₂S₂O₈, A=0.375cm²)

Contrary to the introduction of surface oxygen through quenching at various temperatures, the post-air-annealing treatment proves to be a more effective method for enhancing the photoactivity of CFO-CN films (**Figure 98**).

After being annealed in the air for 1 hour at 200°C, the film showed a ~70% increase in the photocurrent density. At 300°C, the photocurrent density has a slight increase (~30%). While there are fluctuations in photoactivity enhancement at both 250°C and 350°C, the overall performance remains comparable to the standard CFO-CN. When the temperature reached 400°C, the photocurrent density dropped significantly, suggesting a phase transition and decreased thermal stability. The photocurrent density generated at 0.4 V vs RHE in the different CFO films have been summarised in **Table 46**.

Table 46. Summary of the photocurrent density obtained at 0.4 V vs RHE in 1M NaOH with 10% 0.1 M Na₂S₂O₈ of CFO-CN films being annealed for 1h in the air

Air annealing Temperature	j (mA/cm ²)	Enhancement (%)
/	0.2206	/
200°C	0.3775	71
250°C	0.2100	-5
300°C	0.2913	32
350°C	0.2001	-9
400°C	0.0672	-70

Analysing the data from XPS and PEC measurements, it appears that the increased PEC activity is not a result of oxygen interstitials, as indicated by Cu 2p analysis, but rather a consequence of the surface oxygen state. Specifically, the film annealed at 200°C, with a smaller Cu 2p shoulder (indicative of more oxygen interstitials) and a significantly larger surface oxygen peak area (O 1s), achieved the highest photocurrent density. Additionally, among films annealed at other temperatures, those with similar Cu 2p peak areas displayed trends in surface oxygen (O 1s spectra) consistent with PEC performance. For instance, the film annealed at 300°C, featuring a larger surface oxygen peak area, exhibited better

PEC activity. In comparison, the film annealed at 400°C, with the smallest surface oxygen peak area, demonstrated the poorest PEC performance.

6.3.3 Characterization and the PEC performance of CFO-CN films inserted with extra oxygen during post-annealing treatment

In **Chapter 3 (Section 3.3.1.2)**, the annealing gas atmosphere was one of the critical factors during the investigation of optimal annealing conditions for CFO films.

Given the favourable effect of post-air-annealing treatment on enhancing photocurrent generation, it is intriguing to explore the photoelectrochemical performance of the films annealed with variable oxygen concentrations.

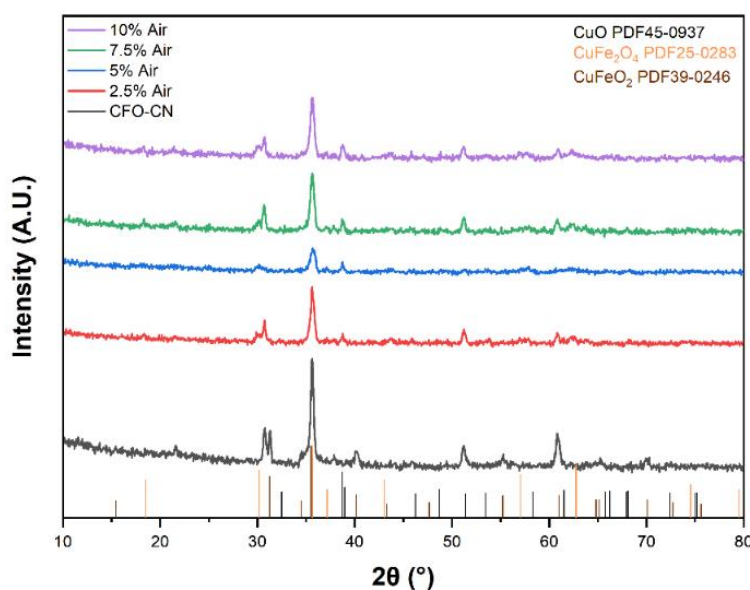


Figure 99. Integrated XRD patterns of CFO-CN films annealed in different gas atmospheres, annealing temperature is 750°C and annealing duration is 5h

Four CFO-CN films deposited with the same AACVD conditions as the standard CFO-CN were annealed at 750°C in N₂ and mixed with different amounts of compressed air for 5 hours. The crystal structure (**Figure 99**) of each film was analysed and confirmed by XRD. CuFe₂O₄ and CuO phases were discovered starting from the 2.5 vol.% air (5,000 ppm O₂), where the typical peaks of CuFeO₂

at $2\theta=31.237^\circ$ (0 0 6), 40.2° (1 0 4), etc. were no longer visible. The overall peak intensities of the film annealed in 5 vol.% air (10,000 ppm O_2) were relatively low. However, as the volume percentage of the air increased to 7.5% (15,000 ppm O_2) and 10% (20,000 ppm O_2), the $CuFe_2O_4$ and CuO peaks became more noticeable again.

When comparing high-temperature annealing with a slight air mixture in N_2 to quenching and post-air-annealing treatments, the crystal structure of the film underwent alterations due to the introduction of oxygen interstitials into the $CuFeO_2$ Delafossite structure. Notably, even a small percentage (2.5 vol.%) of air in the N_2 resulted in the formation of spinel and CuO phases, highlighting the stringent requirements for inert annealing atmosphere when dealing with Delafossite $CuFeO_2$, as well as its sensitivity to oxygen.

From XPS spectroscopy (**Figure 100**), in 2.5% Air mixed with 97.5% N_2 , the film Cu 2p peaks mainly were converted from Cu (I) to Cu (II), where the binding energy of Cu $2p_{3/2}$ right shift from 932.1 eV to 933.2 eV (in the literature Cu(I) Cu $2p_{3/2}$ peaks at 932.18 eV and Cu (II) Cu $2p_{3/2}$ peaks at 933.76 eV³²⁸). There is no noticeable valence state change in Fe 2p peaks as Fe (III) remains the same. In contrast, O 1s peaks offer compelling evidence for the reduction in surface oxygen with an increase in the percentage of air volume, also indicating the phase transition from $Cu(I)FeO_2$ to $Cu(II)Fe_2O_4$ and $Cu(II)O$.

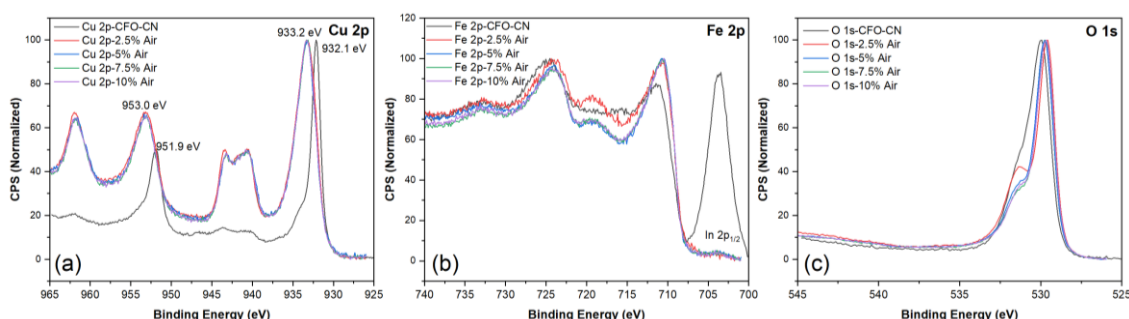


Figure 100. Comparison of XPS of a) Cu 2p; b) Fe 2p; c) O 1s peaks of CFO-CN films being annealed in the different gas atmosphere

CFO-CN films annealed with N₂ mixed with different amounts of air were evaluated for photoactivity through LSV in 1M NaOH (**Figure 101**). Compared with the CFO-CN films annealed in pure N₂, the photocurrent densities of all films annealed mixed with air were greatly enhanced. The highest photocurrent density was obtained in the film being annealed with 10 vol.% air (**Table 47**). The improved percentage is almost doubled (142%) compared with the films annealed with optimal conditions in the post-air-annealing (71%, at 200°C). The results confirmed the effect of oxygen annealing on the photoactivity of CFO thin films, which can effectively enhance the photoelectrochemical activity of CFO thin likely due to the change in crystalline phase.

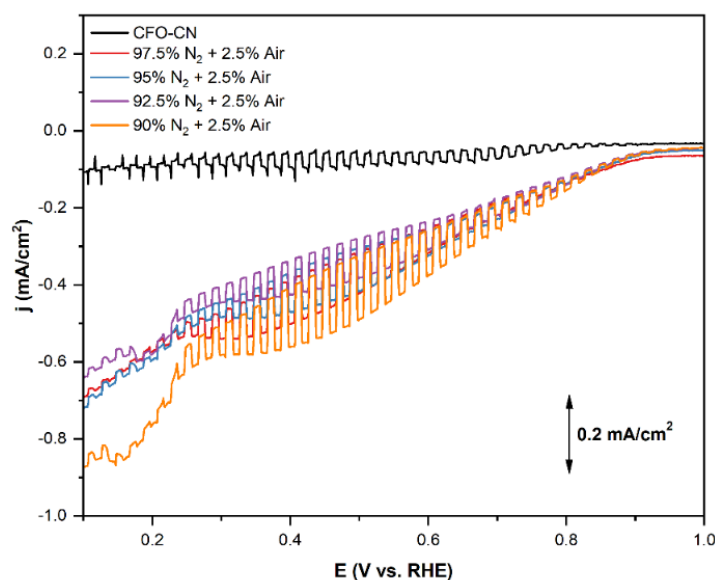


Figure 101. Chopped LSV of CFO-CN films being annealed in the different gas atmospheres (1M NaOH, A=0.75cm²)

Table 47. Summary of the photocurrent density obtained at 0.4 V vs RHE in 1M NaOH of CFO-CN films being annealed under different gas atmospheres

Gas atmosphere (vol.%)	j (mA/cm ²)	Enhancement (%)
N ₂	0.0617	/
97.5% N ₂ + 2.5% air	0.1103	79
95% N ₂ + 5% air	0.1015	65
92.5% N ₂ + 7.5% air	0.0853	38
90% N ₂ + 10% air	0.1496	142

6.4 Summary

In summary, this chapter explores the impact of three distinct post-annealing approaches using air to improve the PEC performance of CFO thin films through defects by introducing oxygen interstitials. This not only offers insights into the material engineering of CFO photocathodes but also establishes connections between Delafossite CuFeO_2 and its spinel 'cousin' CuFe_2O_4 .

The results obtained in this Chapter indicate that treatment with air can indeed serve as an effective method to enhance the photoactivity of CFO films, provided it is constructed appropriately.

The results of the three post-annealing approaches (**Figure 91**) can be summarized as follows:

- 1) Quenching CFO films after being annealed in the inert atmosphere proves ineffective in enhancing photoactivity.
- 2) Conversely, post-air annealing for a brief duration effectively boosts the photogenerated current density of CFO samples while preserving the Delafossite structure. Notably, the highest enhancement percentage, exceeding 70%, was achieved after post-air annealing at 200°C.
- 3) Annealing CFO films in an inert N_2 atmosphere with a small percentage of air mixed in can also enhance photocurrent generation. However, this process leads to the conversion of the crystal phase into a mixed phase of CuFe_2O_4 and CuO .

It is recommended to explore the photoelectrochemical performance of CuFe_2O_4 and CuO using transient absorption spectroscopy (TAS) in the future study to discern the phase responsible for the enhanced performance and understand the mechanism of performance boosting.

Chapter 7. CuO: NiO, CuNiO_x and Effect from Hole Transport Layer on Photoactivity of Delafossite CuFeO₂ Thin Film

7.1 Introduction

Building up heterojunctions is one of the most useful and convenient approaches (as shown in **Chapter 1**) to adjust semiconducting metal oxides' electronic properties, which can further increase the light absorption efficiency, increase the charge carrier transfer efficiency or slow down the charge carriers' recombination rate.

As being introduced in **Section 1.4.4.2**, NiO or CuO:NiO were actively be used as hole transport layer and prove to be effective additives to boost p-type material's PEC performance. In this Chapter, CuO:NiO films were studied in detail and was designed to be constructed with CFO photocathode to enhance its photoactivity.

First, CuO: NiO (two-layer film) and CuNiO_x (precursors were mixed before the deposition) thin films are deposited via AACVD on an ITO-quartz substrate. The PEC performance of CuO: NiO and CuNiO_x were investigated, including the PEC testing environment (electrolyte and pH), film thickness, and the ratio between CuO and NiO. Besides, the electric properties, morphology and photo performance of CuO: NiO and CuNiO_x thin films were investigated. The working mechanism of this heterojunction has been discussed.

Later, CuNiO_x was used as an active layer, deposited between Delafossite CFO film and ITO-quartz substrate, to investigate its feasibility of improving CFO films' photoactivity. 250 nm CFO-CN film, annealed at 750°C for 5 hours under an inert N₂ atmosphere, was used as the standard CFO thin film used for modifications and to compare with modified CFO-CN films (**Figure 102**).

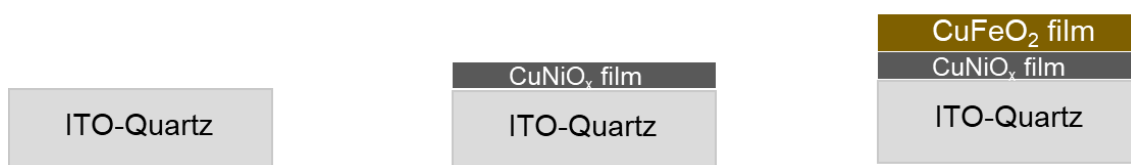


Figure 102. Illustration depicting the sequential deposition process of CuNiO_x (precursors pre-mixed) and CFO-CN film with CuNiO_x engineered as a hole transport layer

During the investigation of post-annealing treatment and the CuNiO_x -CFO-CN heterojunction, the existence of the CuFe_2O_4 phase was found to have a positive effect on the photoelectrochemical performance of Delafossite CFO films. It is worth noting that the XRD patterns of CuFe_2O_4 and NiFe_2O_4 present similar Spinel crystal structures, with typical peaks occurring at near-identical 2θ values, which makes it hard to distinguish their effect on the photoelectrochemical performance of Delafossite CuFeO_2 thin films when co-deposited with Ni.

In order to understand the function of CuFe_2O_4 or NiFe_2O_4 on promoting Delafossite CuFeO_2 thin film's photoelectrochemical performance, pure spinel CuFe_2O_4 thin film as well as NiFe_2O_4 thin film were deposited via AACVD (**Figure 103**). The film's crystal structure, morphology, and photoelectrochemical performance were evaluated.



Figure 103. Illustration depicting the deposition process of CuFe_2O_4 , NiFe_2O_4 and $\text{Cu}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ thin films

7.2 Experimental

7.2.1 Synthesis of CuO : NiO , CuNiO_x hole transport layer and assembly with CFO-CN photocathode

The study on CuO : NiO thin films and the utilization of CuNiO_x layer to build up a heterojunction with the standard CFO-CN films can be divided into three stages.

7.2.1.1 Investigation of AACVD and post-annealing conditions for CuO_x: NiO thin films

In the 1st stage, CuO_x: NiO thin films were deposited using aerosol-assisted chemical vapour deposition (AACVD) on conductive ITO substrates, in which 13 mg (~0.05 mmol) [Cu(acac)₂] was dissolved in 13 ml acetonitrile as the Cu precursor, and 13 mg (~0.05 mmol) [Ni(acac)₂] was dissolved in 13 ml acetonitrile as the Ni precursor.

The two precursors were either deposited separately (as of CuO: NiO), in the order of the nickel precursor followed by the copper precursor or deposited together (as of CuNiO_x) after the two precursors were thoroughly mixed under ultrasound for 20 min prior to AACVD deposition. Cu₂O: NiO films were also synthesized to compare with CuO: NiO.

The effect of the AACVD deposition methods and the sequence were compared, and film thickness was altered by using different amounts of precursors. The AACVD deposition temperature was set at 350°C with the N₂ gas flow fixed at 1 L/min.

After the AACVD deposition, post-annealing treatment was applied to remove the carbon contaminant and to form crystalline metal oxides. At the same time, the annealing atmosphere, annealing temperature and gas atmosphere were varied.

Inert N₂ and air atmosphere were tested as annealing atmospheres in order to control and adjust metal oxide composition (such as Cu₂O and CuO), in which the tube furnace and chamber furnace were used, respectively. Films were annealed at temperatures ranging from 350°C to 750°C with intervals of 50 to 100°C, while the duration was set as 3 hours for the films to complete the phase transition.

PEC measurements were carried out in 1M NaOH electrolyte with the voltage applied from 0.1 V to 1.0 V vs RHE with a scan rate of 1 mV/s. Different pH values

(pH=6.0, 7.0 and 8.0) were altered using K_2HPO_4/KH_2PO_4 buffer solution to test the optimal environment for CuO_x : NiO as photocathodes. Based on the previous research¹⁴⁷, 1 M NaOH and 0.5M Na_2SO_4 were used as electrolytes and were compared.

7.2.1.2 Investigation of AACVD and post-annealing conditions for $CuNiO_x$ thin films with various ratios of Cu and Ni precursors

In the 2nd stage, different volumes of Cu and Ni precursors solution with the same concentration as discussed above were used for the deposition of $CuNiO_x$ thin films with various ratios of Cu and Ni. Pure CuO film and pure NiO film were also deposited and used to compare with the dual-metal oxide films.

PEC stability test was conducted for 2 hours in the $CuNiO_x$ with various Cu and Ni ratios.

1.2.2.4 Assemble $CuNiO_x$ thin films with $CuFeO_2$ for the enhanced PEC performance of $CuFeO_2$ photocathod

In the 3rd stage, the $CuNiO_x$ was assembled with standard CFO-CN film as the catalytic layer to form the heterojunction. The sequence of the deposition is 1) $CuNiO_x$ films deposited on ITO-quartz substrate; 2) CFO films deposited on the $CuNiO_x$ film; 3) The as-deposited multi-metal oxide thin films were annealed in the inert N_2 atmosphere.

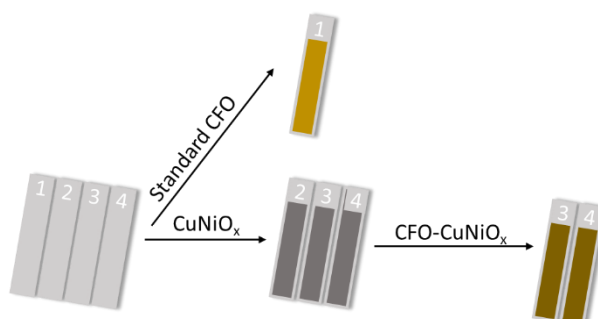


Figure 104. Illustration depicting the deposition process of $CuNiO_x$, CFO-CN and CFO- $CuNiO_x$ films on ITO-quartz substrate

AACVD deposition of different layers (CuNiO_x-ITO-quartz, CFO-ITO-quartz, and CFO-CuNiO_x-ITO-quartz) was carried out separately using the optimal conditions to understand the photo-performance change and the mechanism. A 2*2 cm ITO-quartz substrate was cut into 4 pieces, in which one substrate was used only for standard CFO deposition, three pieces had CuNiO_x deposited on them, of which two had CFO deposited on top, and two for CFO- CuNiO_x (**Figure 104**). The multi-layer CFO-CuNiO_x-ITO-quartz films were annealed at 750°C in the N₂ atmosphere for 5 hours.

7.2.2 Synthesis of CuFe₂O₄ and NiFe₂O₄ films via AACVD and post-annealing treatment

To understand the working mechanism of improved PEC performance from being annealed with a small amount of air in the inert annealing atmosphere, study on the synthesis, characterization and photo-electrical properties of CuFe₂O₄ and NiFe₂O₄ thin films deposited on ITO-quartz substrates were carried out.

Notably, the amount of [Cu(acac)₂] and [Fe(acac)₃] utilized in the investigation of AACVD deposition conditions was halved compared to the quantity typically used for CFO-CN, to reduce unnecessary chemical consumption.

EDX analysis was carried out during optimization experiments to control the atomic ratio of Cu/Fe or Ni/Fe to be 1:2, respectively (i.e. CuFe₂O₄ or NiFe₂O₄). Post-annealing treatment was conducted in the air atmosphere in the chamber furnace. Annealing temperature and duration were briefly investigated.

The crystal structures of CuFe₂O₄ and NiFe₂O₄ thin films on ITO-quartz substrates were examined by XRD, and the film morphology was obtained from SEM. PEC measurements of CuFe₂O₄ and NiFe₂O₄ thin films along with CuFe₂O₄ + CuO (annealed under 90 vol.% N₂ and 10 vol.% O₂), Cu_xNi_{1-x}Fe₂O₄ and CFO films were conducted in 1M NaOH electrolyte with no gas purged in.

7.2.3 Characterization and PEC performance comparison of CuO, Fe₂O₃, standard CFO, CuFe₂O₄-CuO and CuFe₂O₄ thin films

Synthesis, characterization and PEC performance of CuO, Fe₂O₃, standard CFO, CuFe₂O₄ + CuO (annealed under 90 vol.% N₂ and 10 vol.% O₂), and CuFe₂O₄ were conducted and compared to understand the working function of individual or mixed metal oxides in 1M NaOH electrolyte with 10% 0.1M NaS₂O₈. The synthesis conditions are summarized in **Table 48**.

Table 48. Summary of synthesis conditions of CuO, Fe₂O₃, CFO-CN, CuFe₂O₄+CuO, CuFe₂O₄ and NiFe₂O₄ thin films

Film	AACVD deposition	Post-annealing treatment
CuO	The same amount of [Cu(acac) ₂] as standard CFO-CN	Air, 700°C, 3h
Fe ₂ O ₃	The same amount of [Fe(acac) ₃] as standard CFO-CN	Air, 700°C, 3h
CFO-CN	Standard 250 nm CFO-CN	N ₂ , 750°C, 5h
CuFe ₂ O ₄ +CuO	Standard 250 nm CFO-CN	N ₂ /Air vol.% = 90/10; 750°C, 5h
CuFe ₂ O ₄	0.15 mmol [Fe(acac) ₃], 0.065 mmol [Cu(acac) ₂], in 30 ml CH ₃ CN. Take 17.637 ml precursor solution from 30 ml (keep Fe at.% as the same standard 250 nm CFO-CN) as reagent.	Air, 700°C, 3h
NiFe ₂ O ₄	0.15 mmol [Fe(acac) ₃], 0.09 mmol [Ni(acac) ₂], in 30 ml CH ₃ CN. Take 17.637 ml precursor solution from 30 ml(keep Fe at.% as the same as standard 250 nm CFO-CN)	Air, 700°C, 3h

7.3 Results and discussion

7.3.1 Investigation on the CuNiO_x thin film as a hole transport layer for performance improvement of Delafossite CuFeO₂ photocathode

7.3.1.1 Investigation of AACVD deposition and post-annealing conditions of CuO_x: NiO thin film for photocathode

In the first stage, CuO_x: NiO deposited from AACVD were annealed under different conditions. Annealing temperature and gas atmosphere were tested at the same

time, and XRD analysis provided information on phase composition and the phase transition.

XRD patterns of CuO_x: NiO thin films annealed under N₂ and air atmosphere confirmed the proper annealing atmosphere for the formation of CuO and Cu₂O (**Figure 105**). In films deposited by AACVD and annealed at 350°C in an air atmosphere, no crystalline phase was formed. From 450°C, CuO (PDF#45-0937) and NiO (PDF#47-1049) were formed in the air atmosphere and from 650°C, the NiO (1 1 1) peak at $2\theta=37.248^\circ$ was observed alongside the In₂O₃ (4 1 1) peak at $2\theta=37.685^\circ$ which comes from the ITO-quartz substrate.

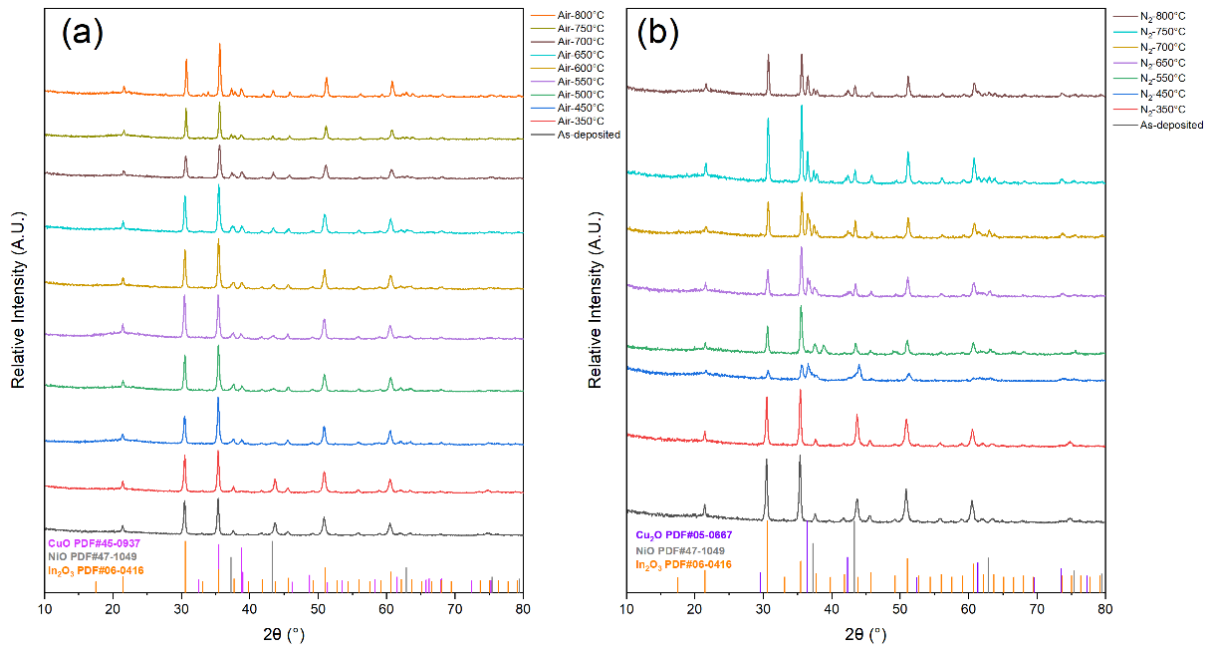


Figure 105. Integrated XRD patterns of CuO_x: NiO films annealed in a) Air and b) N₂ at different temperatures

In the inert N₂ atmosphere, similarly as in the air atmosphere, no crystalline phase was found in the as-deposited film and films annealed at 350°C. However, there was a clear phase transition stage from 450°C to 550°C, where CuO peaks can be observed rather than Cu₂O peaks. Cu₂O (PDF#05-0687) and NiO (PDF#47-1049) peaks were formed and stayed stable when the annealing temperature was over 650°C.

The phase transition process was also observed from the digital images, where as-deposited, amorphous and semi-amorphous films are darker, likely due to carbon contamination, and crystalline films have clean yellow (Cu_2O and NiO) and brown (CuO and NiO) appearance (**Figure 106**).

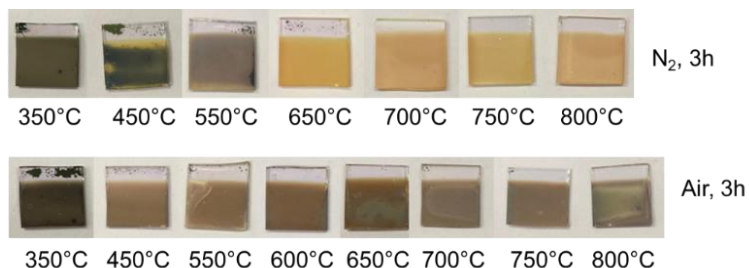


Figure 106. Digital images of CuO_x : NiO films annealed in air and N_2 at different temperatures for 3h

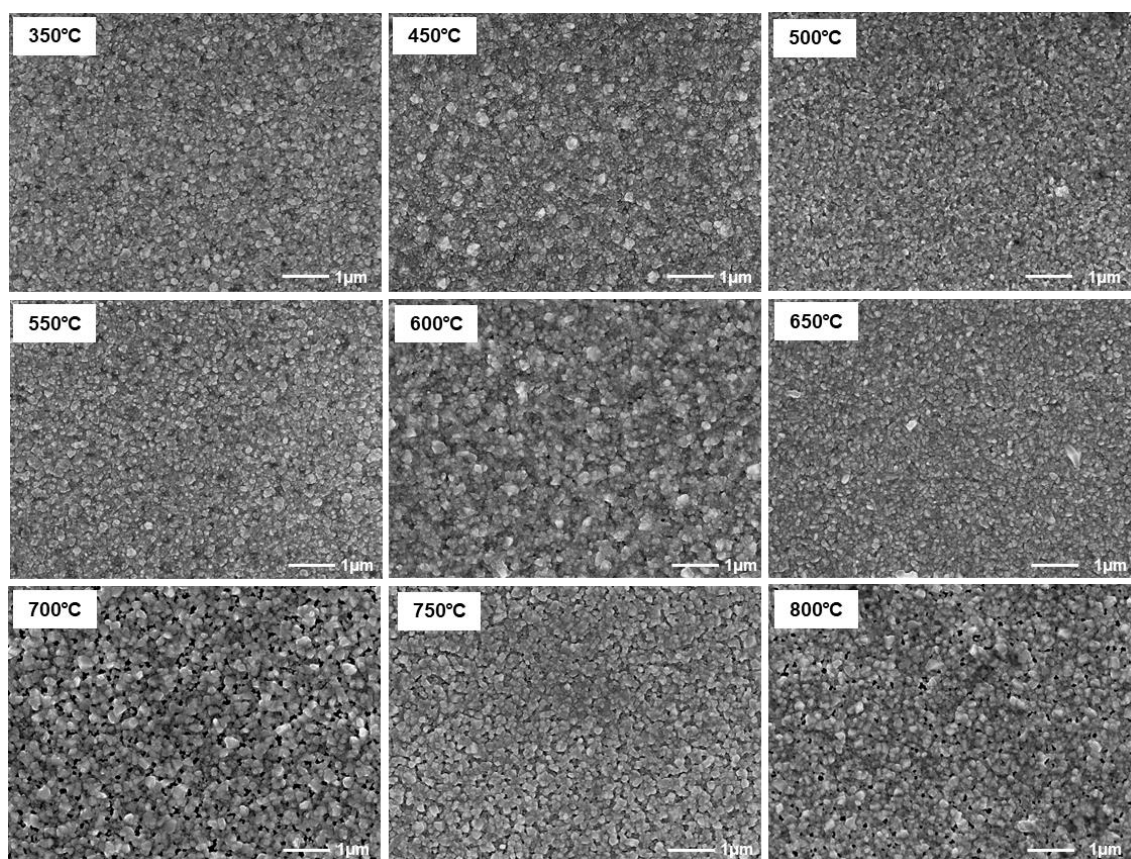


Figure 107. SEM images of CuO : NiO films annealed at different temperatures in air for 3 hours
 CuO : NiO films annealed at different temperatures in air for 3h were analyzed by SEM to characterize film morphology (**Figure 107**). In the SEM images, grains in

the CuO: NiO films annealed at 350°C and 450°C appear disordered. From 550°C, particles were more evenly distributed, and particle sizes were more similar. As the temperature increases, particles seem to grow larger and larger, as well as showing a trend to connect with particles nearby to form a flatter film.

650°C was selected as the annealing temperature while the annealing duration was investigated. Three hours were selected as the annealing duration as the findings from the integrated XRD patterns suggest that CuO (PDF#45-0937) and NiO (PDF#47-1049) phases are formed and remain stable from the first hour of post-air-annealing (**Figure 108**).

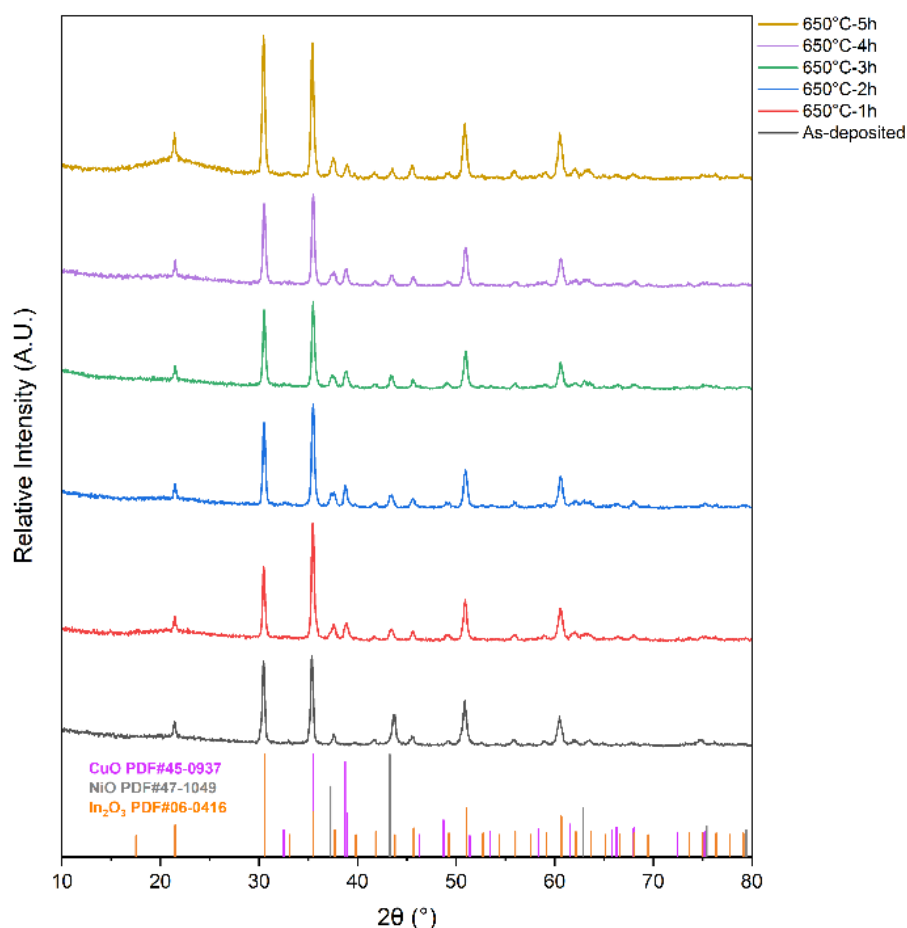


Figure 108. XRD of NiO-CuO films annealed at 650°C for different durations

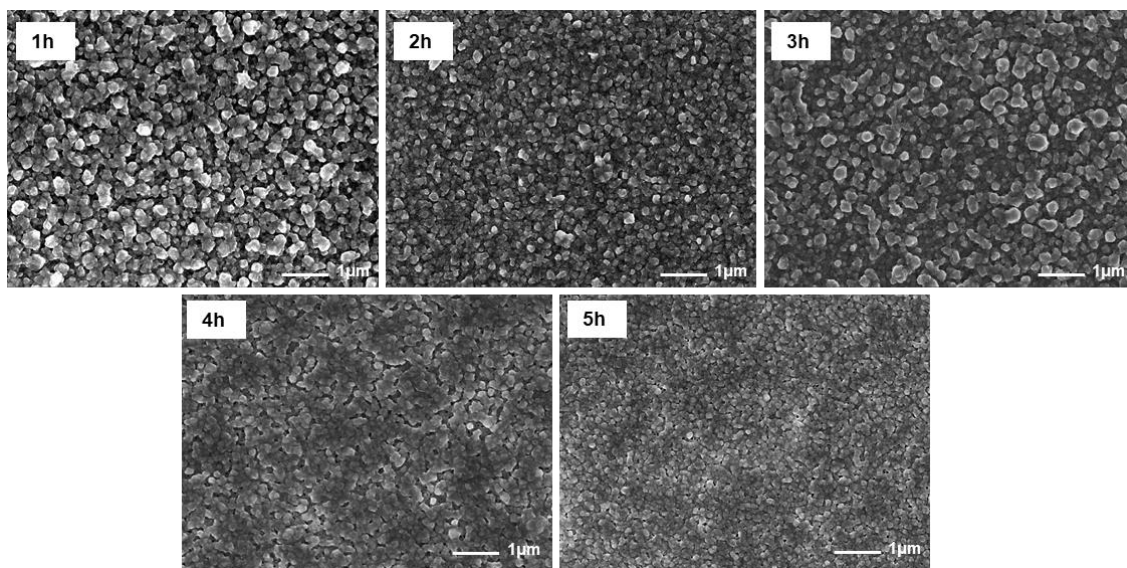


Figure 109. SEM images of CuO: NiO films annealed at 650°C for 1h to 5h

In the SEM images (**Figure 109**), it was observed that particles also tend to connect with nearby particles to form a flatter film. After the first hour of annealing, large grains were formed and were evenly distributed in the film. The distance among grains is large, indicating a relatively high porosity. As the annealing duration increases, the distribution of particles tends to be ordered, while the gaps between particles may decrease.

7.3.1.2 Investigation of the photoelectrochemical performance of CuO: NiO films and the effect of AACVD deposition sequence

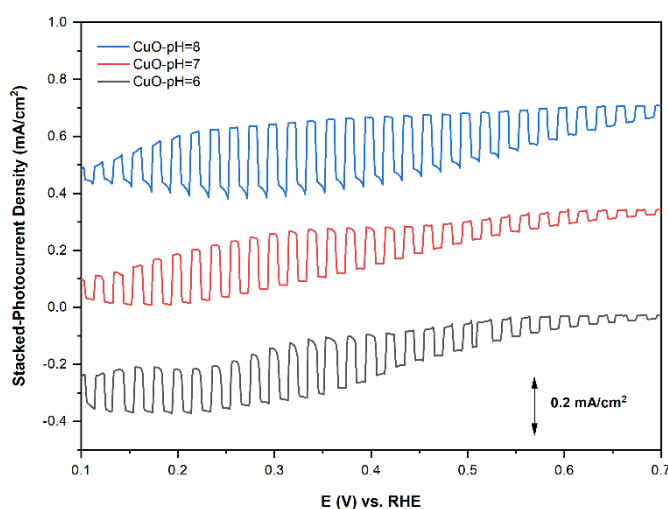


Figure 110. Chopped LSV of CuO: NiO films being measured in K_2HPO_4/KH_2PO_4 buffer solutions with pH=6, 7 and 8

Buffer solution of different pH values (pH =6, 7 and 8) consisting of K_2HPO_4 and KH_2PO_4 was used to confirm the desired electrolyte environment for the CuO: NiO electrode and to evaluate the film's pH resistance (**Figure 110**).

The photocurrent generated from CuO: NiO in an alkaline environment (pH=8, 0.2687 mA/cm²) is more than the one in a neutral environment (pH=7, 0.1802 mA/cm²) and acidic environment (pH=6, 0.1943 mA/cm²) at 0.3 V vs RHE. However, after the LSV test, the CuO: NiO film almost completely faded in the acidic environment, which means that the film is almost completely consumed during the reaction. The strongest photo corrosion and the worst stability indicate that acidic electrolytes are not suitable for bare CuO: NiO thin films to be used as a photocathode.

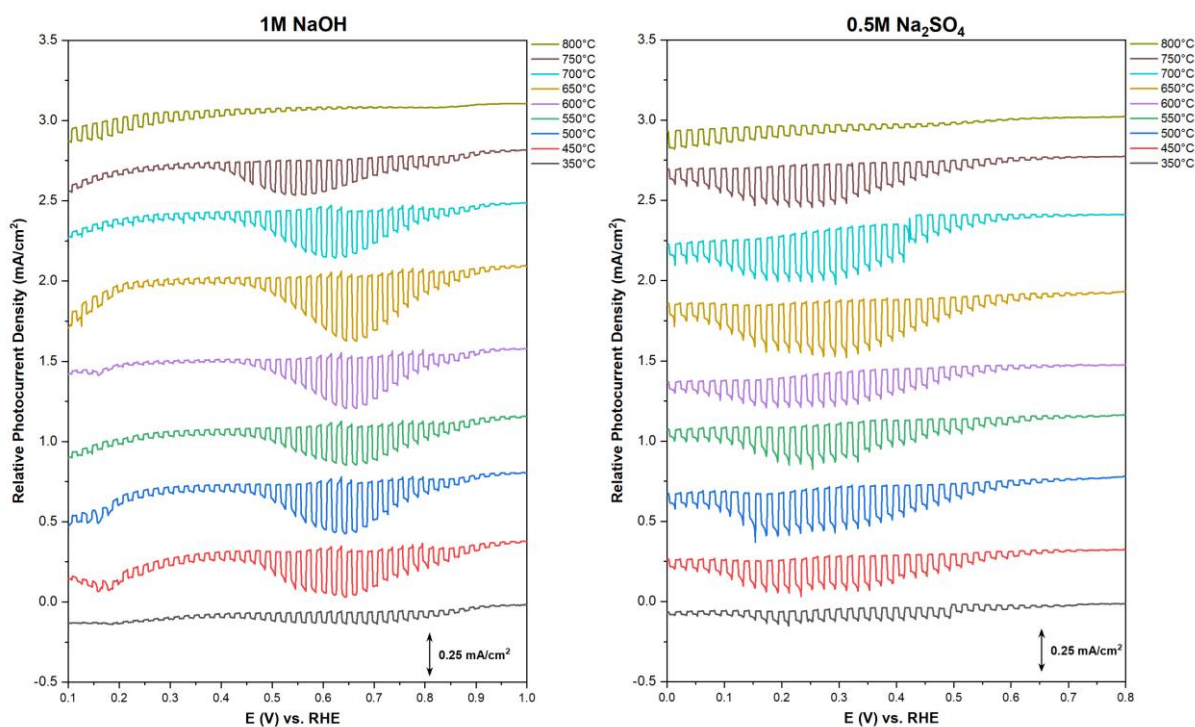


Figure 111. Chopped LSV of CuO: NiO films measured in (Left) 1M NaOH and (2) 0.5 M Na₂SO₄ being annealed in air at different temperatures for 3 hours

Table 49. Summary of photocurrent density of CuO: NiO films measured in 1M NaOH and 0.5 M Na₂SO₄ at 0.4 V vs RHE, all films were annealed in air at different temperatures for 3h

Air annealing Temperature	j (mA/cm ²) - 1 M NaOH @0.65 V vs RHE	j (mA/cm ²) - 0.5 M Na ₂ SO ₄ @0.25 V vs RHE
350°C	0.0731	0.0759
450°C	0.2857	0.2001
500°C	0.3197	0.2647
550°C	0.2352	0.2732
600°C	0.3197	0.1944
650°C	0.4036	0.3242
700°C	0.2964	0.3072
750°C	0.1661	0.2675
800°C	0.0096	0.0538

0.5 M Na₂SO₄ and 1 M NaOH were used as electrolytes to evaluate the photoactivity of CuO: NiO thin films in the neutral and acidic environment (**Figure 111**). CuO: NiO thin films annealed at different temperatures were all tested. Overall, the highest photocurrent density was obtained at ~0.65 V vs RHE in the 0.5 M Na₂SO₄, while in the 1 M NaOH, the most efficient potential left shift to ~0.25 V vs RHE (**Table 49**).

The currents generated in the dark using CuO: NiO films as photocathode are relatively small compared with CFO films. The photoactive window in the neutral environment is wider, ranging from 0-0.6 V, while in the alkaline environment, the photoactive range is from 0.45-0.9 V.

650°C was chosen as the optimal annealing temperature for the further experiment, being the temperature at which the highest photocurrent density was obtained in both electrolytes (**Figure 112**).

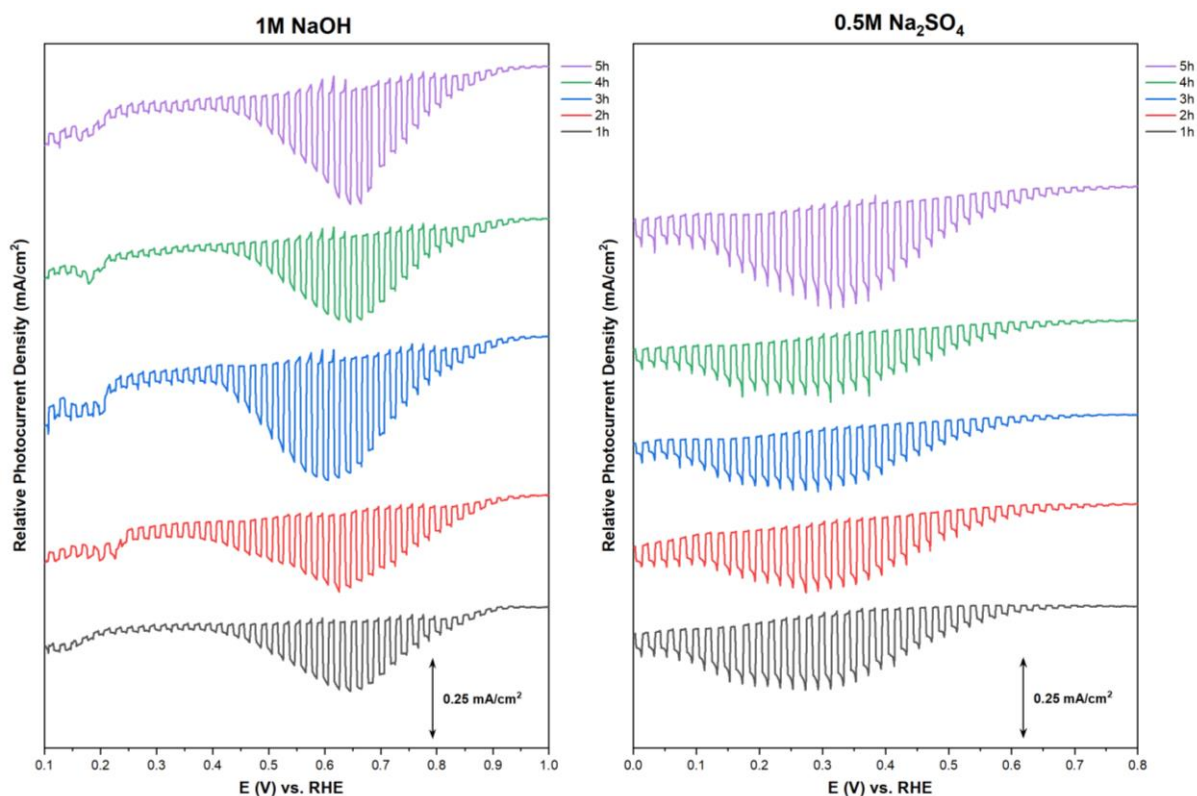


Figure 112. Chopped LSV of CuO: NiO films measured in (Left) 1M NaOH and (2) 0.5 M Na₂SO₄ annealed at 650°C in air for 1h to 5h

The optimal duration was investigated for up to 5 hours when the annealing temperature was set at 650°C. According to the results obtained from both electrolytes, 5 hours of annealing was regarded as the most appropriate annealing duration for CuO: NiO photocathodes (**Table 50**).

Table 50. Summary of photocurrent density of CuO: NiO films measured in 1M NaOH and 0.5 M Na₂SO₄ at 0.4 V vs RHE, all films were annealed in air at 650°C in air for 1h to 5h

Air annealing Duration	j (mA/cm ²) - 1 M NaOH @0.65 V vs RHE	j (mA/cm ²) - 0.5 M Na ₂ SO ₄ @0.25 V vs RHE
1 h	0.2210	0.2238
2 h	0.2474	0.1951
3 h	0.3663	0.1840
4 h	0.2684	0.1696
5 h	0.3663	0.2729

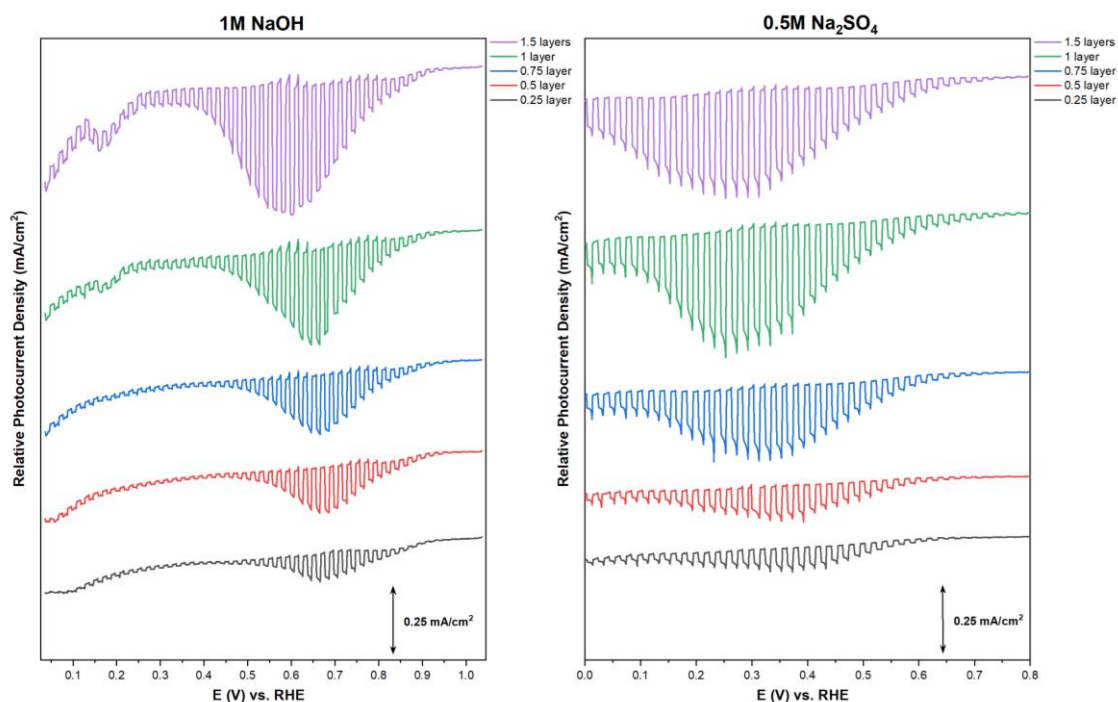


Figure 113. Chopped LSV of CuO: NiO films deposited with various thicknesses measured in (Left) 1M NaOH and (2) 0.5 M Na₂SO₄ annealed at 650°C in air for 3h

As thickness influences the PEC performance of thin film materials, CuO: NiO film with varying thicknesses were deposited and evaluated for their performance in 1M NaOH. The film deposited with 0.13 mol [Cu(acac)₂] in 13 ml acetonitrile and 0.13 mol [Ni(acac)₂] in 13 ml acetonitrile was regarded as one-layer CuO: NiO film, CuO: NiO film with 0.25 to 1.5 layers were deposited and were tested in the LSV using two electrolytes (**Figure 113**).

Contrary to CFO films, the photoactivity of CuO: NiO films was found to be minimally affected by film thickness, as observed in the LSV data. The data indicates that as the film thickness increases, the generation of photocurrents also increases. This observation holds true for both 0.5 M Na₂SO₄ and 1M NaOH electrolytes. Furthermore, the thickness was extended up to 5 layers by using consecutive depositions, and the LSV data in 1M NaOH electrolyte still showed the same trend that thicker CuO: NiO can generate more photocurrent (**Figure**

114). The highest photocurrent density (1.22 mA/cm^2) was obtained in the 5-layer film at $\sim 0.5 \text{ V}$ vs RHE.

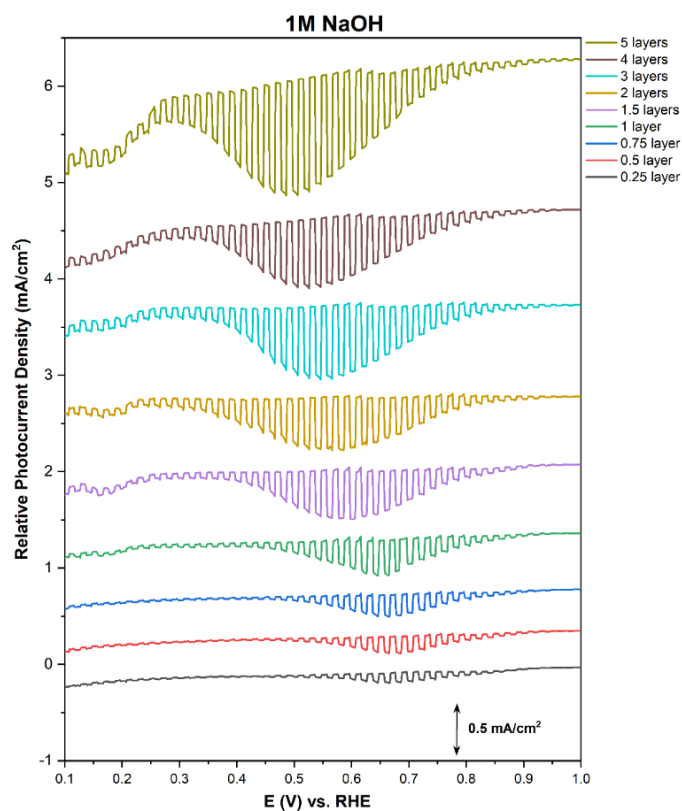


Figure 114. Chopped LSV of CuO: NiO films deposited with different thicknesses from 0.25 layer to 5 layers measured in 1M NaOH annealed at 650°C in air for 3h

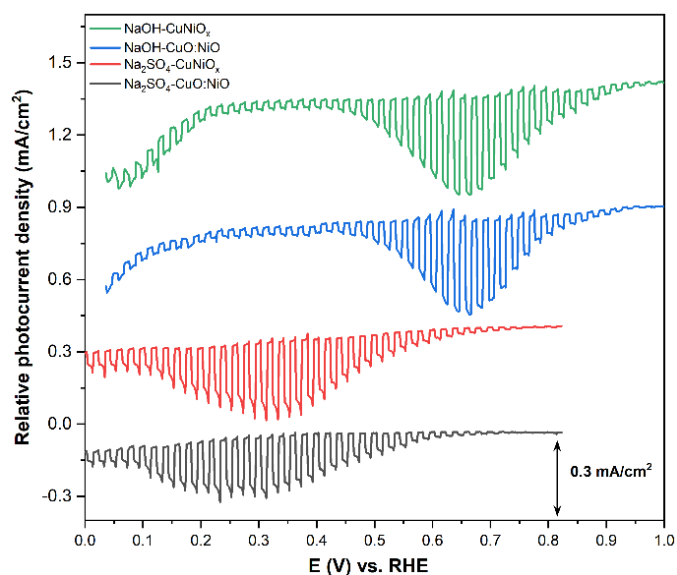


Figure 115. Chopped LSV of CuO: NiO films deposited with different deposition sequences measured in 1M NaOH and 0.5 M Na₂SO₄ electrolyte annealed at 650°C in air for 3h

Similarly, like the previous result, films tested in an alkaline environment generated more significant photocurrent than in the neutral electrolyte (**Figure 115**).

The photoactivity of CuO: NiO films deposited with different sequences in the AACVD deposition was also evaluated and compared in two electrolytes. Overall, CuO: NiO films deposited with two precursor solutions well-mixed before AACVD deposition have a relatively higher photocurrent density than the ones deposited by Cu and Ni precursor solution separately in both 1M NaOH and 0.5 M Na₂SO₄.

As a result of the above test, CuNiO_x films were deposited with a well-mixed precursor solution in the following experiments when investigating the photoelectrochemical performance and used as a hole transport layer (**Table 51**).

Table 51. Comparative photocurrent density analysis of CuO: NiO and CuNiO_x films under 1M NaOH and 0.5 M Na₂SO₄ at 0.4 V vs RHE annealed at 650°C in air for 3h

Air annealing Duration	j (mA/cm ²) - 0.5 M Na ₂ SO ₄ @0.25 V vs RHE	j (mA/cm ²) - 1 M NaOH @0.65 V vs RHE
CuNiO _x	0.2756	0.4046
CuO:NiO	0.2509	0.3913

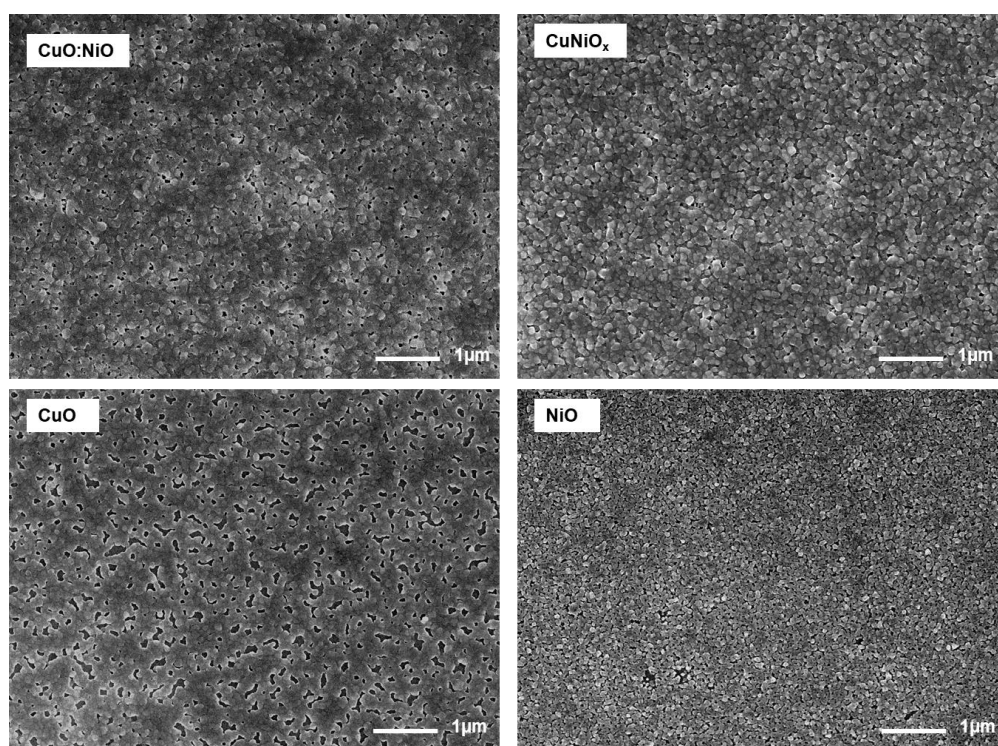


Figure 116. SEM images of CuO, NiO, CuNiO_x and CuO: NiO films

SEM was used to examine the thin film morphologies of CuO, NiO, CuNiO_x and CuO: NiO. CuO thin films appeared to be a 2-dimensional flat film with much space between particles, while NiO thin films were mainly comprised of nanoparticles. There was no apparent difference between CuO: NiO and CuNiO_x films. The combination of CuO and NiO makes CuO: NiO (CuNiO_x as well) a flat film composed of large nanoparticles, as shown in **Figure 116**.

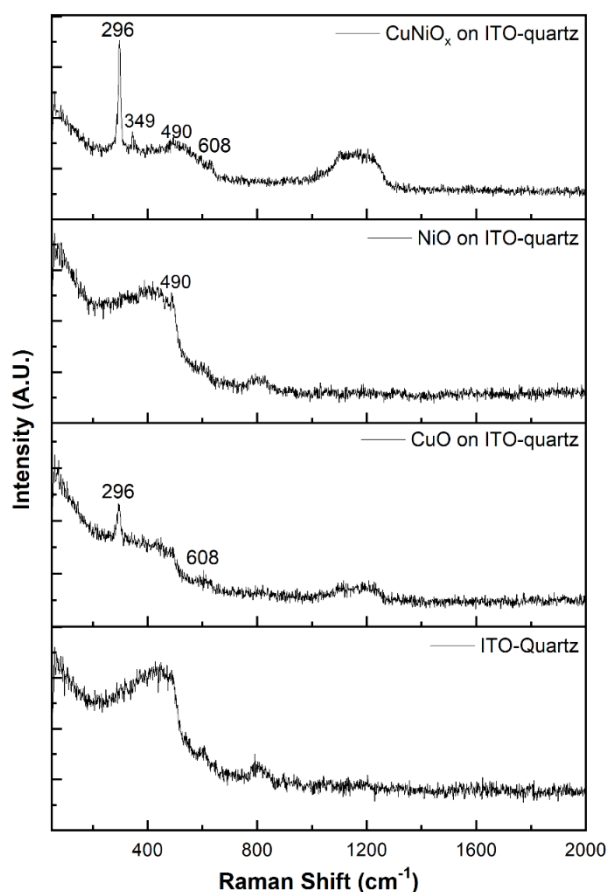


Figure 117. Integrated Raman spectrum of CuO, NiO, CuNiO_x deposited on ITO-quartz and ITO-quartz substrate

Bare ITO-quartz substrate, CuO on ITO-quartz, NiO on ITO-quartz and CuNiO_x on ITO-quartz were analysed using Raman spectroscopy to identify and compare the composition in each layer (**Figure 117**). CuO fingerprint peaks were found at ~296 cm⁻¹, 349 cm⁻¹, and 608 cm⁻¹, according to the RRUFF database (R060978 Tenorite CuO). There is a small peak located peak at ~490 cm⁻¹ in the Raman

spectroscopy of NiO thin film, which coincides with NiO powder (Aldrich, 99.99%) in the literature³²⁹. However, due to the overall area with an ITO-quartz background, it is hard to confirm the existence of NiO. Peaks from ITO-quartz substrates at $\sim 450\text{ cm}^{-1}$ and 800 cm^{-1} were both observed in NiO film. However, it was not shown obviously in the CuO and CuNiO_x films.

The optical properties of CuO, NiO and CuNiO_x films deposited on ITO-quartz substrates were evaluated by UV-vis spectroscopy, where the ITO-quartz substrate was used as a blank background. The indirect band gaps of CuO, NiO and CuNiO_x plotted using Tauc plot were found at 2.5 eV, 3.1 eV and 2.8 eV, respectively. From **Figure 118 a**), the absorption peak in CuNiO_x looks like an amalgamation of the peaks from CuO and NiO, especially from 325-350 nm. From the Tauc plot in **Figure 118 b**), it seems that the band gap of CuNiO_x shifted after the amalgamation, increasing the bandgap in CuO and decreasing the bandgap in NiO.

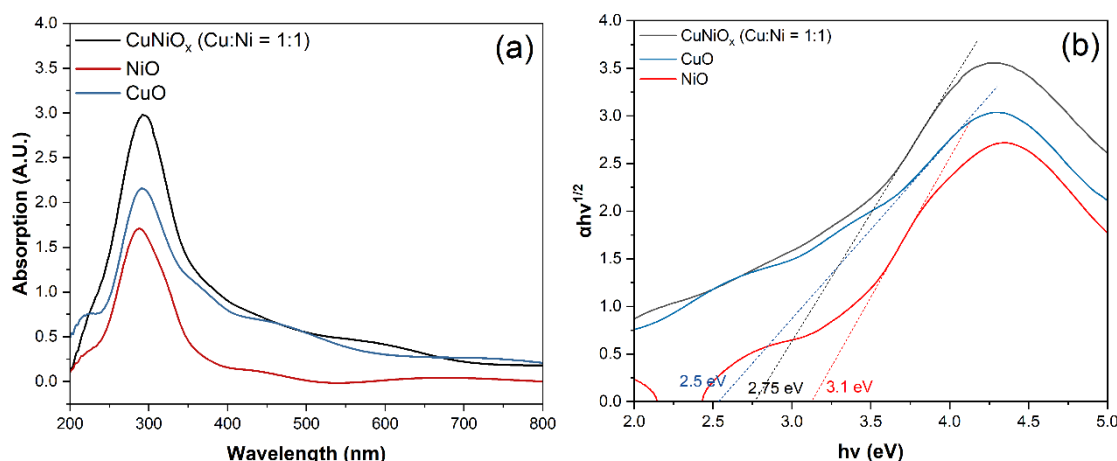


Figure 118. (a) UV-vis absorption spectroscopy and (b) Tauc plot for indirect band gaps of CuO, NiO and CuNiO_x films deposited on ITO-quartz substrate

Insight on the electronic structure and composition of Cu, Ni and O were obtained by XPS analysis (**Figure 119**). High-resolution spectra of Cu 2p, Ni 2p and O 1s peaks for CuO, NiO and CuNiO_x films were compared. In the Ni 2p spectra, the Ni 2p_{3/2} peak at $\sim 853\text{ eV}$ was assigned to Ni²⁺, while the Ni 2p_{3/2} peak at $\sim 855\text{ eV}$

was assigned as Ni^{3+} ³³⁰. The oxygen peaks at ~ 529 eV and ~ 531 eV can still be allocated to lattice oxygen and surface oxygen. Due to the large amount of surface oxygen in the NiO, the amount of surface oxygen in the CuNiO_x thin film was increased compared with the CuO thin film.

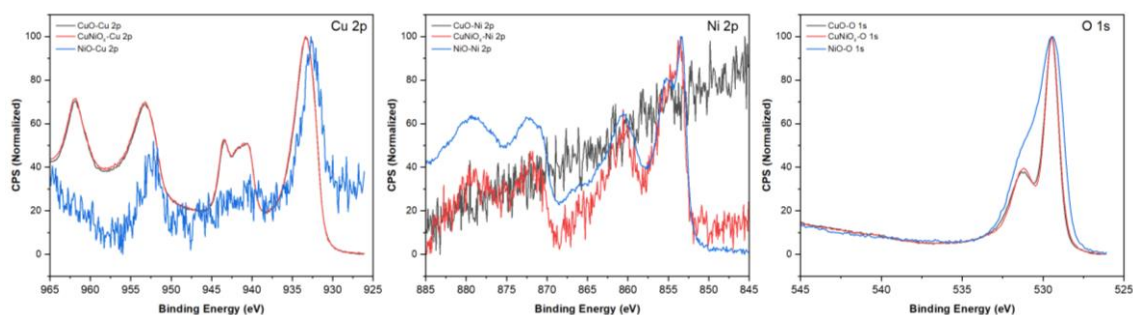


Figure 119. Comparison of XPS of a) Cu 2p; b) Fe 2p; c) O 1s peaks in CuO, NiO and CuNiO_x films deposited on ITO-quartz substrate

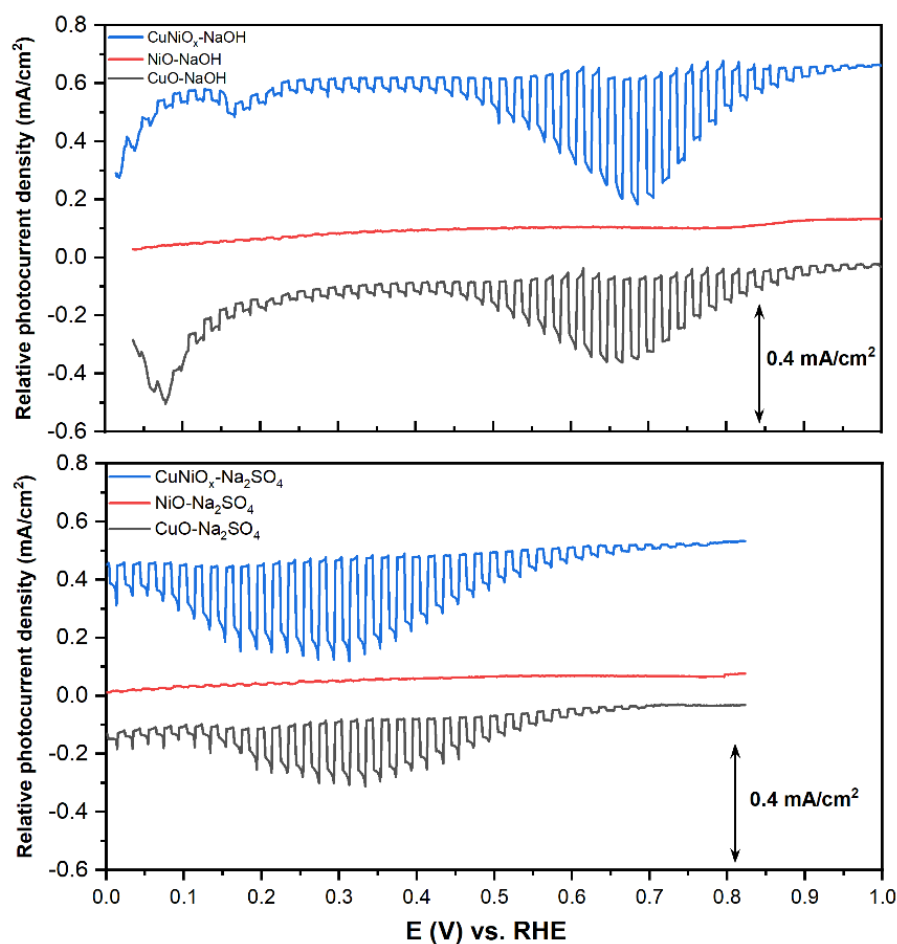


Figure 120. Chopped LSV of CuO, NiO and CuNiO_x films measured in 0.5M Na_2SO_4 and 1M NaOH

The PEC performance of each layer in the CuNiO_x films in two electrolytes was evaluated to see if the CuNiO_x had better performance than the individual metal oxide films (**Figure 120**).

According to the LSV test results, CuO and CuNiO_x showed similar and relatively high photoactivity, while the photocurrents generated from NiO are negligible.

The photocurrent densities of CuO and CuNiO_x in two electrolytes are summarized in **Table 52**, where CuNiO_x generated more photogenerated current than CuO in both electrolytes. In 1 M NaOH electrolyte, the photocurrent density of CuNiO_x was 30% larger than that of CuO, while in 0.5 M Na₂SO₄ solution, the photocurrent density increased by 80% from CuO to CuNiO_x, indicating CuNiO_x is a more effective and efficient as a photocathode.

Table 52. Comparative photocurrent density analysis of CuO and CuNiO_x films under 1M NaOH and 0.5 M Na₂SO₄ electrolytes at 0.4 V vs RHE annealed at 650°C in air for 3h

Films	j (mA/cm ²) - 0.5 M Na ₂ SO ₄ @0.25 V vs RHE	j (mA/cm ²) - 1 M NaOH @0.65 V vs RHE
CuO	0.7694	1.1937
CuNiO _x	1.3926	1.5272
	+80%	+30%

7.3.1.3 Photoelectrochemical performance comparison between CuO: NiO films annealed in the air and Cu₂O: NiO films annealed in the N₂

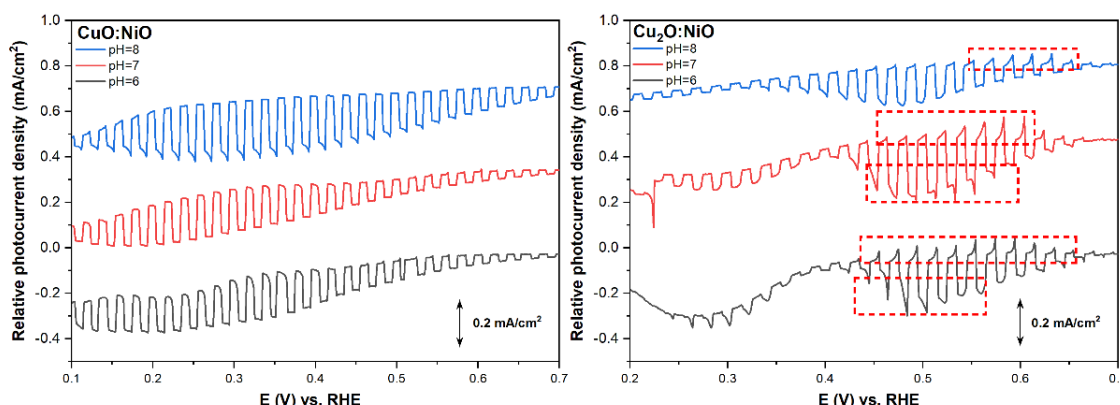


Figure 121. Chopped LSV of CuO: NiO and Cu₂O: NiO films measured in K₂HPO₄/KH₂PO₄ buffer solutions with pH=6,7,8

During the annealing atmosphere investigation, Cu₂O: NiO thin films were formed in the inert N₂ atmosphere from 650°C after 3 hours of annealing. In parallel to copper(II) CuO: NiO, copper(I) Cu₂O: NiO was also tested by LSV under three different pH environments. As can be seen from **Figure 121**, Cu₂O: NiO showed better PEC performance in the neutral and acidic environment. Since after a single LSV test, Cu₂O: NiO film was also primarily corroded, a neutral environment was regarded as its best environment for its photoactivity. Compared with CuO: NiO thin films, Cu₂O: NiO has a narrower active potential window, mainly ranging from 0.4 V to 0.7 V.

Moreover, transient spikes were observed (Highlighted in **Figure 121**) in the LSV chopped light curves in the Cu₂O: NiO thin films, indicating that the consumption of photogenerated holes and electrons is ascribed mainly to the surface recombination, while in the CuO: NiO film the transient spikes are not present³³¹.

Specifically, the surface recombination means the ‘instantaneous’ photocurrent observed when the light is switched on relates to a rapid separation of photogenerated electron-hole pairs that takes place in the space charge layer, with – for a p-type photocathode – electrons moving to the interface to charge the space charge capacitance and holes passing to the external circuit³³².

The subsequent decrease in photocurrent is attributed to the accumulation of photogenerated minority carriers near or at the interface. This accumulation leads to an increased flow of electrons (resulting in a negative current) into the surface due to recombination. Eventually, a steady state is attained where the rate at which holes reach the interface equals the rate at which they are consumed by charge transfer and recombination. Consequently, the photocurrent stabilizes and remains constant, matching the current passing through the semiconductor/electrolyte interface. The spike observed upon turning off the light occurs because the flow of holes is abruptly halted, revealing only the decay of electron flux. This electron flux

diminishes until all excess holes are consumed by recombination and charge transfer, causing the current to return to zero³³².

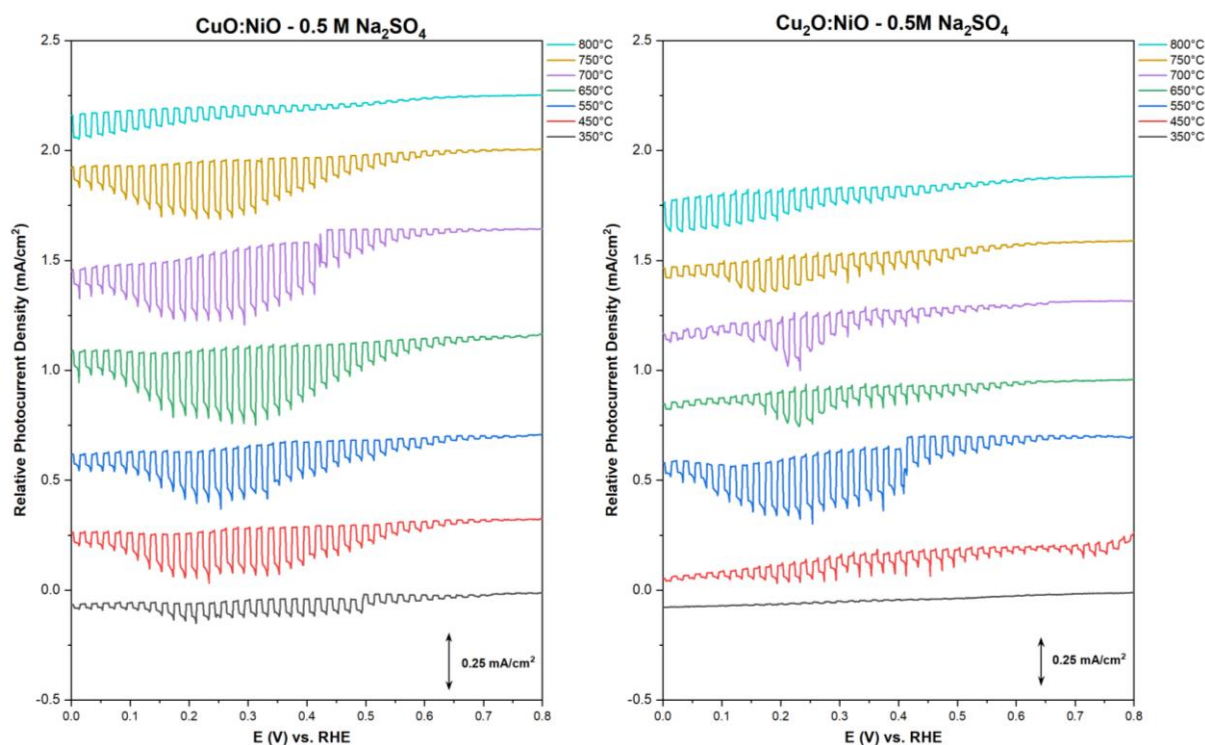


Figure 122. Comparative chopped LSV of CuO: NiO and Cu₂O: NiO films annealed in air and N₂ at different temperatures for 3h and measured in 0.5 M Na₂SO₄

Since Cu₂O: NiO showed better performance in the 0.5M Na₂SO₄, the films annealed under different temperatures were tested and compared with CuO: NiO films in the same electrolyte (**Figure 122**). It seems that after annealing at 550°C, the photocurrent density was the highest at 0.25 V vs RHE. However, as was shown in the XRD patterns (**Figure 105 b**), Cu₂O: NiO formed the stable Cu₂O and NiO phases from 650°C, where at 550°C, CuO: NiO film was observed in a transition stage. Compared with the group of CuO: NiO films annealed at the same temperatures, Cu₂O: NiO films' overall photocurrent densities are smaller (**Table 53**). It can also be deduced that in the alkaline electrolyte, CuO: NiO will still generate a higher photocurrent than Cu₂O: NiO films.

Table 53. Comparative photocurrent density analysis of CuO:NiO and Cu₂O:NiO films under 0.5 M Na₂SO₄ electrolytes at 0.4 V vs RHE annealed at 650°C in air and N₂ for 3h

Annealing temperature	j (mA/cm ²) – Air @0.25 V vs RHE	j (mA/cm ²) – N ₂ @0.25 V vs RHE
350°C	0.0759	0.0098
450°C	0.2001	0.0846
550°C	0.2732	0.3214
650°C	0.3242	0.1790
700°C	0.3072	0.1747
750°C	0.2675	0.1284
800°C	0.0538	0.0930

7.3.1.4 Investigation of the photoelectrochemical performance of CuNiO_x films consisting of various ratios between Cu and Ni

Previously, CuNiO_x thin films were synthesized with the same amount of [Cu(acac)₂] and [Ni(acac)₂] precursors in the precursor solution. In this section, 0.05 mmol [Cu(acac)₂] and 0.05 mmol [Ni(acac)₂] were dissolved in 13 ml CH₃CN, respectively, and pre-mixed for AACVD deposition. The amount of Cu or Ni deposited on the film was adjusted by using various ratios of Cu or Ni precursors.

Table 54. Summary of Cu/Ni precursor ratios utilized during AACVD deposition for CuNiO_x films along with the corresponding EDX results showing the Cu/Ni relative atomic ratio in the as-deposited film

Cu:Ni precursor ratio	Cu precursor (ml)	Ni precursor (ml)	EDX Relative Cu/Ni at.% - as deposited	Standard Deviation (%)	Standard error (%)
Pure NiO	/	13	/	/	/
Cu:Ni = 1:5	2.6	13	28/72	3	1
Cu:Ni = 1:4	3.25	13	38/62	1	0.6
Cu:Ni = 1:3	4.33	13	38/62	0.9	0.4
Cu:Ni = 1:2	6.5	13	43/57	1	0.6
Cu:Ni = 1:1	13	13	61/39	0.5	0.2
Cu:Ni = 2:1	13	6.5	70/30	0.8	0.4
Cu:Ni = 3:1	13	4.33	80/20	0.5	0.2
Cu:Ni = 4:1	13	3.25	85/15	0.5	0.2
Cu:Ni = 5:1	13	2.6	86/14	0.8	0.4
Pure CuO	13	/	/	/	/

EDX was performed to quantify the elemental composition in the as-deposited CuNiO_x films, as shown in **Table 54**. It is also evidenced from XRD patterns that both CuO and NiO phases have been obtained in the CuNiO_x for films with various Cu, Ni ratios (**Figure 123**).

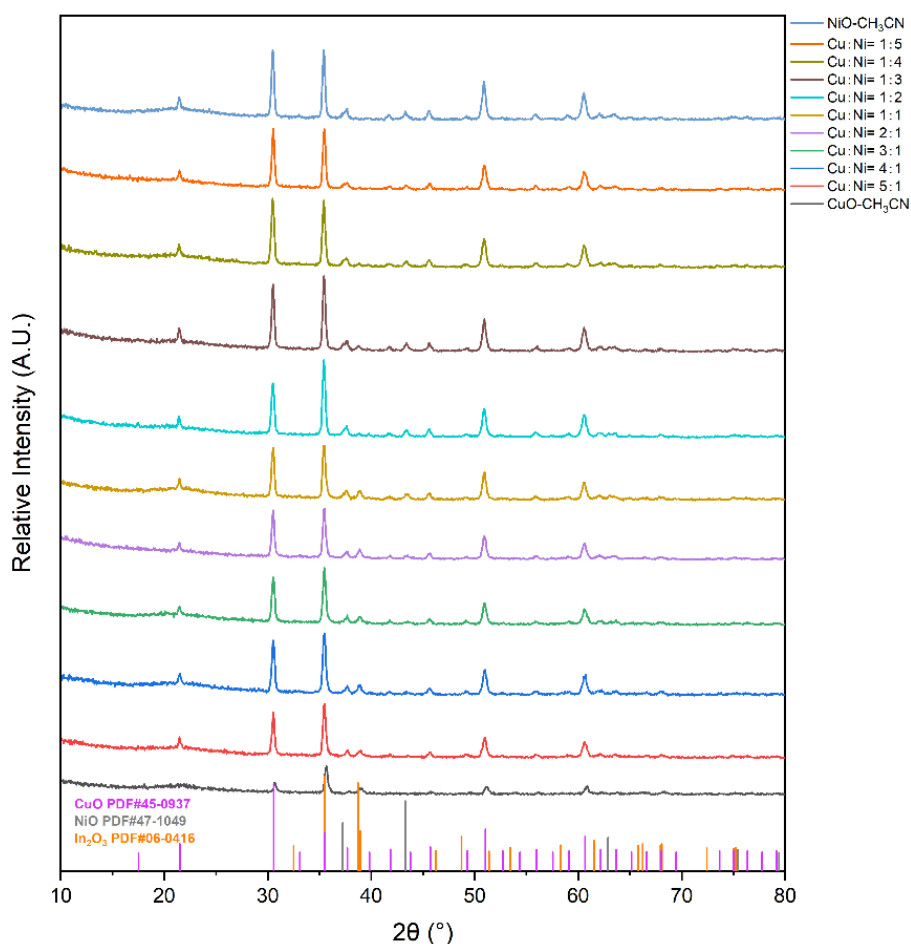


Figure 123. Integrated XRD patterns of CuNiO_x thin films deposited with various ratios of Cu/Ni precursors

PEC performance of CuNiO_x films deposited with various ratios of Cu/Ni precursors was evaluated via the LSV test in 1M NaOH (**Figure 124 a**). The 2h-stability test in 1M NaOH at 0.4 V vs RHE was also conducted to explore if the dual-metal oxide thin film has better stability than the single-metal oxide films (**Figure 124 b**).

From sole CuO film to CuNiO_x film, the potential that generates the most photocurrent slightly shifts left. The sole NiO film hardly produces any

photocurrents under these conditions. With CuO added into NiO thin film, the photoactivity increases. Compared with CuO, CuNiO_x improves the photocurrent generation capacity of CuO. The highest photocurrent density was observed in the Cu: Ni = 1:1 film (**Table 55**).

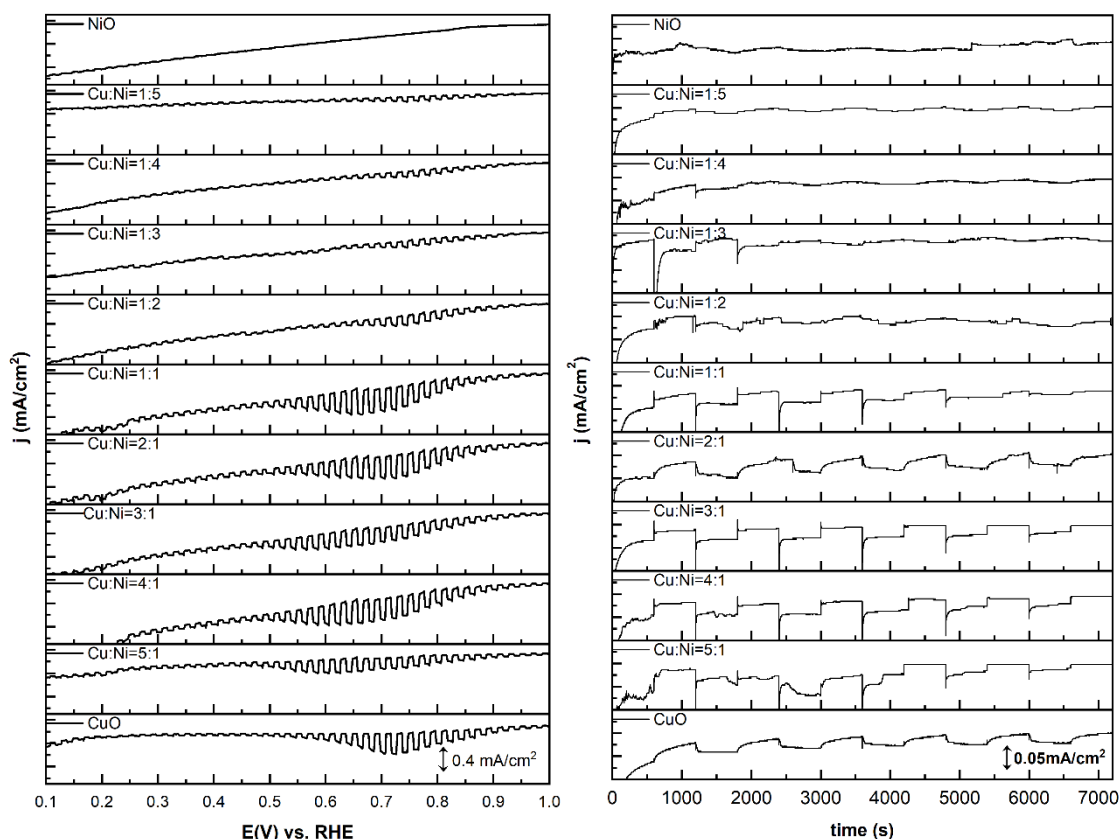


Figure 124. (Left) Chopped LSV and (Right) 2-hour stability test of CuNiO_x thin films deposited with various ratios of Cu/Ni precursors and measured in 1M NaOH

In the 2-hour stability test, Ni-rich CuNiO_x film shows very poor photocurrent generation, while Cu-rich CuNiO_x film has a relatively better and stable ability to produce photocurrents. With NiO added, the recovery speed of CuO, as well as the response rate, becomes faster when turning the light on or off.

Overall, the test data reveals that CuNiO_x dual-metal oxide thin film has better photoactivity than sole CuO thin film or NiO thin film as photocathode material. The addition of CuO greatly enhanced NiO thin film's cathodic photoactivity, while in return, the addition of NiO improved CuO thin film's photoelectrochemical stability.

Table 55. Summary of photocurrent density in the CuNiO_x thin films deposited with various ratios of Cu/Ni precursors and measured at 0.4 V vs RHE in 1M NaOH

The ratio of Cu/Ni	j (mA/cm ²) - Air @0.65 V vs RHE
NiO	/
Cu:Ni = 1:5	0.0626
Cu:Ni = 1:4	0.0723
Cu:Ni = 1:3	0.0771
Cu:Ni = 1:2	0.1093
Cu:Ni = 1:1	0.4771
Cu:Ni = 2:1	0.2663
Cu:Ni = 3:1	0.3349
Cu:Ni = 4:1	0.4386
Cu:Ni = 5:1	0.2699
CuO	0.2120

7.3.2 Investigation of AACVD deposition and post-annealing conditions of CuNiO_x-CFO-CN film deposited on ITO-substrate

7.3.2.1 Characterization of CuNiO_x-CFO-CN film deposited on ITO-substrate

Each layer was deposited via AACVD (**Figure 125**) and analysed by XRD to help us understand the phase formation and transformation.



Figure 125. Illustration depicting the deposition process CuO, NiO, CFO-NiO, CFO-CuO, CFO-CuNiO_x and CuNiO_x films on ITO-quartz substrate

Moreover, the investigation helps to understand the heterojunction in this complicated multi-metal oxide thin film and to explain the photo-performance observed in the PEC measurements.

Different layer and deposition details are shown in **Table 56**:

Table 56. List of compositions in different CN128 thin films

Sample label	Film
CN128-1	NiO on ITO-quartz
CN128-2	CuO on ITO-quartz
CN128-3	CFO-NiO on ITO-quartz
CN128-4	CFO-CuO on ITO-quartz
CN128-5	CFO-CuNiO _x on ITO-quartz
CN128-6	CuNiO _x on ITO-quartz

XRD patterns of CN128-1 NiO on ITO-quartz (**Figure 126 a**)) were collected after depositing 7.5mg Ni precursor on ITO-quartz substrate and after annealing in N₂ at 750°C for 5 hours. There are no obvious NiO peaks in the XRD pattern, but in the noisy background, weakly diffracting NiO peaks might be present.

XRD patterns of CN128-2 CuO on ITO-quartz (**Figure 126 b**)) show the film deposited from 7.5 mg Cu precursor on ITO-quartz substrate. CuO peaks were found (Tenorite (syn), PDF#45-0937), although the typical (002) peak at $2\theta = 35.495^\circ$ was overlapped with an ITO peak.

When depositing CuFeO₂ on NiO on ITO-quartz substrate (Sample CN128-3), after annealing in N₂ at 750°C for 5 hours, NiFe₂O₄ (Trevorite, syn, PDF#54-0964) or CuFe₂O₄ (Cuprospinel, PDF#25-0283) was found in the XRD pattern (**Figure 126 c**)). The peaks in these two patterns (CuFe₂O₄ and NiFe₂O₄) have almost the same intensity at almost the same 2 Theta. They are, therefore, difficult to differentiate from a sample that could contain either (or both) materials. In addition, CuO peaks (Tenorite, syn, PDF#45-0937) peaks were also found in the pattern. Surprisingly, typical CuFeO₂ peaks are not found in this XRD pattern.

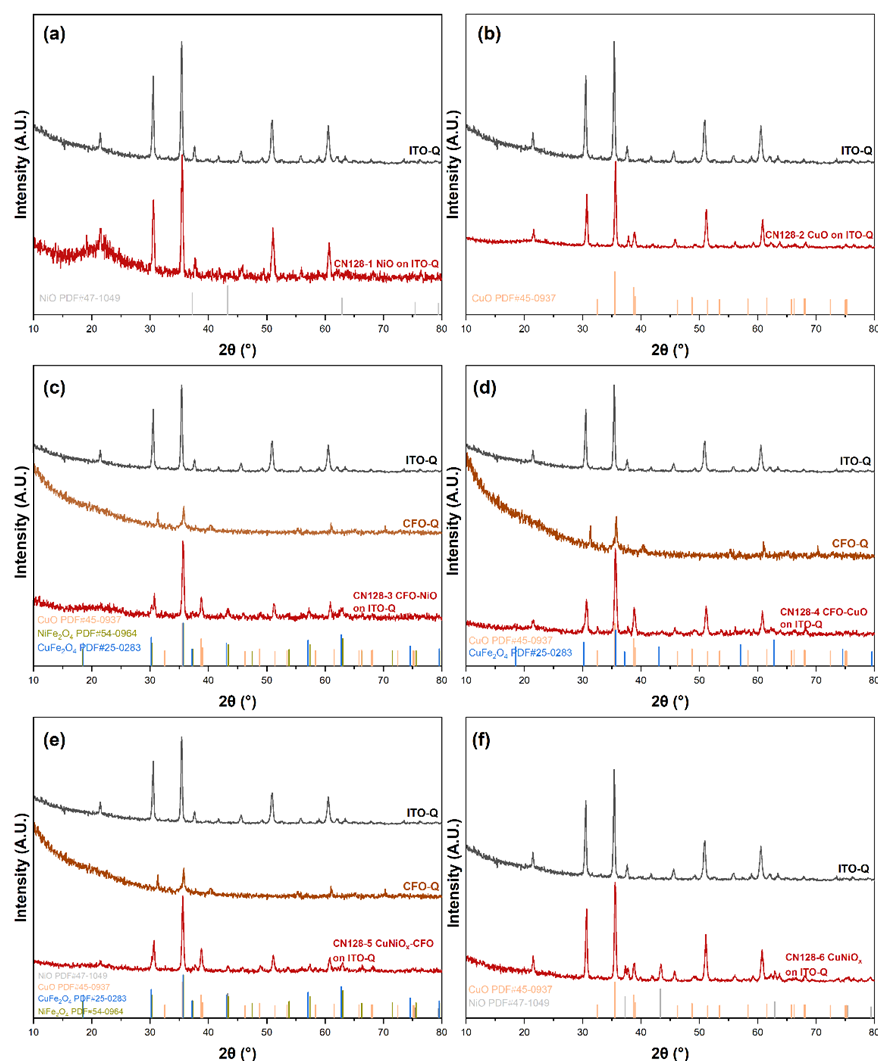


Figure 126. XRD patterns of a) sample CN128-1: NiO deposited on ITO-quartz, b) sample CN128-2: CuO deposited on ITO-quartz, c) sample CN128-3: CFO-NiO deposited on ITO-quartz, d) sample CN128-4: CFO-CuO deposited on ITO-quartz, e) sample CN128-5: CFO-CuNiO_x deposited on ITO-quartz and f) sample CN128-6: CuNiO_x deposited on ITO-quartz substrate

For the deposition of a CuFeO₂ layer on a CuO film on ITO-quartz substrate (Sample CN128-4, **Figure 126 d**), clear CuO peaks (PDF#45-0937) were found. Peaks of CuFe₂O₄ (Cuprospinel, PDF#25-0283) were also observed, but the intensity was relatively low. The Delafossite CuFeO₂ crystal structure was also not found in this XRD pattern either. Though in the inert N₂ atmosphere, Cu₂O instead of CuO phase should be formed, the as-deposited CuFeO₂ can be the protective layer that prevents the CuO from losing oxygen N₂ and could even itself contribute O to the CuO phase, preventing reduction.

In **Figure 126 f)** (Sample CN128-6), CuNiO_x were deposited on ITO-quartz substrate, in which CuO (PDF#45-0937) and NiO (PDF#47-1049) peaks were found, as seen in the previous sections.

In Sample CN128-5, films were deposited with the sequence CuFeO₂ deposited on a CuNiO_x film on ITO-quartz substrate. In this complicated multi-metal oxide film, NiFe₂O₄ (PDF#54-0964) or CuFe₂O₄ (Cuprospinel, PDF#25-0283) and CuO (PDF#45-0937) were found (**Figure 126 e)**). NiO (PDF#47-1049) peaks mostly overlap with CuFe₂O₄ and NiFe₂O₄ peaks, making it hard to identify. No typical CuFeO₂ (PDF#39-0246) peaks were found, which indicates that after post-annealing treatment, any CuFeO₂ phase deposited might be transformed into another crystalline phase due to the presence of CuO and NiO.

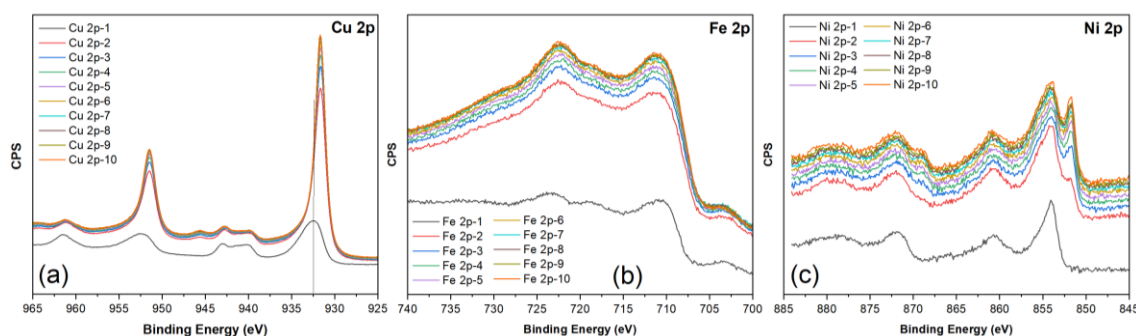


Figure 127. Depth profiling XPS spectroscopy showing information of a) Cu 2p, b) Fe 2p and c) Ni 2p at different depths in the CN-128-5 CFO-CuNiO_x film

XPS depth profiling was performed to understand the elemental change in the multi-metal oxide film with different deposition sequences (**Figure 127**). In theory, only Cu and Fe should be detected in the beginning levels. Ni should be detected only when the signal comes from the deeper film.

However, ion migration was demonstrated to exist among each layer. In the first layer, peaks of Ni 2p_{3/2} were found at ~853 eV (Ni²⁺) and ~855 eV (Ni³⁺), with the satellite at ~861 eV³³⁰. A shoulder of metallic Ni was also found at ~852 eV. As the test signal goes deeper and deeper, the peak intensity of metallic Ni becomes larger.

In the Cu 2p spectra, Cu peaks were observed to be shifted towards higher energy when the signal goes deeper. In the first level, signals for Cu^{2+} and Cu^{+1} were both found, and as the etching went deeper, Cu^{2+} was reduced, and the intensity of Cu^{+1} significantly increased.

Therefore, it can be inferred from the XPS results that during the post-annealing treatment, NiO and CuO in the CuNiO_x layer were partly blended into the CFO layer, where the CuO and NiO reacted with the expected CuFeO_2 deposition to form NiFe_2O_4 or CuFe_2O_4 .

In the XRD patterns of CFO- CuNiO_x -ITO-quartz (**b**), metallic Ni and Cu_2O were not observed. The thin CuNiO_x layer between the ITO-quartz and CFO probably contains or was partly converted to a mixture of reduced Ni or Cu_2O , existing in an amorphous state.

7.3.2.2 Investigation of PEC performance of CFO-CN- CuNiO_x film deposited on ITO-substrate

Due to the potential for use as a photocathode material but to address the poorer stability compared with CFO film, CuNiO_x thin film was designed in a heterojunction with CFO thin film in order to obtain a performance-enhanced multilayer cathodic thin film.

Since the highest photocurrent generation ability was found in the CuNiO_x films with a Cu/Ni precursor ratio of 1/1, CuNiO_x films deposited in this section following the sequence shown in **Figure 128**.

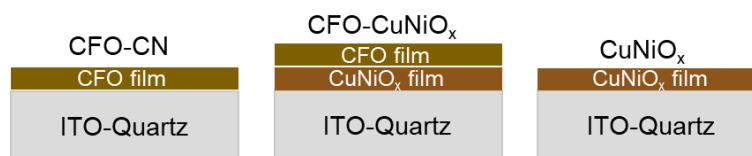


Figure 128. Illustration depicting the deposition process of CuNiO_x , CFO- CuNiO_x and CFO films

In **Figure 129**, the photocurrent generation abilities of CuNiO_x-7.5 mg film, CFO film and CFO-CuNiO_x -7.5 mg film were tested and compared using LSV in 1M NaOH under illumination. To be specific, CuNiO_x-7.5 mg film was deposited with 7.5 mg [Cu(acac)₂] (~0.03 mmol) and 7.5 mg [Ni(acac)₂] (~0.03 mmol), pre-mixed in 10 ml acetonitrile as the precursor solution. The highest photocurrent density was obtained in the CFO- CuNiO_x film when 7.5 mg [Cu(acac)₂] and 7.5 mg [Ni(acac)₂] were used. At 0.4 V vs RHE, the photocurrent density was more than three times (374%) that of standard CFO film.

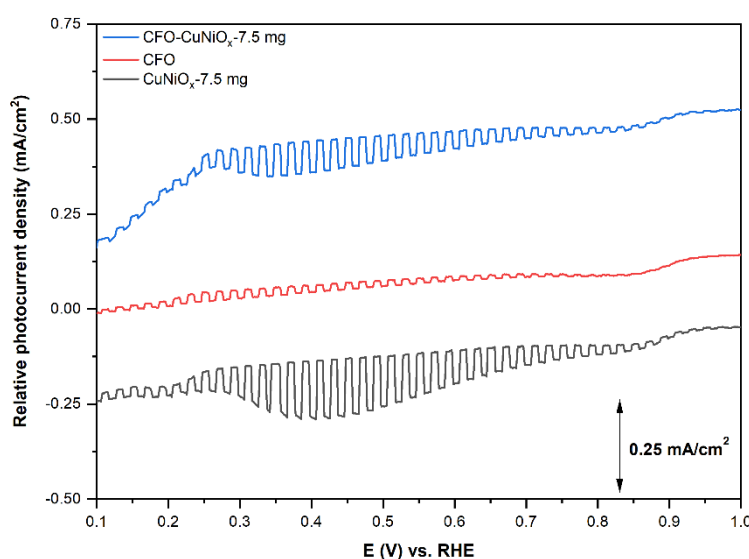


Figure 129. Chopped LSV of CuNiO_x -7.5 mg (film deposited with 7.5 mg Cu and Ni precursors respectively), CFO and CFO-CuNiO_x-7.5 mg film measured in 1M NaOH

To discover the mechanism of the CuNiO_x layer and sort out the complexity of the heterojunctions among different layers, different amounts of Cu and Ni precursors were used for CuNiO_x thin film deposition under CFO film (**Figure 130**) and were evaluated by chopped light LSV. Also, each layer was deposited and evaluated respectively to compare to which extent CuNiO_x dual-metal oxide thin film can improve CFO film's cathodic photoactivity.

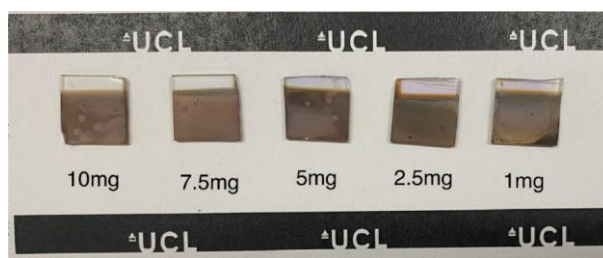


Figure 130. Digital photo of CFO- CuNiO_x thin film deposited with different amounts of Cu/Ni precur

According to **Figure 131 (Left)**, as the amount of Cu and Ni precursor increases (film thickness increases), CuNiO_x film's photocurrent density constantly increases, as we discovered in **Figure 113**, where increasing the number of layers (film thickness) gave higher photocurrent density.

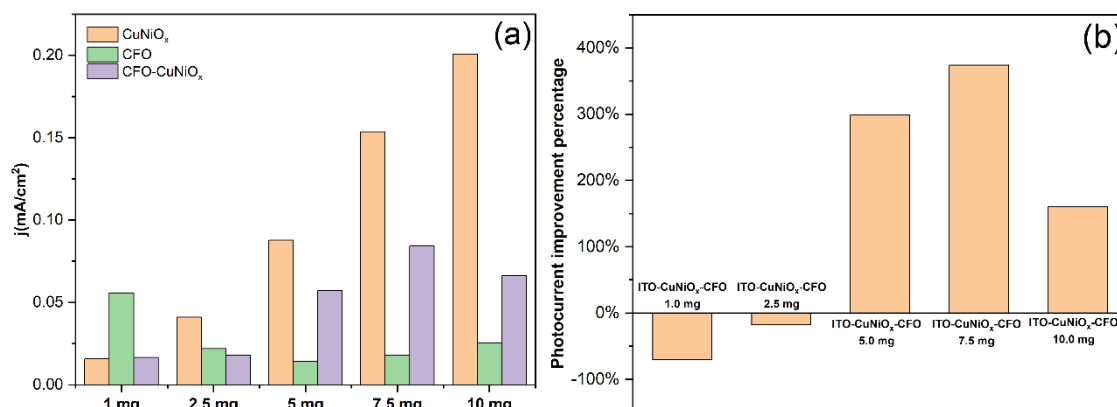


Figure 131. (a) Photocurrent density of CFO, CuNiO_x and CFO-CuNiO_x deposited with the amount of Cu/Ni precursors in the CuNiO_x film and (b) enhancement efficiency of CFO-CuNiO_x film compared with CFO as the amount of Cu/Ni precursors increases

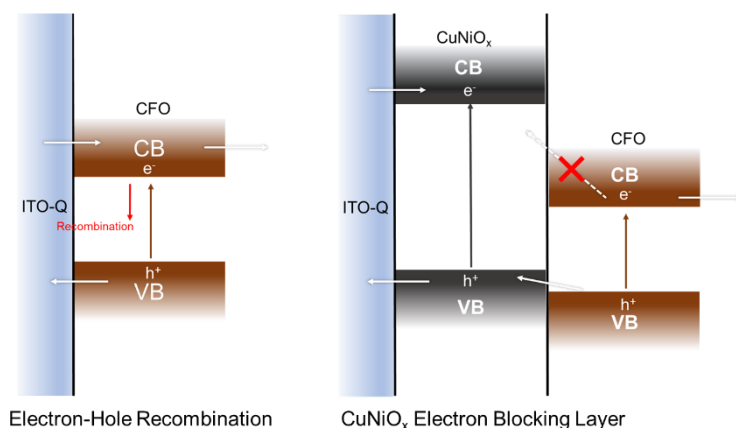


Figure 132. Energy diagram of CuNiO_x assembled with CFO-CN film and the explanation of the inhibited charge carrier recombination

CuNiO_x film was used as the effective hole transport layer to construct a Cu₂O-based photocathode. Its effectiveness with the CFO film can be explained in a similar way^{12,24}. From the energy point of view, the band alignment between CuNiO_x and CFO accumulates electrons in the CFO layer whilst allowing hole migration to the photocathode (**Figure 132**), reducing electron-hole recombination and improving the hole collection efficiency, which results in a more effective structure for CFO films to be used as photocathodic material.

7.3.3 Further investigation on the photoelectrochemical performance of Spinel M(II)Fe₂O₄ samples

Due to the existence of CuFe₂O₄ and NiFe₂O₄ phase in the CFO-CuNiO_x films, the investigation of the photoelectrochemical performance of CuFe₂O₄ and NiFe₂O₄ films started from AACVD deposition, following the similar deposition strategy used for CFO films in **Chapter 3**, as shown in **Table 57** and **Table 58**.

Ultimately, the optimal AACVD deposition conditions of CuFe₂O₄ film were obtained using a precursor solution consisting of 0.0325 mmol [Cu(acac)₂] and 0.075 mmol [Fe(acac)₃] dissolved into 15 ml acetonitrile. The optimal deposition temperature was set as 310°C with a gas flow rate of 1000 sccm.

Table 57. Summary of AACVD deposition conditions for CuFe₂O₄ films deposition and corresponding EDX results showing the Cu/Fe relative atomic ratio in the as-deposited film

Sample	n- [Cu(acac) ₂] (mmol)	n- [Fe(acac) ₃] (mmol)	Temperature (°C)	Substrate	Flow Rate (sccm)	EDX Relative Cu/Fe at. %
Cu precursor's amount initial investigation						
CuFe ₂ O ₄ -1	0.0375	0.075	350	ITO-Quartz	1000	42.34/57.66 ± 0.3
CuFe ₂ O ₄ -2	0.04	0.075	350	ITO-Quartz	1000	49.65/50.35 ± 0.9
CuFe ₂ O ₄ -3	0.03	0.075	350	ITO-Quartz	1000	34.74/65.26 ± 0.6
CuFe ₂ O ₄ -4	0.05	0.075	350	ITO-Quartz	1000	69.60/30.40 ± 1
CuFe ₂ O ₄ -5	0.02	0.075	350	ITO-Quartz	1000	33.61/66.39 ± 0.8
CuFe ₂ O ₄ -6	0.015	0.075	350	ITO-Quartz	1000	22.99/77.01 ± 0.4
CuFe ₂ O ₄ -7	0.01	0.075	350	ITO-Quartz	1000	16.14/83.86 ± 0.3

Sample	n- [Cu(acac) ₂] (mmol)	n- [Fe(acac) ₃] (mmol)	Temperature (°C)	Substrate	Flow Rate (sccm)	EDX Relative Cu/Fe at. %
Temperature investigation						
CuFe ₂ O ₄ -8	0.0375	0.075	325	ITO-Quartz	1000	39.28/60.72 ± 0.2
CuFe ₂ O ₄ -9	0.0375	0.075	300	ITO-Quartz	1000	42.85/57.15 ± 0.6
CuFe ₂ O ₄ -10	0.0375	0.075	275	ITO-Quartz	1000	35.87/64.13 ± 0.4
CuFe ₂ O ₄ -11	0.0375	0.075	250	ITO-Quartz	1000	29.08/70.92 ± 0.5
Temperature investigation with Cu precursor's amount adjusted						
CuFe ₂ O ₄ -12	0.03	0.075	340	ITO-Quartz	1000	38.97/61.03 ± 0.3
CuFe ₂ O ₄ -13	0.03	0.075	330	ITO-Quartz	1000	36.95/63.05 ± 0.2
CuFe ₂ O ₄ -14	0.03	0.075	320	ITO-Quartz	1000	51.65/48.35 ± 0.3
CuFe ₂ O ₄ -15	0.03	0.075	310	ITO-Quartz	1000	34.49/65.51 ± 0.3
CuFe ₂ O ₄ -16	0.03	0.075	300	ITO-Quartz	1000	46.33/53.67 ± 0.4
CuFe ₂ O ₄ -17	0.03	0.075	290	ITO-Quartz	1000	42.07/57.93 ± 0.8
CuFe ₂ O ₄ -18	0.03	0.075	280	ITO-Quartz	1000	34.53/65.47 ± 0.6
Cu precursor's amount adjusted.						
CuFe ₂ O ₄ -19	0.0325	0.075	350	ITO-Quartz	1000	36.03/63.97 ± 0.2
CuFe ₂ O ₄ -20	0.03	0.075	350	ITO-Quartz	1000	36.66/63.34 ± 0.2
CuFe ₂ O ₄ -21	0.0275	0.075	350	ITO-Quartz	1000	41.65/58.35 ± 0.4
CuFe ₂ O ₄ -22	0.0375	0.075	350	ITO-Quartz	1000	40.28/59.72 ± 0.1
CuFe ₂ O ₄ -23	0.045	0.075	350	ITO-Quartz	1000	46.20/53.80 ± 0.4
Temperature finalized						
CuFe ₂ O ₄ -24	0.0325	0.075	340	ITO-Quartz	1000	38.51/61.49 ± 1
CuFe ₂ O ₄ -25	0.0325	0.075	330	ITO-Quartz	1000	36.45/63.55 ± 0.3
CuFe ₂ O ₄ -26	0.0325	0.075	320	ITO-Quartz	1000	38.34/61.66 ± 0.5
CuFe ₂ O ₄ -27	0.0325	0.075	310	ITO-Quartz	1000	33.55/66.45 ± 0.2
CuFe ₂ O ₄ -28	0.0325	0.075	300	ITO-Quartz	1000	35.83/64.17 ± 0.4

Similarly, the optimal AACVD deposition conditions of NiFe₂O₄ film were obtained using a precursor solution consisting of 0.045 mmol [Ni(acac)₂] and 0.075 mmol [Fe(acac)₃] dissolved into 15 ml acetonitrile. The optimal deposition temperature was set as 425°C with a gas flow rate of 1000 sccm.

Table 58. Summary of AACVD deposition conditions for NiFe₂O₄ films deposition and corresponding EDX results showing the Ni/Fe relative atomic ratio in the as-deposited film

Sample	n- [Cu(acac) ₂] (mmol)	n- [FeCl ₂ ·4H ₂ O] (mmol)	Temperature (°C)	Substrate	Flow Rate (sccm)	EDX Relative Cu/Fe at. %
Ni precursor's amount initial investigation						
NiFe ₂ O ₄ -1	0.0375	0.075	350	ITO-Quartz	1000	22.14/77.86 ± 0.5
NiFe ₂ O ₄ -2	0.04	0.075	350	ITO-Quartz	1000	33.40/66.60 ± 0.3
NiFe ₂ O ₄ -3	0.03	0.075	350	ITO-Quartz	1000	17.20/82.80 ± 0.2
NiFe ₂ O ₄ -4	0.05	0.075	350	ITO-Quartz	1000	21.94/78.06 ± 0.3
NiFe ₂ O ₄ -5	0.02	0.075	350	ITO-Quartz	1000	14.52/5.48 ± 0.3
Temperature investigation						
NiFe ₂ O ₄ -6	0.05	0.075	350	ITO-Quartz	1000	21.32/78.68 ± 0.2
NiFe ₂ O ₄ -7	0.05	0.075	375	ITO-Quartz	1000	28.29/71.71 ± 0.2
NiFe ₂ O ₄ -8	0.05	0.075	400	ITO-Quartz	1000	32.31/67.69 ± 0.2
NiFe ₂ O ₄ -9	0.05	0.075	425	ITO-Quartz	1000	38.03/61.97 ± 0.4
NiFe ₂ O ₄ -10	0.05	0.075	325	ITO-Quartz	1000	17.99/82.01 ± 0.1
Temperature investigation with Ni precursor's amount adjusted						
NiFe ₂ O ₄ -11	0.06	0.075	350	ITO-Quartz	1000	25.62/74.38 ± 0.3
NiFe ₂ O ₄ -12	0.05	0.075	410	ITO-Quartz	1000	37.08/62.92 ± 0.2
NiFe ₂ O ₄ -13	0.05	0.075	425	ITO-Quartz	1000	36.33/63.67 ± 0.4
NiFe ₂ O ₄ -14	0.06	0.075	425	ITO-Quartz	1000	37.22/62.78 ± 0.1
NiFe ₂ O ₄ -15	0.065	0.075	425	ITO-Quartz	1000	38.67/61.33 ± 0.3
NiFe ₂ O ₄ -16	0.045	0.075	425	ITO-Quartz	1000	33.30/66.70 ± 0.3
NiFe ₂ O ₄ -17	0.04	0.075	425	ITO-Quartz	1000	31.56/68.44 ± 0.3
NiFe ₂ O ₄ -18	0.06	0.075	425	ITO-Quartz	1000	41.33/58.67 ± 0.4

The post-annealing treatment conditions were briefly tested for both CuFe₂O₄ and NiFe₂O₄, as shown in **Table 59**. Pure CuFe₂O₄ phase was obtained during 700°C to 800°C while pure NiFe₂O₄ was formed between 600°C to 900°C (**Figure 133**).

Table 59. Summary of annealing conditions of as-deposited CuFe₂O₄ and NiFe₂O₄

Sample	Temperature (°C)	Duration (h)	Gas atmosphere	Sample	Temperature (°C)	Duration (h)	Gas atmosphere
CuFe ₂ O ₄ -Q1	500	3	Air	NiFe ₂ O ₄ -Q1	500	3	Air
CuFe ₂ O ₄ -Q2	600	3	Air	NiFe ₂ O ₄ -Q2	600	3	Air
CuFe ₂ O ₄ -Q3	700	3	Air	NiFe ₂ O ₄ -Q3	700	3	Air
CuFe ₂ O ₄ -Q4	800	3	Air	NiFe ₂ O ₄ -Q4	800	3	Air
CuFe ₂ O ₄ -Q5	900	3	Air	NiFe ₂ O ₄ -Q5	900	3	Air

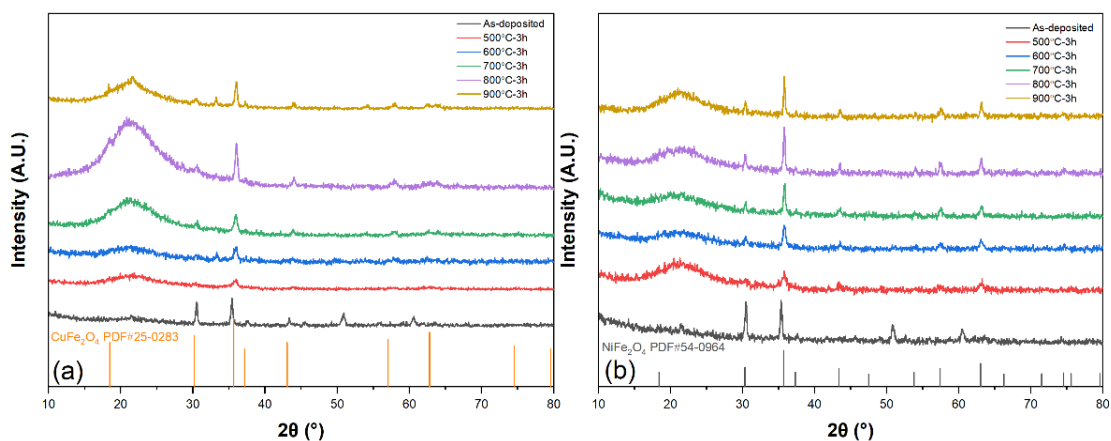


Figure 133. Integrated XRD patterns of a) CuFe_2O_4 and b) NiFe_2O_4 as-deposited films annealed at different temperatures for 3h in air

To finalize the optimal annealing temperature for CuFe_2O_4 and NiFe_2O_4 , as well as evaluate their photoactivity as photocathodic materials, chopped LSVs were performed (**Figure 134**).

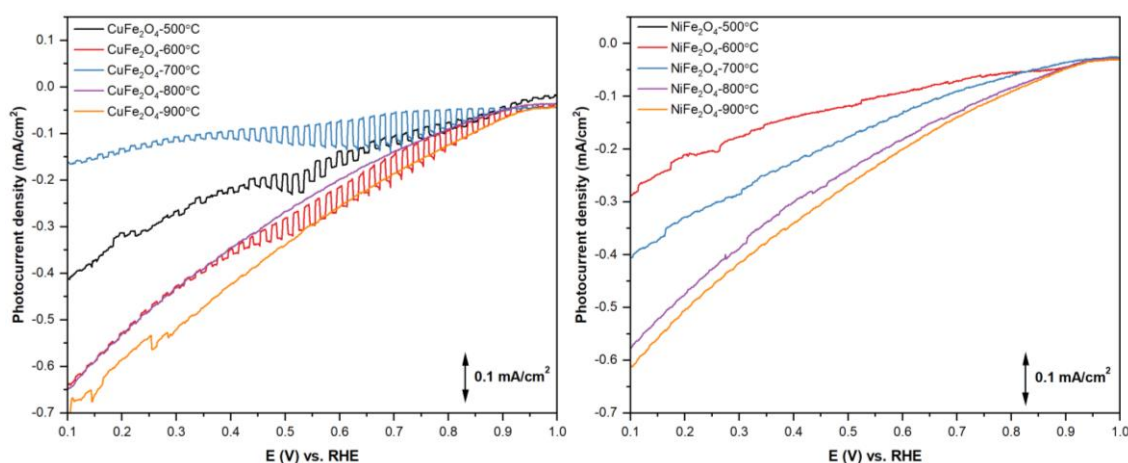


Figure 134. Chopped LSV of CuFe_2O_4 and NiFe_2O_4 films annealed at different temperatures in air for 3h

The highest photocurrent density ($\sim 0.085 \text{ mA/cm}^2$) was achieved at $\sim 0.7 \text{ V}$ vs RHE in the CuFe_2O_4 film annealed at 700°C for 3 hours. The photoactivity exhibited a discernible increase as the annealing temperature was raised within the range of 500°C to 700°C . However, a notable decline in photoactivity was observed when the annealing temperature surpassed 800°C , resulting in a complete absence of

photoinduced activity. Therefore, the annealing temperature of CuFe_2O_4 film was finalized at 700°C .

In contrast, though the NiFe_2O_4 phase was observed when the annealing temperature is maintained within the range of 600°C - 900°C , it is noteworthy that no significant cathodic photoactivity was exhibited in any of the NiFe_2O_4 films.

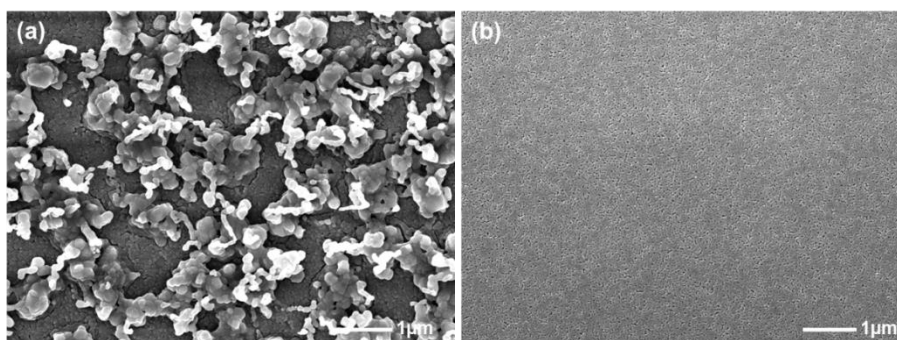


Figure 135. SEM images of (a) CuFe_2O_4 and (b) NiFe_2O_4 films annealed at 700°C for 3h in air

The morphology of the CuFe_2O_4 and NiFe_2O_4 films were examined and characterized using SEM after being annealed at 700°C in the air atmosphere for 3 hours (**Figure 135**).

An underlying film consisting of densely packed and well-organized small particles can be discernibly observed in the CuFe_2O_4 film. In contrast, relatively larger particles grew on the top surface, displaying a propensity to interconnect with adjacent particles.

The NiFe_2O_4 film is comprised entirely of compact and well-organized small particles, exhibiting the characteristics of a two-dimensional planar film.

Since CuNiO_x film showed better PEC performance than sole CuO or NiO films, the investigation of quaternary oxide spinel film $\text{Cu}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ was studied. The precursor solution of CuFe_2O_4 was first deposited on ITO-quartz substrate at 310°C , followed by the precursor solution of NiFe_2O_4 deposited at 410°C . The

volume of CuFe_2O_4 and NiFe_2O_4 precursor solution was adjusted to vary the ratio of Cu and Ni in the mixed Spinel film.

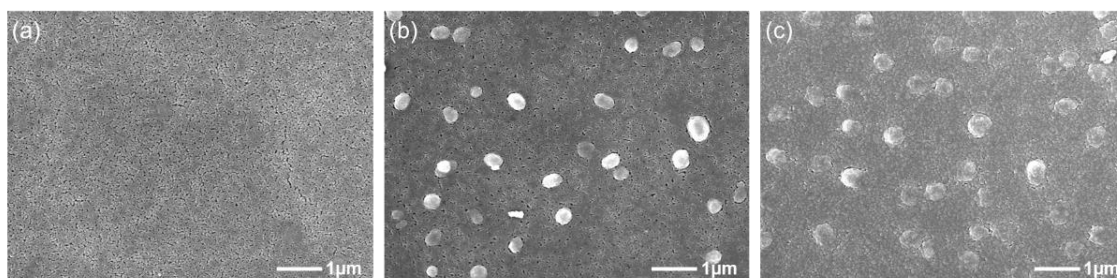


Figure 136. SEM images of (a) $\text{Cu}_{0.33}\text{Ni}_{0.66}\text{Fe}_2\text{O}_4$, (b) $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$, and (c) $\text{Cu}_{0.66}\text{Ni}_{0.33}\text{Fe}_2\text{O}_4$

The introduction of Cu into NiFe_2O_4 film changed the two-dimensional planar film morphology in the NiFe_2O_4 film, as shown in **Figure 136**.

However, the PEC performance was not significantly improved in the $\text{Cu}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ films, although the more Cu was introduced into the spinel film, the higher photocurrent density was obtained (**Figure 137**).

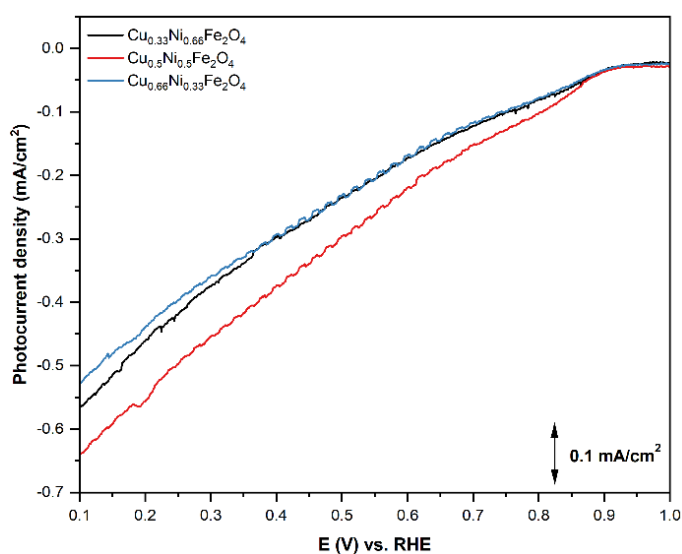


Figure 137. Chopped LSV of $\text{Cu}_{0.33}\text{Ni}_{0.66}\text{Fe}_2\text{O}_4$, $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Cu}_{0.66}\text{Ni}_{0.33}\text{Fe}_2\text{O}_4$ film measured in 1M NaOH electrolyte

In order to assess and compare the photoelectrochemical performance among various film compositions, a comparative study was designed involving the following films: CFO-CN, CuFe_2O_4 , $\text{CuFe}_2\text{O}_4+\text{CuO}$, CuO, and Fe_2O_3 . The CFO-

CN and $\text{CuFe}_2\text{O}_4+\text{CuO}$ films were synthesized using the standard recipe for 250 nm CFO-CN, while the annealing atmosphere for $\text{CuFe}_2\text{O}_4+\text{CuO}$ phase formation consisted of 90 vol.% N_2 and 10 vol.% air.

For the synthesis of the CuFe_2O_4 film, the same amount of Fe precursor as that used in CuFeO_2 was employed, with a reduction in the quantity of $[\text{Cu}(\text{acac})_2]$ to provide the desired metal ratio. Similarly, CuO and Fe_2O_3 films were synthesized using identical amounts of Cu and Fe precursor solutions as those utilized in the deposition of the standard CFO-CN film.

XRD patterns and UV-vis absorption spectroscopy of each sample are shown in **Figure 138**. Digital images of the five films discussed above are shown in **Figure 139**.

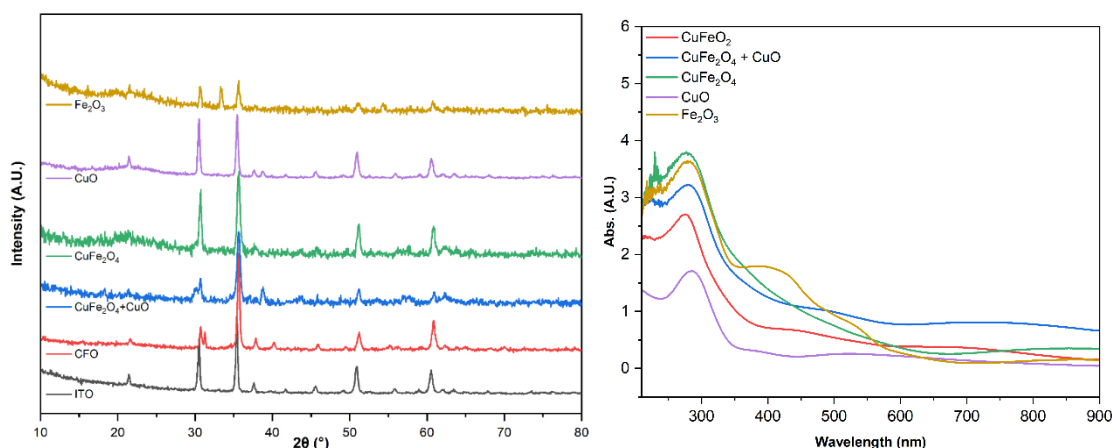


Figure 138. Integrated XRD patterns (Left) and UV-vis absorption spectroscopy (Right, ITO-quartz substrate as background) of CFO-CN, $\text{CuFe}_2\text{O}_4+\text{CuO}$ (annealed at 750°C in N_2 with 10 vol.% Air), CuFe_2O_4 , CuO and Fe_2O_3 films deposited on ITO-quartz substrate

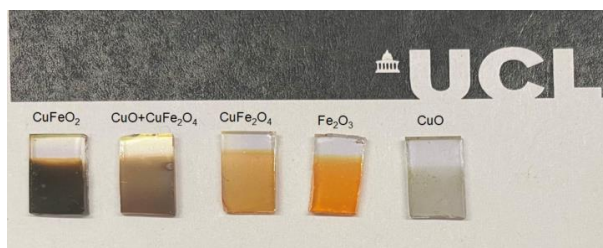


Figure 139. Digital images of CFO-CN, $\text{CuFe}_2\text{O}_4+\text{CuO}$ (annealed at 750°C in N_2 with 10 vol.% Air), CuFe_2O_4 , Fe_2O_3 , and CuO films

LSV tests were conducted to compare the photocurrents generated in the potential range of 0.1-1.0 V vs RHE. From **Figure 138 (Left)**, the highest photocurrent densities obtained in the different films are at different potentials. Specifically, the highest photocurrent density of $\sim 0.27 \text{ mA/cm}^2$ was obtained for CFO-CN at $\sim 0.30 \text{ V}$ vs RHE, $\sim 0.41 \text{ mA/cm}^2$ was obtained for CuFe_2O_4 and CuO at $\sim 0.5 \text{ V}$ vs RHE; $\sim 0.16 \text{ mA/cm}^2$ was obtained for CuFe_2O_4 at $\sim 0.50 \text{ V}$ vs RHE; $\sim 0.40 \text{ mA/cm}^2$ was obtained for CuO at $\sim 0.65 \text{ V}$ vs RHE. Fe_2O_3 showed a very tiny response as a photocathodic material in the alkaline electrolyte. Instead, it showed anodic response when the potential was close to 0.9-1.0 V vs RHE.

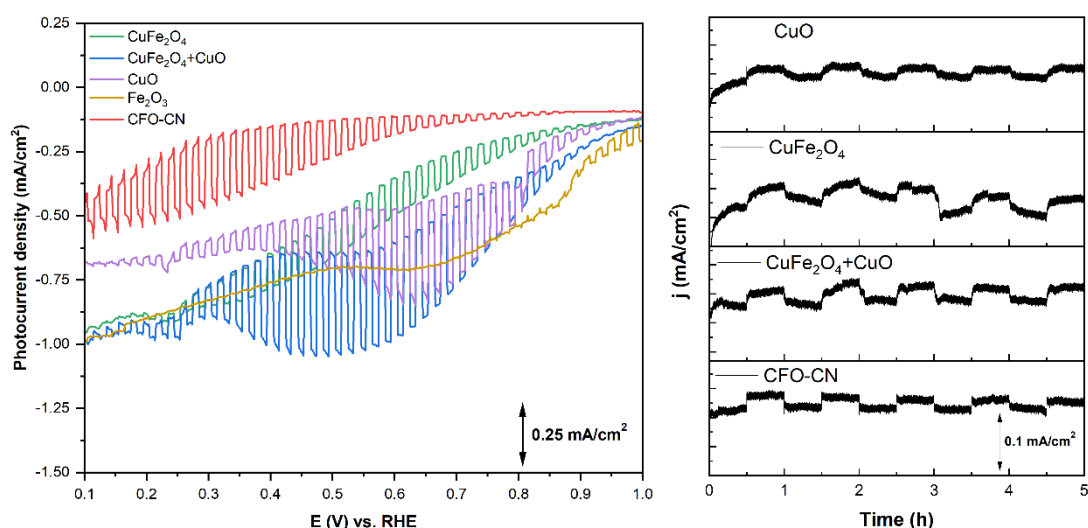


Figure 140. (Left) Comparative LSV analysis of CFO-CN, $\text{CuFe}_2\text{O}_4 + \text{CuO}$ (10 vol.% Air), CuFe_2O_4 , CuO and Fe_2O_3 and (Right) 5h-stability test of CFO-CN, $\text{CuFe}_2\text{O}_4 + \text{CuO}$ (10 vol.% Air), CuFe_2O_4 and CuO @ 0.4V vs RHE measured in 1M NaOH with 10 vol.% 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$

Photoelectrochemical (PEC) stability of four different photoactive films was evaluated under the same conditions as the LSV tests for 5 hours. Stability results are presented in **Figure 140 (Right)**. Among the four films tested, the CFO-CN film exhibited the fastest response speed upon switching the light on and off. During the stability test period, the photocurrent density displayed a slight decrease over time, but the performance remained relatively consistent within each half-hour interval.

CuFe₂O₄-CuO films demonstrated relatively less stable performance compared to the CFO-CN film. However, even after the 5-hour stability test, the photoactivity of CuFe₂O₄ and CuO films remained satisfactory. Notably, in the CuFe₂O₄ and CuO films, the photocurrent density initially exhibited a high value but decreased significantly during the first half-hour of testing. Subsequently, the reduced photocurrent density exhibited fluctuations throughout the later stages of the test, indicating an unstable performance of these films.

LSV test results revealed that as a consequence of exposure to a small amount of oxygen atmosphere, the CuFe₂O₄-CuO film exhibited superior cathodic photoactivity compared to the CFO-CN film, as well as the individual CuO and CuFe₂O₄ films. However, this enhanced photoactivity came at the expense of reduced stability, indicating a trade-off between photoactivity and stability for the CuFe₂O₄-CuO film.

The elemental composition differences were exhibited from XPS spectroscopies (**Figure 141**). Cu 2p, Fe 2p and O 1s peaks were compared among CFO-CN, CuFe₂O₄-CuO, and CuFe₂O₄ films.

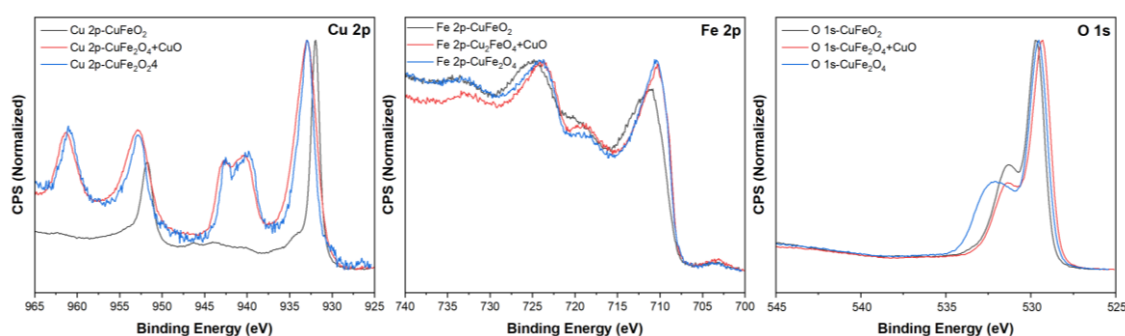


Figure 141. Comparison of XPS of a) Cu 2p; b) Fe 2p; c) O 1s peaks in CuFeO₂, CuFe₂O₄+CuO and CuFe₂O₄ films

In the CFO-CN film, the Cu 2p peaks confirmed the monovalent valence state of Cu. However, upon the introduction of air into the annealing atmosphere, resulting in the formation of the CuFe₂O₄-CuO and CuFe₂O₄ phases, the Cu (II) peaks became significantly prominent in the Cu 2p spectrum. This presence of Cu (II)

species caused a leftward shift in the binding energy of the Cu 2p peaks and led to an increase in the intensity of the satellite peaks associated with Cu 2p.

The O 1s peaks provide insight into the exchange of oxygen between the lattice and surface in the three types of films. A similar trend was observed in the O 1s spectrum in the CFO-CN film to the CuFe₂O₄-CuO film, wherein the peak intensity associated with surface oxygen decreased. This observation has been previously discussed in **Sub-section 6.3.3**.

In contrast, the CuFe₂O₄ film exhibited a significant increase in the area of the surface oxygen peak, accompanied by an increase in its binding energy. The oxygen peak can be split into three peaks at ~529.3 eV, ~530.5 eV and 532.1 eV, which corresponds to chemisorbed oxygen at the surface, the lattice oxygen and hydroxyl oxygen³³³. This increased amount of accumulated oxygen species on the surface may contribute to the unstable performance of the CuFe₂O₄ film, as they are more prone to participate in redox reactions.

7.4 Summary

This chapter further explores the potential of CuFeO₂ as a photocathode by incorporating it with hole transport layer CuNiO_x. Additionally, the properties of the CuNiO_x film have been thoroughly examined, yielding valuable insights. Given that CuFe₂O₄ frequently emerges as a by-product during the development of CuFeO₂ photocathode, and exhibits superior performance, it becomes crucial to ascertain the fundamental factor contributing to this enhancement. In this regard, this study provides significant insights into the matter.

CuO: NiO and CuNiO_x films were successfully deposited on ITO-quartz substrate via AACVD. The optimal deposition conditions were found at 350°C with the N₂ gas flow rate of 1L/min, while the post-annealing was conducted in the air atmosphere at 650°C for 5 hours. The results can be summarized into the following

aspects: 1) CuNiO_x film has a better PEC activity than CuO: NiO film; 2) In the CuO: NiO thin films, the longer the annealing duration, the better the photoactivity (up to 5 hours); 3) Film thickness has a positive correlation with CuO: NiO's photoactivity, in which the higher photocurrent density was obtained when the film thickness is increased.

Cu₂O: NiO was obtained using the same AACVD deposition and post-annealing recipes, while the difference is that the post-annealing was conducted in the inert N₂ gas atmosphere.

The ratio between Cu and Ni was altered while the film's morphology and electronic structure were investigated. The photoelectrochemical properties of CuNiO_x thin film, with different ratios, were evaluated in the different electrolyte and pH environments. According to the results, CuNiO_x thin film exhibited excellent photocathodic properties and can be used as a photocathode in both alkaline and neutral environments. In the alkaline electrolyte, the photocurrent density is higher, while the active potential window is narrower. In contrast, in the neutral electrolyte, the photocurrent density is relatively smaller, but the active potential window is wider. Noticeably, CuNiO_x thin film exhibited a high photocurrent density in the acidic electrolyte with relatively low stability due to the severe electro- and photo-corrosion.

In addition, CuNiO_x thin film was deposited as a hole transport layer (HTL) for the first time to improve the photoactivity of CFO film. This build-up heterojunction was proved to be an effective structure to block the electrons and slow down the electron-hole recombination rate. The highest photocurrent density was promoted from 17.8 μA/cm² to 84.3 μA/cm² at 0.4 V vs RHE in 1M NaOH electrolyte, in which the enhancement efficiency reached 373%.

Moreover, Spinel CuFe₂O₄ and NiFe₂O₄ thin films were successfully deposited via AACVD on ITO-quartz substrate. CuFe₂O₄ thin film showed its potential as a

photocathode, while the photocathodic activity in NiFe_2O_4 is not desirable. When depositing CuFe_2O_4 together with NiFe_2O_4 with various ratios, the photoactivity showed a positive relevance with CuFe_2O_4 . Among CuO , NiO , CuFeO_2 , CuFe_2O_4 , and CuO , CuFe_2O_4 thin films, Delafossite CuFeO_2 thin film showed the greatest stability in 5 hours' stability test at 0.4 V vs RHE in 1M NaOH with 10% 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ electrolyte.

Chapter 8. Surface Decoration with Excessive Fe₂O₃ on Delafossite CuFeO₂ Photocathode

8.1 Introduction

In the research, an abnormal PEC measurement result was noticed when the tube furnace was changed, where the photocurrent density of CFO-CN film was unexpectedly significantly improved. To figure out the reason for the unexpected photo-performance change, EDX and XPS analyses were carried out, and an exciting phenomenon was discovered that the Fe-rich surface may improve CFO thin film's photoactivity.

To confirm this assumption, in this Chapter, surface decoration with a thin layer of iron oxide (Fe₂O₃) thin film as a buffer layer¹⁴⁶ was proposed as one of three modification strategies to improve the photoelectrochemical performance of Delafossite CFO thin film. The film's composition has been characterized, and the elemental distribution on the film surface was illustrated via XRD, EDX and XPS. The film's morphology was evaluated under SEM, where various amount of Fe₂O₃ was deposited on the CFO film's surface.

The effect of the extra amount of Fe precursor deposited on the CFO-CN film's surface on the CFO's photoactivity was investigated, and the promoted performance was illustrated and reaffirmed with the current understanding of charge carrier transportation and separation.

8.1 Experimental

0.15 mmol [Fe(acac)₃] dissolved in 15 ml acetonitrile was used as Fe precursor solution, with a concentration of 0.01 mmol/mL. The concentration of Fe³⁺ was the same as in the standard CFO-CN precursor solution.

Three deposition strategies were used, and the according photoactivity was examined, as shown in **Figure 142**:

(1) After using the well-mixed Cu and Fe precursor solution in the AACVD chamber for the standard CFO-CN deposition, a small amount of Fe-only precursor solution was passed through the reactor to enrich the surface with Fe_2O_3 . Due to the different sequence of applying post-annealing, two different Fe-rich films were obtained, shown as (1.1) and (1.2).

(2) The same Cu and Fe precursor solutions from standard CFO-CN precursor were prepared separately. During deposition, the copper oxide film was first deposited, followed by iron oxide film deposited on the top.

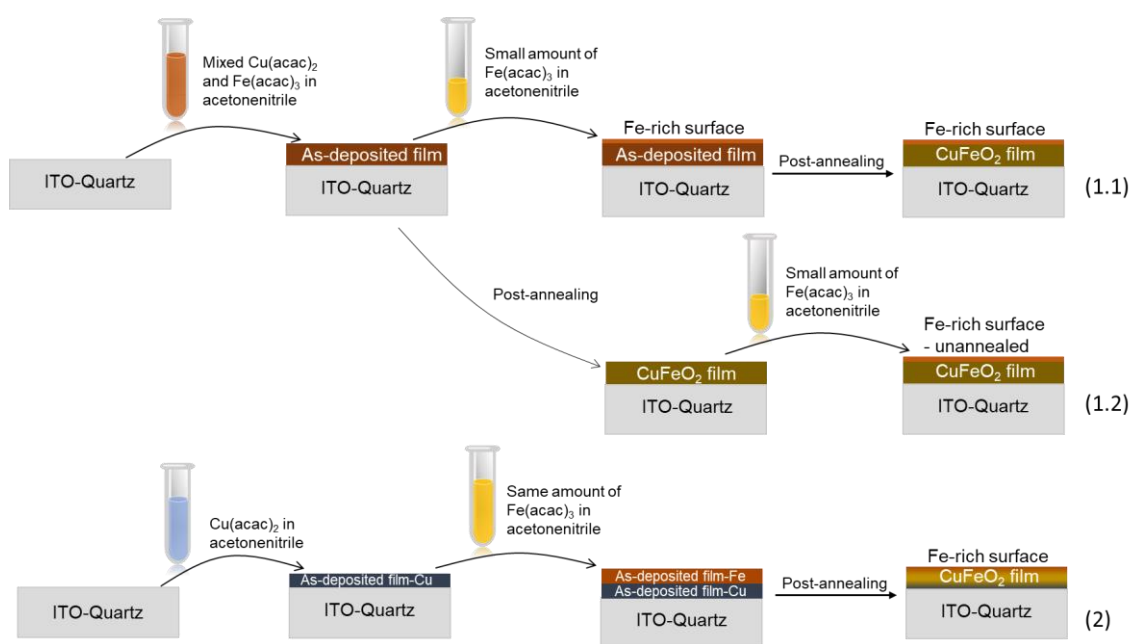


Figure 142. Illustration depicting two AACVD deposition processes of Fe-rich CuFeO_2 thin film. EDX and XPS were used to confirm the element distribution in the overall thin film and the surface of the thin film, respectively. XRD was used to confirm the crystalline phase. SEM compared the morphologies between standard CFO-CN and films enriched with different amounts of surface Fe_2O_3 . PEC measurements were conducted to compare the photoactivity of standard CFO-CN films and Fe-surface-enriched CFO-CN. 1M NaOH with 10% 0.1M $\text{Na}_2\text{S}_2\text{O}_8$ was used as the

electrolyte, while no gas was purged into the electrolyte during the PEC test. The improved films with the highest photoactivity were repeatedly deposited and confirmed by the results of LSV, which will be discussed later in detail.

8.2 Results and discussion

In the case of the abnormal CFO film, where the PEC performance exhibited a remarkable increase of over 100%, the EDX analysis (**Table 60**) revealed that the atomic ratio of Cu and Fe elements in the overall film closely approximated a 1:1 ratio. However, the result from XPS (**Table 61**) shows that the Cu/Fe atomic ratio on the film surface was completely different, where the atomic ratio of Fe/Cu was ~2:1, indicating the excessive amount of Fe on the CFO-CN film's surface.

The Cu/Fe atomic ratio of the previous normal sample is shown in **Table 62**. It is suspected that the excessive surface Fe has a positive impact on the CFO film's photoactivity. Therefore, experiments were designed to examine if a Fe-rich surface will have a positive impact on the CFO film's photoactivity.

Table 60. EXD analysis of CFO-CN film with excessive Fe

Point	O	Na	Si	Fe	Cu	In	Sn	Total	Fe at. %	Cu at. %
1	59.99	3.16	15.46	6.66	6.32	7.97	0.44	100	51.3	48.7
2	59.92	3.19	15.25	7.12	6.14	7.92	0.46	100	53.7	46.3
3	60.13	2.92	15.45	6.99	5.99	7.96	0.55	100	53.8	46.2
4	61.4	/	16.38	7.19	6.25	8.31	0.47	100	53.5	46.5
5	61.59	/	16.84	6.83	6.01	8.21	0.53	100	53.2	46.8

Table 61. Analysis of surface elemental distribution of Fe-rich CFO-CN film from XPS

Name	Position	FWHM	Area	At%
O 1s	530.30	3.70	1940982.04	58.16
C 1s	284.30	2.69	274809.97	24.13
Cu 2p	931.30	2.60	1476761.64	5.11
Fe 2p	710.30	7.44	2198583.46	11.75
Sn 3d	485.30	2.50	55957.82	0.20
In 3d	443.30	2.51	169296.33	0.66

Table 62. Surface element distribution of standard CFO-CN film from XPS

Name	Position	FWHM	Area	At%
O 1s	530.30	3.23	516964.26	38.85
C 1s	284.30	2.82	59413.90	13.08
Cu 2p	931.30	2.72	2753270.24	23.88
Fe 2p	710.30	10.30	1709389.01	22.92
Sn 3d	485.30	2.65	45418.64	0.40
In 3d	443.30	2.58	88202.27	0.86

As explained in **Figure 142**, Cu and Fe precursors were deposited via two methods to construct a Fe-rich surface in the CFO film. The film produced using method (2) not only failed to exhibit any enhancement in photoactivity but actually displayed a decrease, as illustrated in **Figure 143 (Left)**. Significant enhancement in the photo-induced current generation capability was observed when an additional amount of Fe precursor was deposited onto CFO, followed by a post-annealing treatment as method (1.1) in **Figure 142** (the result is shown in **Figure 143 (Right)**). In contrast, films deposited with an extra amount of Fe precursor on the surface without subsequent annealing did not exhibit noticeable photoactivity (deposited by method (1.2) in **Figure 142**. The result is shown in **Figure 143 (Right)**).

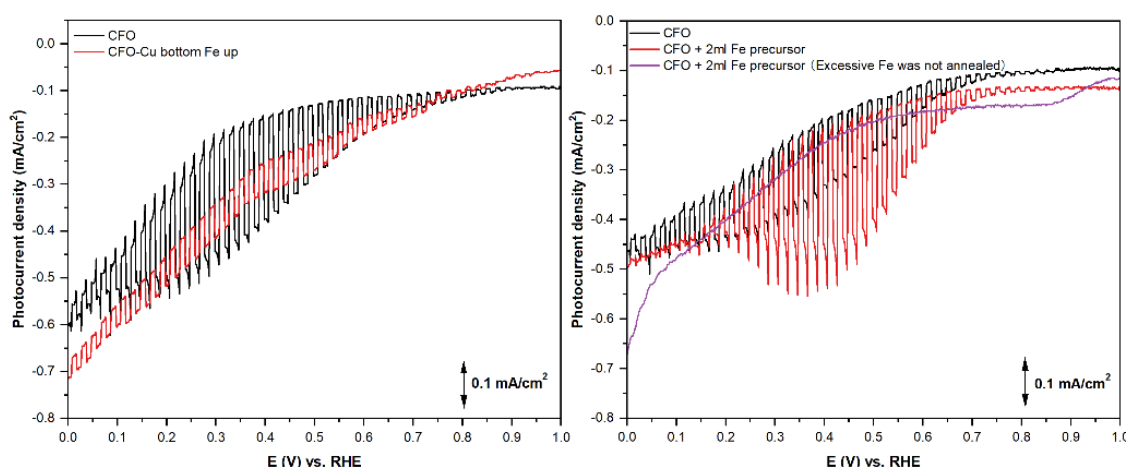


Figure 143. Chopped LSV of CFO films with excessive Fe deposited on the film surface, (a) CFO film being deposited by first Cu precursor and then Fe precursor separately; (b) 2 extra ml Fe precursor was deposited on the CFO film before and after post-annealing in N₂ at 750°C for 5h to assure the Fe-rich surface

Additionally, the quantity of excess Fe precursors employed to modify the surface of the CFO-CN film was systematically adjusted to determine the optimal amount that would contribute to the best photo performance.

Four different volumes (1 ml, 2 ml, 5 ml, and 10 ml) of Fe precursor solution, all having the same concentration, were individually deposited onto multiple small pieces of the CFO-CN film, which were prepared in one reaction and cut to be of equal size. Additionally, one piece of the unmodified CFO-CN film was set aside as a blank sample for comparison purposes.

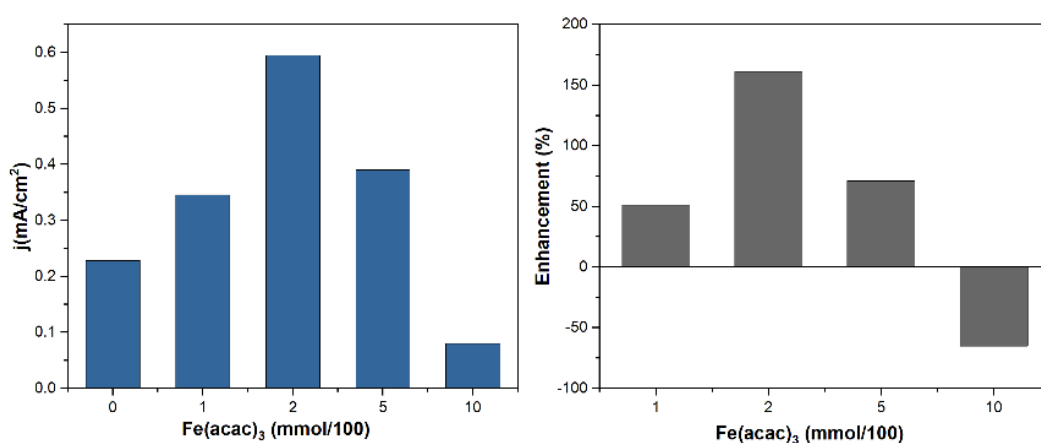


Figure 144. (Left) Photocurrent density and (Right) percentage increase in photocurrent density compared to standard CFO-CN films after adding various amounts of Fe precursor on top of the surface, measured at 0.4 V vs RHE in 1M NaOH with 10% 0.1 M NaS₂O₈

The obtained results provide compelling evidence regarding the influence of excess Fe on the surface of the CFO-CN film. Notably, the deposition of 2 ml of additional Fe precursor solution had the most pronounced effect on the photocathodic capability of the CFO-CN film, which resulted in the most remarkable enhancement of the photocurrent density (**Figure 144**). The photocurrent density obtained at 0.4 V vs RHE was increased from ~0.228 mA/cm² to ~0.595 mA/cm², representing a substantial 160% enhancement compared to the standard CFO-CN film.

With the continuous addition of Fe precursor solution, the photocurrent generation capability decreased significantly. From the SEM images of the modified film morphology (**Figure 145**), it can be seen that when an excess volume of Fe precursor was deposited, the surface of the CFO-CN film was entirely covered by the non-photocathode active Fe_2O_3 film, which led to a significant drop in the photocurrent generation ability.

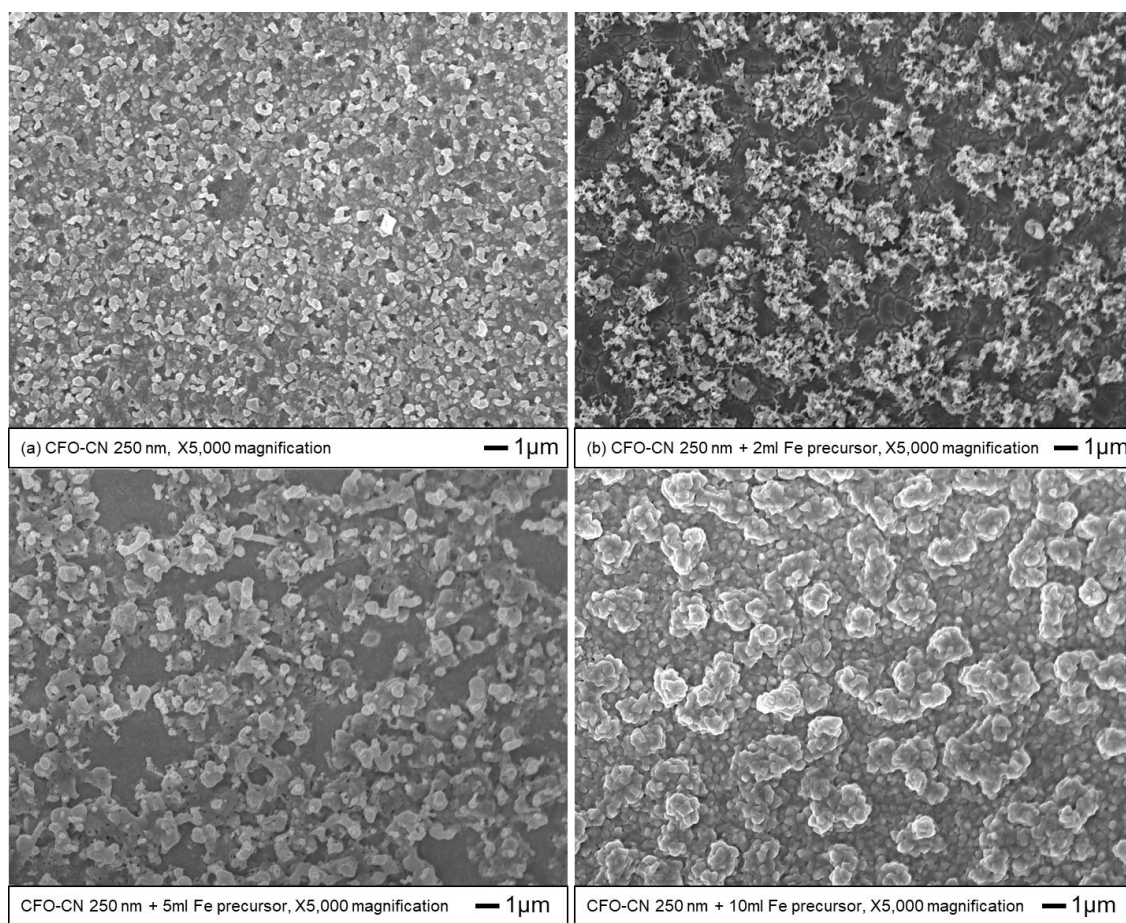


Figure 145. SEM images of (a) CFO-CN film, (b) CFO-CN film with 2 ml extra Fe precursor, (c) CFO-CN film with 5 ml extra Fe precursor and d) CFO-CN film with 10 ml extra Fe precursor deposited on the film surface

XRD analysis was conducted on both the CFO-CN films and the Fe-rich CFO-CN films prepared with an additional 2 ml of Fe precursor solution. A comparison was made between their respective XRD patterns (**Figure 146**). Notably, the distinctive peaks, such as when $2\theta^\circ = 33.152$, were observed, which indicates the presence

of Fe_2O_3 within the films. The other iron oxide phases, such as Fe_3O_4 and FeO , were not observed.

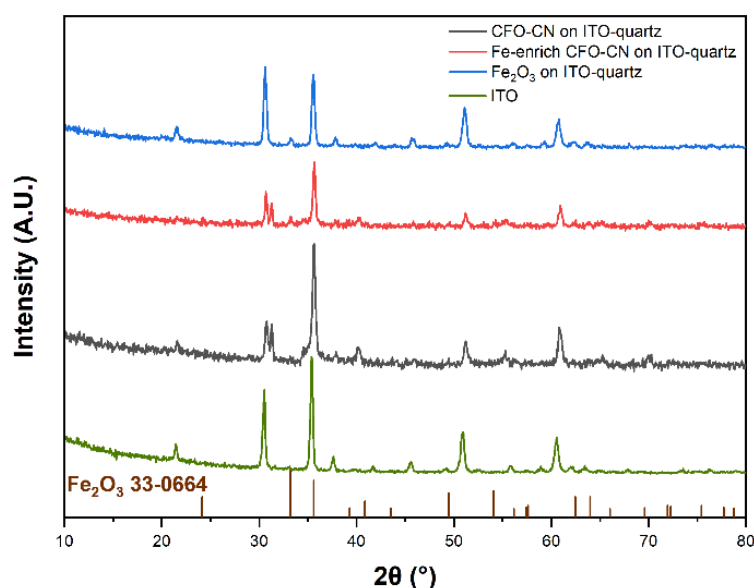


Figure 146. Integrated XRD patterns of ITO-quartz substrate, standard CFO-CN, Fe_2O_3 enriched CFO-CN and Fe_2O_3 deposited on ITO-quartz substrate

In order to validate the efficacy of the surface modification method, a series of experiments were performed. CFO-CN films and excess Fe precursor solutions were prepared separately in different batches (**Table 63**) using the same process: standard 250 nm CFO film with 2ml extra Fe precursor deposited on the surface ($T=350^\circ\text{C}$, $\text{FR}=1000\text{sccm}$). The films were annealed at 750°C for 5 hours separately to ensure that all samples were parallel and replicated.

Table 63. Summary of photocurrent density from repeated PEC measurements using unmodified and modified CFO-CN with 2ml Fe precursor deposited on the surface

Sample	Electrolyte	$J_{\text{CFO-CN}}$ (mA/cm^2)	$J_{\text{Fe-rich CFO-CN}}$ (mA/cm^2)	Enhancement %
1	1M NaOH 0.1M 10% $\text{Na}_2\text{S}_2\text{O}_8$	0.228	0.595	161
2	1M NaOH 0.1M 10% $\text{Na}_2\text{S}_2\text{O}_8$	0.149	0.323	117
3	1M NaOH 0.1M 10% $\text{Na}_2\text{S}_2\text{O}_8$	0.201	0.285	42
4	1M NaOH 0.1M 10% $\text{Na}_2\text{S}_2\text{O}_8$	0.109	0.294	169
5	1M NaOH 0.1M 10% $\text{Na}_2\text{S}_2\text{O}_8$	0.077	0.275	255
6	1M NaOH 0.1M 10% $\text{Na}_2\text{S}_2\text{O}_8$	0.154	0.335	117
7	0.1 M NaHCO_3	0.017	0.045	172

The collective findings demonstrate a significant enhancement in the photocurrent density of the CFO-CN film when excessive Fe was introduced onto its surface. On average, there was a remarkable enhancement rate of $143 \pm 29\%$ observed in the presence of 1M NaOH with 10% $\text{Na}_2\text{S}_2\text{O}_8$.

In **Section 7.3.1**, when the CuNiO_x layer was added as the hole transport layer, the recombination rate was slowed down because the electrons were blocked.

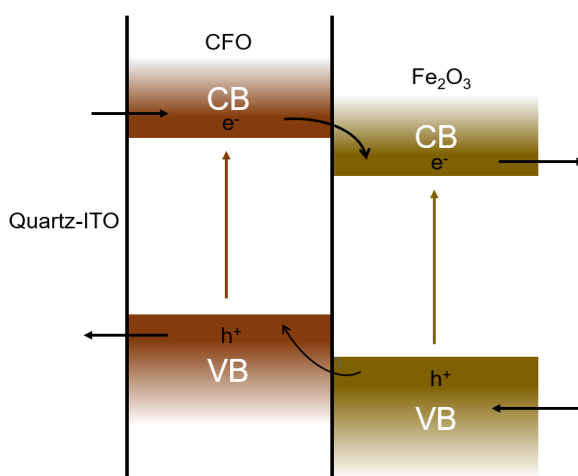


Figure 147. Energy diagram of Fe-rich CFO-CN and the explanation of the enhanced charge carrier separation

Here, standing from the energy point of view (**Figure 147**), the addition of the thin layer of n-type Fe_2O_3 constructs a p-n junction with CFO-CN and acts like a buffer layer¹⁴⁶, effectively removing the electrons and therefore increasing the charge carriers' separation rate.

8.3 Summary

The study on the constructing CuFeO_2 using Fe_2O_3 has received little attention in the past. In this Chapter, the application of surface modification through the incorporation of a small amount of Fe_2O_3 has been investigated and proven as a valuable strategy to enhance the photocathodic performance of CuFeO_2 . The formation of a desired p-n heterojunction significantly enhances the separation

speed of charge carriers, resulting in consistent, reliable, and repeatable improvements observed in the LSV test. Various amount of Fe precursor was investigated, and the optimal condition was discovered where the highest photocurrent density was promoted from 0.228 mA/cm^2 to 0.595 mA/cm^2 in 1M NaOH with 10% 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ electrolyte.

It is noteworthy that the highest photocurrent density achieved in this study significantly surpasses literature reports. In previous studies where CuFeO_2 was wrapped with Fe_2O_3 and Pt served as the cocatalyst on the surface, the photocurrent density reached $-274 \text{ }\mu\text{A/cm}^2$ at 0 V vs. Ag/AgCl in 0.1M Na_2SO_4 .

In future studies, to conduct measurements on CuFeO_2 with Fe_2O_3 coated on the surface under identical conditions to further evaluate and validate the enhancement. Additionally, XPS analysis should be performed on the samples after PEC measurement to examine the chemical state of Fe and gain insights into the working mechanism of this buffer layer.

TAS analysis should also be conducted to compare CuFeO_2 with and without the Fe_2O_3 buffer layer. This will help verify the effectiveness of charge carrier separation and the reduction in recombination rates.

Chapter 9. Conclusion and Prospect

This thesis used aerosol-assisted chemical vapour deposition (AACVD) and post-annealing treatment as the synthesis techniques to deposit a series of semiconducting metal oxides. The primary material under investigation is Delafossite CuFeO_2 . By adjusting the deposition conditions and reagents, the morphology and the thickness of this p-type semiconducting metal oxide thin film were successfully controlled and adjusted and later on used for the investigation of application performance, including gas sensing ability and photoactivity for water splitting. The deposition and post-treatment annealing conditions for single-phase Delafossite CuFeO_2 were studied in-depth in **Chapter 3**. These carefully polished deposition conditions and profoundly summarized deposition influenced factors provide valuable guidance for CuFeO_2 thin film construction, improve the benchmark of film purity and quality while save time to a large extent.

So far, there are still few studies on using Delafossite CuFeO_2 thin film as a p-type gas sensor. **Chapter 4** has investigated on Delafossite gas sensor with various morphology towards oxidized analyte gas and humidity at different temperatures addressed the research gap in the area. The observed variation in film morphology was found to correlate with changes in gas sensing performance. These findings offer valuable insights for refining film engineering strategies aimed at enhancing or modifying the gas sensing performance. The gas sensing sensitivity showed temperature dependence, whereas gas sensors have higher sensitivity in the oxygen and humidity tests. The p-to-n transition was observed when films were exposed to an oxidising environment for a period, adding significant value investigation of the p-type gas sensing mechanism.

The best gas sensing performance was observed in CFO-CN film compared to CFO-ACCL and CFO-ACAC, with the highest resistance, fastest response rate and

recovery speed, especially at 300°C. Due to the lack of a mature gas sensor assembly technique at UCL, the gas sensing performance was only evaluated from the sensitivity aspect of response towards oxidising gas and humidity and temperature dependency. The evaluation of stability and selectivity should be done in the future study.

Additionally, a high-temperature, inert atmosphere post-annealing should be set up when the n-type property appears to see if this phenomenon is reversible. This can provide a clearer understanding of the stability or the lifetime of the Delafossite CuFeO_2 gas sensor.

In **Chapter 5**, three Delafossite CuFeO_2 thin films with distinct morphologies were deposited on ITO-quartz substrates for photocathode applications. In addition to morphology, film thickness was varied to enhance photoactivity. The investigation revealed the significant influence of film morphology and thickness on the PEC performance of CuFeO_2 thin films. Although grain size and surface area affect surface reaction rates, they are not the only factors that affect the photoactivity of CuFeO_2 films. Notably, there is a complex interplay between surface reactions and charge carrier separation, with grain size exerting a more pronounced influence than surface area on grain boundaries. Furthermore, the impact of film thickness becomes predominant when it exceeds 300 nm.

All three CuFeO_2 variants exhibited their best PEC performance in alkaline electrolytes, followed by moderate photoactivity in a neutral environment and the lowest performance in an acidic environment considering stability and photogenerated current density. 1M NaOH was selected as the electrolyte for comparison with literature results, although CuFeO_2 thin films demonstrated superior performance in NaHCO_3 electrolyte, attributed to electron removal by HCO_3^- . Oxygen (O_2) was observed to play a vital role in the electrolyte, acting as an electron scavenger, which can boost the photoinduced current density of

CuFeO₂ thin films. Later, Na₂S₂O₈ served as a sacrificial reagent and showed its effectiveness in removing trapped electrons on the surface of CuFeO₂ thin film, thereby enhancing the photoactivity of CuFeO₂ thin film and revealing its potential.

The best performance of Delafossite CuFeO₂ thin film observed, with a photocurrent density of approximately 240 $\mu\text{A}/\text{cm}^2$ at 0.4 V vs RHE in 1M NaOH containing 10% 0.1 M Na₂S₂O₈, was achieved with the CFO-CN film at an optimal thickness of ~250 nm, aligning with literature findings. In O₂-saturated 1M NaOH electrolytes with 10% 0.1 M Na₂S₂O₈, performance can be further improved due to the increased concentration of electron scavengers.

Further improvements were developed from several aspects: post-air-annealing treatments, heterojunction, and surface decoration.

Chapter 6 explores the impact of three different air-involved treatments on the CFO-CN 250 nm thin film. The results confirm that treatments involving air are effective in enhancing CuFeO₂ films' photoactivity due to structural defects, providing insights for further exploration in this specific direction. Quenching during inert gas annealing is not practical for improving photoactivity. In contrast, short post-air annealing significantly boosts photogenerated current density while preserving the Delafossite structure, with the highest enhancement efficiency exceeding 70% after annealing at 200°C and the highest photocurrent density of 0.3775 mA/cm² at 0.4 V vs RHE in 1M NaOH with 10% 0.1 M Na₂S₂O₈. Annealing in an inert N₂ atmosphere with a small air percentage also enhances photocurrent generation up to 142% (with the highest photocurrent density of 0.1496 mA/cm² at 0.4 V vs RHE in 1M NaOH) but leads to a crystal phase transition into a mixed CuFe₂O₄ and CuO phase.

In **Chapter 7**, CuO and NiO films were successfully deposited on an ITO-quartz substrate using AACVD, with the optimal conditions identified at 350°C and an N₂ gas flow rate of 1L/min, followed by post-annealing at 650°C for 5 hours. Key

findings include: 1) CuNiO_x bilayer thin film outperforms CuO: NiO single layer thin film in terms of PEC activity; 2) Longer annealing durations (up to five hours) enhance photoactivity in CuO: NiO thin films; 3) CuO: NiO photoactivity positively correlates with film thickness. Cu₂O: NiO bilayer thin film was similarly synthesized but with post-annealing in an inert N₂ atmosphere. Varying the Cu: Ni ratio led to investigations into film morphology and electronic structure, revealing CuNiO_x thin film's excellent photocathodic properties in both alkaline and neutral environments. While alkaline electrolytes offer higher photocurrent density and narrower active potential windows, neutral electrolytes provide a wider active potential window. Notably, CuNiO_x exhibits high photocurrent density in acidic electrolytes with lower stability due to electro- and photo-corrosion.

Additionally, CuNiO_x thin film was employed as a hole transport layer (HTL) for the first time to improve the photoactivity of CuFeO₂ thin film, and the photocurrent density was significantly increased by 373% (from 17.8 $\mu\text{A}/\text{cm}^2$ to 84.3 $\mu\text{A}/\text{cm}^2$) at 0.4 V vs RHE in 1M NaOH. Furthermore, CuFe₂O₄ and NiFe₂O₄ thin films were successfully deposited via AACVD on ITO-quartz, with CuFe₂O₄ showing promise as a photocathode. The photoactivity of mixed CuFe₂O₄ and NiFe₂O₄ thin films positively correlated with CuFe₂O₄ content. Among the thin films studied so far (CuO, NiO, CuFeO₂, CuFe₂O₄ and CuO, CuFe₂O₄ thin films), Delafossite CuFeO₂ thin films exhibited the most excellent stability in a 5-hour test at 0.4 V vs RHE in 1M NaOH with 10% 0.1 M Na₂S₂O₈ electrolyte.

Chapter 8 has demonstrated the effectiveness of surface modification through the addition of a small quantity of Fe₂O₃ in enhancing photocathodic performance of CuFeO₂ thin film. The creation of a buffer layer significantly boosts charge carrier separation rates, consistently yielding notable improvements in LSV tests. After investigating various Fe precursor quantities, the optimal condition was identified that elevated the photocurrent density from 0.228 mA/cm² to 0.595 mA/cm² in 1M

NaOH with 10% 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$ electrolyte. As mentioned before, in future research, XPS and TAS measurements will be favourable to explain the reasons for the enhanced photoactivity of CuFeO_2 thin film from the aspects of chemical state changes and photogenerated charge carrier dynamics, respectively.

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