

**MXENE-METAL OXIDE NANOCOMPOSITES FOR
ENHANCING CO₂ ELECTROCHEMICAL REDUCTION TO
VALUABLE PRODUCTS**

BY

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A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMISTRY

MAY 2023

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN- 31261, SAUDI ARABIA
DEANSHIP OF GRADUATE STUDIES

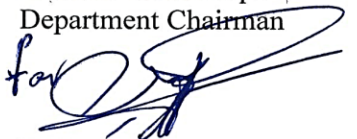
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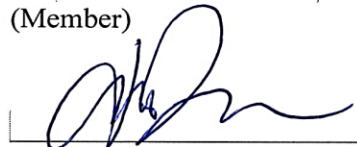
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[DEDICATION]

The work is dedicated to Almighty Allaah and to the research community for the benefit of others.

ACKNOWLEDGMENTS

My unreserved praises, adorations, and gratitude is due to Almighty Allaah the Lord of the universe, who granted me the great blessings of life, health, sound state of mind to accomplish this great achievement and all others since birth till date. I am indeed grateful to my beloved family members, my father and mother, Mr. and Mrs. Abdullahi Shafiu for their parental love, guidance, support and constant prayers all through my life. My siblings and other close relatives for their heartwarming encouragements and prayers, I sincerely appreciate you all. To my beloved and amiable wife, who has given me a deep sense of understanding, immeasurable patience, endurance, and unrelenting support that kept me motivated and moving till the achievement of this remarkable success, I say a loud thank you to an amazing personality like you.

I sincerely appreciate the efforts, guidance and patience of my amiable and indispensable advisor, Dr. Saheed Ganiyu and my thesis committee members, Dr. Abdulrahman Albetar and Dr. Almaz Jalilov for being distinctively and unadulteratedly supportive. Dr. Saheed Ganiyu offered me the opportunity to explore and improve my knowledge and skills in the field of research to accomplish this feat, he is indeed a rare gem to be with, words cannot complete capture his level of support tendered to me day and night. I am thankful also to my committee members for their wealth of wisdom and informative input from the start of the proposal till the accomplishment of this work.

My profound appreciation goes to the chairman of the department Dr. Khalid Alhooshani for his love, concern, and support to ensure my growth in the research field, he is indeed like a father to me here in Saudi Arabia and at KFUPM. To my mentor and a personality that is more than just a senior colleague, Mr. Mustapha Umar, I do appreciate all the

countless knowledge and soft landings during my moments of challenges, I am honored that our path crossed. Big thanks to all the faculty and staff members of chemistry department KFUPM, my research team colleagues, and all the lab technicians, especially Mr Malak Alkhalidi for their assistance with XRD, FTIR, FESEM, TEM, and EDS analysis.

The governing arm of King Fahd University of Petroleum and Minerals, the Deanship of Graduate Studies (DGS) and the government of the kingdom of Saudi Arabia, I am profoundly delighted for this great opportunity of a fully sponsored scholarship to achieve this degree, improve my academic career, and interact with a larger society. Shukran!!!

Lastly, I want to unfailingly acknowledge my alma mater Federal University of Technology Minna, for the robust grooming and setting the pace for my academic journey in the field of chemistry. To all others who have contributed to my success that haven't been mentioned in this write up by name, I say a big and unreserved thank you.

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LIST OF ABBREVIATIONS

Ag/AgCl	:	Silver/Silver chloride
CCS	:	Carbon Capture and Storage
CE	:	Counter Electrode
CO ₂	:	Carbon dioxide
CO ₂ RR	:	Carbon dioxide Reduction Reaction
CTAB	:	Cetyltrimethylammonium bromide
DI H ₂ O	:	Deionized Water
EDS	:	Energy Dispersive X-ray Spectroscopy
FESEM	:	Field Emission Scanning Electron Microscopy
FID	:	Flame Ionization Detector
FTIR	:	Fourier-Transform Infrared Spectroscopy
GC	:	Gas Chromatography
GHG	:	Greenhouse Gases
LSV	:	Linear Sweep Voltammetry
NMR	:	Nuclear Magnetic Resonance
ppm	:	Part per Million

RE	:	Reference Electrode
RHE	:	Reversible Hydrogen Electrode
rpm	:	Revolution per Minute
sccm	:	Standard Cubic Centimeters per Minute
SHE	:	Standard Hydrogen Electrode
TCD	:	Thermal Conductivity Detector
TEM	:	Transmission Electron Microscopy
WE	:	Working Electrode
XRD	:	X-ray Diffraction

ABSTRACT

Full Name : AbdulHakam Abdullahi Shafiu
Thesis Title : Mxene-Metal Oxide Nanocomposites for Enhancing CO₂
Electrochemical Reduction to Valuable Products
Major Field : Chemistry
Date of Degree : June, 2023

This study reports the use of a novel nanocomposite material composed of MXene-metal oxide nanoparticles (ZnO nanorods and CuO nanoflakes) for CO₂ reduction via electrochemical technique which have proved to be a strategic way to obtain valuable feedstocks to curtail the global concern of skyrocketing concentration rise of CO₂ in the atmosphere which is detrimental to human health and weather/climate conditions in a more economically viable way. Metal oxide nanoparticles, MXene and MXene-Metal oxide nanocomposites were synthesized via a thermal treatment, hydrothermal and wet impregnation methods respectively. XRD, EDS, SEM, TEM, and FTIR characterization techniques were utilized to confirm the materials. Linear sweep voltammetry, cyclic voltammetry and controlled potential coulometry were used to evaluate the electrochemical performance of the nanocomposites, while the gaseous products were detected and quantified using gas chromatography. The ZnO₉₀-MX₁₀ nanocomposite showed a high selectivity towards the production of CH₄ at 79.3% FE and low applied potential of -0.56 V_{RHE}, while suppressing H₂ evolution greatly. The CuO₇₀-MX₃₀ showed more selectivity towards formate. This improved electrochemical activity may be linked to a constructive cooperative effect between the MXene and ZnO/CuO components, which promotes efficient charge transfer, increased active sites and high surface area for CO₂ reduction. Overall, this study presents a viable approach for CO₂RR electrochemically using MXene-Metal oxide nanocomposites which could have significant implications to produce valuable feedstocks sustainably.

ملخص الرسالة

الاسم الكامل: عبد الحكم عبد الله شافيو

عنوان الرسالة: المركبات النانوية لأكسيد المعادن مكسين لتعزيز خفض الكهروكيميائية لثاني أكسيد الكربون للمنتجات القيمة

التخصص: الكيمياء

تاريخ الدرجة العلمية: يونيو 2023

تقدم هذه الدراسة استخدام مادة نانومركبة جديدة تتكون من جسيمات نانوية من المعدن وأكسيد الـ إم إكسين (عصيات نانوية من أكسيد الزنك وشرائح نانوية من أكسيد النحاس) لتحويل ثاني أكسيد الكربون (CO_2) عبر تقنية كهروكيميائية، والتي ثبتت كونها وسيلة استراتيجية للحصول على مواد خام قيمة للحد من القلق العالمي حيال زيادة تركيز ثاني أكسيد الكربون بشكل متسارع في الغلاف الجوي والذي يضر بصحة الإنسان والظروف الجوية/المناخية بطريقة اقتصادية أكثر جدوى. تم تحضير جسيمات أكسيد المعادن والإم إكسين ونانومركبات الإم إكسين-أكسيد المعادن بواسطة المعالجة الحرارية، والمعالجة الحرارية بالماء، وطرق التشريب الرطب على التوالي. تم استخدام تقنيات التوصيف باستخدام أشعة الإكس-راي (XRD) وطيف الانبعاث والتشتت الإلكتروني (EDS) والمجهر الإلكتروني الماسح (SEM) والمجهر الإلكتروني ذو الانتقال الناقل (TEM) والتحليل الطيفي بالأشعة تحت الحمراء (FTIR) لتأكيد المواد. تم استخدام تقنيات الفولتامبرية ذات التمرير الخطي والفولتامبرية الدورية والكولومترية بالتحكم في الجهد لتقييم الأداء الكهروكيميائي للنانومركبات، في حين تم اكتشاف وكمية المنتجات الغازية باستخدام الكروماتوغرافيا الغازية. أظهرت النانومركبة $ZnO_{90}-MX_{10}$ انتقائية عالية في إنتاج ثنائي الميثان (CH_4) بنسبة من الكفاءة الكهروكيميائية وجهد تطبيق منخفض قدره $-0.56 V_{RHE}$ ، مع قمع تطور الهيدروجين بشكل كبير. أما النانومركبة $CuO_{70}-MX_{30}$ فأظهرت انتقائية أعلى نحو الفورمات. قد يكون النشاط الكهروكيميائي المحسن مرتبطاً بتأثير تعاوني بناء بين مكونات الإم إكسين وأكسيد الزنك/أكسيد النحاس، مما يعزز نقل الشحنة بكفاءة وزيادة المواقع النشطة والمساحة السطحية العالية لتحويل ثاني أكسيد الكربون. بشكل عام، تقدم هذه الدراسة نهجاً قابلاً للتطبيق في تحويل ثاني أكسيد الكربون كهروكيميائياً باستخدام نانومركبات الإم إكسين-أكسيد المعادن، مما يمكن أن يكون له آثار هامة في إنتاج مواد خام قيمة بشكل مستدام

CHAPTER 1

INTRODUCTION

1.1 Overview of Carbon dioxide (CO₂)

Carbon dioxide (CO₂) is an odorless, colorless gas that occurs naturally in the atmosphere. Despite been considered a trace gas in the atmosphere in comparison with the concentrations of nitrogen or oxygen, it is essential in the Earth's life cycle and in regulating the world's climate with current concentrations of approximately 417 ppm [1]. Aerobic respiration results in the emission of CO₂. As part of photosynthesis, plants absorb CO₂ and exhale oxygen. Up to 15 ppm of seasonal variations in atmospheric CO₂ can be attributed to shifts in the worldwide photosynthesis-respiration balance. [2]. Carbon dioxides constitute part of the carbon cycle in the ecosystem, from the environment (surface water and atmospheric air), decomposition, photosynthesis, through respiration (aerobic and anaerobic), to carbon sink release during combustion (from fossil fuels like petroleum, coal, CaCO₃). Furthermore, CO₂ is a greenhouse gas that slows down the escape of long-wavelength radiation into space by absorbing it in the atmosphere. CO₂ along with other greenhouse gases like ozone, methane, water vapor, chlorofluorocarbons, and nitrous oxide trap radiation and causes the earth to be warmer than it would be without the atmosphere [2].

Societies and economies around the globe rely largely on fossil fuels like natural gas, coal, and petroleum for generation of the major forms of energies needed in industrial activities and processes [3]. As a result of constant emission of gases from these industrial activities, the atmospheric CO₂ content globally has skyrocketed and has contributed significantly to the acidification of water bodies, increased global warm up, adverse weather conditions, and the extreme annihilation of important natural species [2,3], which have created a great deal of concern because of the unceasing rise of greenhouse gases (GHG) generated from these processes. Carbon dioxide is the major greenhouse gas that promotes climate change due to anthropogenic human activities among other sources such as deforestation, cement production, and biomass burning [6]. About 412 ppm of CO₂ is currently held by the Earth's atmosphere with a steady increase with a rise of 11% compared to year 2000, when the concentration was 370 ppm, and a 47.5% increase since the start of the industrial age [5,6]. This figure has been projected to reach 950 ppm by 2100 by the International Panel on Climate Change (IPCC) [7,8].

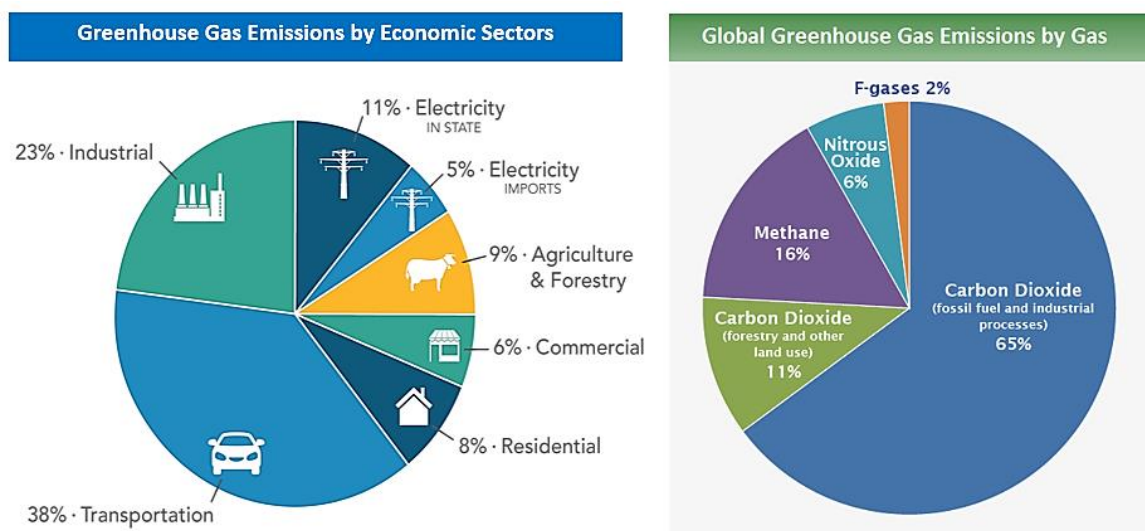


Figure 1: Greenhouse gas emissions by economic sectors and gases [11]

Food, oil, and chemical industries use carbon dioxide commercially. CO₂ is mostly utilized in the synthesis of urea as a major component, with a minor portion employed in methanol and host of other chemicals production [12]. The Kolbe-Schmitt reaction uses CO₂ to produce certain carboxylic acid derivatives, like sodium salicylate [13]. At the research level, electrochemical techniques are also being investigated. Particularly appealing is the use of green energy to synthesize fuels from carbon dioxide (like methanol), as this might produce fuels that are simple to transport and use with conventional combustion methods while emitting no net CO₂ [14]. In the food industry, CO₂ is a food additive that is employed as a propellant and an acidity regulator legally used in Australia, and New Zealand [15], the EU [16], and US [17]. It is also employed for manufacturing carbonated products like seltzer water and soft drinks giving them sparkling tastes. Carbon dioxide serves as flame extinguisher achieved by swamping the flame environment with it. It works by starving the flame of oxygen due to oxygen displacement. Carbon dioxide extinguishers are primarily used in server rooms and does not work well with usual combustible flames, due to their inability to significantly cool the affected material [18]. Supercritical carbon dioxide is utilized in the production of various aerogels, removal of caffeine from coffee and serve as an excellent solvent for numerous lipophilic chemical molecules [19]. In the pharmaceutical sectors, carbon dioxide has drawn interest as a less hazardous substitute compared to conventional solvents like organochlorides. For this reason, certain dry cleaners also use it. However, these utilizations constitute less than 1% of the anthropogenic CO₂ generated around the globe while the remaining is discharged to the atmosphere because of limited resources to convert them into valuable chemicals and fuels.

1.2 CO₂ Mitigation

The development of methods and technologies to trap CO₂ and its conversion to value-added products and fuels have received enormous attention by scientists to curb this menace and to preserve the serenity of our atmosphere and immediate environment. There are several techniques for CO₂ emission extenuation, which include carbon capture and storage, renewable energy, nuclear power, forestry, and bioenergy. Proven handy techniques that have been suggested to reduce carbon emissions in light of forestry activities include: afforestation (planting forests where they previously did not exist), reforestation (planting forests where they once existed), existing forests carbon density increase, reducing deforestation, bioenergy with CCS (BECCS) [20,21], and degradation activities [22].

Carbon capturing at the emission source is considered an effective approach in mitigating the anthropogenic releases of carbon dioxide to the environment, factoring in the fact that the globe will still rely on fossil fuels for energy generation for an ample duration. Separating, processing, and transporting a flow of carbon dioxide from industrial sources to amenities for long-term storage constitute the carbon capture and storage (CCS) process [23]. For example, CO₂ from fossil fuels burn or biomass. Furthermore, a good number of methods, such as adsorption, membrane gas separation, absorption, gas hydration, and chemical looping, CO₂ can be directly captured from an industrial sources like cement kiln [23,24]. In 2022, around one thousandth of the world's CO₂ emissions are trapped by CCS, with the major focus on the processing of gaseous fossil fuels [26], with a success rate between 50 to 68% [27]. However, despite all the materials developed to achieve this

objective, majority of these materials suffer from inadequate adsorption capacities, and need for elevated temperatures, coupled with the limited resources to continually store the huge amount of CO₂ released on daily to annual basis are some consequential drawbacks which hinders carbon capture and storage as an efficient and sustainable technology to sufficiently achieve the needed goal [9 – 11]. Additional drawbacks of CCS include the high energy and resource costs involved in capturing, transporting, and safely storing CO₂. Moreover, there are chances of CO₂ storage facilities leakage over time.

Novel alternative techniques are currently being explored with the motivation of harnessing CO₂-capture and utilization (CCU) techniques which provides a commercial opportunity to convert CO₂ to value-added products. The biochemical method [31], photochemical [13,14], electrochemical [15,16], thermochemical [17,18], and catalytic hydrogenation [19,20] are techniques which have been explored.

The biological technique involves the conversion of CO₂ into useful products like food and chemicals by use of biological systems, like microorganisms or enzymes. While this approach has the potential for CO₂ conversion to give valuable products, some of its limitations include Low efficiency/selectivity, limited feedstocks such as microorganisms or enzymes, requires a complex and multi-step process which involves several biological and chemical reactions. The photochemical method of CO₂ reduction involves using light energy to drive CO₂ reduction to value-added products. Catalyst stability, high cost of materials and equipment, and the environmental impact because of use of toxic solvents, the release of harmful by-products, and the disposal of waste materials are some of the drawbacks of this technique. The thermochemical method involves using heat energy to transform CO₂ to valuable feedstocks. This technique is faced with the challenge of easy

degradation of equipment and materials, high energy requirements, release of pollutants and greenhouse gases from the feedstocks for the process (coal and natural gas), and the production of large quantity of wastes.

Despite the contribution of these techniques to the utilization/conversion of CO₂, factors such as limited feedstocks, low efficiency/selectivity, environmental impact of waste generated from their processes, technical challenges, catalyst instability or easy deactivation, high energy requirement (due to the inertia of CO₂), corrosion and degradation of materials, are some of predicaments limiting their industrial scaling.

The electrochemical technique, which involves utilizing electrical energy for converting CO₂ into more useful chemicals, offers a competitive advantage among others [21,22] because it utilizes green and sustainable energy source [23,24], has mild and easily tunable reaction conditions, and generates a wide range of industrial chemicals and useful fuels such as hydrocarbons, syngas, formate, alcohols [44].

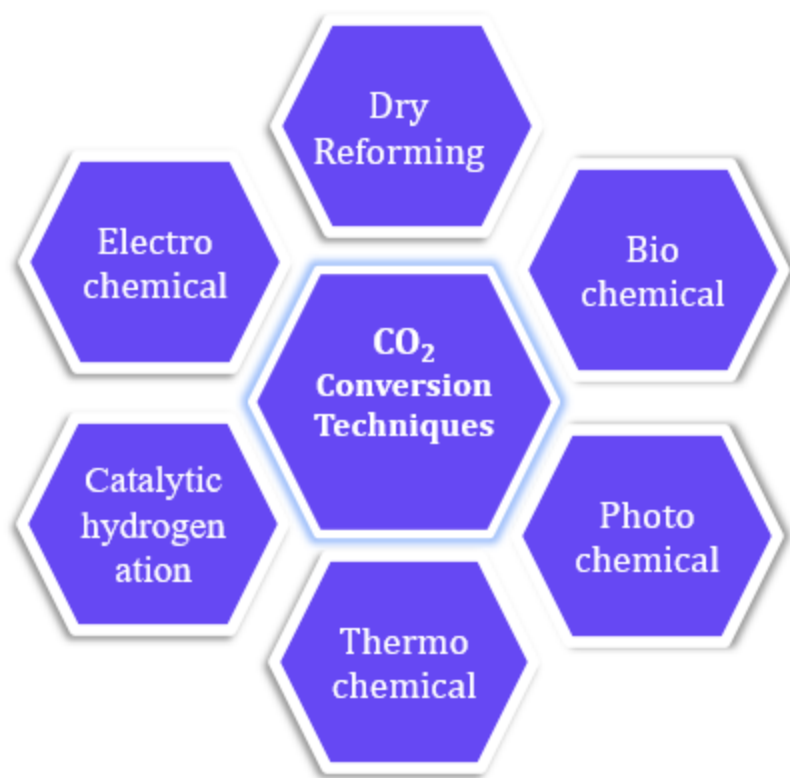


Figure 2: Techniques of CO₂ conversion/utilization

1.3 Electrochemical CO₂ Reduction

Electrochemical carbon dioxide reduction, commonly referred to as electrolysis of CO₂, is the transformation CO₂ into a more reduced chemical species using electrical energy. It is deemed one of the most promising methods in carbon capture and utilization from among the numerous methods utilized in this field [45]. Electrochemical methods can be used to convert carbon dioxide into valuable feedstocks, including methane (CH₄), formic acid (HCOOH), carbon monoxide (CO), [46] ethylene (C₂H₄), and ethanol (C₂H₅OH) by reduction [46,47]. Different metallic catalysts exhibit varying degrees of selectivity for electrochemical CO₂RR into value-added products. Silver is a more selective metallic

catalyst for CO, tin for HCOOH, and copper is for C₂H₄, CH₄, or C₂H₅OH. Additionally, though sparingly, CO₂ electrochemical reduction has been used to make methanol, propanol, and 1-butanol [49].

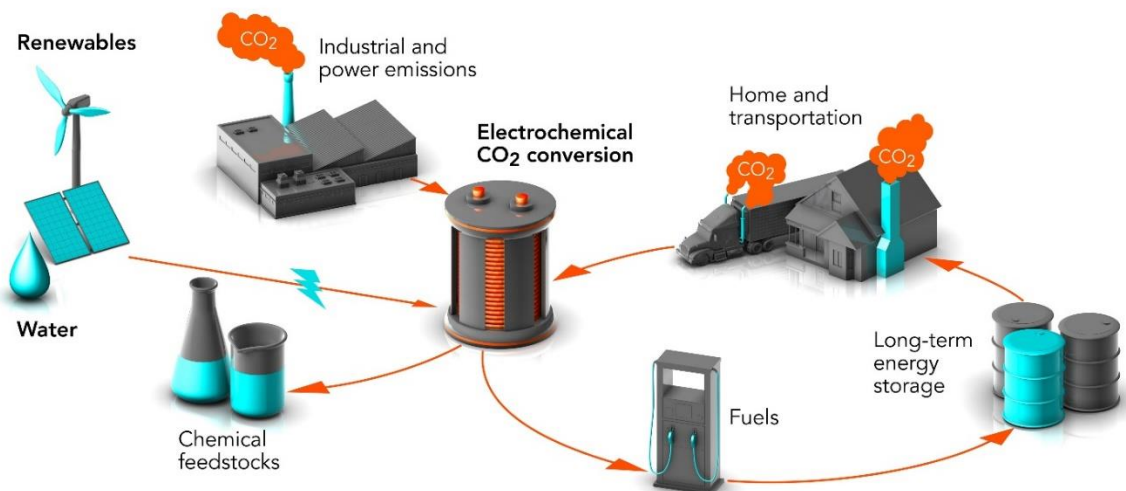


Figure 3: Electrochemical technique for CO₂ conversion to valuable feedstocks using renewable energy source [50]

In general, obtaining C₁ products like CO & HCOO⁻ are relatively easier to obtain compared to the slow kinetics needed for coupling carbon atoms [51] to generate C₂₊ products. Previous studies have demonstrated C–C coupling process to be a crucial step in the production of C₂₊ species [27 – 29]. Activation of CO₂ requires substantial amount of energy due to its inertness. Poor product selectivity consequently results due to numerous operational reaction pathways. Therefore, development of catalysts that promotes product selectivity while maintaining good stability, low overpotential, low cost, and decent faradaic efficiency is highly desirable for CO₂RR and economic viability [55]. In light of this, numerous kinds of electrocatalytic materials which have been explored by researchers

so far include: metal chalcogenides [31,32]; metals nanomaterials [33,34]; metal alloys [35,36], Mxenes [37,38], metal organic frameworks (MOFs), carbon-based [64], metallic oxides [40–42].

MOFs, also known as metal-organic frameworks, are a category of compounds where metal ions or clusters are bound to organic ligands, creating structures that can be one-dimensional, two-dimensional, or three-dimensional. MOFs belong to the subclass of coordination polymers and are characterized by their porous nature. This unique property makes them highly versatile and widely employed in various applications such as catalysts, support materials and other applications. In a study conducted by Gutterød *et al.* [69], they investigated a highly stable MOF catalyst composed of Pt nanoparticles (NPs) embedded within a Zr-based UiO-67 MOF. The researchers conducted steady-state and transient kinetic studies, focusing on H/D and $^{13}\text{C}/^{12}\text{C}$ exchange, to examine the production of methanol from CO_2/H_2 feeds. The results revealed that methanol formation occurred selectively at the interface between the Pt NPs and defect Zr nodes, facilitated by formate species attached to the Zr nodes. This mechanistic pathway allowed for the separation of methanol from other byproducts such as CO and methane. Additionally, Tianqinji *et al.* [68] reported a bimetallic MOF ($\text{Cu-ZnO}/\text{Al}_2\text{O}_3$) catalyst synthesized via a templated strategy (termed $\text{Cu-ZnOMOF} \subset \text{Al}_2\text{O}_3$). They linked the formation of methanol to be highly influenced by Cu-Zn@MOF precursor system because of the substantial Cu metal active sites and surface-enriched Cu-ZnOx interfaces with improved H_2 and CO_2 adsorption. The developed catalytic system ($\text{Cu-ZnOMOF} \subset \text{Al}_2\text{O}_3$) demonstrated an excellent selectivity for methanol at 86.9% faradaic efficiency.

Metal oxides are solid crystalline compounds that consist of a metal cation bonded with an oxide anion. These compounds have the characteristic ability to react with water, resulting in the formation of bases, or with acids, leading to the formation of salts. Many researchers have explored the use of metal oxides for CO₂RR with resounding results. In a study, the performance of different morphologies of ZnO was investigated by Kang *et al.* [69]. The different morphologies were synthesized using the hydrothermal method. Among the morphologies (nanospheres, nanorods, and nanosheets synthesized), The ZnO nanorod exhibited superior performance over others, demonstrating a high current density of 100 mA·cm⁻² and a Faradaic efficiency of 68.3% for the production of carbon monoxide at an applied potential of -0.76 V_{RHE}. The exceptional performance of ZnO nanorods can be attributed to the presence of higher O-deficient surface, which are facilitated by their larger surface area. These conditions promote the effective adsorption of *CO species, leading to enhanced performance in CO₂ reduction [70], [71].

They further doped the catalyst with Ag to improve its efficiency, the ZnO morphology was maintained after doping. At a current density of 150 mA·cm⁻² and an applied potential of -0.76 V_{RHE}, ZnO nanorods doped with 1 atom% of silver (Ag) exhibited the highest FE_{CO} value of 91.9%, with about 23% CO selectivity improvement, higher current densities, and maintaining a 10h stable performance compared to the pristine ZnO which lasted for 4 h. In another study, Wei Liu *et al.* [72] synthesized an ultrathin Copper (ii) oxide nanoplate containing oxygen-rich arrays forming Cu/Cu₂O heterogeneous interfaces by self-evolution during electrocatalysis. The catalyst demonstrated 84.5% FE for C₂H₄ while maintaining a stability of ~55 h in a flow cell

containing KCl as its electrolyte, and a full-cell ethylene energy efficiency of 27.6% at 200 mA cm⁻². They attributed the prolonged ethylene production to the improved adsorption of *OCCOH species and stable Cu/Cu₂O interfaces.

Mxenes have been utilized in recent time for CO₂RR to value-added feedstocks and have shown great potential in that application. Zhao *et al.*, [73] demonstrated an effective approach to synthesize single atom immobilized copper MXene which electrocatalytically reduces CO₂ to CH₃OH. The developed electrocatalyst showed great electrocatalytic stability. The high efficiency of the process can be attributed to the low energy barrier encountered during the rate-determining step, which involves the conversion of HCOOH* to the absorbed CHO* intermediate. They achieved a 59.1% FE_{CH₃OH}. Albertus and colleagues conducted a comprehensive study that combined experimental and theoretical approaches to investigate the electrocatalytic carbon dioxide reduction reaction (CO₂RR) on MXene catalysts based on titanium and molybdenum [63]. The Mxenes (Mo₂CT_x & Ti₂CT_x) produced HCOOH as the main product with peak FE of over 56% on Ti₂CT_x and partial current density of up to -2.5 mA cm⁻² on Mo₂CT_x. Additionally, they postulated that at smaller quantity terminal -F group, smaller overpotential was observed from the simulations carried out by the team which reveals the crucial role of the Tx group in the CO₂RR.

Metal alloy nanoparticles have also been utilized for reducing CO₂ to various value-added products electrochemically. Yeongdong *et al.* [74] synthesized various compositions of monodisperse Cu-Pd nanoparticles via colloidal method. The NPs demonstrated a catalytic efficiency other than the bulk Cu catalysts when alloyed with Pd, suppressing hydrocarbon formation. According to their report, the catalyst with 1:1 Cu-Pd composition was best for

the conversion of carbon dioxide to carbon monoxide efficiently with a FE of 87% at $-0.9 V_{\text{RHE}}$. The energy barrier for the CO^* protonation process is increased when Pd is alloyed with Cu according to density functional theory simulations which help to control the formation of hydrocarbons from CO_2RR process. Jiwon *et al.* [61] reported a bimetallic electrocatalysts of Sn–Zn (oxide-derived). The developed electrocatalysts displayed excellent efficiency for the transformation of CO_2 to HCOOH . 80% FE for CO was attained using a pure Zn catalyst in the reduction of CO_2 electrochemically, whereas a FE_{HCOOH} of 80% was achieved on Sn_1Zn nanoporous catalyst which promotes CO_2 conversion at $-1.0 V_{\text{RHE}}$ overpotential to formic acid. The synergistic effect of Sn and Zn performs a vital role in modulating the selectivity and catalytic activity towards formic acid. Additionally, the electrocatalyst effectively localizes electrons to metallic Sn, facilitating its selectivity and high stability, while maintaining its efficiency even after a duration of 18 h for CO_2RR .

Typically, the half-cell reduction reaction of carbon dioxide to various products electrochemically is shown in table 1, along with the number of electrons required for each process.

Table 1: Reduction potential for variety of products during electrochemical reactions in aqueous electrolyte (at 1 atm, 25 °C, and pH 7 Vs SHE)

CO₂ Reduction Reaction	Product	Number of Electrons	Reduction Potential E° (V vs SHE) [75]
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	Formic acid	2	−0.610
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	Carbon monoxide	2	−0.530
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	Methane	8	−0.240
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	Ethylene	12	−0.349
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$	Ethanol	12	−0.329
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	Methanol	6	−0.380
$2\text{CO}_2 + 14\text{H}^+ + 14\text{e}^- \rightarrow \text{C}_2\text{H}_6 + 4\text{H}_2\text{O}$	Ethane	14	−0.270
$3\text{CO}_2 + 18\text{H}^+ + 18\text{e}^- \rightarrow \text{C}_3\text{H}_7\text{OH} + 5\text{H}_2\text{O}$	Propanol	18	−0.310

In this work, inspired by the quest to develop a novel two-dimensional (2D) catalyst to tune the selectivity on product(s) towards specific product via CO₂ electrochemical conversion process. Thus, we report the synthesis of titanium based MXenes composited with copper (ii) oxide and zinc oxide nanomaterials via different methods described in the methodology section. The morphological and structural states of the synthesized catalysts were confirmed using XRD, FTIR-KBr, TEM, SEM, EDS characterization techniques. Furthermore, intercalation of the base material (MXene) with varying metal oxide loadings to produce MXene-metal oxide nanocomposite to boost their faradaic efficiency and selectivity towards specific products based on the synergistic property of the fabricated material is also reported.

1.4 Research Objectives

The fundamental objective of this thesis work is to develop an improved electrocatalyst to enhance its selectivity towards specific product(s) via CO₂ electrochemical conversion process.

The specific objectives include:

- i. Design and synthesis of an efficient electrocatalyst and electrode
- ii. Modification of the synthesized catalysts (MXene – metal oxide nanocomposite Ti₂C/MO) which are very selective and efficient for reduction of CO₂ electrochemically.
- iii. Characterization of the synthesized and modified catalysts' morphology and properties

Application and evaluation of the efficiency of the catalysts

CHAPTER 2

LITERATURE REVIEW

Materials used in electrochemical assessment should be largely available, application-driven designed, exhibit enhanced sensitivity, stability, and selectivity to specific products, with high efficiency while maintaining low costs to ensure its economic sustainability. In the literature, a collection of catalysts utilized for electrochemical reduction of CO₂ have been identified and explored. Some of which include, metal-free electrodes, metal nanostructure such as Cu, Au, Pt and Ag, metal alloys like Cu–Pd, Cu–Ag, Cu–Ni, Cu–Zn, Cu–In, and Cu–Sn, metal oxide; CuO, SnO₂, ZnO, and CeO₂, MXenes; Ti₃C₂, V₂C and chalcogenides; MoS₂, WS₂ [76].

2.1 Overview on MXenes

Mxenes, first discovered by Gogotsi and his team in 2011, are a class of two-dimensional (2D) transition metal carbides, nitrides or carbonitrides [77]. They are obtained by selectively etching out from MAX precursors, the 'A' layers. They are generally represented as M_{n+1}AX_nT_x. (M, A and X denotes transition metal, group 13 element, and C and/or N respectively), n can range from 1 to 3, T_x represents terminating atom(s) on the surface like -OH, -O, and/or -F as a result of the etching process [27–29]. Typically, element “A” within the framework is etched with mineral acids like and a fluoride agent HCl + LiF (or NaF) (forming HF *in-situ*), HF + HCl, HF only, or NH₄HF₂ to obtain Mxenes [81]. Chemical vapor deposition and high-temperature synthesis are some other methods

employed in the synthesis of MXenes [82]. Ti_2C , Cr_2TiC_2 , Ti_3CN , Mo_2C , Mo_2TiC_3 , Nb_4C_3 , V_4C_3 , Ti_3C_2 , Zr_3C_2 , Ti_4N_3 , V_2C , and Mo_2ScC_2 are variety of literature reported MXenes, synthesized experimentally [73,74].

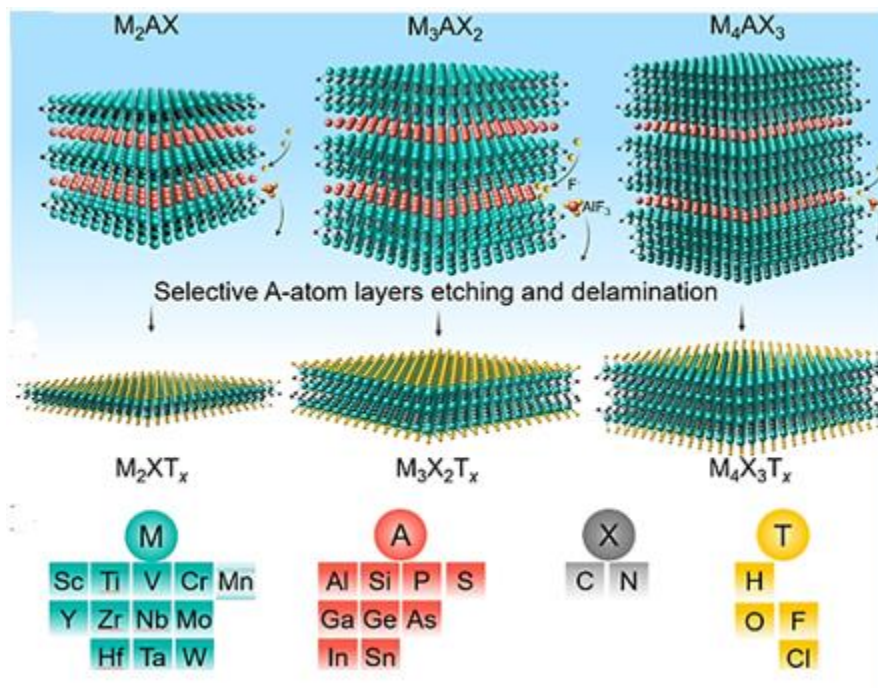


Figure 4: Scheme of variety of MXenes and their exfoliation process [85]

Batteries, energy storage, separation, catalysis, and biomedicine are some of the fields in which these materials have found applications [75,76]. The outstanding chemical characteristics and structures of MXenes have attracted scientists' curiosity in exploring their applicability in various technological needs [44,45]. Furthermore, their inherent properties such as tunable terminal functional groups, decent chemical and mechanical stability, hydrophilicity, higher surface area, high electronic conductivity, easily accessible active sites make them prominent catalysts, as well as co-catalysts [46,47]. MXenes have been explored extensively in CO_2 reduction as an electrocatalyst or photocatalyst [82,83].

MXene plays a significant role in several catalytic reactions, including the photocatalytic synthesis of H_2 and CO_2 as well as the evolution and reduction of hydrogen (H_2), oxygen (O_2), nitrogen, and nitrogen (N_2) [71,81]. The cycling stability and specific capacitance of Mxenes are excellent and outstandingly high, hence widely employed in high-performance supercapacitors and lithium-ion batteries [83,84]. They also have been explored for water treatment applications because of their effective and efficient heavy metal ions removal capacity [85,86].

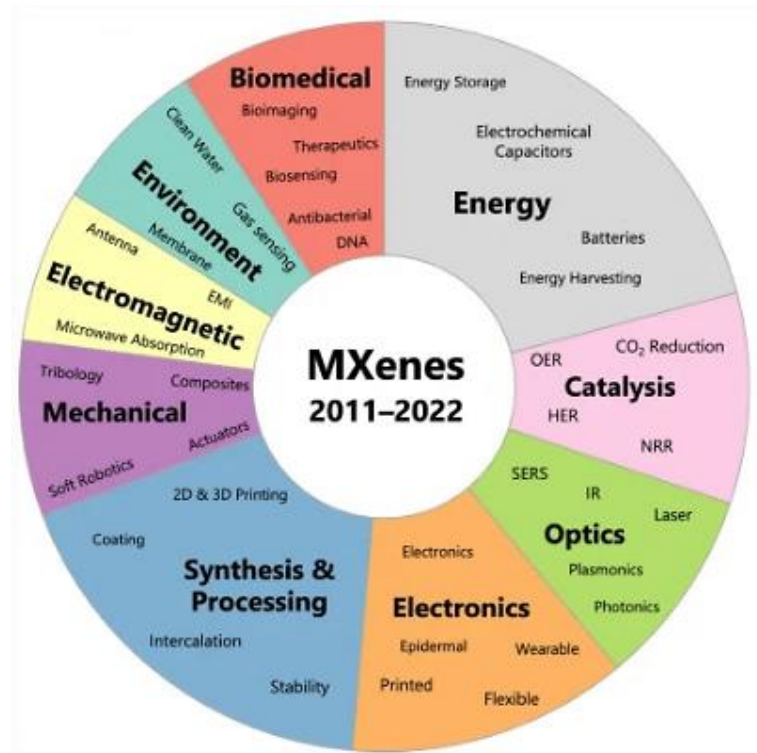


Figure 5: Fields of MXenes application since its discovery [99]

2.2 Metal Oxides and CO₂ Reduction

Researchers have explored numerous metal oxide materials for CO₂ conversion to valuables, among which include CuO, ZnO, TiO₂, WO₃, and CdO which have demonstrated notable prospects and applications in this field. Compared to the others, copper (ii) and zinc oxide nanoparticles have been explored more with excellent FE and decent overpotential for carbon monoxide, ethylene, methane, methanol, ethanol. Zinc-based electrocatalysts are highly selective towards CO, and the abundant availability of zinc on Earth, have shifted attention to it as a promising resource [48,49]. A low selectivity for CO to approximately 40% is shown by bulk Zn metal in reality [102]. However, some research teams have recently reported nanostructured metallic Zn electrocatalysts, such as hexagonal, dendrite, nanoscale, and nanowire, achieved by modulating the morphological properties of the Zn metal and gave a resounding yield of ~90% faradaic efficiency (FE) for CO [50–54]. According to Geng *et al.* [107], they achieved a FE of 83% for CO at a current density of 16.1 mA/cm⁻², they tied it to the high density of oxygen vacancies in ZnO nanosheets. Copper has acquired the distinction of being the only catalyst capable of selectively and efficiently converting CO₂ into multi-carbon compounds [55,56], most importantly C₂ and C₂₊ hydrocarbon products in considerable quantity [57,58]. Copper and its derivatives, such as oxides, alloys, and composites have demonstrated tremendous potential for CO₂RR conversion into valuable chemical feedstock. Additionally, because of the intermediate binding strength of copper to *CO and its high surface adsorption coverage to *CO, *CO₂, and *H₂, hydrocarbons such as ethylene, ethanol, methane, formate, methanol, and longer-chain products can be generated [57,58]. Wei *et al.* [72] reported an ultrathin CuO nanoplate arrays which form Cu/Cu₂O heterogeneous interfaces

for electrochemical CO₂ reduction to ethylene, which demonstrated a FE of 84.5%, with an excellent stability of ~55 h in a flow cell using a neutral KCl electrolyte, and a full-cell ethylene energy efficiency of 27.6% at 200 mA cm⁻² in a membrane electrode assembly electrolyzer.

2.3 Two-Dimensional (Hybrid) Materials for CO₂ Reduction Reaction

The electrochemical method of CO₂ reduction has attracted more interest in recent times due to its numerous advantages over other techniques of CO₂ conversion. The reduction process (CO₂RR) thermodynamically progresses via proton-coupled multi-electron transfer reactions at the cathode of either an electrolyzer or a fuel cell, producing a variety of chemical fuels with a large global demand like hydrocarbons (C₂H₆, C₂H₄, and CH₄), alcohols (CH₃OH, C₂H₅OH and n-C₃H₇OH) carbon monoxide (CO), and formate (HCOO⁻) [114]. Despite this, significant obstacles like slow electroreduction reaction kinetics of CO₂, high energy barrier requirement to generate intermediates (*COOH), high overpotential, pervasive H₂ evolution reaction competition, low faradaic efficiency, and low selectivity on products have limited the electrocatalysts' catalytic performance. Hence, to achieve a significant breakthrough in this field, it is crucial to develop CO₂RR catalysts that show great selectivity, activity, durability, and efficiency is crucial.

The advent and advancement of 2D materials, such as graphene, in recent years has opened novel possibilities to fabrication of highly effective catalysts. In comparison to conventional materials, they possess high proportion of available surface atoms and excellent specific surface area, which are greatly advantageous for them being used in the catalysis industry [115]. Additionally, 2D materials chemical properties can be tuned

through surface adjustments, doping, and manufacturing defects, which is very essential in engineering and design of high-performance electrocatalysts. Nanostructured two-dimensional (2D) materials refer to materials with atom-thicknesses of one or a few which are intrinsically layered [116]. Materials such as transition-metal dichalcogenides (TMDs), transition-metal oxides (TMOs), transition metals (TMs), and carbon-based materials [117] are some of the examples these class of novel catalysts. Example to this the case of a pristine graphene which is basically shows chemical inertness, doping it with nitrogen (N) can activate the 2D material to catalyze CO₂RR significantly [118].

2.4 Reaction Mechanisms for Product Formation

The electrochemical reduction of CO₂ in aqueous medium can take several reaction paths depending on the desired product(s) which involves the transfer of several electrons and protons. Adsorption and activation of CO₂ happens in the first step requiring a -1.90 V (vs SHE) redox potential to transfer one electron to CO₂ to generate the (CO₂^{•-}) radical in the presence of suitable electrocatalyst to minimize the overpotential [119]. In theory, a good catalyst should be able to either facilitate proton-electron transport with relatively low energy barriers or separate hydrogen sources like water and H₂ into atomic H^{*} and to potentially introduce electrons into the CO₂ antibonding orbital. The adsorption of CO₂ on an electrocatalyst surface happens via two possible modes, either as *COO or as *OCO. Adsorption through *OCO leads to the formation of only formic acid, while via *COO can result in the formation of numerous possible products [120]. According to theoretical calculations and experimental findings, main group metals like Sn and Bi binds to CO₂ via oxygen preferably (i.e., *OCO) to produce formic acid, whereas transition metals prefer

via carbon binding (i.e., $\ast\text{COO}$) and generate CO or $\ast\text{CO}$ intermediate [121]. Formic acid and CO can be achieved with comparatively good selectivity and low overpotentials, involving a reaction of only one intermediate and two-electrons transfer. The possible pathways for the realization of a variety of valuable feedstocks are indicated in the scheme of Figure 6.

The C_2 products formation is more difficult because it requires more available protons and higher C – C bond(s) formation energy which can limit the rate. This process involves the dimerization of $\ast\text{CO}$ and through several possible protonation sites arrangements [122]. Copper-based electrocatalysts are the only group of materials with the capacity to transform carbon dioxide to multi-carbon alcohols and hydrocarbons but suffer from high product selectivity [111,112]. Typically, the site at which CO_2 binds determines the product selectivity. Usually, C_2 products develop when CO_2 is adsorbed on Cu(100), but on Cu(111), methane and ethylene can both be the main products [125]. Higher hydrocarbon (C_{3+}) products can also be produced on copper-based catalysts but however at a low selectivity ($< 20\%$) [126]. Consequently, catalyst optimization is required to increase their capacity for charge transfer and target products can be selectively attained from CO_2RR by tuning the adsorption and desorption capacity of electrocatalysts.

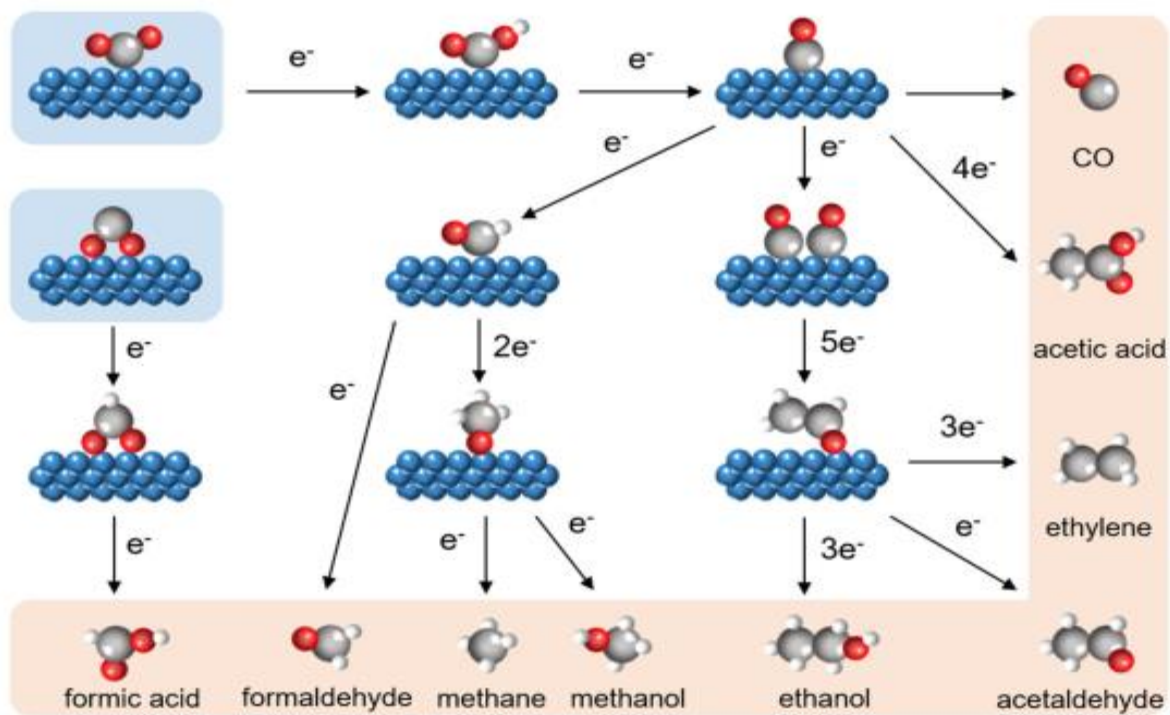


Figure 6: Scheme CO₂RR pathways to form the C₁ and C₂ products (catalysts, hydrogen, oxygen and carbon: blue, white, red, grey spheres respectively) [127]

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Materials and Chemicals

The materials and chemical reagents utilized in this study include:

- i. Methanol (CH_3OH), Ethanol ($\text{C}_2\text{H}_5\text{OH}$), Nafion (5 wt%), CO_2 (99.99%)
- ii. Platinum wire (counter electrode)
- iii. Electrochemical cell (H-type)
- iv. Carbon paper (support material for the catalyst)
- v. Aluminum (granular, <1 mm, 99.7% purity)
- vi. Titanium (powder, 100 mesh, 99.7% purity)
- vii. Potassium bicarbonate (KHCO_3 , granular, 99.7% purity)
- viii. Sodium hydroxide (NaOH , 99%)
- ix. Copper (ii) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, >99%)
- x. Hexadecyl trimethyl ammonium bromide CTAB (99%)
- xi. Tetrabutylammonium hydroxide (TBAOH) ($\text{C}_{16}\text{H}_{37}\text{NO}$, ~40%)
- xii. Hydrochloric acid (HCl , ~38% wt)
- xiii. Hydrofluoric acid (HF , ~48% wt)
- xiv. Sodium fluoride (NaF , 99%)
- xv. Potassium hydroxide (KOH , 99%)
- xvi. Zinc Chloride (ZnCl_2 , 98%)
- xvii. Carbon graphite (powder, 99%)

All chemical reagents were procured from Sigma-Aldrich and of standard analytical grades which were used without further purification or refinement.

3.2 Synthesis of Catalysts

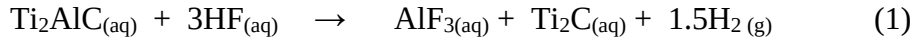
3.2.1 Titanium Carbide MXene (Ti_2C) Synthesis

A ratio of 2:1:1 of Ti, Al, and C graphite, the precursor materials, were mixed and finely grinded together using a mortar and pestle to prepare the MAX (Ti_2AlC). Tubular furnace was then used to anneal the resultant mixture for 2 hrs in an argon atmosphere at 1400 °C (at 10 °C/min heating rate). DI H_2O was added to the annealed sample in a beaker, ultrasonicated for about 1hr and the resultant mixture was paper filtered, oven dried and meshed into a fine powder.

The Al layer from the Ti_2AlC was selectively etched to produce Ti_2C MXene adopting the synthesis procedure documented by [21] with slight modifications. Using a 500 mL polypropylene bottle, 84 mL HCl (38% wt) was added to 42 mL DI and then 14 mL HF (~48% wt) was introduced carefully and stirred continuously for 5 mins. While stirring continuously, 7 g of the finely grinded MAX was gradually introduced to the acid mixture over the course of 5 – 10 minutes. The system was placed on an oil bath with a temperature setting of 55 °C, and it was agitated for 24 hours. Centrifuging at 5000 rpm afterwards, the mixture washed repeatedly with DI until the supernatant pH did not cause any change to litmus paper. The residue was dispersed in 25mL deionized H_2O , followed by the addition of 15mL tributylammoniumhydroxide (TBAOH) (10% wt/v). The colloid was stirred continuously for 12 hrs after ultrasonication for 15min. The resulting mixture was

centrifuged and rinsed repeatedly with DI H₂O to achieve neutrality of supernatant's pH. It was then subjected at 80 °C vacuum drying for 5h, and further meshed to obtain a fine uniform powder.

The following equation illustrates the fundamental reactions involved in etching the MAX phase:



The etching process in reaction (1) eliminates the Al layer. While processes (2) and (3) occur concurrently, to functionalize the surface. Additionally, research has been conducted to determine how the bifluoride compounds (NaHF₂, KHF₂, NH₄HF₂) utilized to etch the MAX phase affects the nanosheets' surface spacing and functionalization [128].

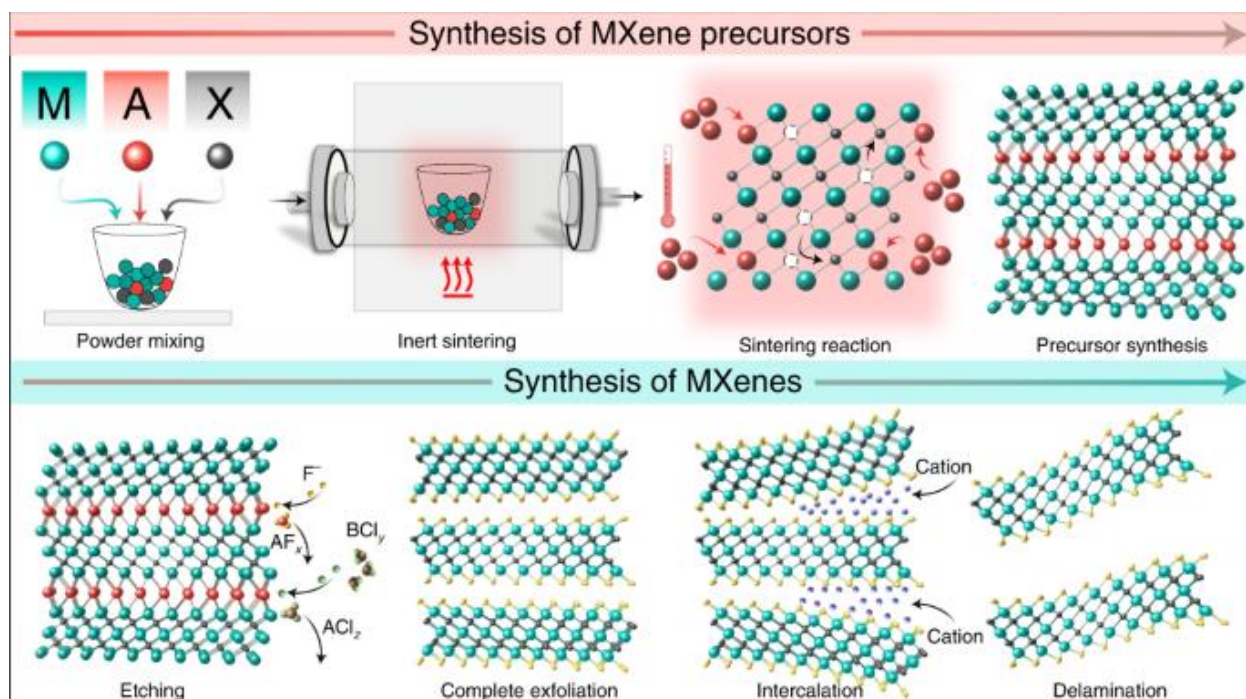


Figure 7: Synthesis of Mxenes from MAX phase precursors, etching and delamination process [129]

3.2.2 Copper (ii) Oxide Nanoflakes Synthesis

CuO nanoflakes were synthesized by simple precipitation method from sodium hydroxide (NaOH) and copper (ii) sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) as precursors. Copper (ii) sulphate solution was prepared by dissolving 4g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 20mL of deionized water, while a 20% NaOH solution was made by the dissolution of 10g NaOH pallets in 40mL DI H_2O . The nanoparticles were obtained by a gradual addition of 20% NaOH solution to the Copper (ii) sulphate solution while stirring and heating on a magnetic hot plate stirrer at 90 °C until a significant amount of black precipitate was achieved. The precipitate was thereafter centrifuged for 5 mins at 3500 rpm after cooling down naturally. The sediment was washed thrice with DI and absolute ethanol alongside decantation of the

supernatant to remove any form of remnant impurity in the mixture. The resultant sediment was oven dried at 90 °C for 8 hrs.

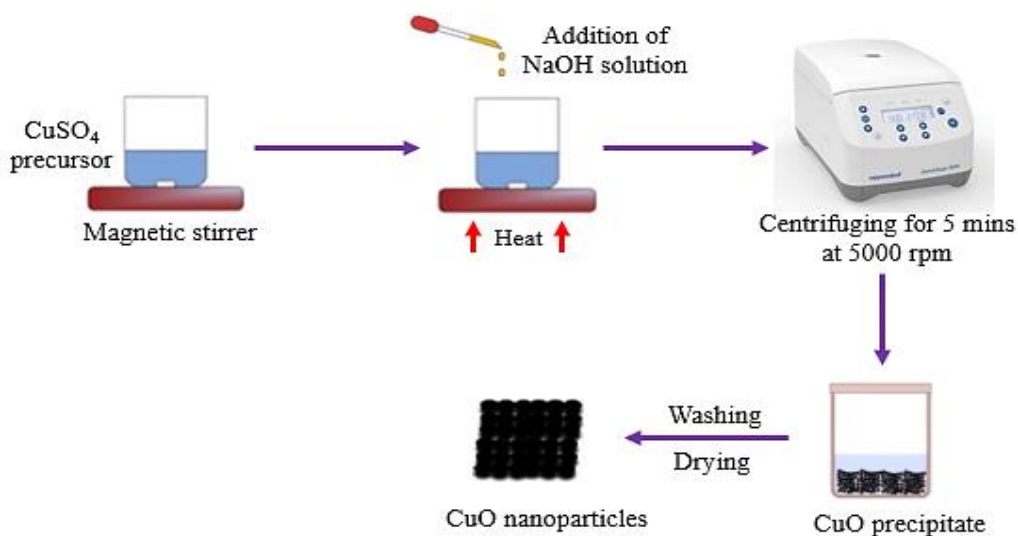
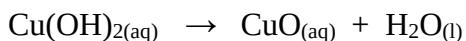
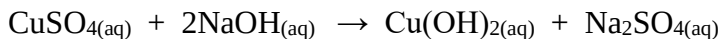


Figure 8: Copper (ii) oxide nanoflakes synthesis scheme

3.2.3 Zinc Oxide Nanoflakes Synthesis

Zinc oxide nanorods was synthesized adopting a simple hydrothermal method procedure from [130]. In a little amount of distilled water, 5.03g ZnCl_2 and 4.15g KOH were dissolved in separate beakers and on combination, produced a white floccule rapidly while stirring using a magnetic stirrer. 6.66g of cetyltrimethylammonium bromide (CTAB) was gradually added to the mixture under a continuous stirring condition. CTAB plays the role of a surfactant which helps to control crystal growth of the nanoparticles and regulate their size and shape. Controlling both the surfactant's architecture and its self-assembly behavior enables tailoring the morphologies in the desired way. After 5 hours of hydrothermal

treatment of the resulting mixture in an autoclave at 120 °C, the autoclave (Teflon stainless-steel) was then given time to naturally cool down. The resulting precipitate were collected, centrifuged at 5000 rpm, repeatedly rinsed with DI and absolute ethanol at 60:40 combining ratio respectively to eliminate contaminants while decanting the supernatant after every wash. The sediment was then dried at 80 °C for a duration of 5 hours.

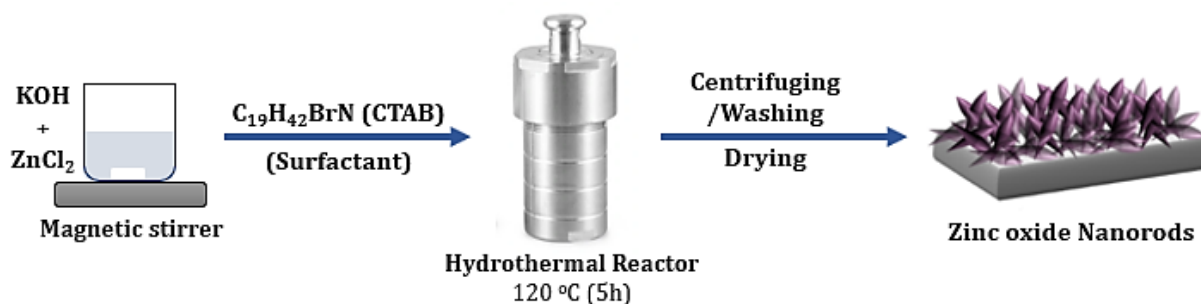


Figure 9: Zinc oxide nanorods synthesis via hydrothermal technique

Zinc oxide nanorods could also be synthesized using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$ or $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ as the zinc precursor as an alternative to ZnCl_2 or changing the reaction time and/or temperature adopting the same procedure.

3.3 Nanocomposite Intercalation

Mxene – zinc oxide nanocomposite was realized by wet impregnation of the synthesized Mxene sheets with Zinc oxide powder via dispersion of varying masses of ZnO and Mxene (0.09g & 0.01g (10% Mxene), 0.085g & 0.015g (15% Mxene), and (0.08g & 0.02g (20% Mxene), in 20 mL of ethanol. The mix was continuously stirred for 2 hrs at 65 °C to enhance the evaporation of ethanol and dried in an oven afterwards. The resulting product was heat treated under Ar condition at 600 °C using tubular furnace for 2 hrs (at 5 °C/min heating

rate). Mxene – copper oxide nanocomposite was prepared adopting the same procedure at a mix of CuO and Mxene 0.085g & 0.015g (15% Mxene), (0.08g & 0.02g (20% Mxene), and (0.07g & 0.03g (30% Mxene)

The modified catalysts were termed sample A ($\text{ZnO}_{90}\text{--MX}_{10}$), Sample B ($\text{ZnO}_{85}\text{--MX}_{15}$), sample C ($\text{ZnO}_{80}\text{--MX}_{20}$) for ZnO nanocomposites, while the CuO nanocomposites are labelled sample D ($\text{CuO}_{85}\text{--MX}_{15}$), sample E ($\text{CuO}_{80}\text{--MX}_{20}$), and sample F ($\text{CuO}_{70}\text{--MX}_{30}$).

CHAPTER 4

RESULTS AND DISCUSSION

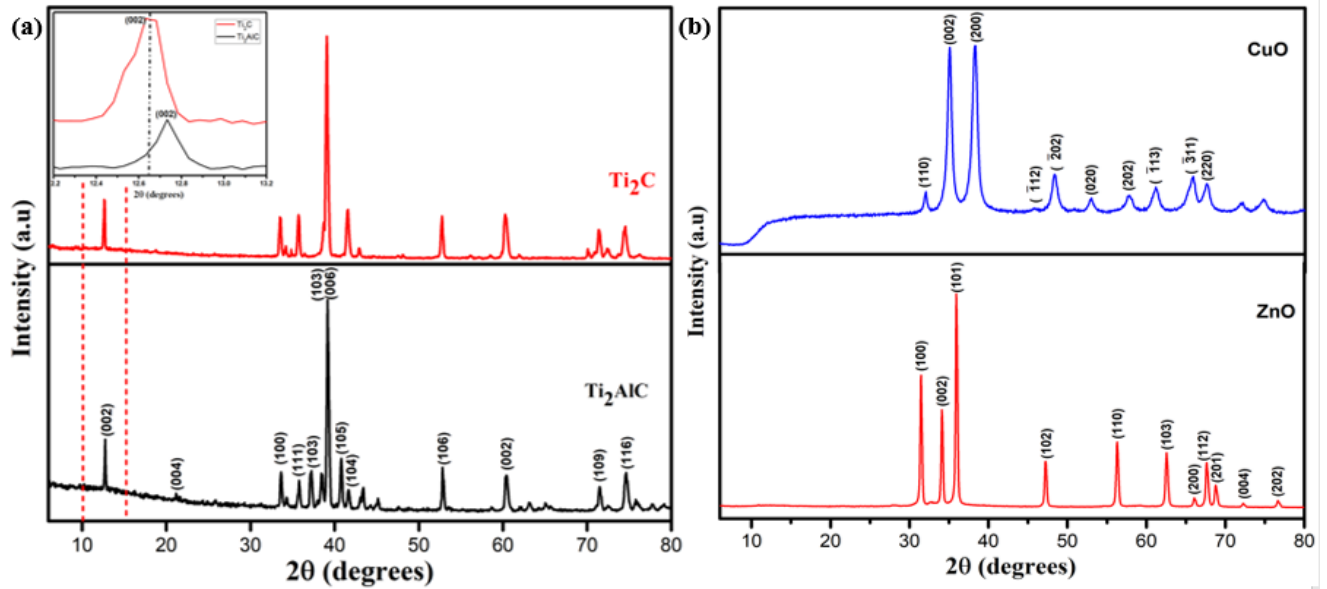
4.1 Catalysts Characterization

The structural investigation of the synthesized catalysts was carried out using D2 phaser 2nd Generation XRD diffractometer at an applied voltage of 40 kV and a $3^\circ/\text{min}$ scan rate. A JSM-6460 model field emission scanning electron microscope (FESEM) was used to access the morphological structures of the catalysts. Additionally, the growth of catalysts layer and their compositions were studied using field emission transmission electron microscope (FETEM), JEM2100F model, while a NICOLET iS10 model Fourier-transform infrared spectrophotometer (FTIR) was used to measure the as-obtained powders surface properties.

4.1.1 X-Ray Diffraction Analysis

The X-ray diffraction (XRD) spectrum was used to confirmed structures of Ti_2AlC (MAX), Ti_2C (Mxene), ZnO nanorods, CuO nanoflakes, and MO – Mxene nanocomposites as presented in Figure 10. Figure 10a displays the various peak patterns of MAX powder (Ti_2AlC) alongside that of Ti_2C MXene. According to Wang and co-worker's study [125], the typical $\text{Ti}_2\text{AlC}/\text{TiC}/\text{Ti}_3\text{AlC}_2$ standard spectrum was used to index each peak. The typical peaks (103) and (104), at $2\theta = 37.5^\circ$ and 42.1° of "Al", observed in Ti_2AlC a close

to disappearing in the case of MXene due to its etching out selectively from Ti_2AlC to give well separated layers of MXene sheets. TiC impurity is denoted by the diffraction peaks (100), (111), and (105) at positions 33.8, 36.1, and 41.8°, respectively. The ensuing peaks are wider, weaker, and rougher as a result of subjecting Ti_2AlC to HF treatment for 24 hours indicating planes disorderliness of the crystalline structure of Ti_2AlC and the formation of a new material of layered network. The (002) peak's backward shift in the MXene spectrum, which is similarly magnified in Figure for clarity, is another intriguing modification that was observed, which is most likely attributed to the c-lattice increment, an intrinsic attribute of the layered structure of MXene [131]. These alterations verify that the MXene flakes were successfully synthesized.



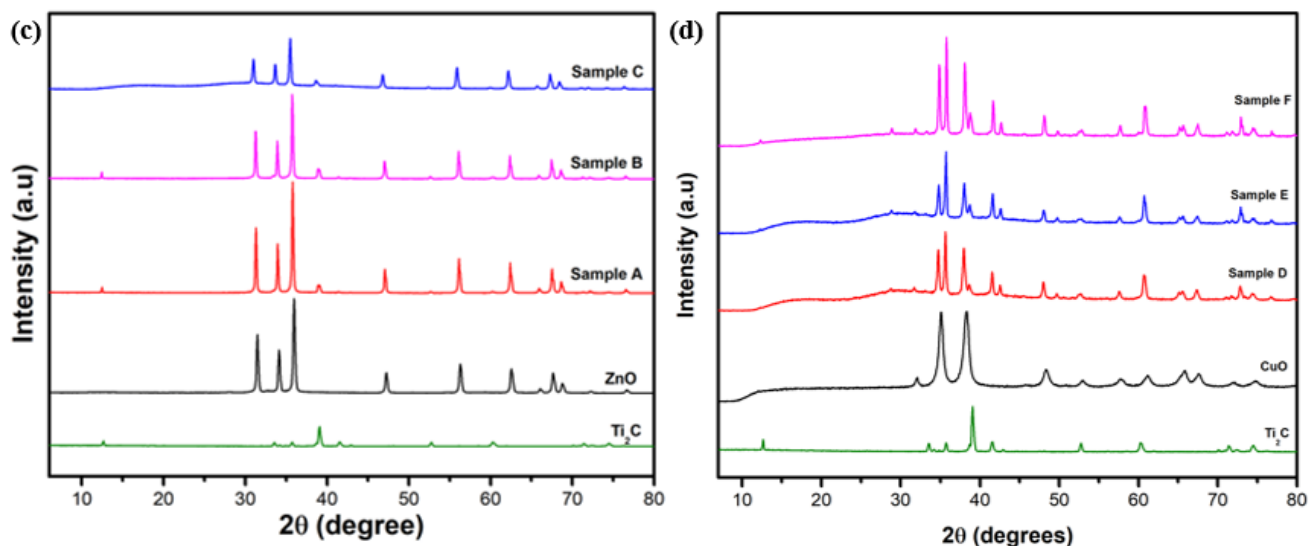


Figure 10: XRD pattern of (a) Ti_2AlC (MAX) and Ti_2C (Mxene) with magnification showing (002) peak shift. (b) CuO nano flakes and ZnO nanorods (c) ZnO-MXene nanocomposite (d) CuO-MXene nanocomposite

The ZnO diffraction pattern shows peak matching to (101), (103), (111), (200), (002), (201), (102), (110), and (112) crystal planes as in Figure 10b which match reports in the literature quite well [122–124]. In the same vain, the diffraction pattern of CuO shows peaks in-line with crystal planes (110), (002), (111), (-202), (020), (202), (-113), (-311) and (220) which are inherent diffraction peaks of CuO according to reports [125–127]. Additionally, the nanocomposites formed shows characteristic peaks of both the Mxene and the corresponding metal oxide nanoparticles which were intercalated as shown in Figure 10c-d. This is an indication of a successful synthesis of the base catalysts and hybridization of the base materials to produce the nanocomposite catalysts.

4.1.2 Catalyst Morphology

The catalysts' morphologies and surfaces were investigated using field emission scanning electron microscopy (FESEM). Figure 11a-c shows the uniformly formed sheets of Ti_2C MXene and metal oxide nanoparticles. The SEM images of Figure 11 shows the modified forms after incorporation with zinc oxide (samples A – C) and copper oxide (samples D – F) at different ratios which clearly indicates the growth and entrapment of the MXene sheets on the metal oxide nanoparticles. Additionally, some of the ZnO formed secondary specks on top of the MXene layer. The MO – MXene nanocomposite's synthesis is verified by the well-dispersed distribution of both materials on one another.

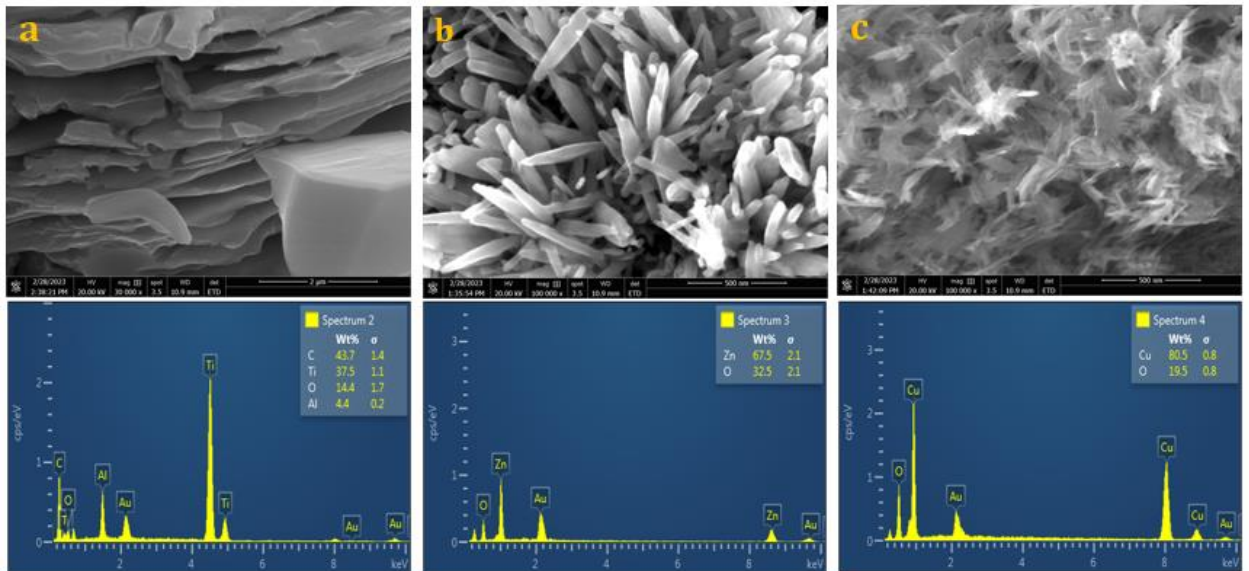


Figure 11: Scanning electron micrograph of (a) Ti_2C MXene (b) ZnO nanorods (c) CuO nano flakes and their respective EDS mapping

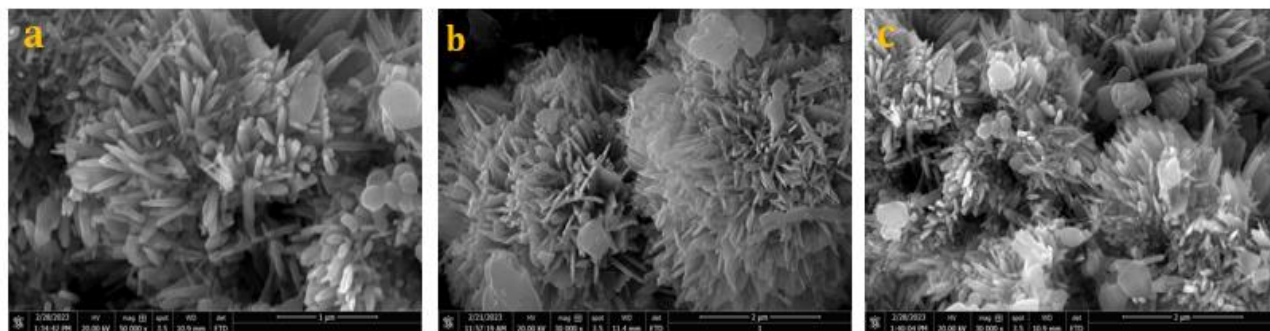


Figure 12: Scanning electron micrograph of (a) ZnO₉₀-MX₁₀ (b) ZnO₈₅-MX₁₅ (c) ZnO₈₀-MX₂₀

The base catalysts and the nanocomposites TEM images are presented in Figures 13, 14 (a-d) and 15 (a-d), which shows a good correlation with literature reports and correlates with the XRD and SEM analysis. The catalysts has particles sizes in the nanometer range having a particle size of 49.1 nm, 71.0 nm, 17.3 nm, 17.9 nm, 27.0 nm, 44.4 nm, 7.0 nm, 8.4 nm, and 11.3 nm for MXene, ZnO nanorod, sample A (ZnO₉₀-MX₁₀), Sample B (ZnO₈₅-MX₁₅), sample C (ZnO₈₀-MX₂₀), CuO nanoflakes, sample D (CuO₈₅-MX₁₅), sample E (CuO₈₀-MX₂₀), and sample F (CuO₇₀-MX₃₀) respectively averagely at an image scale of 100 nm for all samples.

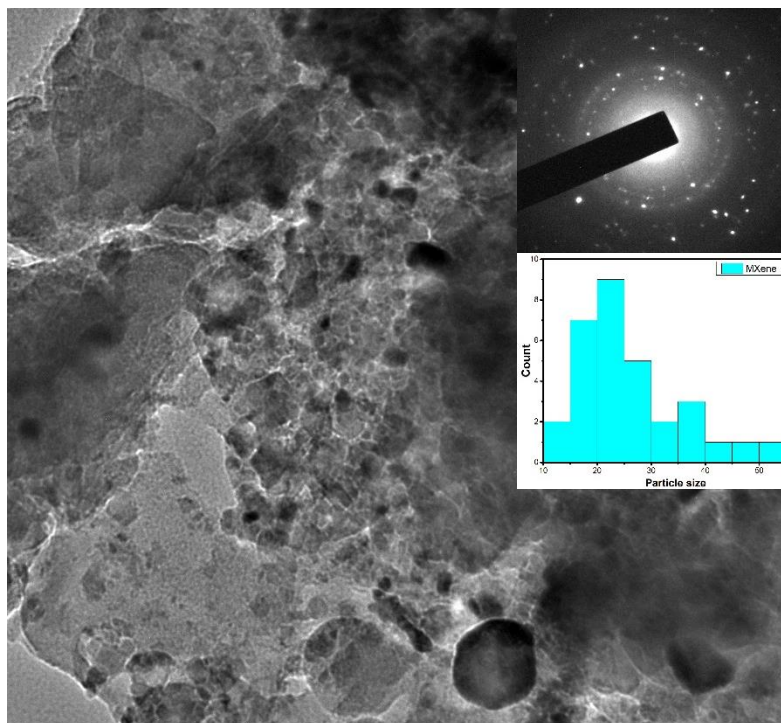


Figure 13: TEM images of Ti_2C MXene

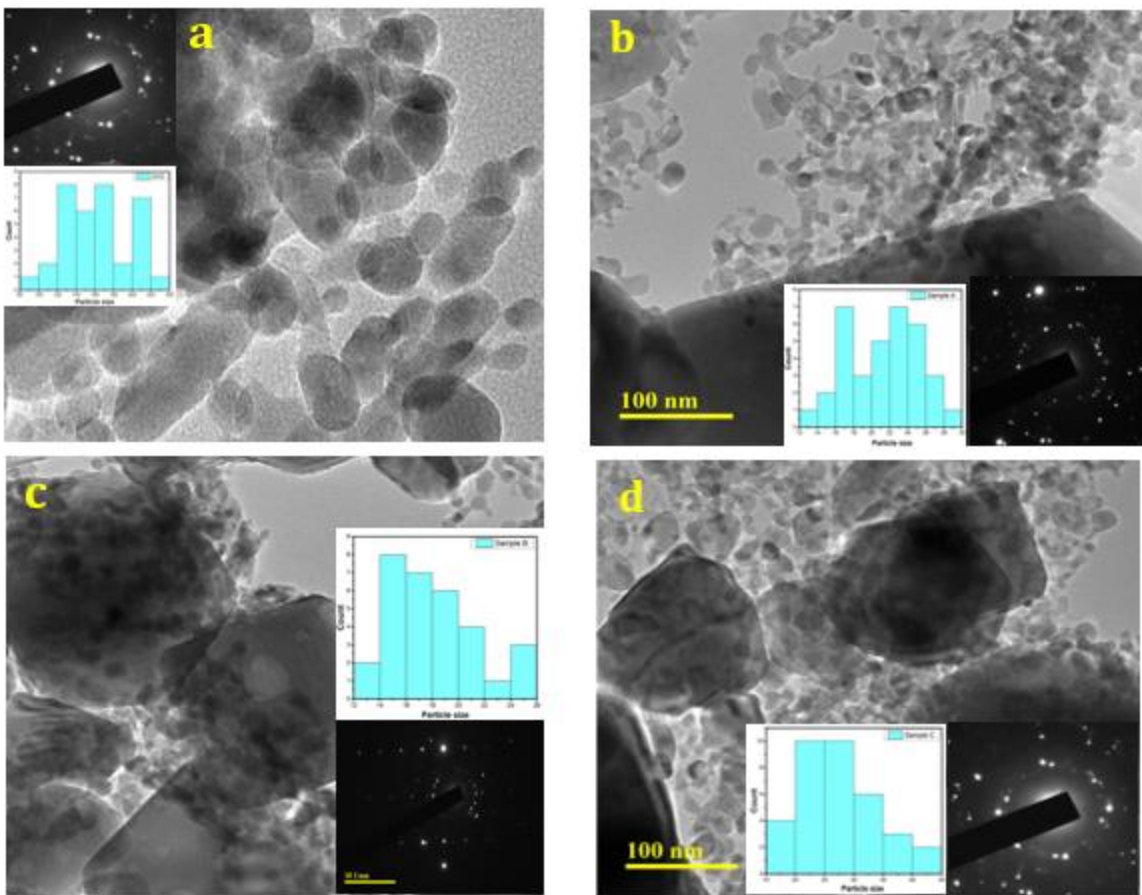


Figure 14: TEM image of (a) ZnO (b) ZnO₉₀-MX₁₀ (c) ZnO₈₅-MX₁₅ (d) ZnO₈₀-MX₂₀

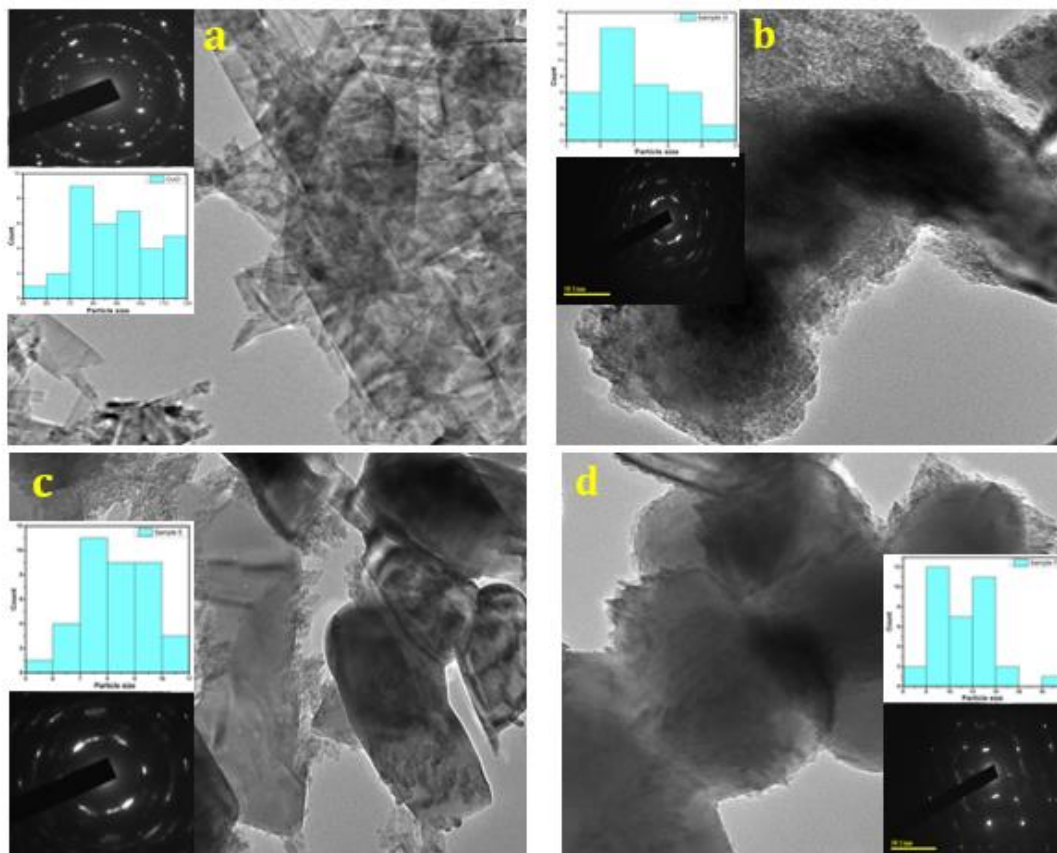


Figure 15: TEM image of (a) CuO nanoflakes (b) $\text{CuO}_{85}\text{-MX}_{15}$ (c) $\text{CuO}_{80}\text{-MX}_{20}$ (d) $\text{CuO}_{70}\text{-MX}_{30}$

4.1.3 FTIR-KBr Analysis

The FTIR spectra of all the catalysts which reveal absorption bands at from 3899 to 450 cm^{-1} are presented in Figure 15 (a-b), which agrees with reported literature. Variations on the signal intensities are observed for the modified catalysts, this is an indication of the growth of the metal oxide nanorods on the MXene sheets, and with increase in the quantity ZnO added, the change in the peak intensities are more pronounced.

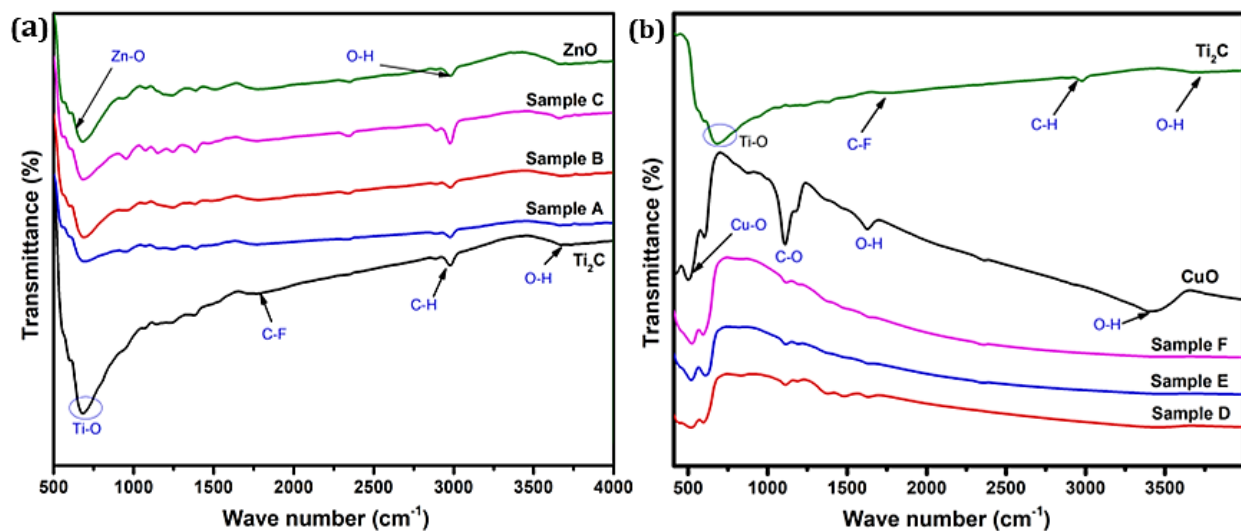


Figure 16: (a) Ti₂C MXene, ZnO nanorods and ZnO based nanocomposites (b) Ti₂C MXene, CuO nanoflakes and CuO based nanocomposites FTIR spectra.

The 1641, 3670, and 3749 cm⁻¹ vibration bands indicate the occurrence of the -OH group attributed to external H₂O absorbed as a result of the hydrophilicity of MXene [138]. The Ti-C vibrations are shown by the band at 606 cm⁻¹ [139]. Additionally, the Ti-O bond's deformation vibration is likely what caused the peak at 529 cm⁻¹ [140]. Asymmetric/symmetric stretching bands for methyl and methylene are seen in the FTIR spectra of MXene at 2894 and 2985 cm⁻¹, respectively. Peaks at 545–600 cm⁻¹ correspond to the Zn-O and Ti-O stretching [141], [142]

Bands at around 601, 508 and 487 cm⁻¹ ascribed to Cu-(II)-O vibrations. CuO nanoparticles spectra exhibit a prominent peak at 601 cm⁻¹, an indication of the production of Cu-O bond.

4.2 Electrochemical Measurements

4.2.1 Linear Sweep voltammetry (LSV)

The electrocatalytic activity of CO₂ reduction on base catalysts and the nanocomposites was evaluated using LSV technique in a 0.5 M KHCO₃ solution saturated with CO₂. The onset potential of the base catalysts is presented in Figure 16. The zinc oxide electrode showed the lowest current density amongst the base materials. A controlled LSV experiment was conducted (using the same electrolyte saturated with Ar) to establish the electrocatalytic activity of the synthesized catalysts. The insignificant current density observed proved that the catalyst was less active in an inert atmosphere (Ar) and more active in the CO₂ saturated condition. The current density observed is attributed to hydrogen evolution reaction or residual current of the electrocatalytic system.

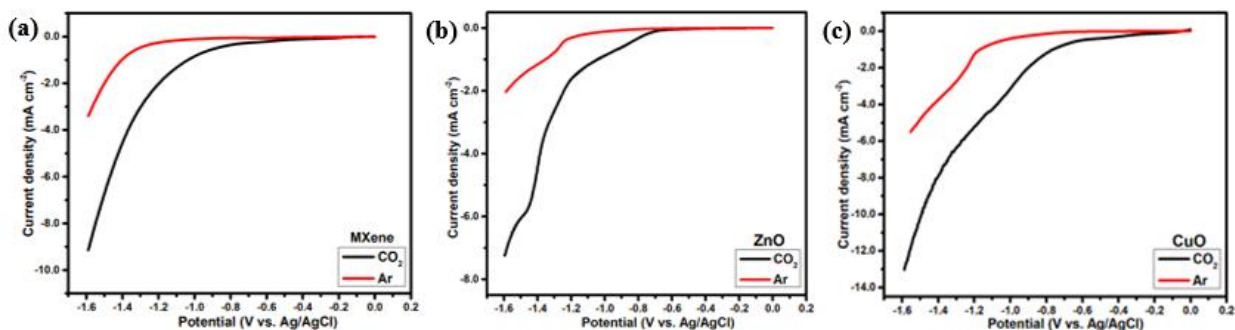


Figure 17: Linear sweep voltammetry of (a) Ti₂C MXene (b) ZnO nanorod (c) CuO nanoflakes

The LSV of the nanocomposites are presented in Figure 17. Sample B (ZnO₈₅–MX₁₅) among the ZnO based nanocomposite series and sample F (CuO₇₀–MX₃₀) in the CuO based nanocomposites series showed the highest current densities of -10.20 mA cm⁻² and -18.30

mA cm^{-2} respectively. Additionally, the linear sweep voltammetry provides information of the on-set potential for each of the catalysts, which serves as a guide on promising potentials to scan through during the controlled potential analysis for CO_2 reduction.

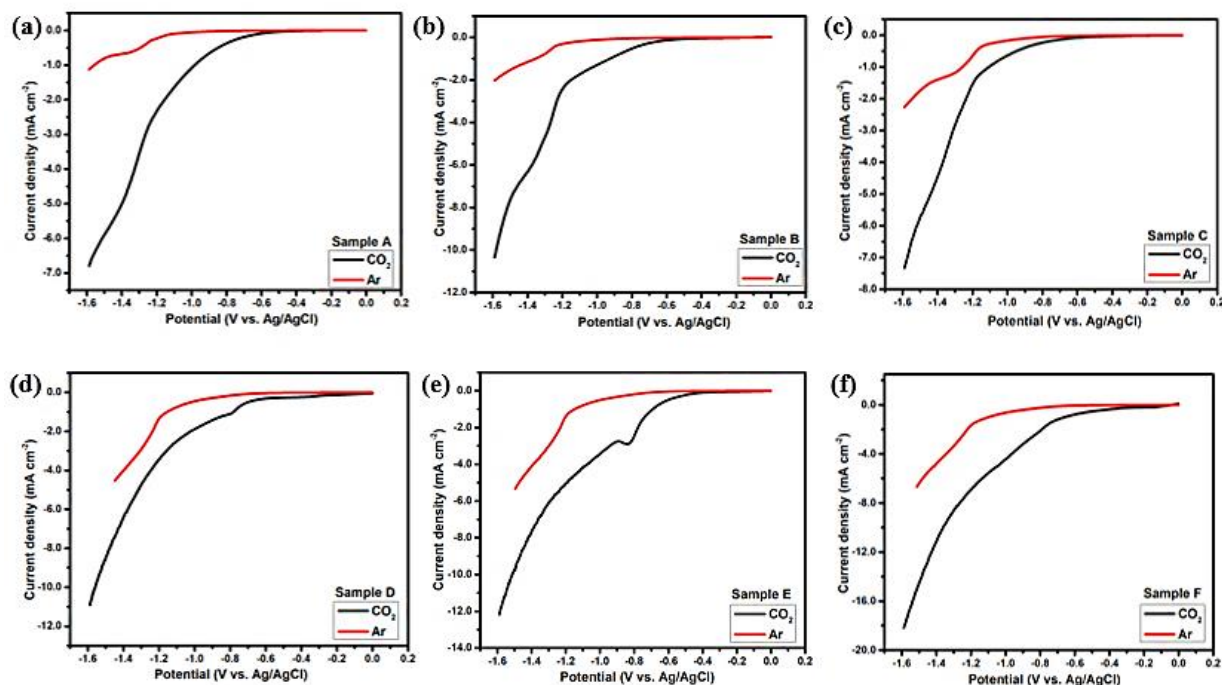


Figure 18: Linear sweep voltammetry of (a) $\text{ZnO}_{90}\text{-MX}_{10}$ (b) $\text{ZnO}_{85}\text{-MX}_{15}$ (c) $\text{ZnO}_{80}\text{-MX}_{20}$ (d) $\text{CuO}_{85}\text{-MX}_{15}$ (e) $\text{CuO}_{80}\text{-MX}_{20}$ (f) $\text{CuO}_{70}\text{-MX}_{30}$

Additionally, controlled potential experiments were carried out to assess each of the catalysts selectivity and activity based on their products analysis and quantification.

4.2.2 Controlled Potential Analysis

The electrochemical experiments were conducted using a conventional H-cell of three-electrodes system, a reference electrode (RE) - Ag/AgCl , the counter electrode (CE) - platinum wire, and a working electrode (WE) - carbon paper support doped with ink of the

synthesized electrocatalyst. The working electrode was made by combining 1 mL of methanol with 5 mg of the catalyst powder, then adding 50 μ L of the dispersant Nafion (5 wt%) and sonicated for 15 min to achieve the ink. Thereafter, a carbon paper support (1.5 cm $\times$ 1 cm) was doped with 50 μ L of the prepared ink and set aside overnight to dry.

Conventional H-type electrochemical cells with Nafion-117 proton exchange membranes between the anode and cathode compartments are used to conduct CO₂ reduction measurements. 15 mL of 0.5 M potassium hydrogen bicarbonate of pH 6.8 was added to each cell compartment as the anodic and cathodic electrolytes. The electrolyte of the WE compartment cell was purged at 50 sccm flow rate with high purity CO₂ (99.999%) for 30 min before the electrolysis process. A 5 sccm flow rate was maintained throughout the process to remove residual air and ensure continuous CO₂ saturation. On a Clarus 580 GC (Perkin Elmer) fitted with Hayesep and Molecular sieve columns as well as flame ionization (FID) and thermal conductivity (TCD) detectors, the gaseous products like H₂, CO, CH₄, and C₂H₄ were analyzed online. The electrolyte solution was collected after 1h of continuous electrolysis, and the liquid product content was analyzed using a JEOL 600 MHz NMR utilizing ¹H-NMR analysis to qualify and quantify the contents of its liquid product(s).

The products Faradaic efficiency was evaluated with the formula:

$$FE = \frac{Z n F}{Q} \times 100 \quad (1)$$

Where Z represents the number of electrons transferred during electrolysis, n is the mole of products formed, F is the Faraday's constant (96485 C mol⁻¹ of electrons), and Q is the amount of charge passed during the electrolysis in coulombs.

The results of gaseous products as presented in table 2 for the base materials shows that the Ti₂C MXene display better selectivity towards methane at applied potential of -0.56 V_{RHE} with a faradaic efficiency (FE) of 61.4%, while at higher applied potential, it retains its activity but loses selectivity towards a specific product. The Zinc oxide (ZnO) catalyst shows a good activity for CO₂RR with more selectivity for CO than CH₄ at an FE of 64.6% and 33.5% respectively at an applied potential of -0.76 V_{RHE}. It shows no gaseous product, alongside the CuO catalyst at a low potential of -0.56 V_{RHE}. Furthermore, the CuO electrocatalyst has a distribution of products with no selectivity for a specific product except for CO at -0.76 V_{RHE} and trace amount of ethylene.

Table 2: Table of Faradaic Efficiencies and Overpotentials for the Base Electrocatalysts

Catalyst	Applied Potential (V)		Product(s) and Faradaic Efficiency FE (%)				Overpotential (mV)
	Ag/AgCl	RHE	CH ₄	CO	H ₂	C ₂ H ₄	
Ti ₂ C MXene	-1.2	-0.56	61.4	ND	ND	ND	309.15
	-1.3	-0.66	26.1	ND	29.2	ND	409.15
	-1.4	-0.76	15.6	2.1	17.4	ND	229.15
ZnO	-1.2	-0.56	ND	ND	ND	ND	29.15
	-1.4	-0.76	33.5	64.6	ND	ND	229.15
	-1.5	-0.86	6.3	62.3	ND	ND	329.15
CuO	-1.3	-0.66	ND	ND	ND	2.4	129.15
	-1.4	-0.76	2.9	35.2	3.2	ND	229.15
	-1.5	-0.86	2.0	22.8	2.1	ND	329.15

The ZnO nanocomposite electrocatalysts were highly active towards CO₂RR and gave CH₄, CO and H₂ as the major gaseous products at different applied potentials and varying faradaic efficiencies as presented in table 3. Sample A (ZnO₉₀-MX₁₀) shows the best

efficiency and selectivity among all the catalysts examined. It demonstrated a great tuning capacity and high selectivity towards CH₄ at a low at applied potential of -0.56 V_{RHE} and a high FE of 79.3%, converse to most literature reports of Zn-based electrocatalyst being selective towards CO. Catalysts A, B and C were more selective towards CO at high potentials with a FE of 59.5%, 54.2% and 45.7% respectively and a steady increase in the competing hydrogen evolution reaction (HER).

Table 3: Table of Faradaic Efficiencies and Overpotentials for the ZnO Nanocomposite Electrocatalysts

Catalyst	Applied Potential (V)		Product(s) and Faradaic Efficiency FE (%)				Overpotential (mV)
	Ag/AgCl	RHE	CH ₄	CO	H ₂	C ₂ H ₄	
Sample A (ZnO ₉₀ -MX ₁₀)	-1.2	-0.56	79.3	ND	ND	ND	309.15
	-1.3	-0.66	31.4	7.91	ND	ND	409.15
	-1.4	-0.76	11.1	44.9	12.8	ND	229.15
	-1.5	-0.86	5.8	59.5	6.5	ND	329.15
Sample B (ZnO ₈₅ -MX ₁₅)	-1.3	-0.66	24.6	12.2	27.2	ND	129.15
	-1.4	-0.76	ND	37.9	7.5	ND	229.15
	-1.5	-0.86	ND	54.2	4.0	ND	329.15
Sample C (ZnO ₈₀ -MX ₂₀)	-1.3	-0.66	20.8	12.9	ND	ND	129.15
	-1.4	-0.76	6.7	32.9	7.5	ND	229.15
	-1.5	-0.86	2.7	45.7	3.1	ND	329.15

On the other hand, the CuO nanocomposite electrocatalysts was less selective towards any of the gaseous products except at high potential of -0.86 V_{RHE} with a faradaic efficiency of 26.1% and 20.8% for CO in catalysts D and E. Catalyst F showed the poorest activity for CO₂RR to gaseous products among the CuO nanocomposites.

Table 4: Table of Faradaic Efficiencies and Overpotentials for the CuO nanocomposite Electrocatalysts

Catalyst	Applied Potential (V)		Product(s) and Faradaic Efficiency FE (%)				Overpotential (mV)
	Ag/AgCl	RHE	CH ₄	CO	H ₂	C ₂ H ₄	
Sample D (CuO ₈₅ -MX ₁₅)	-1.3	-0.66	8.8	1.4	9.7	12.8	129.15
	-1.4	-0.76	4.7	26.1	5.1	3.0	229.15
	-1.5	-0.86	2.7	21.4	2.9	ND	329.15
Sample E (CuO ₈₀ -MX ₂₀)	-1.3	-0.66	ND	ND	ND	ND	129.15
	-1.4	-0.76	ND	ND	ND	ND	229.15
	-1.5	-0.86	3.2	20.8	3.1	ND	329.15
Sample F (CuO ₇₀ -MX ₃₀)	-1.3	-0.66	9.0	10.2	10.1	ND	129.15
	-1.4	-0.76	ND	ND	ND	ND	229.15
	-1.5	-0.86	ND	ND	ND	ND	329.15

The optimum performance of each of the catalysts is summarized in table 5 and shown in the histogram in Figure 18.

Table 5: Summary of the Optimal Performance of Individual Catalysts

Catalyst	Applied Potential (V)		Product(s) and Faradaic Efficiency FE (%)				Overpotential (mV)
	Ag/AgCl	RHE	CH ₄	CO	H ₂	C ₂ H ₄	
Ti₂C MXene	-1.2	-0.56	61.4	ND	ND	ND	309.15
ZnO	-1.4	-0.76	33.5	64.6	ND	ND	229.15
CuO	-1.4	-0.76	2.9	35.2	3.2	ND	229.15
(ZnO ₉₀ -MX ₁₀)	-1.2	-0.56	79.3	ND	ND	ND	309.15
(ZnO ₈₅ -MX ₁₅)	-1.5	-0.86	ND	54.2	4.0	ND	329.15
(ZnO ₈₀ -MX ₂₀)	-1.5	-0.86	2.7	45.7	3.1	ND	329.15
(CuO ₈₅ -MX ₁₅)	-1.4	-0.76	4.7	26.1	5.1	3.0	229.15
(CuO ₈₀ -MX ₂₀)	-1.5	-0.86	3.2	20.8	3.1	ND	329.15
(CuO ₇₀ -MX ₃₀)	-1.3	-0.66	9.0	10.2	10.1	ND	129.15

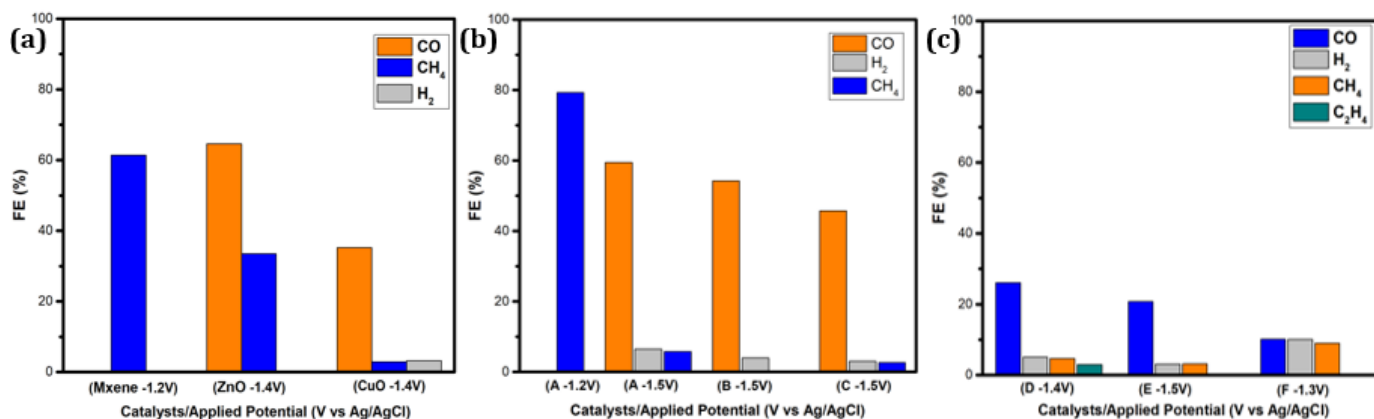


Figure 19: Histogram of (a) Ti₂C MXene, ZnO and CuO (b) ZnO nanocomposites (c) CuO nanocomposites

Table 6: Comparison of Result with other Literatures

Catalysts	Electrolyte	FE (%)	Potential (Vs RHE)	Product	Ref.
ZnO-derived catalysts	0.1 M KHCO ₃	91.6%	−0.62 V	CO	Cat. B: Environ., 2020, 273:119060
ZnO-NR	1 M KOH	80 %	−0.8 V	CO	ACS Appl. Energy Mat. 2022, 5, 11, 13928–13938
Zn nanoplates	0.1 M KHCO ₃	85 %	−1.0 V	CO	Chem. Europe, 2021, 13(8): 1998-2004
ZnO nanosheets	0.1 M KHCO ₃	83 %	−1.1 V	CO	Angewandte Chemie., 130(21): 6162-6167
Cu–ZnO catalyst	0.1 M KHCO ₃	84 %	−0.95 V	CO	eScience, 2(5): 518-528
ZnO–MX nanocomposites	0.5 M KHCO ₃	79.3 %	−0.56 V	CH ₄	This work

Table 6 shows a comparison of the result obtained from this study with other literature studies using modified ZnO catalysts where an improved faradaic for CO was obtained after modification of the ZnO catalyst. In this work, where we modified the ZnO nanorod by the introduction of Ti₂C MXene into its cavity, the usual product (CO) was observed to be tuned towards the production of methane alongside suppressing the formation of side products like CO and H₂. This could serve as an efficient and greener technique of methane production in contrast to the conventional methods which generate lots of greenhouse gases and expose our environment to greater danger and health conditions.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this study, we successfully synthesized Ti_2C MXene sheets, ZnO nanorods, CuO nanoflakes and prepared nanocomposite of the base materials (MX-Metal oxide) at different loading ratios to examine their efficiencies for CO_2 reduction electrochemically. The modified catalysts exhibited a morphology and crystal planes that depicts the characteristics of MXene and ZnO/CuO which confirms the successful intercalation of both materials. Among the MX-ZnO nanocomposite catalysts, Sample A ($\text{ZnO}_{90}\text{-MX}_{10}$) demonstrated the best efficiency and tuning ability towards a specific product than others. It demonstrated the potential for CO_2 conversion to CH_4 at a low applied potential of $-0.56 \text{ V}_{\text{RHE}}$, a FE up to 79.3% and 59.5% FE for CO at $-0.86 \text{ V}_{\text{RHE}}$. Additionally, it completely suppressed hydrogen evolution reaction and other side products. The observed electrocatalytic activities were attributed to the presence of substantial catalytic active sites on the catalyst surface coupled with the excellent electrical conductivity of the MXene which avails it the supply of electrons for the reduction of CO_2 and a constructive synergistic effect of the nanocomposite. The obtained results demonstrate the potential of the $\text{ZnO}_{90}\text{-MX}_{10}$ for the effective transformation of CO_2 to valuable chemicals and could be further explored.

5.2 Recommendations

The synthesis of Ti_2C MXene sheets and the incorporation of metal oxide nanomaterials into its sheets for CO_2 electrochemical reduction application was feasible and gave promising results. Nevertheless, it is possible to get more promising outputs with further studies. The following are recommendations worthy of noting:

- i. Development and exploration of other synthesis pathways for MXene synthesis to get highly exfoliated sheets and excellent yield, to maximize its economic viability.
- ii. Optimization of the nanocomposites, especially those of CuO series is necessary to get a good tune of the selectivity of the catalyst(s) towards a specific product. This study has laid a foundation for selecting appropriate ratio of the base catalyst mix.
- iii. Exploring other transition metal MXene like vanadium, molybdenum which share similar periodic properties with titanium and/or other composites materials to tune the selectivity and improve the faradaic efficiency and overpotential in CO_2RR .
- iv. Conducting post electrolysis analysis on the electrodes to establish the performance stability and possible re-usability of the electrodes.

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Vitae

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Academic Publications

- “The role of morphology on the superior performance of d-block metal oxides: towards an efficient electrocatalytic reduction of CO₂”. Mustapha U., Churchill C., I Hussain, Maria A., Umar Y., **A.S Abdulhakam**, S.A Ganiyu, K.R Alhooshani, A.A Al-Saadi, (2023) – (*Accepted for publication – Journal of Energy Chemistry (IF=13.599)*)
- “Investigation of Titanium Carbide MXene for CO₂ Electrochemical Reduction”. **A.S Abdulhakam**, Mustapha U., S.A Ganiyu, K.R Alhooshani, (2023) – (Manuscript under preparation)
- “Ti₂C–ZnO Nanocomposites for Methane Production via CO₂ Electrochemical Reduction”. **A.S Abdulhakam**, Mustapha U., S.A Ganiyu, K.R Alhooshani, (2023) – (Manuscript under preparation)
- “Prospects of Polymer Nanocomposite-Based Electrochemical Sensors as Analytical Devices for Environmental Monitoring: a Review”. A.B Olabintan, **A.S Abdulhakam**, C. Basheer (2023) – (Manuscript under preparation)
- “Ti₂C-Mxene/Activated Carbon Nanocomposite for Efficient CO₂ Capture: Insights into Thermodynamics Properties”. Mansur Aliyu, **A.S Abdulhakam**, S.A Ganiyu, Idris A. Bakare (2023) – (Manuscript under preparation)

INSTRUMENTS UTILIZED



Smart OMNI-Transmission FTIR Spectrophotometer NICOLET iS10 model



D2 phaser 2nd Generation XRD diffractometer



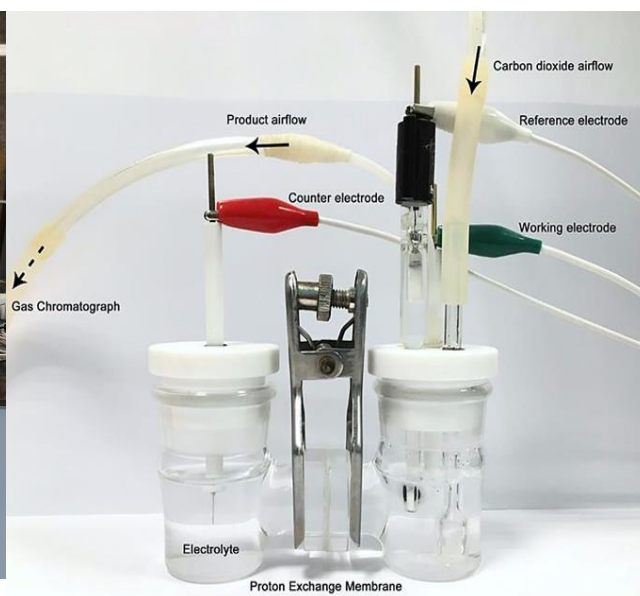
JEOL NMR 600 MHz



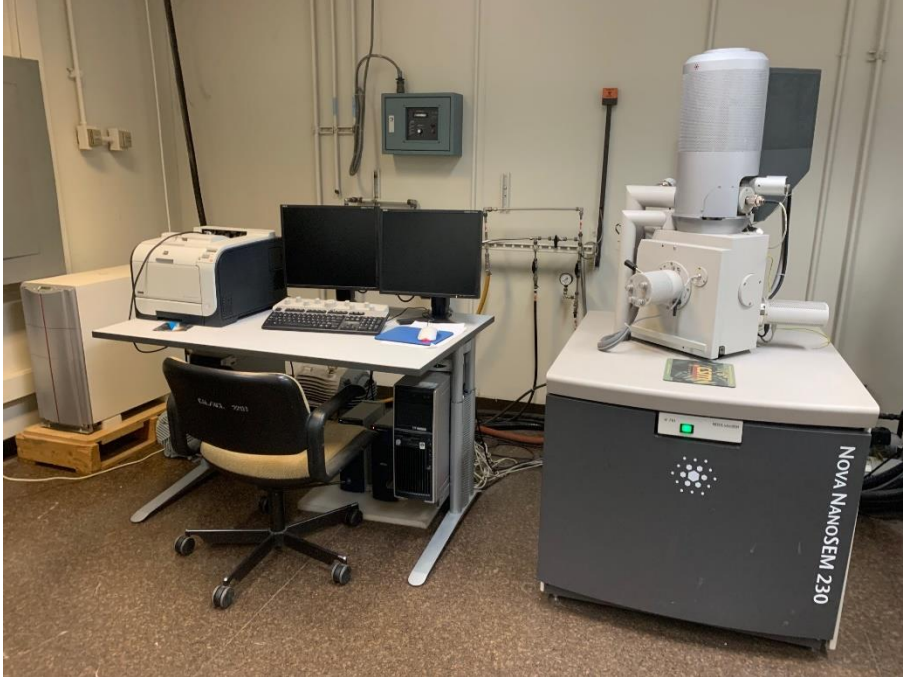
Clarus 580 GC (Perkin Elmer)

Columns: Hayesep and Molecular sieve

Detectors: TCD and FID detectors



Electrochemical H-cell



Field Emission-SEM

Model No. : NOVANANOSEM230



Field Emission TEM

Model No.: JEM2100F