

**SPUTTER COATED SILVER-ZINC ALLOYED THIN FILM
CATALYSTS FOR ELECTROCHEMICAL CO₂ REDUCTION**

BY

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Requirements for the Degree of

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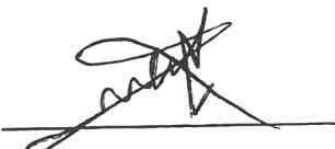
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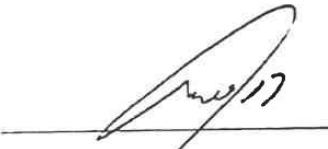


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Dedication

Firstly, I dedicate this thesis to my beloved parents and family as their endless support, motivation and unwavering encouragement and continuous prayers guided me through every step of my academic journey.

Secondly, to my respected supervisor, co-supervisor, teachers and mentors, who have motivated and inspired me as well as shaped my passion for scientific research and innovations.

Lastly, I dedicate this work to all those, conducting their research in KFUPM, for a sustainable and brighter future, may our collective efforts contribute effectively and positively to the society around us and even all over the globe.

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LIST OF ABBREVIATIONS

- **CO₂**: Carbon Dioxide
- **CO**: Carbon Monoxide
- **ECR**: Electrochemical Reduction
- **ECO₂R**: Electrochemical Carbon Dioxide Reduction
- **ECO₂RR**: Electrochemical Carbon Dioxide Reduction Reaction
- **GHGe**: Green House Gas emissions
- **Au@Ag-Zn**: Gold decorated Silver-Zinc
- **IPCC**: Intergovernmental Panel on Climate Change
- **Gt**: Gigatons
- **PPm**: Parts Per millions
- **PVD**: Physical Vapor Deposition
- **XRD**: X-ray Diffractions
- **FE-SEM**: Field Emission Scanning Electron Microscopy
- **EDS**: Energy Dispersive x-ray Spectroscopy
- **TEM**: Transmission Electron Microscopy
- **XPS**: X-ray Photoelectron Microscopy
- **WCA**: Water Contact Angle
- **LSV**: Linear Sweep Voltammetry
- **CV**: Cyclic Voltammetry
- **EIS**: Electrochemical Impedance Spectroscopy
- **ECSA**: Electrochemical Surface Area
- **CA**: Chronoamperometry
- **GC**: Gas Chromatograph
- **UPLC**: Ultra Performance Liquid Chromatograph
- **F.E**: Faradic Efficiency

ABSTRACT

Full Name : ARSHAD FARID MUHAMMAD HANIF
Thesis Title : Sputter coated Ag-Zn alloyed thin film catalysts for electrochemical CO₂ reduction
Major Field : Materials Science and Engineering
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The electrocatalytic reduction of CO₂ (ECO₂RR) into high-value products like CO presents a viable strategy for achieving carbon neutrality. While Ag-Zn catalysts have demonstrated high activity for CO-selective electroreduction, their limited stability under electrochemical conditions hinders large-scale applications. To overcome this challenge, Au and Bi was incorporated into Ag-Zn to develop an Au@Ag-Zn and Bi@Ag-Zn ternary catalyst. Experimental results confirmed that introducing a small amount of Au and Bi significantly enhanced both the catalyst's stability and its CO production efficiency. Among the fabricated catalysts, 5.7 weight percent of Au and 7.64 weight percent of Bi at Ag-Zn catalyst surface showed the highest CO faradic efficiency 94.2% and 93.5% respectively at -1V vs. RHE with the current density -20.26 mAcm⁻² and -63.5 mA cm⁻² respectively in H-type cell at ambient conditions. Additionally, the Au-decorated Ag-Zn catalyst demonstrated excellent durability of over 12 hours, 2.4 times higher than the Ag-Zn catalyst alone. The incorporation of Au and Bi on the Ag-Zn surface increases the catalyst's hydrophobicity, helping to prevent CO₂ mass transport limitations while preserving the intrinsic Ag-Zn dendritic structure, thereby enhancing catalyst activity and durability during CO₂ reduction.

ملخص الرسالة

الاسم الكامل: ارشد فريد محمد حنيف

عنوان الرسالة: محفزات الأغشية الرقيقة المطلية بالرش من سبائك الفضة والزنك لتقليل ثاني أكسيد الكربون كهروكيميائيًا

التخصص: علوم وهندسة المواد

تاريخ الدرجة العلمية: ذو القعدة 1446 هـ 7

يُمثل الاختزال الكهربائي التحفيزي لثاني أكسيد الكربون إلى منتجات عالية القيمة مثل أول أكسيد الكربون استراتيجية فعالة لتحقيق الحياد الكربوني. في حين أظهرت محفزات الفضة والزنك نشاطًا عاليًا في الاختزال الكهربائي الانتقائي لثاني أكسيد الكربون، إلا أن استقرارها المحدود في الظروف الكهروكيميائية يُعيق التطبيقات واسعة النطاق. وللتغلب على هذا التحدي، أُدمج الذهب والبيزمت في الفضة والزنك لتطوير محفز ثلاثي Au@Ag-Zn و Bi@Ag-Zn . أكدت النتائج التجريبية أن إضافة كمية صغيرة من الذهب والبيزمت عززت بشكل كبير استقرار المحفز وكفاءته في إنتاج أول أكسيد الكربون. من بين المحفزات المُصنَّعة، أظهرت نسبة 5.7% وزناً من الذهب و7.64% وزناً من البزموت على سطح محفز Ag-Zn أعلى كفاءة فارادية لثاني أكسيد الكربون، حيث بلغت 94.2% و93.5% على التوالي في خلية من النوع H في الظروف المحيطة. بالإضافة إلى ذلك، أظهر محفز Ag-Zn المزخرف بالذهب متانة ممتازة لأكثر من 12 ساعة، أي أعلى بـ 2.4 مرة من محفز Ag-Zn وحده. يزيد دمج الذهب والبزموت على سطح Ag-Zn من كراهية المحفز للماء، مما يساعد على منع قيود نقل كتلة ثاني أكسيد الكربون مع الحفاظ على البنية الشجرية الجوهرية للسبيكة المكونة من الفضة والزنك، مما يعزز نشاط المحفز ومتانته أثناء اختزال ثاني أكسيد الكربون.

CHAPTER 1

INTRODUCTION

Chapter 1. Introduction

1.1. Research background

1.1.1. Global energy and environmental challenges

Today, climate change stands as one of the most pressing global challenges. Climate change refers to long-term shifts in the average values of key meteorological indicators, such as surface air temperature and mean sea level. [1]. The rapid increase in urbanization, industrialization and deforestation in the past few decades led to increased energy demand globally, whereas the main source of energy is fossil fuels. The boost in greenhouse gas emissions (GHGe) into the atmosphere due to continuous use of fossils to meet the worldwide increasing energy demands, has emerged as a serious threat to life on our planet due to its negative effects on climate. CO₂ release in our environment is considered as a major constituent of the GHGe [2].

Since the late 1800s, atmospheric CO₂ levels have risen from about 280 ppm to roughly 400 ppm [3]. The IPCC 2013, Fifth Assessment Report highlighted that human activities has released an estimated 555 gigatons (Gt) of CO₂ between 1750 and 2011 of which roughly 240 Gt are still resident in the atmosphere which is now the dominant contributor to modern global warming [4]. According to IPCC AR6 what is this climate change 2023 reports that atmospheric CO₂ levels have climbed to roughly 410 parts per million, the highest recorded value with in the previous 2-million years [5]. In the year 2019, there was a recorded increase in CO₂ emissions at a rate of 0.9%, which stands to the annual growth rate, +1.9% seen in 2018[4]. The cumulative concentration of carbon dioxide in the Earth's atmosphere has reached a value of 38 Gt. The COVID-19 epidemic resulted in a decrease in worldwide GHGe emissions in 2020, with a significant decrease of 5.8% or 2 Gt CO₂ [5]. This represents the most significant decrease in carbon emissions documented since the industrial revolution. The magnitude of this loss was

fivefold greater than the decline saw in 2009 as a result of the global financial crisis. However, other statistical models imply that there will be a resurgence in CO₂ emissions in the future when the global economy strengthens once more. In the year 2021, CO₂ emissions had a notable increase of 4.9% [6]. The steadily increasing concentration of atmospheric CO₂, attributed to rapid industrial growth and the relentless use of fossil fuels, have spurred the scientific community to seek an economical, efficient, and scalable approach to mitigate CO₂ emissions for sustainable life on the planet. Fig. 1(a,b), highlights the historical CO₂ emissions since 1980, models of carbon emissions until 2100 and annual surface global CO₂ concentrations [7].

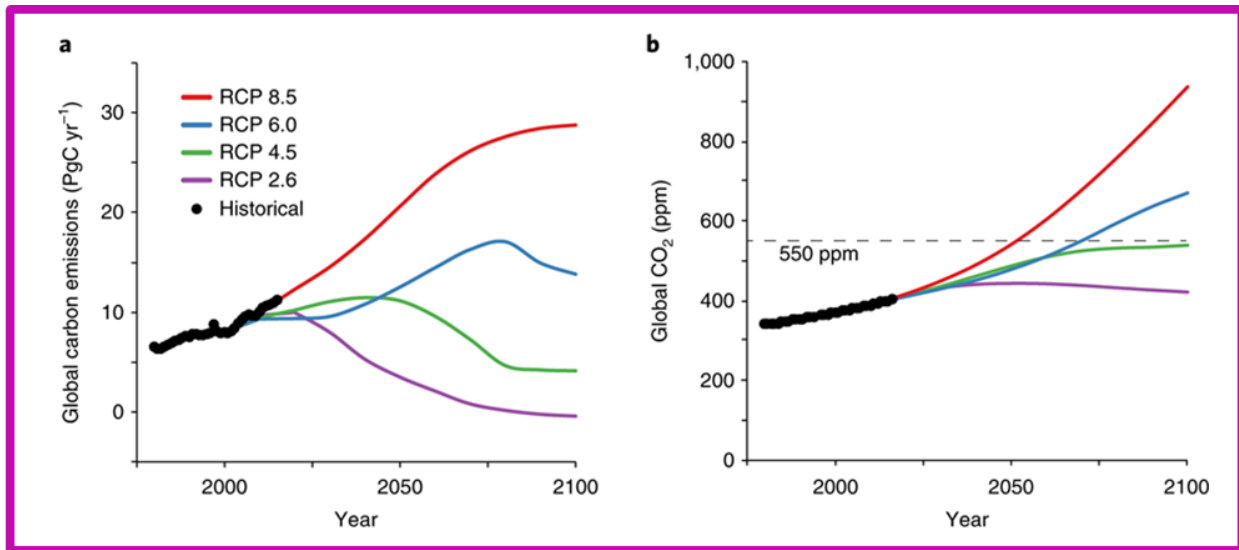


Figure 1. (a) Evolution of anthropogenic CO₂ emissions from 1980 to the present, with forward projections to 2100 under the high-emissions scenario outlined in RCP 8.5. (b) Year-to-year global mean atmospheric CO₂ concentration. Staying on the RCP 8.5 path would push levels to ≈ 550 ppm by mid-century, whereas lower-emission scenarios postpone or, under stringent mitigation, completely avoid crossing that threshold. Adapted from Ref. [7], copyright (2018), Nature.

1.1.2. Rising CO₂ emissions and climate change

In recent years, the connection between CO₂ emissions and intensifications of climate related issues are very clear. The negative impacts of CO₂ on climate change such as global

warming is causing melting of glaciers, sea level rise and acidifications, extreme weather conditions and ecological imbalance is a serious threat for human and nature. According to NASA observations in 2020, the increasing trend in average atmospheric temperature accounted 0.15°C-0.20°C in each ten years since 1975[2]. The worldwide excessive use of fossil fuels, industrial processes and deforestation to meet the increasing energy demands is the major source of CO₂ emissions, which is likely to increase the global atmospheric temperature from 2.3 to 5.4 °C by the end of 21st century [8][9]. Yin et al., reported that energy consumption is expected to become two times more than the present consumption by 2050. If fossil fuels remain a major source of energy, it is predicted that 500 gigatons of CO₂ will be produced by 2060 [10].

Extreme weather conditions such as wildfires, hurricanes and flooding events wreak havoc on communities, demolish infrastructure, destabilize economies, and result in loss of life. For example, the record-breaking number of storms in 2020 Atlantic hurricane season and in the worst in the history Australian wildfires between 2019-2020 claims a huge loss of biodiversity and sustainable economy [11]. NCDC-NOAA (National Climate Data Centre) recently reported that in 2024, global temperature exceeded historical averages across most of the earth land and ocean surfaces as shown in Fig. 2. Notably, North America, South America, Europe, Africa, and Oceania had their warmest year on record whereas Asia and Arctic were ranked at second. The most significant temperature increases occurred in the Arctic, northeastern North America, eastern Europe, the North Atlantic, and the western North Pacific. A few regions such as southern Greenland, eastern Antarctica, the southeastern Pacific Ocean, and the Drake Passage, recorded cooler-than-average temperatures. Overall, 2024 is recorded as the warmest year for land and ocean surfaces globally.

According to the Paris agreement the rise in atmospheric temperature needs to be limited to 1.5°C pre-industrial level and now the net zero carbon emission goal is the part of climate control policies of various countries to cop up with the carbon threat for sustainable future [12][13]. On the other hand, the depletion of non-renewable energy sources will result in the worldwide energy crisis [14]. Rising atmospheric CO₂ propelled by fast paced industrialization and due to the ongoing fossil fuels consumption, that has spurred the researchers to pursue cost-effective, energy efficient, and scalable methods for conversion CO₂ into value-added chemicals and fuels. While renewable energy offers an environmentally friendly solution to address the energy demand challenge, the hurdle lies in large-scale storage and transportation of renewable energy [15][16].

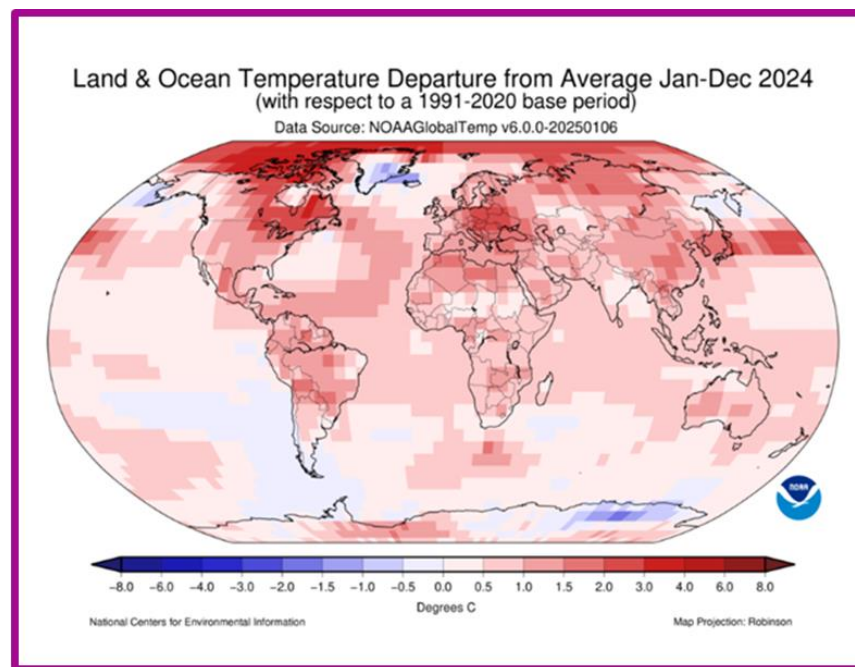


Figure 2. In 2024, the global average surface temperature exceeded the 20th-century mean by 2.32 °F (1.29 °C), marking the warmest year in the instrument-record period from 1850 to 2024 and surpassing the previous record set in 2023 by 0.18 °F (0.10 °C). Notably, the ten hottest years have all occurred within the last decade. Compared to the pre-industrial baseline (1850–1900), 2024 showed an increase of 2.63 °F (1.46 °C). Adapted from Ref. [17], copyright (2025), NCDC-NOAA.

Capturing CO₂ from the atmosphere and transforming it into useful chemicals and hydrocarbons presents a compelling strategy to controlling carbon concentration in the atmosphere and the worldwide energy crisis. With the atmospheric CO₂ concentrations rise, researchers worldwide are developing technologies to both capture the CO₂ gas and re-use it as a plentiful, value-added carbon feedstock for producing higher-value chemicals and fuels. [18][19][20]. Various routes exist for converting CO₂, encompassing enzymatic, electrochemical, photocatalytic, and thermochemical reactions. Among these methods, direct electro-reduction of CO₂ into hydrocarbons, oxygenates, or CO holds appeal due to its environmental compatibility when paired with carbon-free renewable energy sources (e.g., solar, tidal, and wind) and its operation under ambient conditions of temperature and pressure [21]. Thermochemical reduction of CO₂ demands not only high temperature and pressure but also the equivalent concentration of hydrogen as a reducing agent, whereas in photochemical reduction, production rate and selectivity of the final product hinder the scalable application of these methods.

1.2. Electrochemical CO₂ reduction (ECO₂R)

ECO₂R offers a sustainable solution to traditional CO₂ mitigation approaches by directly converting CO₂ into useful products using renewable energy sources such as electricity which itself is not a carbon emission source as shown in Fig 3. Furthermore, conventional conversion methods such as thermochemical routes operate at high temperature and pressure whereas ECO₂R can be conducted under ambient temperature and pressure using an appropriate catalyst. This approach reduces energy consumption which makes it a suitable approach for CO₂ conversion into chemicals and fuels by coupling renewable energy sources.

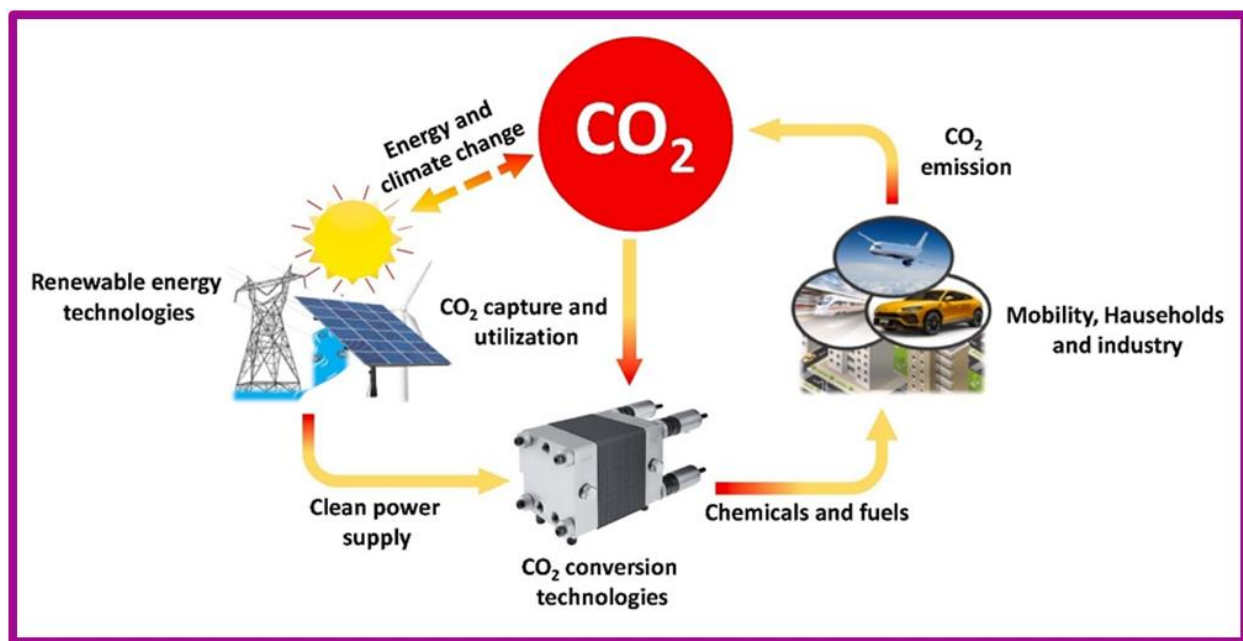


Figure 3. Carbon loop, a CO_2 electrolyzer powered by renewable electricity converts captured CO_2 into high-value chemicals or energy-rich fuels, suitable for immediate use or long-term energy storage. Adapted from Ref. [22], copyright (2020). Elsevier.

1.2.1. Basic H-cell design

Electrochemical reaction (ECR) takes place in an electrochemical cell which involves a chemical reaction that produces electricity or electricity can be used to run the chemical reaction, shown in Fig 4. It works on the principle of interconversion between chemical and electrical energy [23]. Electrocatalytic cells serve as reactors for electrochemical CO_2 reduction reactions, a complete electrochemical reaction in reactor consists of independent anodic (oxidation) half-reaction and cathodic (reduction) half-reaction. A typical electrolytic cell consists of four major components, cathode and anode coated with catalyst for CO_2 reduction and hydrogen evolution reactions respectively, electrolyte allows the mass transportation during reaction and conducting that divides the cell into separate anode and cathode compartments [24]. Carbon is oxidized at anode and converted into molecular oxygen, whereas reduction of CO_2 into reduced carbon species occurred at cathode [25].

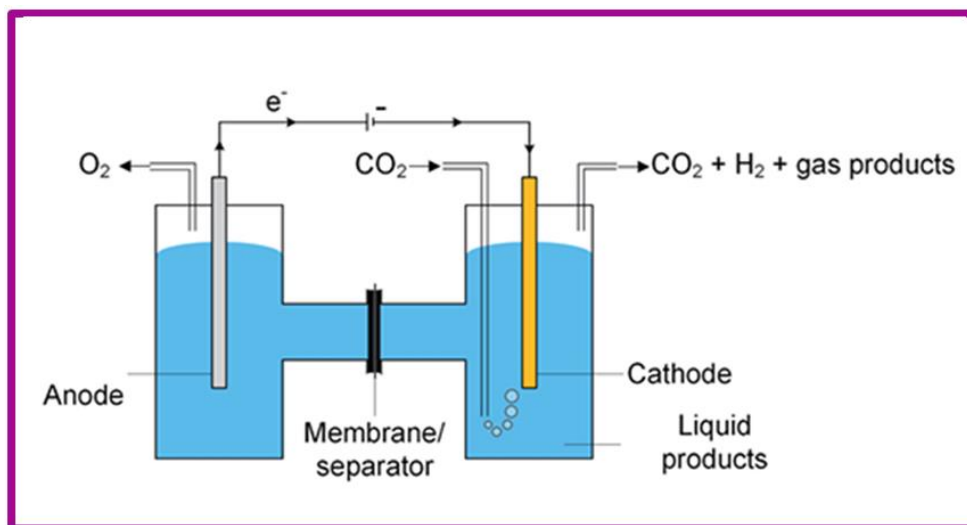


Figure 4. Representative diagram of a CO₂ electrolyzer featuring an ion-conducting membrane.

Adapted from Ref. [26], copyright Royal Society of Chemistry (2020).

CO₂ is a linear and thermodynamically stable molecule, featuring two carbon–oxygen double bonds (C=O), each with a bond length of approximately 1.12 Å [27]. The C=O bond in CO₂ has a high bond energy of around 750 kJ mol⁻¹, which is substantially greater than that of C–C (336 kJ mol⁻¹), C–O (327 kJ mol⁻¹), and C–H (411 kJ mol⁻¹) bonds. As a result, the electrochemical conversion of CO₂ into products containing C–C, C–O, or C–H bonds requires a considerable activation energy input. [28]. Particularly the first electron reduction of CO₂ into CO*⁻ radical required very negative thermodynamic redox potential i.e., $E^{\circ} = -1.90$ V vs SHE (Standard Hydrogen Potential) at standard conditions in aqueous media (PH=7) [29][30]. However, electrochemical CO₂RR is multiple proton-coupled electrons transfer process and occurs at lower potential in the range of -0.2V to -0.6v vs SHE [29], which can lead to formation of various CO₂ products (such as CO, CH₄, C₂H₄ etc.) depending upon the electrolyte and electro-catalyst [30]. Overcoming this challenge is essential to harness the potential of converting stable CO₂ molecules into diverse carbon-based products. One can address this challenge effectively by designing a novel nanostructure catalysis having unique structural and compositional properties.

1.2.2. Elementary steps of ECO₂RR

As CO₂ is thermodynamically a very stable molecule, high overpotential is required to proceed with the reaction. Particularly the first electron reduction of CO₂ into CO₂ radical required extremely negative thermodynamic redox potential i.e., $E^{\circ} = -1.90$ V vs SHE (standard hydrogen potential) at standard conditions in aqueous media (PH=7). However, electrochemical CO₂RR is multiple proton-coupled electrons transfer process and occurs at lower potential in the range of -0.2V to -0.6v vs SHE [25], which can lead to formation of various CO₂ products (such as CO, CH₄, C₂H₄ etc.) depending upon the electrolyte and electro-catalyst [27]. The ECO₂RR proceeds in four elementary steps as follows:

- [1] Chemisorption of CO₂ molecules onto the cathode surface.
- [2] Chemical activation of CO₂ molecules, leading to the formation of the CO₂*⁻ radical intermediate.
- [3] Transfer of multiple elements and protons to form carbonaceous products.
- [4] Desorption of formed carbonaceous products from the electrocatalyst surface.

Worth noting is the demanding nature of the reduction processes of CO₂, particularly the intricate process of single-electron reduction from CO₂ to CO₂*⁻, which proves highly unfavorable. This is mostly owing to the significant reorganizational energy that arises from the structural transformation from linear CO₂ to the bent CO₂*⁻ radical anion. On the other hand, the proton coupled multielectron conversion process exhibits favorability, as evidenced by Equations (1.1) - (1.7), conditions of pH=7 in an aqueous electrolyte relative NHE [31][32]. In theory, the reaction can be driven by any given potential that is more negative than the redox potential associated with ECO₂RR. The high reduction potentials during the ECO₂RR could be detrimental because This process demands extra electrical energy and promotes competing side reactions, such as the

hydrogen evolution reaction (HER), which reduced the product selectivity and efficiency to reduce CO₂ into required product [33]. Therefore, reducing the required reduction potential in CO₂ reduction is one of the major challenges to achieve high efficiency and product selectivity in ECO₂RR.

Table 1. CO₂ reduction products along with their associated standard reduction potentials [34].

Half-electrochemical thermodynamic reactions	Electrode potentials (V vs. SHE)	Equation
$CO_2 + e^- \rightarrow CO_2^-$	$E = -1.90\text{ V}$	(1.1)
$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$	$E = -0.61\text{ V}$	(1.2)
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	$E = -0.53\text{ V}$	(1.3)
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	$E = -0.48\text{ V}$	(1.4)
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	$E = -0.38\text{ V}$	(1.5)
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	$E = -0.24$	(1.6)
$CO_2 + 4H^+ + 4e^- \rightarrow C + 2H_2O$	$E = -0.20\text{ V}$	(1.7)

1.2.3. Evaluation criteria of catalysts for ECO₂R

The efficiency of CO₂RR largely depends on the choice of the electrocatalyst. Ideal catalysts should exhibit high selectivity towards desired products, minimum onset potential, long time durability, and high conversion F.E. There are different scientific terms and parameters that are important to analyze the potential of the electrocatalysts in CO₂ reduction [35][36].

- **Onset potential (η):** the minimum potential required to initiate the ECO₂RR, which can be measured by linear sweep analysis using potentiostat. It is worth noting that it can also be measured by CO₂ product analyzers used in CO₂ reduction such as, Gas chromatograph (GC), Nuclear magnetic resonance spectroscopy (NMR) and High-performance liquid chromatograph (HPLC).
- **Total current density (j_{total}):** the total quantity of the charge that passes through the unit area of the electrocatalyst per unit time is known as total current density, an important term which is used to identify the transformation rate of CO₂ into other products
- **Partial current density (j_{partial}):** It represents the portion of the total current density that is specifically used to generate a targeted product from CO₂ during electrochemical reduction. Determining the partial current density of the desired product is essential, as it reflects the catalyst's selectivity toward that product.
- **Faradic efficiency (F.E):** the efficiency of the charges that transferred to a product in ECO₂RR
- **Energy efficiency (E.E):** the percentage of the energy that is stored in a specific product in comparison to the energy used to transfer CO₂ into that product, which can be calculated by multiplying the FE with cell voltage efficiency and dividing the actual voltage of the cell.
- **Catalyst stability:** the catalyst durability in ECO₂RR is its stability to maintain its performance with time. The catalyst stability is an important parameter that gives the indications of the use of the catalyst in real life applications.

1.2.4. Catalysts for electrochemical CO₂ reduction

Till now a variety of electrocatalysts have been designed and tested for ECO₂RR including metallic [37], non-metallic such as carbon-based boron and nitrogen doped materials [38][39], and MOFs [40][41], the primary challenge lies in developing cost effective and long-term stable electrocatalysts that can effectively and selectively reduce CO₂. Efficient catalysts are crucial for improving the kinetics of electrochemical CO₂ reduction and enhancing product selectivity. Among reported electrodes metallic catalysts gain much attention due to their tunable electronic properties, during the synthesis process of the electrodes, substantial surface area as well as the potential of many metals to bind CO₂ molecules after the easy transfer of initial electrons required for CO₂ activation. In the beginning bulk metallic electrodes were explored for CO₂ electro-reduction [42][43][44]. Traditional catalysts have suffered from limitations such as limited product selectivity and poor durability. The pure metallic electrodes for electrochemical CO₂ reduction are generally divided into different categories depending on their ability to produce specific products from CO₂. Pt, Fe, Ni, Ga, Ti and Al based electrodes lead to produce CO as a major CO₂ product, but the HER dominates during the reduction process on these metals which limits their application in this field [45][46]. Another group of materials: Au, Ag, and Zn more effectively reduce CO₂ in CO with high selectivity and current density [47][48]. The format selective CO₂ reduction follows different reaction pathways and mechanisms of metal electrodes, Cr, Mo and Bi based metal catalysts have been discovered for format production [49]. Cu is an important element in the field of CO₂ electroreduction due to its efficiency to produce hydrocarbons in ECO₂RR. However, the formation of multi-products results in on Cu surface results in poor product selectivity which includes the separation costs of different products economically remains a challenge to use Cu at large scale applications [50].

Recently the advancement in the synthesis processes, in-situ and ex-situ characterization technologies led explore the nano-metallic catalysts and the effect of their electronic properties, facets engineering, morphology, and composition on ECO₂RR. The state of the art to optimize the overall catalytic performance, various metallic electrodes have been designed and tested for ECO₂RR including single atomic, alloyed bimetallic, phase separated bimetallic and ternary catalysts, and metal organic frameworks [51][52][53][54]. For example Ma et al., fabricated gold-platinum thin films with tunable Au/Pt ratios to uncover the effect of surface composition of the catalyst on the activity and selectivity towards ECO₂RR Activity of catalyst for CO and H₂ products tuned by adjusting the Au:Pt atomic ratio in thin films during fabrication which influenced the electronic structure of catalyst, the d-band centroid moves to an energy farther from the Fermi level with increasing in Au content in Au-Pt catalyst, reduced the adsorption energy of CO, COOH and H intermediates, resulting in distinct catalytic activity on compositionally varied Au-Pt bimetallic films for CO₂ reduction [55]. Yang and co-workers., synthesized Zn doped Cu electrocatalyst by magnetron sputtering technique, the incorporation a trace amount of Zn in Cu matrix pushed the d-band downward consequently reduced the CO binding strength on catalyst surface and favors C-C coupling which facilitates selectivity toward C₂⁺ products. Faradic Efficiency of the catalyst was improved with Zn doping in Cu from 65% (single metallic Cu catalyst) to 80.1% (Cu: Zn=9:1) for C₂⁺ hydrocarbons at -1.17 V potential and - 120 mA/cm² current density [56]. Table. 2 shows recently reported highly efficient metallic catalysts and their product selectivity in ECO₂R.

Among the various CO₂ reduction products CO is one of the important molecules which is used as feedstock for multi-carbon products in the Fisher-Tropsch reaction.

Table 2. Recently highly efficient metallic catalysts reported and their product selectivity in ECO₂R.

Catalysts	Cell type	Electrolyte	Potential (V vs. RHE)	Main products	Potential (V vs. RHE)	Faradic Efficiency (%F.E)	Stability	References
Cu/GDE	Flow cell	1MKOH	-0.7V vs. RHE	C ₂ +	-0.7V vs. RHE	~ 79%	10 h	[57]
Ag nanoneedles/Zn	H-cell	0.5 m KHCO ₃	-1V vs. RHE	CO	-1V vs. RHE	90%	12 h	[58]
Bi-600/CF	H-cell	0.1 M KHCO ₃	-1.3V vs. RHE	HCOOH	-1.3V vs. RHE	96.9%	N/A	[59]
Bi-600/CF	Flow cell	0.5 M KHCO ₃	-1.1V vs. RHE	HCOOH	-1.1V vs. RHE	81.7%	27h	
Sn/SnO₂	Flow cell	1 M KOH	N/A	HCOOH	N/A	>94 %	70 h	[60]
Cu/GDE	Microfluidic flow cell	1M KOH	-0.65 V vs. RHE	C ₂ H ₄	-0.65 V vs. RHE	51%	N/A	[61]
In₂O₃ films	H- cell	0.1M KHCO ₃	- 0.85 V vs. RHE	HCOOH and CO	- 0.85 V vs. RHE	70%	6 h	[62]
Ag-Zn	H- cell	0.1 M KHCO ₃	-1.0 V vs. RHE	CO and H ₂	-1.0 V vs. RHE	84.2%	9 h	[63]
Bi₄₅Sb₅₅/CP	Flow-cell system	0.5 M KHCO ₃	-1.0 V vs. RHE	HCOOH	-1.0 V vs. RHE	76.7%	N/A	[64]
Cu-Ag	Flow cell system	N/A	N/A	C ₂ H ₄	N/A	43%	6 h	[65]
Au nanoparticles	H-cell	1 M KHCO ₃	-0.8 V vs.RHE	CO and H ₂	-0.8 V vs.RHE	100%	4 h	[66]
Pd₈₃Cu₁₇ bimetallic aerogel	H-cell	[Bmim]BF ₄	- 2.1 vs. Ag/Ag ⁺	CH ₃ OH	- 2.1 vs. Ag/Ag ⁺	80%	24 h	[67]
PtZn nano- alloys	- 0.90 vs. RHE	0.1 M NaHCO ₃	- 0.90 vs. RHE	CH ₃ OH	- 0.90 vs. RHE	81.4%	16	[68]

Formation of CO is thermodynamically more feasible reaction relative to higher carbon products because it is only 2 electron transfer process in aqueous electrolyte at ambient conditions. At ambient pressure, CO exists in gaseous state and unlike other liquid products the separation costs excluded for the further use of CO [69].

The combination of P-block metals such as Tin (Sn) and Bismuth (Bi) with transition metals like Ag and Zn in a single catalyst can reduce CO₂ into C₁ products specifically formate (HCOOH) [64]. For example, Ag-Sn bimetallic core with partially oxidized 1.7nm Sn shell structure effectively reduced CO₂ into HCOOH with 80% FE at -0.8 V vs. RHE. In this core shell structure, the bimetallic core aimed to provide high electronic conductivity and the SnO shell provide sites for CO₂ reduction [70]. Formate is a chemically stable and liquid product at room temperature which provides ease in its storage and transportation. Electrochemical CO₂ to formate conversion is 2 electron transfer process results in less product cost compared to the C₂ products. Bi being a non-toxic, environmentally friendly and low cost, is a promising choice for the formate and CO production from CO₂ [71].

1.3. Challenges in ECO₂R

Despite the benefits CO₂ to CO electroreduction, scalable electrocatalytic conversion CO₂ to CO at standard temperature and pressure (STP) still encounter many issues including, poor catalytic stability, high reduction potential, low current density due to CO₂ mass transfer limitations in electrolyte, formation of other bi-products leads to poor CO₂ selectivity, and competent HER reaction during CO₂ reduction, most importantly catalysts instability in sluggish reaction conditions [72][73]. Similarly, CO₂ to COOH electroreduction still requires high onset potential to get high F.E and current density in ECO₂RR. Further to improve the Bi catalytic

activity and F.E it can be incorporated into other CO₂ reduction active materials to obtain the synergy to modify its catalytic properties for CO₂ electroreduction [64].

Currently methanol production by ECO₂RR is in its preliminary stages where several challenges exist that need to be overcome before making it feasible for practical applications. Recent reports highlighted that in thermodynamic point of view the formation of methanol from CO₂ is more unfavorable than the CO₂ reduction to syngas under ambient conditions whereas, at high temperature and pressure additional challenges come into account during ECO₂RR such as overheating and excessive pressure can lead to catalysts sintering, agglomeration and dealloying from substrates which eventually reduce the intrinsic properties of electrodes in terms of compromised stability, low activity and selectivity of the catalysts [74]. The high overpotential and multi electrons coupled protons transfer process for methanol production, the small lifetime of the catalysts to maintain their performance, ability of limited materials that are selective for methanol production, competitive H₂ evolution and the limited solubility of CO₂ in the aqueous electrolytes at ambient conditions because of its high ionic strength are the major challenges need to overcome to commercialize ECO₂RR to methanol [75][76][77].

1.4. Research objectives

- Synthesis of porous Ag-Zn bimetallic electrocatalyst from metallic salts solutions by co-electrodeposition method.
- Sputter coating of different metals onto electrodeposited Ag-Zn thin film alloy to study their effect on alloy catalyst performance.
- Optimization of electrodeposition and sputtering parameters to engineer nanostructured surfaces to improve the catalytic activity for electrochemical CO₂ reduction.

- Comprehensive characterizations of the catalysts including structural (XRD), morphological (SEM), compositional (EDS, XPS), and electrochemical (CV, LSV, EIS, ECSA, CA) analyses, to determine the physical and chemical properties of the prepared samples.
- Investigation of the electrochemical performance of the catalyst under ECO₂RR conditions to evaluate its product selectivity, catalytic activity, and long-term durability in CO₂ reduction reactions.

CHAPTER 2

LITERATURE REVIEW

Chapter 2. Literature review

2.1. Reaction mechanism for ECO₂R reduction

ECO₂R is a complex reaction which can be driven in multiple possible pathways depending on the transfer of the electrons from catalysts surface to CO₂ molecules and formation of different intermediates during the reaction. Due to the kinetic and thermodynamic barriers, the electrons transfer to CO₂ can result in different products with varying selectivity and efficiency [78]. Numerous valuable products such as CO, formate, methanol, methane, ethylene, ethanol, formaldehydes, oxalic acid can be obtained at specific standard reduction potentials depending on the nature of catalyst used during CO₂ reduction as highlighted in Table. 2 [79]. However, significant challenges remain for selective production of CO through ECO₂RR in the aqueous electrolytes. The minimum thermodynamic potential differences between various reaction products necessitate highly selective electrocatalysts to achieve the desired product such as CO. Another major issue HER often appears alongside the ECO₂RR in aqueous solution, which lessens the selectivity and F.E of the desired product [80][81].

To initiate the ECO₂RR, CO₂ molecule should Chemi-adsorb onto the catalysts surface and subsequently an electron transfer into the anti-bond orbital of a CO₂ molecule from the catalyst leads to the formation of *CO₂⁻ key intermediate. The binding mode of intermediate *CO₂⁻ on the catalysts surface depends on the final product formed during the reaction. If *CO₂⁻ binds on the electrode surface through the oxygen atom, the final product is expected to be formate or formic acid whereas, if it binds by carbon atoms then the reaction pathway leads to the formation of CO or hydrocarbons as reaction products [82].

Table 3. Overview of electrochemical CO₂ reduction products, showing each balanced half-reaction, its standard reduction potential (E°), and the metal catalysts most frequently employed. Adapted from Ref. [79], copyright (2019), Chemistry Europe

Products	E° [V vs. SHE at pH 7]	Reactions	Most common metal catalysts
CO	-0.530	$\text{CO}_2 + 2 \text{e}^- + 2 \text{H}^+ \rightarrow \text{CO} + \text{H}_2\text{O}$	Au, Ag, Pd, Bi, Zn, etc.
HCOOH	-0.610	$\text{CO}_2 + 2 \text{e}^- + 2 \text{H}^+ \rightarrow \text{HCOOH}$	Sn, Hg, Pb, Ga, and In, etc.
H ₂ C ₂ O ₄	-0.913	$2 \text{CO}_2 + 2 \text{e}^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{C}_2\text{O}_4$	Pb, Tl, Hg
HCHO	-0.480	$\text{CO}_2 + 4 \text{e}^- + 4 \text{H}^+ \rightarrow \text{HCHO} + \text{H}_2\text{O}$	Pt, Pd, Cu
CH ₃ OH	-0.380	$\text{CO}_2 + 6 \text{e}^- + 6 \text{H}^+ \rightarrow \text{CH}_3\text{OH} + 2 \text{H}_2\text{O}$	Ru, Cu
CH ₄	-0.240	$\text{CO}_2 + 8 \text{e}^- + 8 \text{H}^+ \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}$	Cu
C ₂ H ₆	-0.349	$2 \text{CO}_2 + 12 \text{e}^- + 12 \text{H}^+ \rightarrow \text{C}_2\text{H}_4 + 4 \text{H}_2\text{O}$	Cu
C ₂ H ₅ OH	-0.329	$2 \text{CO}_2 + 12 \text{e}^- + 12 \text{H}^+ \rightarrow \text{C}_2\text{H}_5\text{OH} + 3 \text{H}_2\text{O}$	Cu
C ₂ H ₆	-0.270	$2 \text{CO}_2 + 14 \text{e}^- + 14 \text{H}^+ \rightarrow \text{C}_2\text{H}_6 + 4 \text{H}_2\text{O}$	Cu
C ₃ H ₇ OH	-0.310	$2 \text{CO}_2 + 18 \text{e}^- + 18 \text{H}^+ \rightarrow \text{C}_3\text{H}_7\text{OH} + 5 \text{H}_2\text{O}$	Cu
H ₂	-0.420	$2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$	Cr, Mo, W, Ti, Pt, Fe, Ni,
CO ₂ ⁻	-1.90 in water; -1.97 in aprotic solvents	$\text{CO}_2 + \text{e}^- \rightarrow \text{CO}_2^-$	

The different reaction pathways of ECO₂RR on the heterogeneous catalysts surface are mentioned in Fig. 5. The activation step of thermodynamically stable linear CO₂ molecules involves the structural rearrangement of CO₂ molecules to bent structure which is usually known as the rate limiting step in ECO₂RR. The formation of *CO₂⁻ radicals requires higher energy in the

form of overpotential relative to the other final reaction products in the aqueous electrolyte. The $^*\text{CO}_2^-$ intermediate can further undergo different reaction pathways which involves proton coupled multi electron transfer process on the catalysts surface. Depending on the nature of the catalysts e.g., composition, structure and morphology, the different numbers of electron transfers to $^*\text{CO}_2^-$ and variations in the binding ability of different catalysts toward CO_2 intermediates lead to the formation of different end products as the result of ECO_2RR . For instance, the p-block elements such as Sn, In, Pb and Hg do not exhibit strong binding affinity to $^*\text{CO}_2^-$ which results in the formation of HCOOH as the reaction product via binding through oxygen atoms [82].

However, the noble metals such as Au, Ag, Pd and earth abundant non-noble metal Zn have ability to stabilize $^*\text{CO}_2^-$ and $^*\text{COOH}$ intermediate which formed due to the further protonation of $^*\text{CO}_2^-$ radicals on the catalyst surface. As the reaction proceeds, an electron-proton transfer from $^*\text{COOH}$ leads to form $^*\text{CO}$ intermediate which exhibits poor binding affinity on Au, Ag, Pd and Zn surfaces, results in the formation of CO as the final product obtained on these metal electrodes in CO_2 electroreduction [83]. In contrast to Au and Ag the Cu metallic catalysts show strong binding strength towards $^*\text{CO}$ intermediates, which favors the dimerization of $^*\text{CO}$ to $^*\text{C}_2\text{O}_2\text{H}_5$ intermediates and result in conversion of $^*\text{CO}$ to $^*\text{COH}$ and $^*\text{CHO}$ through one electron and proton transfer. Further, proton assisted multi-electron transfer process of these intermediates, $^*\text{CO}$ to $^*\text{COH}$ and $^*\text{CHO}$ can result in the formation of higher carbon products such as alcohols and hydrocarbons [84]

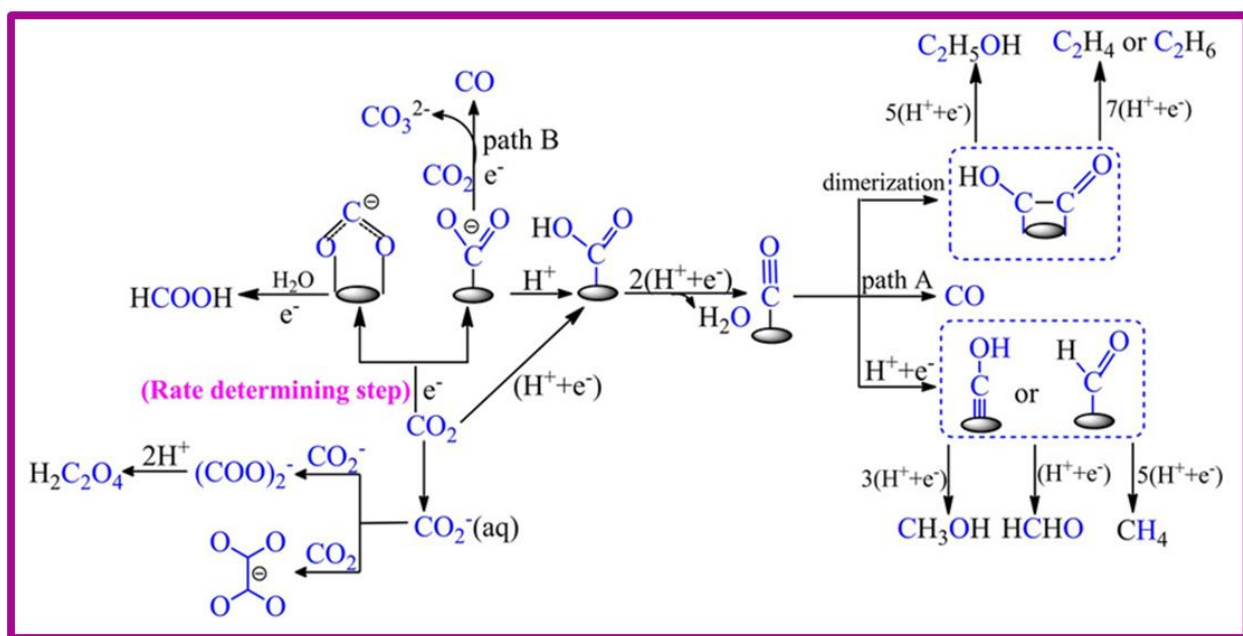


Figure 5. Illustrated pathways for electrochemical CO₂ reduction in aqueous electrolytes. Adapted from Ref. [84], copyright (2019), Chemistry Europe

2.2. Catalysts for ECO₂R to CO

As highlighted in Table. 3, a variety of products can be produced by ECO₂R depending on the nature of the catalyst. Among the various products C1 products, such as CO and formate are simple, easy to achieve and have high potential economic values [85][86]. CO is an important intermediate to produce chemicals and synthetic fuels at industrial scale [87]. Many metallic catalysts have been explored for CO selective CO₂ reduction. High overpotential, dominating HER in aqueous electrolyte, and slow kinetics of the ECO₂RR are the major limitations in CO₂ reduction. The noble metals such Au, Ag, and Pd are mainly used for CO selective production because of their high activity and selectivity in ECO₂RR [88][89]. Side-by-side performance evaluation of carbon-supported gas-diffusion electrodes (GDEs) carrying assorted metal electrocatalysts, operated with alkaline ion-exchange membranes, reported by Lee et al. [90], mentioned in Table. 4.

A lot of modifications have been made to design noble metals based electrocatalysts to improve their performance. Yang et al., reported that the Au size and facets effect on the catalyst's performance. The 50nm Au trisoctahedron exhibited F.E for CO ($F.E_{CO}$), 1.5 folds higher than the Au colloids whereas the F.E was linearly decreased with an increase in Au particle size up to 100nm.

Table 4. Under a 3.0 V cell bias, electrodes containing Pd, Ag, Zn, Cu, Sn, Ru, Pt, and Ni (all at a loading of 1.0 mg cm^{-2}) were benchmarked for total current density and for their Faradaic efficiency toward CO formation. Redrawn from Ref. [90]

Metallic electrode	%$F.E_{CO}$	Current density at -3V (mAcm^{-2})
Pd	96.7%	-202
Ag	96.7%	-162
Zn	91.6%	-84
Cu	90.4%	-171
Sn	7.4%	-108
Ru	0%	-760
Pt	0.2%	-268
Ni	0.3%	-78

The XRD analysis revealed that the formation of (211) facets in trisoctahedron provides active sites to stabilize the reaction intermediates for CO_2 to CO reduction [91]. Similarly, Zhu et al., studied the AuNPs size effect on CO selective reduction where 8nm AuNPs exhibit 90% F.E at -0.67 V. DFT analysis confirmed that 8nm AuNPs have highest ratio of CO selective edge sites which reduced the HER during ECO_2RR [92].

Kwon and co-workers., examined how variations in surface roughness and wettability influence performance of Au electrodes. Among the different degrees of roughness, the roughest Au catalyst surface showed the high hydrophobicity and exposure of high index planes in the catalyst surface. Coupling surface hydrophobicity with high-index crystal facets increased the triple phase interaction during ECO₂RR and active sites respectively. The hydrophobic Au catalysts exhibited 6 folds higher FE_{CO} and 327 folds higher J_{CO} at -0.75V vs. RHE in comparison to the smooth surface Au electrodes [93]. However, Au is a low abundant precious and expensive material, a large-scale production and commercial use of single Au electrocatalyst economically not a feasible approach.

Ag is economically more favorable substitute for Au which exhibits comparable CO₂ to CO reduction potential at lower cost. Silver catalysts strike the right balance that can bind the *CO₂⁻ intermediate just firmly enough to activate it, yet weakly enough that CO desorbs easily. This optimum adsorption energy underpins their excellent selectivity for CO in electrochemical CO₂ reduction (ECO₂RR) and in many studies Ag-catalysts even outperforms Au. By comparison, shrinking Au nanoparticles tend to intensify the competing hydrogen-evolution reaction (HER). whereas Ag nanoparticles showed better selectivity and catalytic performance with decrease in size [94].

In principle, for CO selectivity the electrocatalyst should have low binding energy towards CO and low activity towards HER to restrict the reaction pathway for CO formation, otherwise the reaction pathway can lead to formation of other products resulting in poor catalysts selectivity. Hori et al., study suggests that metallic Ag electrocatalysts showed high CO selectivity ~82% at -1.3V vs NHE in the aqueous electrolyte while the sum of selectivity of side products only ~13% including H₂ and formate. Mechanistic insights revealed that the high availability of d-electrons in

Ag facilitates CO generation because d-electron-rich metals enhance back-donation of electrons which accelerate the formation and stabilization of the key intermediate $^*\text{CO}_2^-$ by transferring electrons from Ag occupied orbitals to CO_2 anti-bonding orbitals [95]. Hatsukade et al., reported that besides the H_2 as side product, minor products such as HCHO , CH_4 , CH_3OH , and $\text{C}_2\text{H}_5\text{OH}$ were also detected on poly Ag at high reduction potentials due to high overpotentials favors the conversion of $^*\text{CO}$ to $^*\text{CHO}$ or $^*\text{COH}$ rather than CO desorption [96].

The poor selectivity at higher overpotentials, competitive HER, low current density and stability of the Ag catalysts remain major challenges in the field of ECO_2R . Researchers have proposed many approaches to overcome these hurdles. For example, as shown in Fig. 6 (a), the nanoporous Ag electrode exhibited 150 folds higher surface area than polycrystalline Ag was able to reduce CO_2 to CO with high current density -18mAcm^{-2} and 92% CO selectivity with the reaction kinetics 3000 folds higher than poly Ag at -0.6V vs RHE in 0.5M KHCO_3 aqueous electrolyte [97].

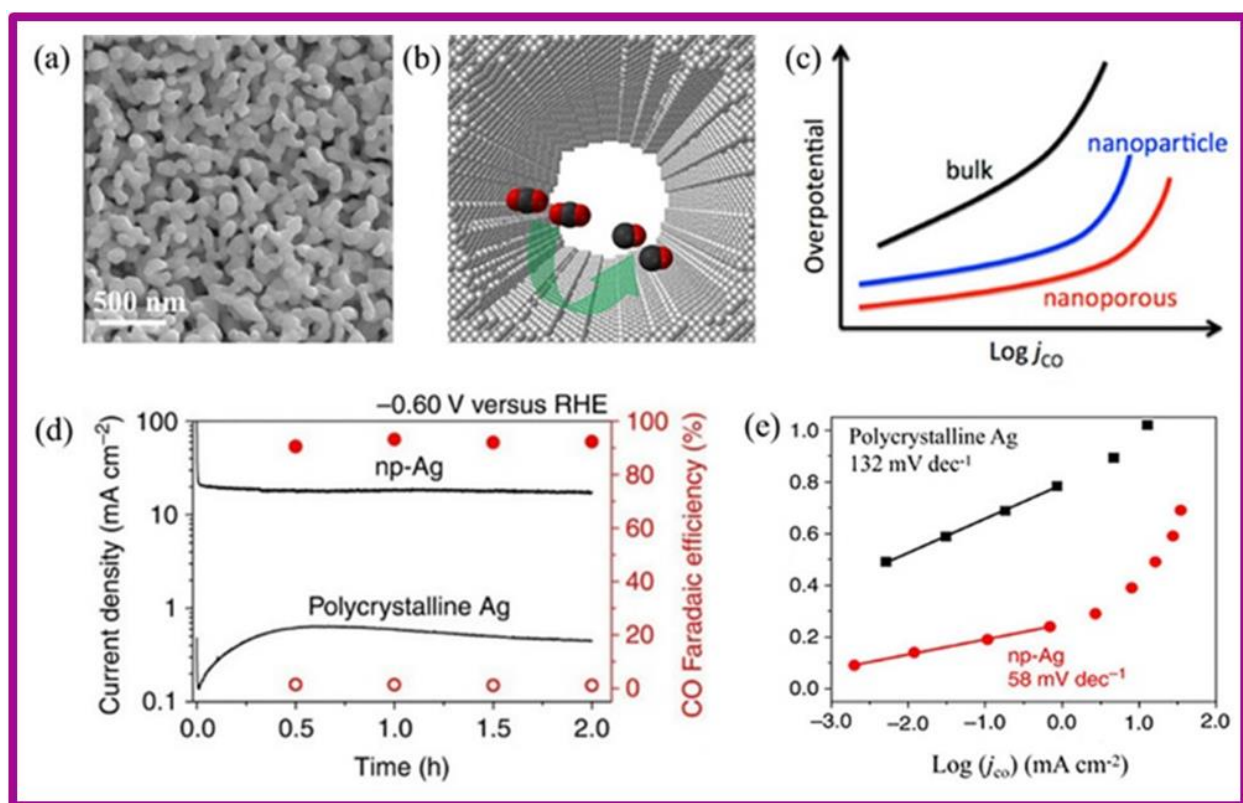


Figure 6.(a) SEM micrograph of nanoporous silver (np-Ag), (b) schematic illustrating a single nanopore with its highly curved interior surface, (c) the relationship between CO partial current density and overpotential for polycrystalline Ag and nanoporous Ag (np-Ag), Reproduced from Ref. 13, Copyright 2015, American Chemical Society. (d) CO₂-to-CO activity of np-Ag and polycrystalline Ag at -0.60 V vs RHE, (e) comparison of CO electrocatalytic performance among Ag catalysts with differing morphologies. reproduced from Ref. [97], Copyright 2015, Nature.

Due to the uncoordinated sites and high surface area of nanoporous Ag Fig. 6(b), it effectively stabilized reaction intermediates as shown in Fig. 6(c-e), during CO₂ reduction. In short, the study revealed that the nan-structured Ag electrodes showed promising catalytic advantages over their bulk counterparts for ECO₂R [98].

It can be depicted from Table. 4, only Pd achieved current densities and F.E higher than 200mAcm⁻² and 95% respectively. At a cell bias of -3.0 V, silver generates a lower current density than palladium, it surpasses Pd at higher potentials, suggesting superior kinetics for Ag as shown

in Fig. 7(a,b). However, Pd is more susceptible to CO poisoning which results in blockage of active sites and favors HER through interstitial sites during long-term electro-reduction of CO₂ [99].

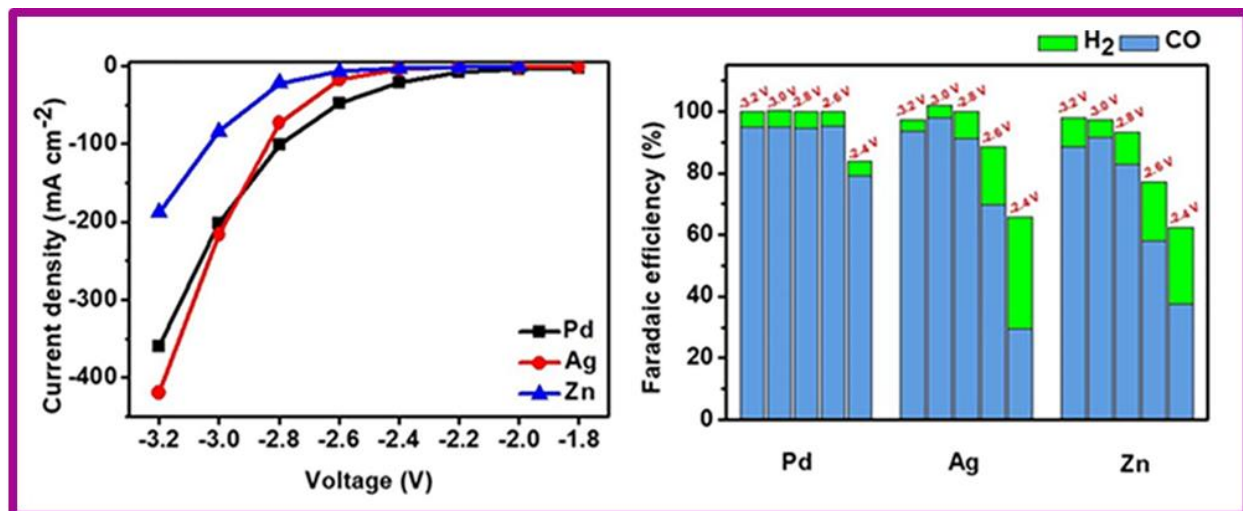


Figure 7. (a) Current–voltage (polarization) profiles and, (b) corresponding Faradaic efficiencies of Pd, Ag, and Zn electrodes recorded across the potential window -2.4 to -3.2 V. Reproduced from Ref. [90], copyright 2022, Elsevier.

Previous reports demonstrate the Au-Ag bimetallic catalysts exhibit superior performance in terms of low overpotential and high activity in ECO₂RR in comparison to pure Ag or pure Au due to variation in binding energy of intermediates in alloyed catalyst [100][101]. For example, Ismail et al., study shows that alloying Au with Ag (Au₆₀Ag₄₀) improve the current density and stability of electrocatalyst at higher overpotential and the product selectivity can be controlled by changing Ag:Au ratio in catalyst, these improvements attributed to change in Fermi level of Ag-Au alloy which lowers the adsorption energy of COOH* and CO* on catalyst, results in higher CO Selectivity by increasing Au concentration [102]. Ag electrocatalysts are economically a better choice than Au but still an expensive element not ideal to be used at large scale applications. The high expense and limited supply of noble metals significantly constrain their viability for

widespread, large-scale deployment; therefore It is important to consider catalyst consists of compositionally less concentrations of precious elements with high CO selectivity.

Despite the noble metals, Zn is a non-toxic earth abundant cheap metal found to be a promising element, intrinsically active in ECO₂RR to get CO as final product [103][104]. Even so, bulk metallic zinc catalysts typically require substantial overpotentials and deliver only limited selectivity for CO production, mainly due to low surface area, insufficient active sites and limited CO₂ adsorption capabilities [105]. Furthermore, various strategies have been applied to synthesize nanostructured Zn and ZnO electrocatalysts such as reconstruction strategy, mixed oxides-based Zn electrodes [105], alloying Zn with other CO₂ reduction active elements [106], morphology and under coordinated Zn facets effect [107], to effectively reduce CO₂ into other products. The Zn dendritic structure prepared by electrodeposition method exhibited high surface area and active sites, showed three folds higher F.E_{CO} (80%), than the Zn foil [108]. Won et al., employed electrodeposition (ED) to synthesize a hierarchical hexagonal Zn catalyst, achieving high selectivity and durability for CO production, with an F.E_{CO} of 95% [109]. Another study by Moreno et al., showed the importance of Zn alloying with other metals, the Zn-based bimetallic (Zn₉Cu₆) foam like morphology of electrodes synthesized by ED technique with high surface area and surface roughness exhibited F.E_{CO} 90% at -0.95V vs. RHE [110]. These studies collectively indicate that modifying morphology or the structural changes in Zn based catalysts is an interesting approach to enhance ECSA. These modifications can provide more active sites for stabilizing reaction intermediates at lower reduction potentials and improve the catalytic efficiency of Zn based electrodes. A recent report by Subash et al., [111], to Zn₈₇ and ZnO₅₂ electrocatalysts have nanosheet and dendritic morphology respectively as shown in Fig. 8(a,b), exhibited different electrochemical CO₂ reduction (ECR) activities due to variations in surface area and phase

formation. From Fig 8. (c,d) it can be observed that Zn₈₇ achieved an FE_{CO} 67% at -0.98V vs. RHE. In contrast, ZnO₅₂ demonstrated superior CO selectivity, achieving a Faradaic efficiency of 88.6% at -0.87 V vs. RHE. This enhancement is attributed to its strong CO₂ adsorption capability, efficient electron transfer, expanded electrochemically active surface area (ECSA), and the presence of Zn²⁺ active sites, as illustrated in Fig. 8(e, f). These results emphasize the critical role of morphology, electronic structure, and crystallinity in governing catalytic performance and product selectivity in electrochemical CO₂ reduction.

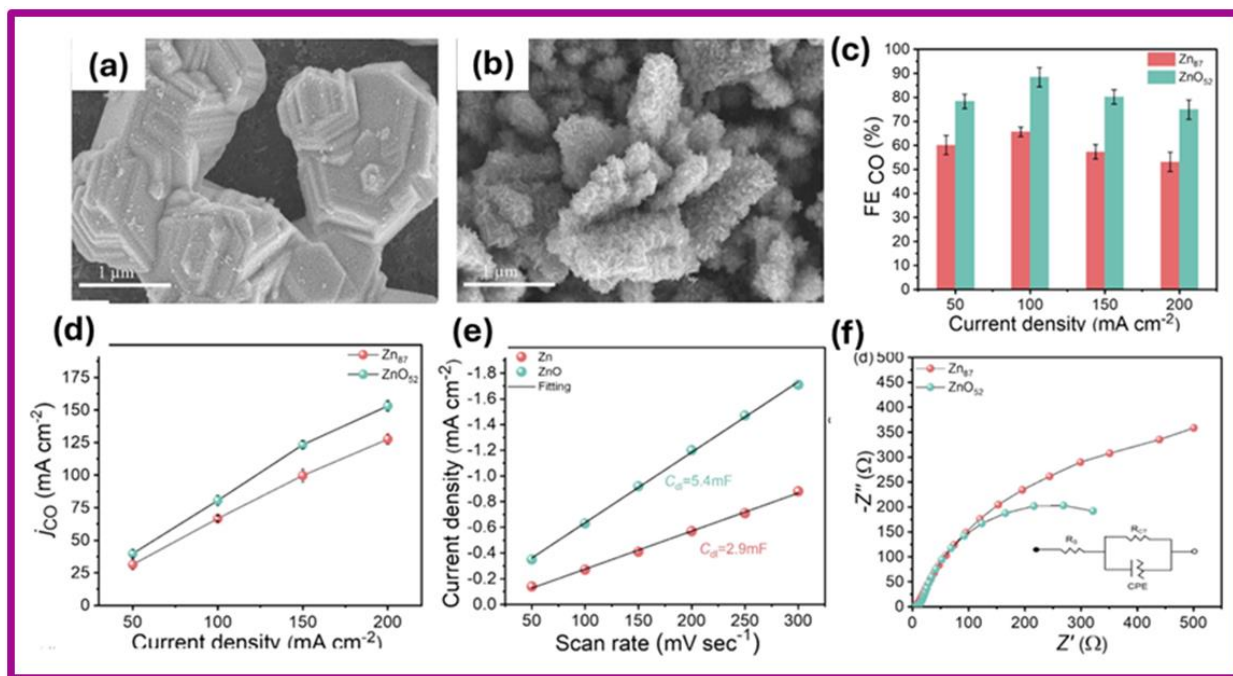


Figure 8. Electrodeposited Zn catalysts: (a, b) FE-SEM micrographs of the Zn₈₇ and ZnO₅₂ samples, (c, d) CO Faradaic efficiency (FE_{CO}) and corresponding CO partial current density for Zn₈₇ and ZnO₅₂, respectively, (e) double-layer capacitance (C_{dl}) and, (f) electrochemical impedance spectra (EIS) obtained in CO₂-saturated 1.0 M KHCO₃. Adapted from Ref. [111], copyright (2025), Elsevier

As revealed by prior studies, bimetallic and ternary catalysts overperforms in CO₂ electroreduction rather than single atomic crystals due to the synergistic effects of more than one element or presence of homogeneously mixed phases in catalyst [112]. Zn-Ag bimetallic catalysts also exhibit

desirable CO selectivity. Catalyst design by combining earth-abundant metal with precious metals reduced the required amount of Ag and Au as well as catalyst often outperforms single metallic counterparts in ECO₂RR due to synergistic effect of alloyed elements. For instance, Y. Zhou et al., [113], used vacuum thermal evaporation (VTE) to deposit a uniform porous Zn coating on Ag nanoneedles (AgNNs@Zn), successfully preserving the pristine AgNNs structure, as shown in Fig. 9(a). The deposition time was adjusted to control the thickness of the Zn layer. Among the tested thicknesses of 10, 15, and 20 nm, the 15 nm Zn film (AgNNs@Zn15) was found to be optimal. This thickness not only stabilized the high-curvature Ag structure but also enhanced the electronic interaction between Zn and Ag at the Ag-Zn interfaces. This interaction effectively stabilized *COOH intermediates, promoting CO production at lower potentials during CO₂RR as illustrated in Fig. 9(b-e).

Lamaison et al. Electrodeposited Ag alloyed Zn (Zn_{0.87}Ag_{0.13}) demonstrated 90% CO selectivity in CO₂ electroreduction at 1 atm pressure [114]. Guo et al., achieved 84.2% F.E towards CO at -1.0 V vs RHE on Ag-Zn electrodes which was 1.8-fold higher than that of poly Au, which discloses that the synergistic effect between Zn and Ag favors formation of CO [115]. The findings of these studies highlight that the catalyst design by combining earth-abundant metal with precious metals reduced the required amount of Ag and Au as well as catalyst often outperforms single metallic counterparts in ECO₂RR due to synergistic effect of alloyed elements.

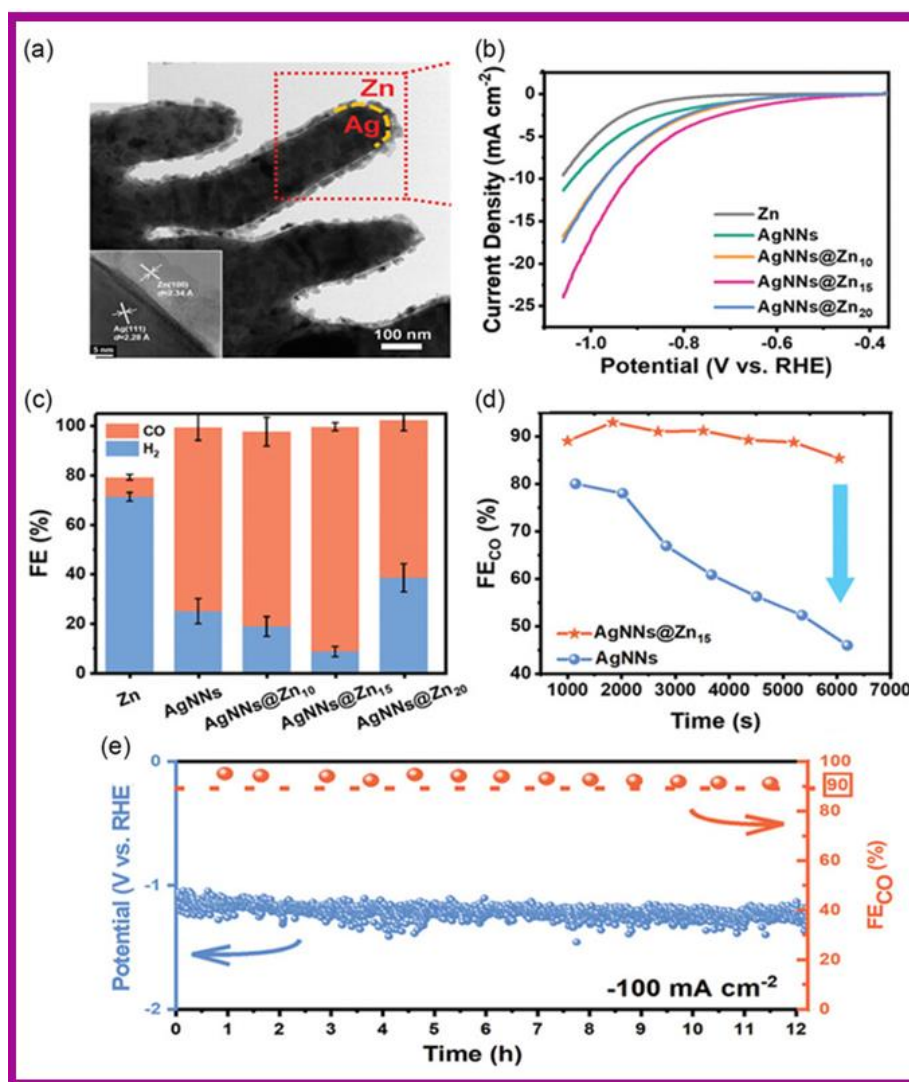


Figure 9. (a) TEM micrographs of Ag nanonets on Zn (AgNNs@Zn15), (b) linear-sweep voltammograms for Zn, AgNNs@Zn10, AgNNs@Zn15, AgNNs@Zn20, and bare AgNNs, (c) Faradaic efficiencies for CO and H₂ at -0.86 V vs RHE in an H-cell for each sample, (d) time-resolved CO Faradaic efficiency of AgNNs@Zn15 versus AgNNs in an H-cell, (e) durability assessment of AgNNs@Zn15 at 100 mA cm⁻² in a flow-cell setup. Adapted from Ref. [112], Copyright 2023, Wiley.

However, long-term stability, formation of side products at higher reduction potentials, slow reaction kinetics and low current density at ambient conditions of Zn based catalyst are the critical challenges in ECO₂RR applications. It may experience dissolution, dealloying and redeposition, catalyst layer etching, disfigurement and agglomeration during CO₂RR and the long term

preserved performance of catalyst compromised [116][117]. Such as decrease in CO evolution on Ag-Zn bimetallic electrodes with time in electrochemical testing was attributed to weak interaction between catalyst and substrate [116]. These factors cause morphological and structural changes results in degradation, poor stability, non-uniform activity and selectivity of the catalyst in electrochemical reactions [118]. Therefore, it is a crucial factor in development of ECO₂RR catalysts to maintain intrinsic catalytic structure by preventing dissolution and morphological changes during electrochemical reactions.

2.3. Catalysts for ECO₂R to HCOOH and CH₃OH

Formic acid is a valuable product of the ECO₂RR which is widely utilized in diverse industrial applications, including pharmaceuticals, pesticides, chemical manufacturing, leather processing, electrowinning, and aircraft deicing agent [119]. Due to its non-toxic nature, chemical stability, transportability and storage at room temperature make it one of the most interesting practical and economical products [120]. Furthermore, formic acid can be directly used as a fuel in formic acid fuel cells, offering a benefit over direct methanol fuel cells. Formate also serves as an efficient hydrogen storage medium due to its high volumetric (53 g H₂/L) [121]. Several metallic catalysts including Pb, In, Sn, and Hg have been explored for ECO₂R towards formate selective production. Pb and Sn exhibit high formate F.E but suffer from poor stability and require high overpotential which hinders their applications as CO₂ reduction electrocatalysts [122][123]. Pb, Hg, Cd, and Tl have attracted limited attention due to their toxic nature and environmental safety concerns [124].

In contrast, bismuth-based catalysts are garnering interest as cost-effective, non-toxic, and widely available materials that deliver excellent selectivity for producing formate [125]. Furthermore, Bi +ve-std potentials exhibit (Bi³⁺/Bi=0.308 V), which hinders the HER domination

in ECO₂RR and results in enhanced selectivity towards formate production [126]. For example, Yang et al., [127], explored the single atomic Bi-based catalyst deposited on carbon paper. The catalyst exhibited high F.E towards formate, 83.6% around -1.1V. The catalyst achieved highest j_{total} -12mA/cm² at -1.2V, which was 3.4 folds than Bismuth oxides clusters deposited on carbon black. Table. 5 highlighting the HCOOH production from ECO₂RR on different electrodes.

Table 5. Compilation of formate electrosynthesis metrics, current density and Faradaic efficiency, reported for a variety of CO₂-reducing electrode materials.

Electrodes	F.E _{formate}	V vs. RHE/ j_{total} (mA/cm ²)	Formate production rate ($\mu\text{mol} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$)	References
Bi plate	15.2%	0.69 V	5.41	[128]
Nanosized Bi/Cu	91.3%	0.69 V	52.4	[128]
Bi nanodendrites/TCP	96.4%	0.95 V	283.7	[129]
Bi nanoflakes/Cu	100%	0.40 V	35	[130]
Sn foil	40.2%	0.95 V	N/A	[131]
Sn/GDE	78.6%	0.99 V	325.14	[132]
SnOx/GDE	87.1%	0.99 V	171.6	[133]
Sn56.3Pb43.7 alloy	79.5%	1.20 V	852.5	[134]
Pb foil	60%	0.8 V	N/A	[135]
Hg	12.9%	200 mA cm ⁻²	N/A	[136]
In	15.3%	200 mA cm ⁻²	N/A	[136]
Cu foam	37%	0.68 V	N/A	[137]

*N/A=Not Available.

Dendritic nanostructures represent an ideal electrocatalyst morphology due to their extensive surface area, superior electrical conductivity, and abundant active catalytic sites. For

instance, Hyun Koh et al., [138], employed Bi-based dendrites for ECO_2R to formate in 0.5M KHCO_3 . The dendritic structured electrocatalyst showed high performance with the 89% formate F.E at 0.7V vs. RHE with high stability of 12 hours continuous electrolysis. The high-index crystal facets of the Bi dendrites significantly contribute to their catalytic activity by effectively stabilizing the $^*\text{OCHO}$ reaction intermediates. In another study, Li and colleagues employed thermal evaporation to fabricate $\text{Sn-Bi}_{0.1}/\text{SnO}_2$ films on polytetrafluoroethylene (PTFE) gas diffusion substrates [139]. $\text{Bi}_{0.1}\text{Sn}$ composition was achieved by controlling the evaporation rate of Bi and Sn at 0.1 and 1nm s^{-1} respectively. Linear sweep voltammetry curves reveal that the $\text{Bi}_{0.1}\text{Sn}$ catalyst possesses the most positive onset potential for CO_2 reduction Fig. 10(a). As depicted in Fig. 10(b) this catalyst achieves over 95% FE for formate across a broad spectrum of current densities. Further insights from Fig. 10(c, d) demonstrate that the formate FEs remain consistently above 90% across all pH levels from 8 to 14, at current densities spanning from 25 to 300 mA cm^{-2} . Remarkably, this catalyst sustaining performance over 2400 hours (100 days) of continuous operation at a current density of 100 mA cm^{-2} as shown in Fig. 10(e).

The alloying of Bi with other elements can precisely tune the electronic structure and consequently alters the binding strength of intermediates on the catalysts surface and optimize the products selectivity. Furthermore, the incorporation of other metals in Bi can help to boost the stability of the catalyst by forming stable alloyed structure which can help to improve the catalyst life in ECO_2RR . The combination of P-block metals such as Sn and Bi with transition metals like Ag and Zn in a single catalyst can reduce CO_2 into C_1 products specifically formate (HCOOH). For example, Ag-Sn bimetallic core with partially oxidized 1.7nm Sn shell structure effectively reduced CO_2 into HCOOH with 80% FE at -0.8 V vs. RHE. In this core shell structure, the

bimetallic core aimed to provide high electronic conductivity and the SnO shell provide sites for CO₂ reduction [140].

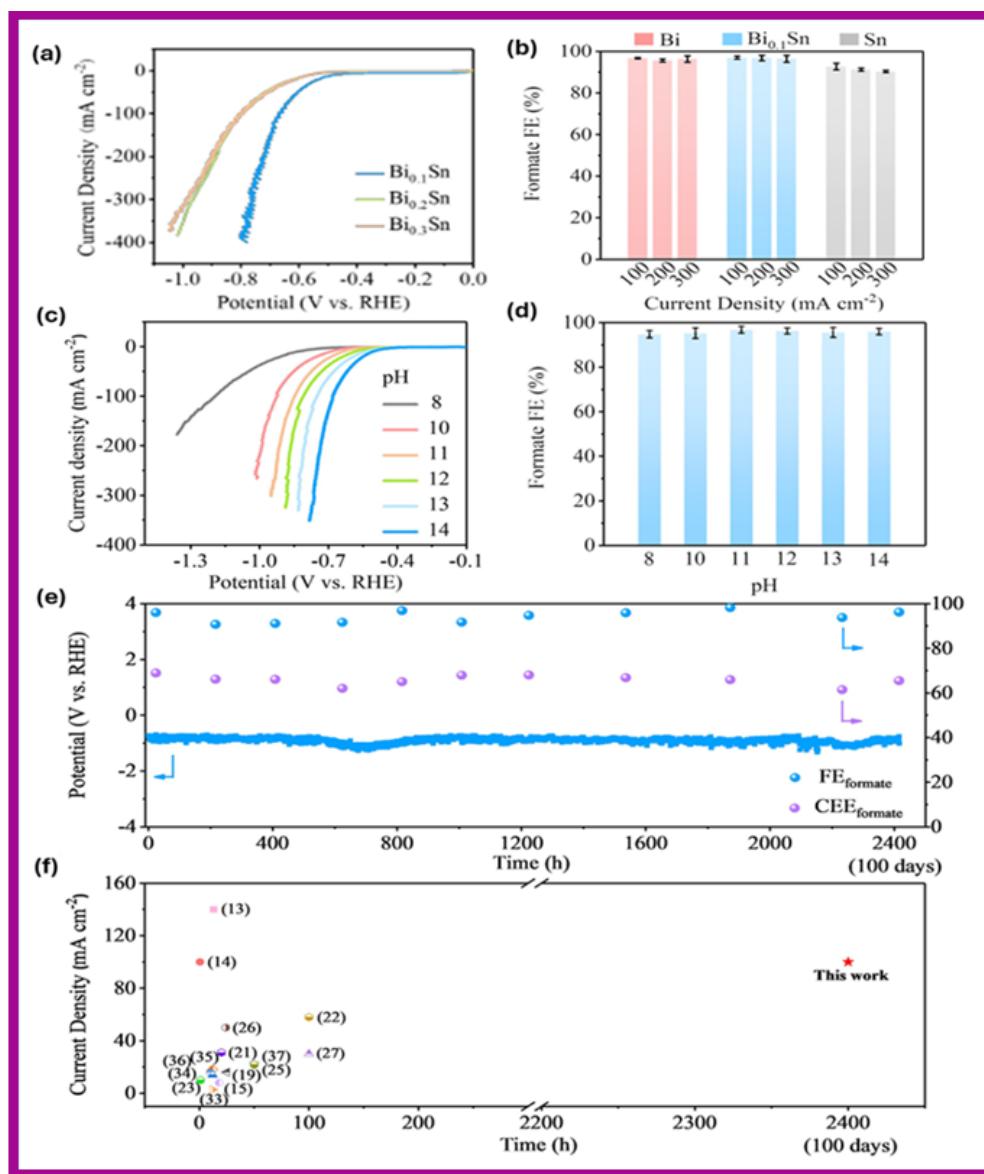


Figure 10. (a) Linear-sweep voltammograms of Bi_{0.1}Sn, Bi, and Sn electrodes in 1 M KOH, (b) resulting formate Faradaic efficiency versus current density for the same electrodes, (c) linear-sweep response of Bi_{0.1}Sn at different pH values, (d) formate Faradaic efficiency of Bi_{0.1}Sn in 1 M KHCO₃ and 1 M KOH across the pH range, measured at 100 mA cm⁻², (e) CO₂-reduction chronopotentiogram (blue line), accompanying formate Faradaic efficiency (blue symbols) and half-cell energy-conversion efficiency to formate (purple symbols) for Bi_{0.1}Sn in pH 11 electrolyte (1 M KHCO₃/KOH) under a constant current of 100 mA cm⁻². Adapted from Ref. [139], with copyright permission from Nature.

In the present study we synthesized a novel, highly porous Au decorated Ag-Zn catalysts, where a small amount of Au (4-10 wt%) is incorporated by magnetron sputtering in co-electrodeposited Zn-Ag alloy to explore the effect of Au on the activity and stability of bimetallic Zn-Ag electrodes towards CO selective reduction of CO₂. In our study we designed catalysts, keeping Zn as major constituent alloyed with Ag whereas, a small amount of Au (5.7% wt%) on the Ag-Zn surface further improved CO selectivity 94.2% F.E_{CO} and 2.4 folds increase in catalyst stability in Nafion-117 separated two compartment H-type cell.

CHAPTER 3

MATERIALS AND METHODS

Chapter 3. Materials and Methods

3.1. Materials and chemicals

Gold (Au-99.999%) and Bismuth (Bi-99.99%) sputter targets purchased from ACI Alloy, INC. 0.1mm thick Silver Foil (Ag-99.99%) was purchased online from Amazon, Silicon carbide #800 fine grit paper was purchased from MAXMAN sandpaper sheets and Platinum mesh counter electrode was purchased online from AliExpress, Silver nitrate (AgNO_3 -99.99%, BDH), Zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ -99.99%, Techno pharmChem India), Sulfuric acid (H_2SO_4 -99%, Sigma-Aldrich), Acetone A.R ($\text{C}_3\text{H}_6\text{O}$, 99.8% Scientific laboratory supplies Ltd), Ethanol ($\text{C}_2\text{H}_5\text{OH}$ -99.9%, Duksan) and Potassium bicarbonate (KHCO_3 -99.9%, Honeywell) was used to fabricate and electrochemical testing of cathode catalyst. All chemicals and materials utilized in this study as received without further purification.

3.2. Catalyst synthesis

In the last decade, many methods have been reported for the fabrication of electrocatalysts such as chemical methods, impregnation, Colloidal solution synthesis approaches, Sol-gel method, microemulsion etc., to control the catalyst's structure and properties [141]. These catalysts fabrication approaches involve multistep complex processes and high temperatures requirements, produced uncontrolled structure and morphology which require surfactants and capping agents. Furthermore, in chemical reduction synthesis methods the catalysts activity compromise due to the generation of impurities during the deposition reaction. Taking into account these reasons, there is a need to adopt simple and facile catalysts synthesis approaches with high purity and controlled morphology, in energy conversion reactions.

In this study two thin films synthesis techniques, electrodeposition and Direct current (DC) magnetron sputtering, were sequentially combined to fabricate the electrocatalysts for ECO₂RR. Both methods were carried out at room temperature and without using any capping agents or surfactants.

3.2.1. Electrodeposition technique

Electrodepositions are typically known as the electroplating process, efficiently used for the synthesis of numerous thin films nanostructures. This process has emerged as a prominent method for synthesizing nanomaterial-based electrocatalysts for various energy conversion applications. This technique allows precise control over the morphology and size of the electrocatalysts deposited on conductive surfaces by simply adjusting electrochemical deposition parameters. A major advantage of this process of electrodeposition is the elimination of capping or surface-active agents which significantly simplify this process and enhance its practical applications.

For instance, Sarfraz et al., [142], demonstrated the fabrication of bimetallic catalyst by electrodeposition of Sn on the oxide-derived copper (OD-Cu). The Sn-decorated Cu catalyst exhibited high FE_{CO} (>90%) and a current density of -1.0 mA cm^{-2} at -0.6 V vs. RHE, significantly outperforming the pristine OD-Cu (63% F.E and -2.1 mA cm^{-2}). However, excessive Sn deposition led to an increase in HER and reduce in current density. This study provides an effective approach to develop a cost-effective, metallic electrocatalysts for highly selective and efficient ECO₂R.

- Basic mechanism of electrodeposition technique

Fig. 11. shows electroplating cell setup. In general, this process involves the immersion of two conductive electrodes e.g., anode and cathode in a specific electrolyte and then the application of external electric field leads to the deposition of specific metal on the cathode material. DC power supply provides unidirectional current across the electrodes. Electron flow occurs through the external circuit whereas, ionic conduction occurs within the electrolyte solution as shown in Fig. 11. When external potential is applied the negatively charged ions called anions migrate toward the positively charged anode and the positively charged ions known as cations move towards the negatively charged cathode. The composition of the electrolyte solution significantly influences the deposition characteristics and outcomes of the electroplating process [143][144]. The counter electrode in the setup is used to complete the circuit of electrochemical cells.

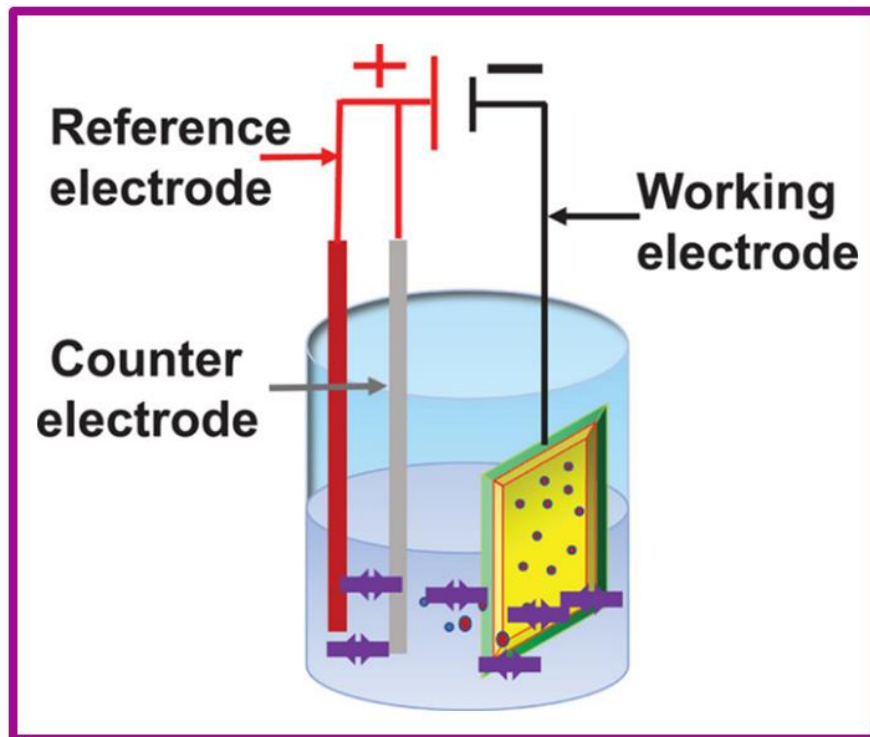


Figure 11. Representative electroplating cell. Adapted from Ref. [144], copyright (2021), Wiley

Electrodeposition is favorable for synthesizing dispersed metal nanoparticles used as catalysts in ECO₂RR, as it does not require surfactants, capping or active agents instead the process depends on the controlled transfer of the electrons through the electrochemical setup. This makes electrodeposition a cost-effective, simple and facile approach to produce highly pure nanomaterials and thin films fabrications. The deposition in this method can be performed either by galvanostatic deposition where a constant current is applied to achieve uniform nanoparticle size or by potentiostatic deposition, where a constant potential is maintained for a specific duration [145][146]. Typically, these methods employ a two or three-electrode configuration including substrate as working electrode, a platinum mesh as counter electrode and an Ag/AgCl reference electrode.

3.2.2. Sputtering technique

Magnetron sputtering (MS) is one of the PVD techniques that involves depositing thin film coatings by bombarding a target material's surface atoms with high-energy ions [147]. MS offers many advantages, it is cost-effective, has no harmful byproducts, and can be readily scaled up for commercial applications. There are several types of MS including Direct Current (DC), Radio Frequency (RF), and Pulsed DC MS, each with unique applications and characteristics. DC is utilized for depositing metallic materials, while a radio frequency (RF) sputtering technique is employed for insulating target materials. The RF sputtering system functions at a high frequency, typically at 13.56 MHz during the deposition process, electrodes are periodically reversed for a brief RF cycle to prevent charge accumulation on the insulator target [148]. Co-sputtering method involves simultaneous deposition from more than one target materials on several supports. This method allows to deposit thin film catalyst with the combination of metallic elements such as metallic alloys, binary and ternary catalysts, and metallic-nonmetallic films such as metal oxides

to fabricate a variety of compositions and properties in the catalysts [149][150]. During co-deposition the power of the target material is controlled independently to control the deposition rate of each target which leads to controlling the composition in fabricated films [151].

- The Fundamentals of sputtering technique

In conventional sputtering setups, the essential components include a power supply, a vacuum chamber, substrate holder, a target positioning system, and a chamber for mixing the working gas Fig. 12. In the basic sputtering system, the target surface is bombarded by high-energy ions accelerated by the electric field, leading to momentum transfer and the ejection of target atoms. These atoms then travel toward the substrate, where they deposit to form a thin film [152]. However, the inefficiencies caused by low secondary electron usage, ionization rates, and deposition rates have limited the effectiveness and wider use of sputtering technology [153]. A new approach to these issues involves incorporating strong magnetic fields created by carefully positioned magnets or coils close to the target surface. This development converted conventional sputtering systems into the commonly used magnetron sputtering technique [154].

Sputtering relies on gas discharge and plasma production. Ar is commonly used as an inert gas to create plasma in non-reactive sputtering. Reactive sputtering involves using reactive gases such as N₂ and O₂ during the deposition to form coating containing the elements present in the reactive gas.

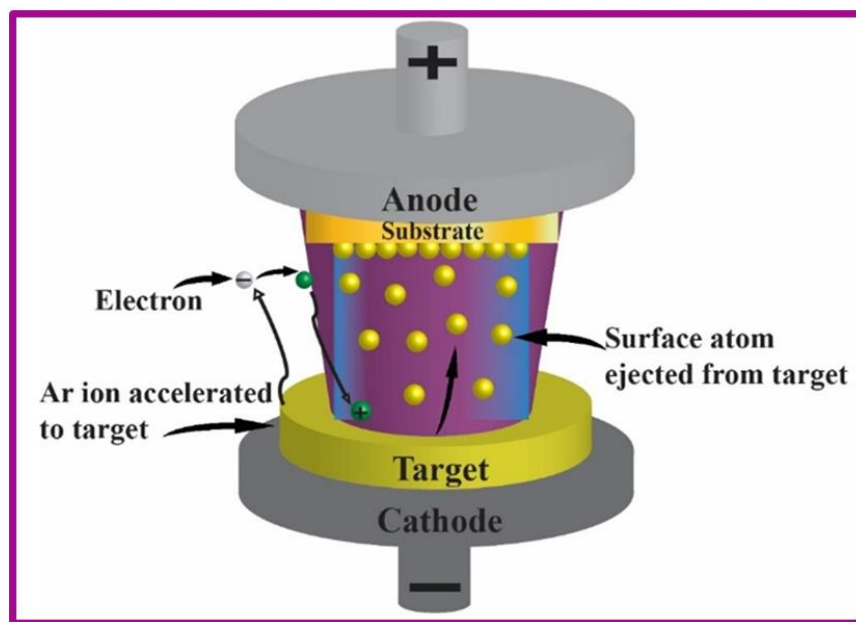


Figure 12. illustration of reactive magnetron sputtering.

3.3. Synthesis of Ag-Zn catalysts

Ag-Zn thin film alloy catalysts were fabricated by electrodeposition technique as reported in the literature [155], on 1cm^2 , 0.1mm thick Ag foil (99.99% pure). Prior to deposition, Ag foil was grinded by 800 grade silicon carbide sandpapers and then sonicated in 0.5 H_2SO_4 , ethanol and De-ionized water respectively (5 minutes in each), to remove any kind of contamination. After drying at room temperature 1cm^2 Ag foil was used as support material to prepare electrodes. To fabricate Ag-Zn thin films each Ag substrate was dipped into 1.5M H_2SO_4 solution containing 0.2M AgNO_3 and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ metallic salts. The solution pH was measured using a calibrated glass electrode and was found to be 0.20 ± 0.05 at 25°C (without external heating or cooling). All electrodepositions were conducted on Ag substrate at room temperature with a constant current density of -1 A cm^{-2} for 30 seconds in a two-electrode configuration cell, using a Pt mesh as the counter electrode. The concentration of Ag and Zn in electrode was controlled by the molarity of AgNO_3 and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in the solution.

3.3.1. Synthesis of Au decorated Ag-Zn catalysts

After deposition Ag-Zn electrodes were instantly rinsed by distilled water and dried at room temperature for 24 hours followed by deposition of Au using DC magnetron sputtering process for 5, 10 and 20s result in 4.3, 5.7 and 9.7 weight percent (wt%) of Au in Ag-Zn will be named as 5sAu@Ag-Zn, 10sAu@Ag-Zn and 20sAu@Ag-Zn in this study. The Au content in the catalyst was controlled by deposition time during sputtering process. The two step catalysts synthesis approach is shown in Fig. 13.

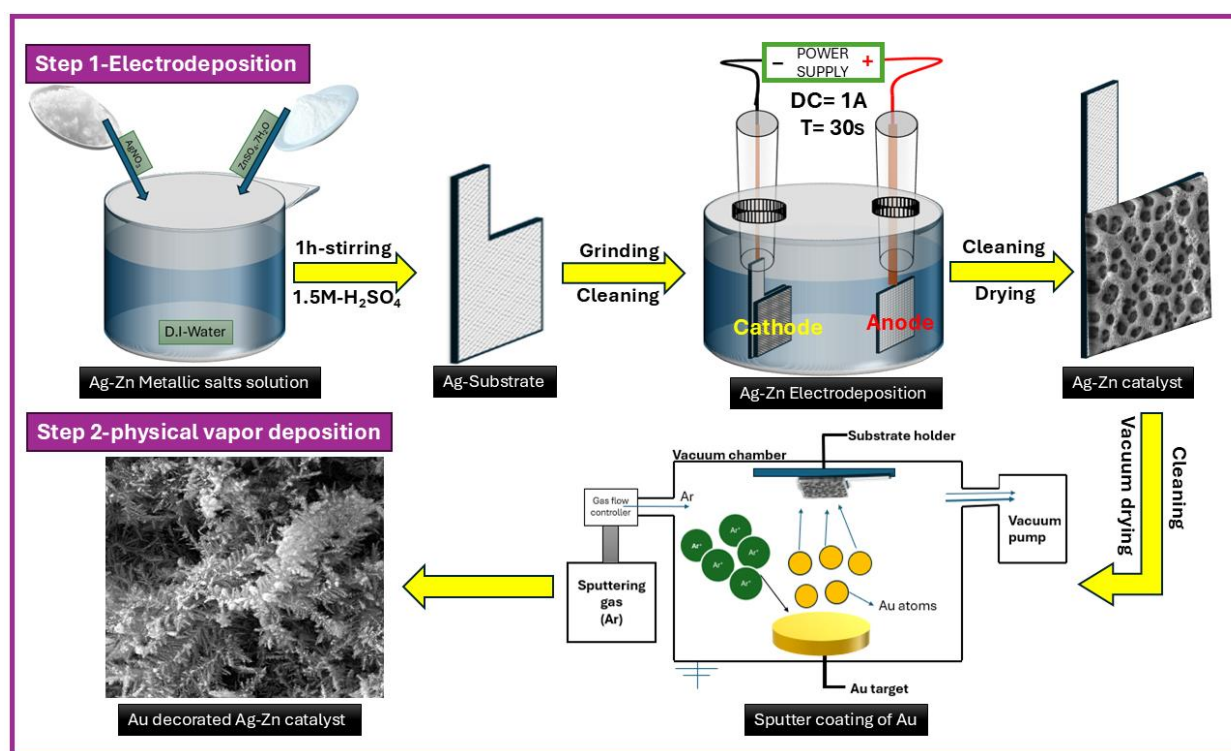


Figure 13. Schematic illustration of Au decorated Ag-Zn catalysts synthesis process.

3.3.2. Synthesis of Bi decorated Ag-Zn catalysts

Synthesis of Bi decorated Ag-Zn catalysts Bi-decorated Ag-Zn catalysts were synthesized following a procedure similar to that described for Au-decorated Ag-Zn catalysts (section 3.3.1). After electrodeposition, the prepared Ag-Zn electrodes were thoroughly rinsed with distilled water

and dried at room temperature for 24 hours. Subsequently, Bi deposition was carried out using the DC magnetron sputtering process with a Bi target. The sputtering times were set at 1, 2, and 3 minutes, resulting in Bi-decorated Ag-Zn catalysts. These catalysts are referred to as 1minBi@Ag-Zn, 2minBi@Ag-Zn, and 3minBi@Ag-Zn, respectively. The Bi content within the catalysts was adjusted by varying the deposition duration during the sputtering process.

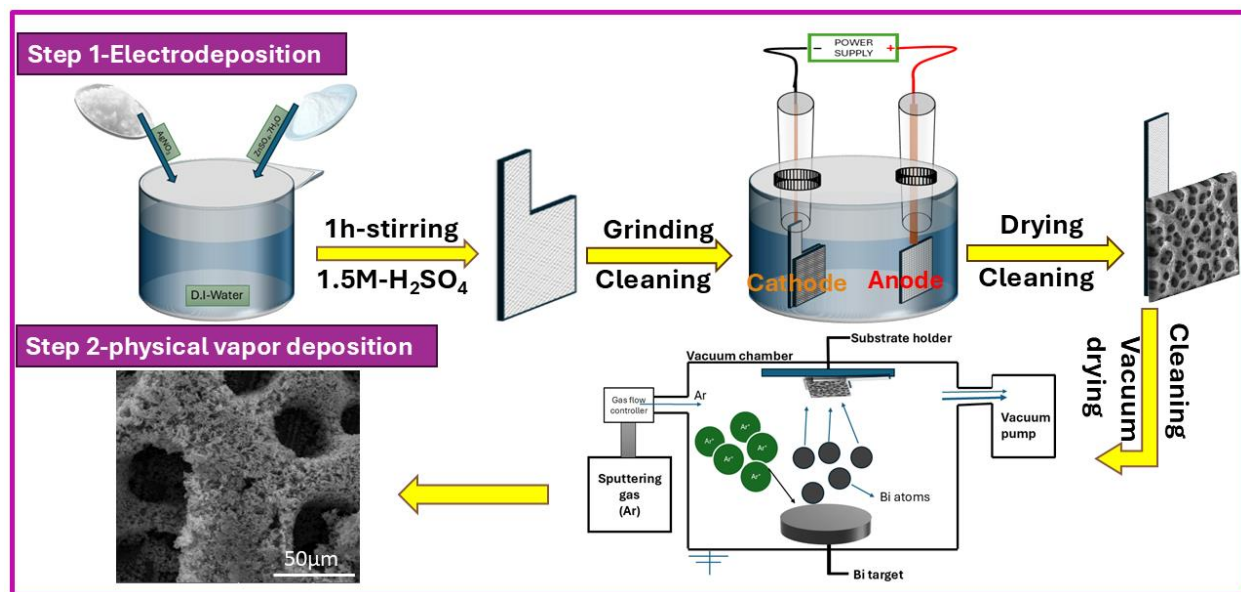


Figure 14. Schematic illustration of Au decorated Ag-Zn catalysts synthesis process.

3.4. Catalysts's characterizations

To get insight of the morphological, structural and compositional properties of fabricated thin film catalyst were characterized by various techniques. The structural properties were analyzed by X-ray diffraction (XRD, MiniflexII diffractometer, Rigaku) with Cu-K α (λ =1.5416Å), 30KV accelerating voltage and keeping the tube current at 10mA. Scanning electron microscopy (SEM) was employed to examine the morphology of the samples. (FESEM, Tescan Lyra-3) combined with energy dispersive spectrometry (EDS) and Transmission electron microscopy (TEM, JEOL 2010). The TEM samples were prepared by removing the catalyst thin

film from substrate and dissolving them in ethanol and then depositing a solution drop on copper grid covered with amorphous carbon. Chemical states of elements and surface chemistry of the catalyst were depicted by X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi, Thermo Fisher Scientific). The wettability of the electrodes was tested in water contact angle measuring equipment (KYOWA interface science co., Ltd, DMS-501).

3.5. Electrochemical testing

Electrochemical tests were conducted with a dedicated potentiostat/galvanostat workstation (Gamry 620, potentiostat/ZRA) in customized gas-tight two compartment H-type cell, a Nafion-117 ion exchange membrane was employed to separate the cell compartment. Pt mesh (2cm×2cm) and saturated KCl, an Ag/AgCl electrode were utilized as counter and reference electrodes, respectively.

3.5.1. Linear sweep voltammetry

Linear sweep voltammetry (LSV) analysis was performed in Ar, and CO₂ saturated 0.1M KHCO₃ solution with scan rate of 5mVs⁻¹ and potential range, -0.25V to -2V vs. Ag/AgCl. Each catalyst was tested in both gas environments where a fresh electrolyte was filled in the cell before each saturation to ensure consistency and accuracy in the measurements.

3.5.2. Cyclic Voltammetry and Electrochemical impedance spectroscopy

The electrochemically active surface area (ECSA) was probed by cyclic voltammetry in N₂-purged 0.1 M KHCO₃, sweeping the non-faradaic window from -0.6 to -1.0 V versus Ag/AgCl at scan rates of 25–100 mV s⁻¹. The double layer capacitance (CDL) of catalysts was measured by calculating the capacitive current density by equation (3.1) and then calculating the slop of Δj Vs scan rate plot as shown in Fig. 39(c).

$$\Delta j = \frac{j_a - j_c}{2} \quad (3.1).$$

Where, j_a and j_c represent the anodic and cathodic current density during forward and reverse CV scans respectively. Charge-transfer resistance was evaluated using electrochemical impedance spectroscopy (EIS), by recording spectra at -1.0 V versus RHE in CO_2 -saturated 0.1 M KHCO_3 , with all measurements collected at the respective open-circuit potentials of the catalysts.

3.5.3. CO_2 reduction performance

The CO_2 electro-reduction performance of the catalyst was evaluated in 0.1M KHCO_3 by chronoamperometry (CA) technique at different potentials. The cathode chamber of the H-cell containing 0.1M KHCO_3 electrolyte, Ag/AgCl reference electrode and synthesized catalysts as working electrode, was purged with high purity CO_2 for 30 minutes with constant flowrate of 30ml/min was controlled by gas flow controller (SIERRA SmartTrack MFC) and continuous stirring prior to ECO_2RR . The gas products were analyzed by online gas chromatograph (Clarus SQ 8 GC/MS, PerkinElmer), taking gas samples directly from the cathode chamber of the cell during ECO_2RR . Faradic Efficiency (F.E) for the gaseous products was determined using the equation presented below.

$$F.Ei = \frac{Zi \times F \times P \times V \times xi}{J_{total} \times R \times T} \times 100 \quad (3.2).$$

Where, Zi is the number of electrons transferred to produce 1 mole of gaseous product, xi is the mole of the product detected by GC, V is the gas flow rate in ml/min observed by digital gas flow meter, J_{total} is total measured current from potentiostat, whereas, the $P= 1.013 \times 10^5$ Pa, $T=293.15$ K, $F=96485$ C mol^{-1} , $R=8.3145$ J mol^{-1} K^{-1} are the constants used in the equation (3.2). To analyze the liquid products electrolyte samples from cathode compartment of cell were collected after the reduction reaction and followed by testing in ultra performance liquid chromatograph (UPLC,

Acquity system with R.I detector) with the injection volume 2ml and flow rate 0.5ml/min. The F.E of the liquid products was calculated using the following equation.

$$\%F.E = \frac{z \times n \times F}{Q} \times 100 \quad (3.3).$$

Where, z is the number of electrons transferred to produce 1 molecule of liquid product, n is moles of the liquid product, Q is the total transferred charge through the catalyst during ECO₂RR, and F is the Faraday constant, has the value 96485C.mol⁻¹.

All electrochemical tests were carried out under ambient temperature and pressure. Potentials recorded versus Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale using the relation shown below:

$$E_{RHE} = E_{Ag/AgCl} + 0.197 \text{ V} + (0.0591 \times \text{pH}) \quad (3.4).$$

3.5.4. Identify and Quantify Liquid Products Using UPLC

To analyze the liquid products of ECO₂RR on Ag-Zn and Au decorated Ag-Zn catalysts, the liquid product samples were directly taken from the cathode chamber of the H-Cell after 1h electrolysis for each sample at different potentials. To find the concentration of liquid products the liquid samples were collected separately at each potential after electrolysis. Ultra-high performance liquid chromatograph (UPLC) equipped with R.I detectors were used to identify and quantify the liquid products by standard curve calibration method.

The standard solution of all the expected liquid products like, HCOOH, CH₃OH, propanol, iso-propanol, CH₃COOH and Ethanol were prepared at different concentrations for each of the compounds. The UPLC test was run for each known concentration under identical conditions, and the peak area was recorded for each concentration.

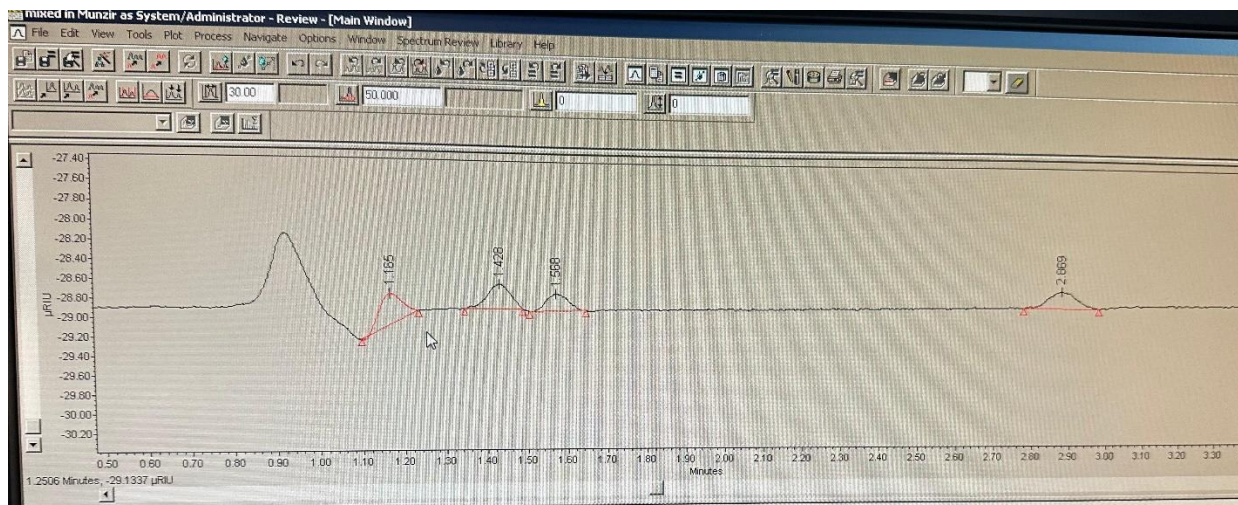


Figure 15. The UPLC standard curve highlights the peak position of different liquid products at different retention times.

The plot between the different concentrations of each product and peak area obtained by UPLC was fitted by linear regression as equation 3.5.

$$Y = mx + b \quad (3.5).$$

Where Y represents the peak area, m is the slope of linear fit, x is the concentration of the product, and b is the intercept.

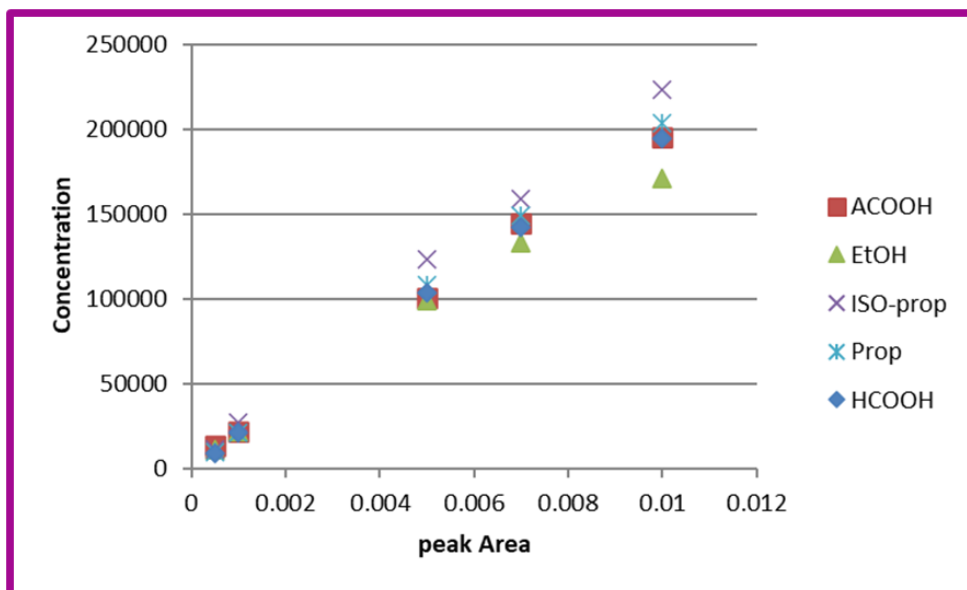


Figure 16. Standard curves of different products obtained from UPLC

Then the liquid product samples obtained from ECO₂RR were tested in UPLC and the peak area of each product was measured. Standard curve equation was used to find the unknown concentration of the liquid products. The moles of each product as calculated as follows,

$$n = C \times V \quad (3.6).$$

In this relation, **n** is the number of moles of product, **C** is the concentration determined by UPLC, and **V** is the volume of electrolyte that was analyzed. The F.E of the liquid products was subsequently analyzed with e.q, 3.3. Where, **z** is the number of electrons transferred to produce 1 molecule of liquid product, **n** is moles of the liquid product, **Q** is the total transferred charge through the catalyst during ECO₂RR, and **F** is the Faraday constant, has the value 96485C.mol⁻¹.

CHAPTER 4

RESULT AND DISCUSSION

Project 1

Chapter 4. Sputtered Au decorated Ag-Zn alloyed thin films for electrochemical CO₂ reduction

The Au@Ag-Zn catalysts was fabricated via two-step synthesis strategy, electrodeposition followed by magnetron sputtering technique. The Ag-Zn thin films was fabricated by constant current electrodeposition using ZnSO₄·7H₂O and AgNO₃ metallic salt solutions as a source of Zn and Ag respectively. The Au@Ag-Zn catalysts was prepared by Au sputter coating on electrodeposited Ag-Zn thin films. Many physical and electrochemical characterization techniques were used to study the properties and electrochemical performance of the fabricated catalysts. In the present study we synthesized a novel, highly porous Au decorated Ag-Zn catalysts, where a small amount of Au (4-10 wt%) is incorporated by magnetron sputtering in co-electrodeposited Zn-Ag alloy to explore the effect of Au on the activity and stability of bimetallic Zn-Ag electrodes towards CO selective reduction of CO₂. In our study we designed catalysts, keeping Zn as major constituent alloyed with Ag whereas, a small amount of Au (5.7% wt%) on the Ag-Zn surface further improved CO selectivity 94.2% F.E_{CO} and 2.4 folds increase in catalyst stability in Nafion-117 separated two compartment H-type cell. These findings indicate the potential of Au decorated Ag-Zn thin films as promising catalyst for sustainable CO production. We proposed a simple facile 2-step approach to fabricate nano-structured trimetallic electrode system at room temperature without using any capping agents or surface stabilizer ligands. Our approach establishes a framework for the fabrication of multi-metallic catalysts by integrating electrodeposition with PVD techniques which offers a versatile strategy for advanced catalytic applications.

4.1. Field Emission Scanning Electron Microscopy

Field Emission Scanning Electron Microscopy (FE-SEM), was used to study the morphological properties of the Ag-Zn and Au decorated Ag-Zn catalysts. Fig. 16(a-f), 17(a-h), 18(a-h), 19(a-e) represent the morphology of Ag-Zn, 5sAu@Ag-Zn, 10sAu@Ag-Zn and 20sAu@Ag-Zn electrodes respectively, obtained by FE-SEM at different resolutions.

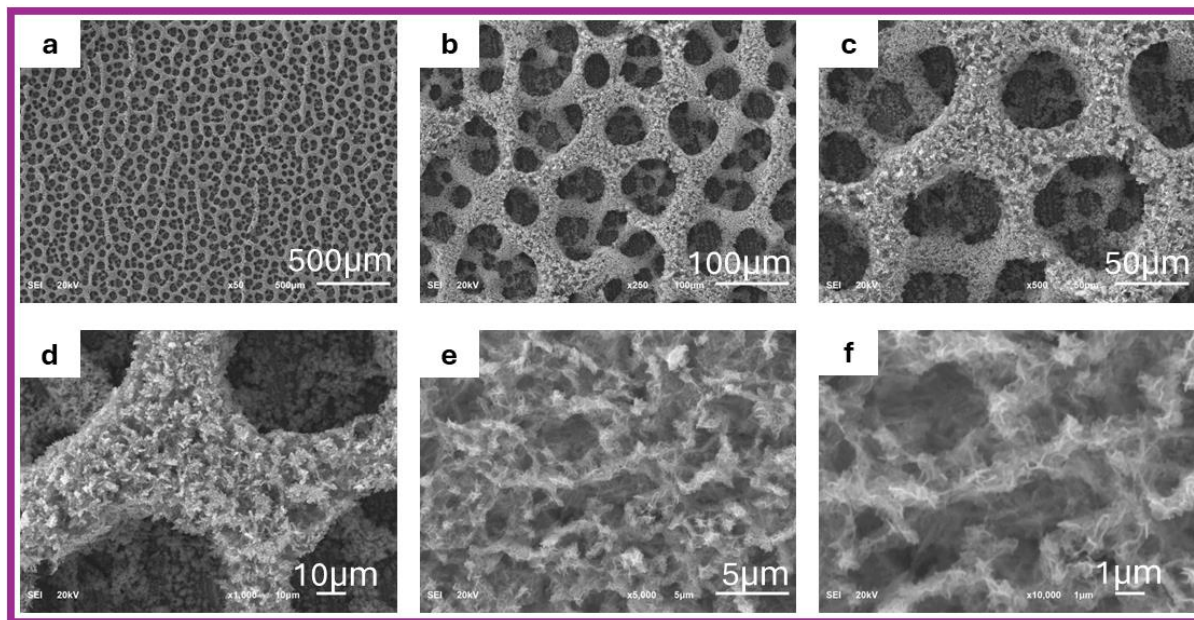


Figure 17. SEM images of Ag-Zn catalyst

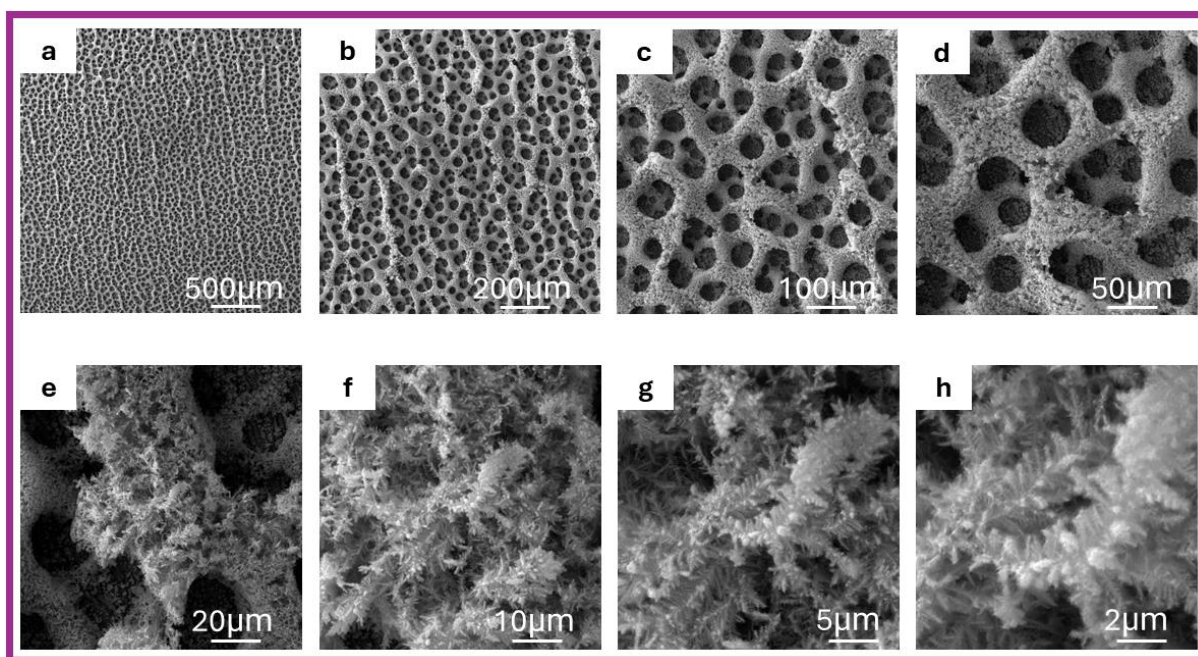


Figure 18. SEM images of 5sAu@Ag-Zn catalyst

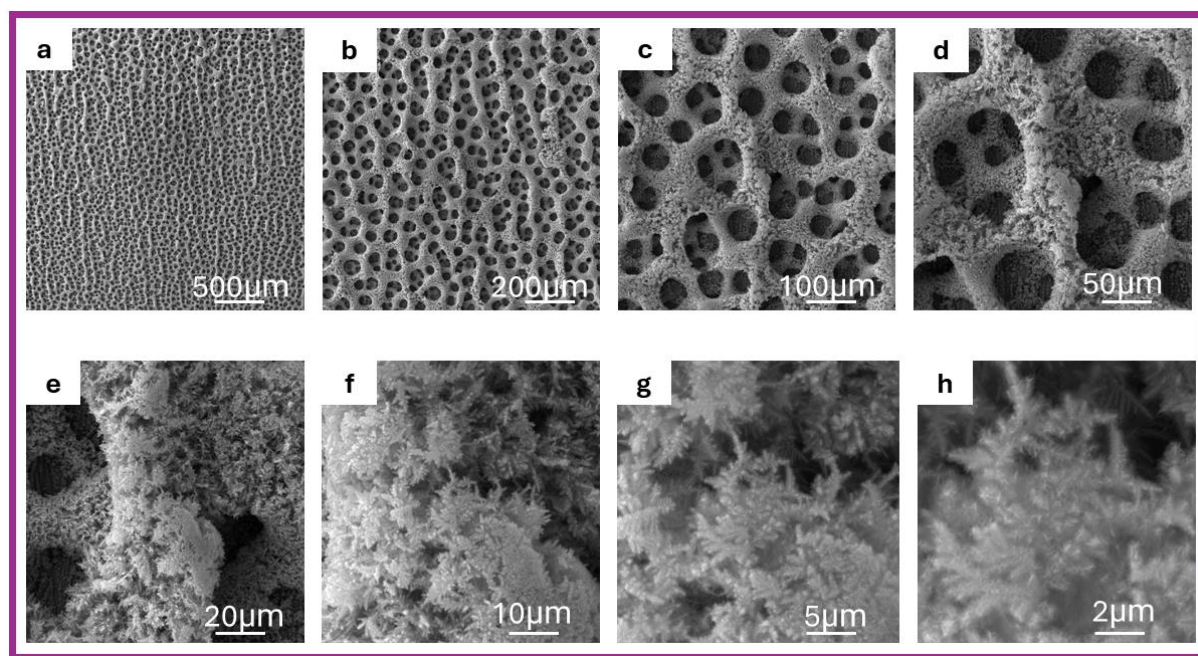


Figure 19. SEM images of 10sAu@Ag-Zn catalyst

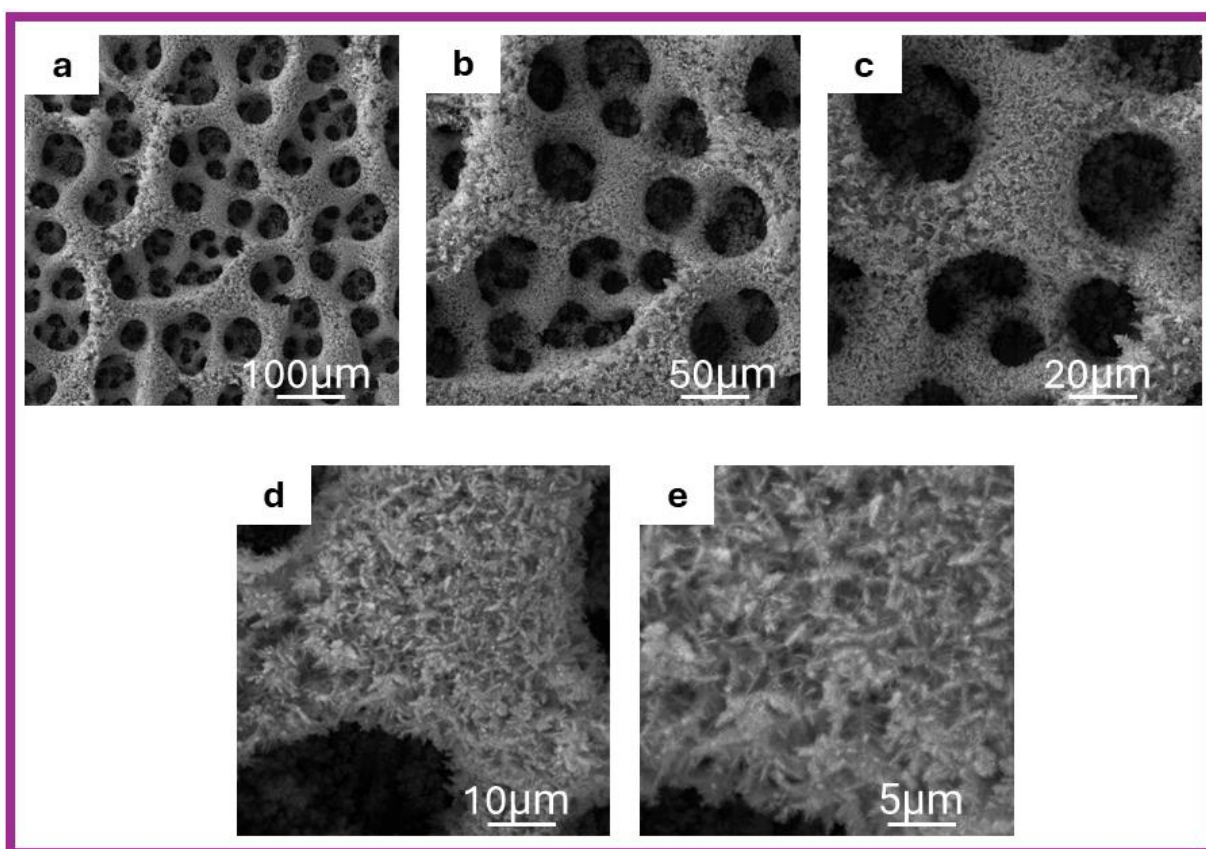


Figure 20. SEM images of 20sAu@Ag-Zn catalyst

FESEM analysis clearly demonstrates the successful synthesis of highly porous Ag-Zn and Au@Ag-Zn catalysts, having a foam like morphology as shown in Fig 16-19. These morphology was achieved by co-electrodeposition of Ag and Zn followed by DC magnetron sputter deposition of Au onto the Ag-Zn thin films surface. During electrodeposition, along with the metal ions reduction constant evolution of hydrogen bubbles at the cathode surface, results in the pores formation in the thin films of the catalysts [156].

The highly porous Ag-Zn foam with the preferential growth of Ag-Zn dendrites surrounding the micropores provides high surface area and active sites for ECO₂R. Moreover, Ag-Zn structure remained intact with the homogeneous distribution of Au sputtered atoms at the surface. The dentritic Ag-Zn structure observed around the micropores further favors the catalytic

efficiency. These dendrites not only increase the surface roughness but also facilitate effective mass transport of CO_2 and electron transfers during ECO_2RR . Following the sputtering step, the SEM images of Au decorated Ag-Zn catalysts shown in Fig. 17-19, confirm that the catalysts structure and morphology remain intact after the Au deposition on Ag-Zn surface. It also highlights that the Au is homogeneously distributed on the Ag-Zn surface which was also confirmed by elemental mapping. Overall the hierarchical and highly porous Ag-Zn and Au decorated Ag-Zn morphology is conducive to achieve high catalysts performance in ECO_2RR .

4.2. Energy-dispersive X-ray spectroscopy

Elemental composition and spatial distribution in the catalyst were probed by pairing scanning electron microscopy with energy-dispersive X-ray spectroscopy (EDS). The elemental mapping of bimetallic Ag-Zn catalyst is shown in Fig. 20, which shows the homogeneous distribution of all the constituents, Ag and Zn are homogeneously distributed throughout the catalyst surface. Quantitative analysis from the EDS data reveals the weight percentage composition of Zn at approximately 69.6% and Ag at approximately 18.7%. These results demonstrate that Zn constitutes a significant portion of the catalyst. The presence of Oxygen in the EDS spectrum indicates that surface oxidation process converts the exposed zinc into a thin layer of ZnO. This is attributed to the inherently high sensitivity and reactivity of metallic Zn toward environmental oxygen especially when it is exposed to atmospheric conditions during the characterization and transportation of the samples after synthesis process. This spontaneous Zn oxidation leads to the formation of a thin native oxide layer on the catalyst surface which was confirmed by the appearance of a distinct oxygen peak in the EDS composition [157].

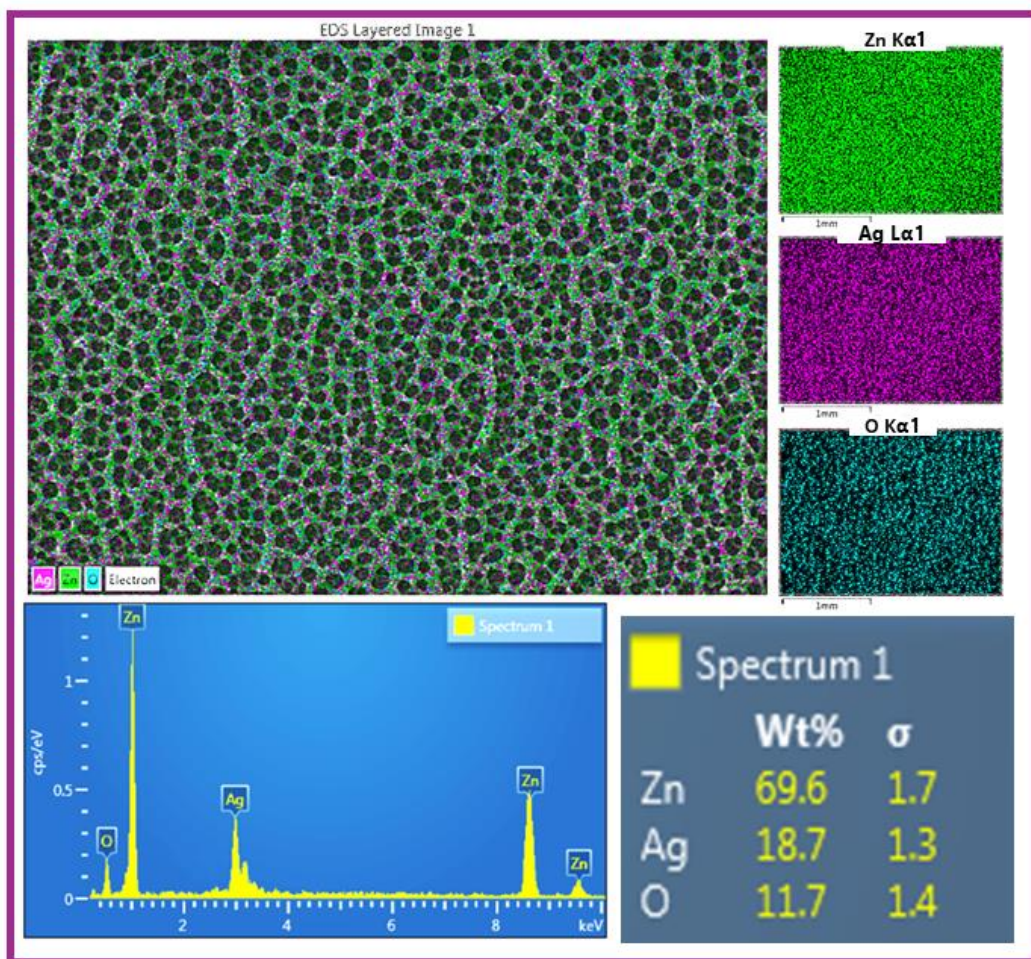


Figure 21. EDS mapping and composition spectrum of Ag-Zn catalyst

The elemental mapping and EDS spectrum of Au decorated Ag-Zn, 5sAu@Ag-Zn, 10sAu@Ag-Zn, 20sAu@Ag-Zn catalysts shown in Fig. 20-23, respectively. In case of the Au decorated Ag-Zn electrodes the elemental mapping reveal uniform and well dispersed distribution of Au atoms on the existing surface of Ag-Zn thin films. These results indicate that the sputtering process successfully applied to produce the homogenous modifications across the Ag-Zn thin films. The consistent distribution of Au indicates that the sputtering technique effectively deposited Au atoms on the surface of Ag-Zn without significant changes in the underlying porous morphology of the electrodeposited Ag-Zn thin films.

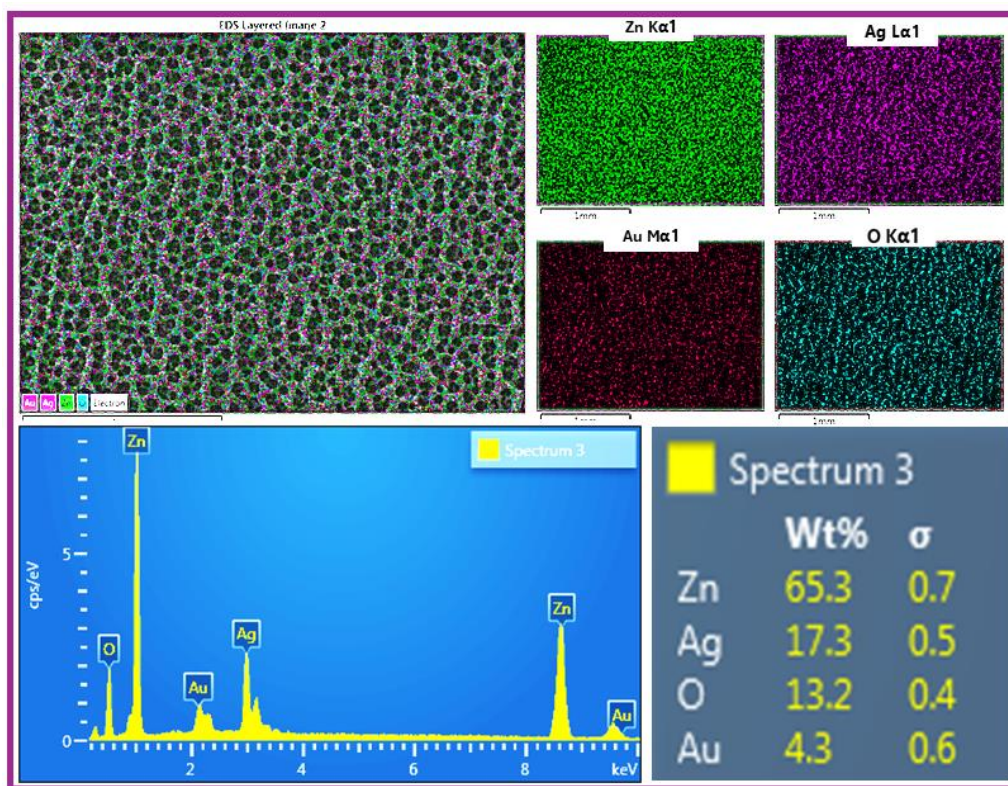


Figure 22. EDS mapping and composition spectrum of 5sAu@Ag-Zn catalyst

However, the persistent detection of the oxygen content in all Au@Ag-Zn electrodes further emphasizes that the susceptibility of the Zn to form oxides when exposed to the environment. Notably it is important to highlight that the surface oxide layer in the electrodes does not affect the performance of the catalysts in ECO₂RR. It has been reported that the native oxide layer of Zn rapidly reduced to metallic Zn under the reducing conditions that are applied during the CO₂ electroreduction which helps to study the intrinsic activity of pure metallic Zn based electrodes. Furthermore, the Au is highly active material towards CO₂ to CO reduction, and a small amount of it can not only improve catalytic efficiency but also helps to improve the charge transfer properties and prevents the further undesired oxidation during the long-term reaction conditions.

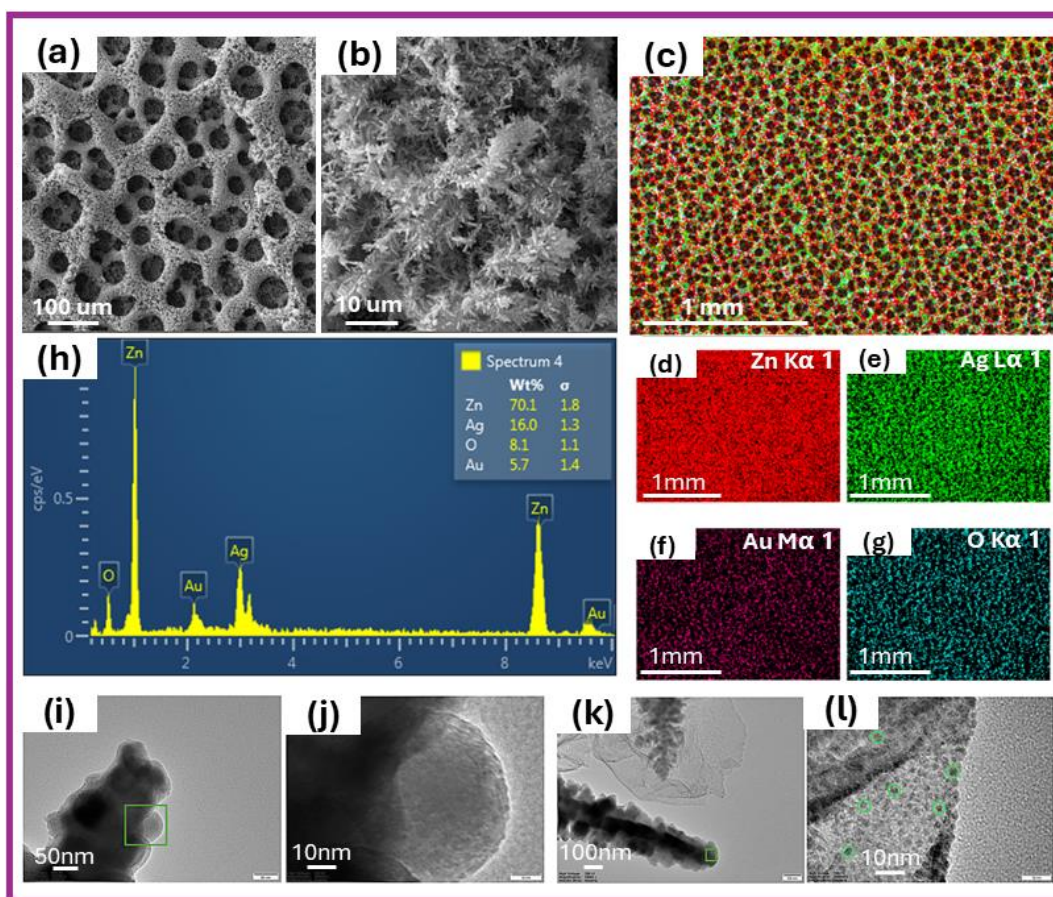


Figure 23. Catalyst morphological and compositional analysis; (a-b) FESEM images, (c-g) EDS mapping of 10sAu@Ag-Zn catalyst, (h) EDS spectrum

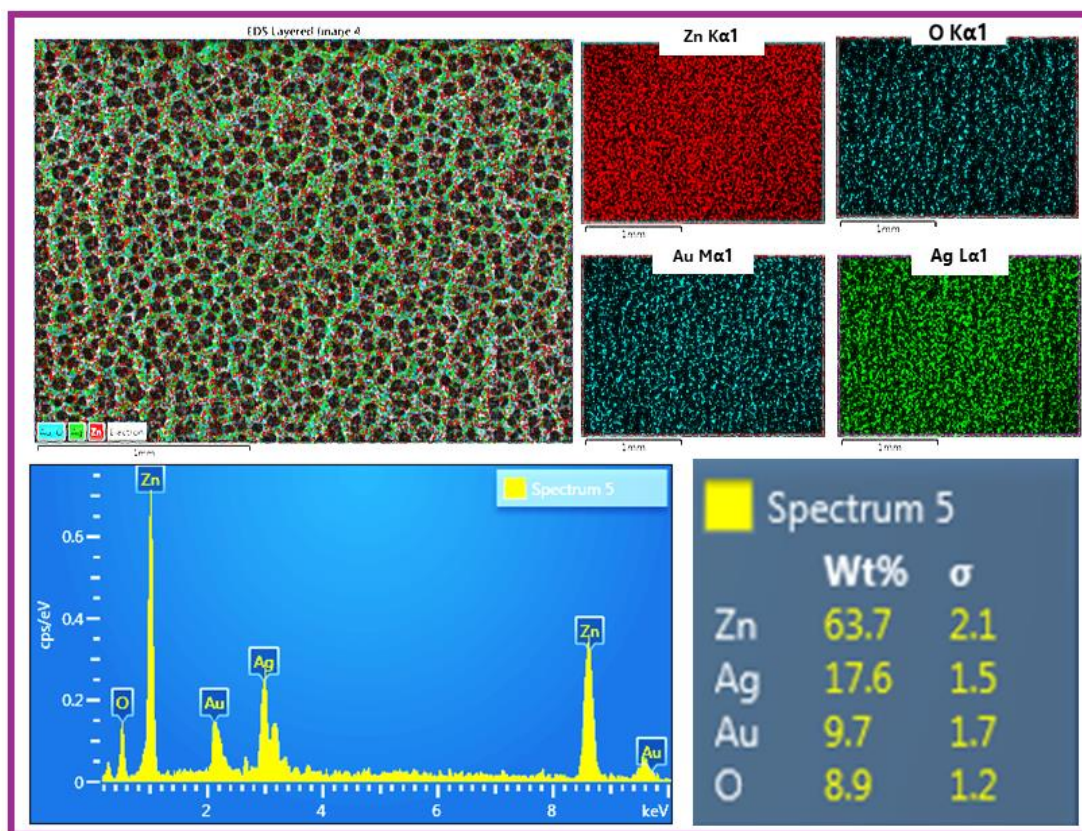


Figure 24. EDS mapping and composition spectrum of 20sAu@Ag-Zn catalyst

4.3. X-ray Diffraction analysis

As revealed by prior studies, bimetallic and ternary catalysts overperforms in CO₂ electroreduction rather than single atomic crystals due to the synergistic effects of more than one element or presence of homogenously mixed phases in catalyst [158][159].

The XRD spectra of Ag-Zn and Au sputter coated Ag-Zn thin film electrodes compared with the standard patterns shown in Fig. 24, which confirms the alloyed nature of the catalyst. The characteristic diffractions signals from Ag-Zn and all the Au@Ag-Zn electrodes at $2\theta = 36.78^\circ$, 40.48° , 42.2° , 56.18° , 66.14° , 75.34° corresponding to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) crystal planes showed exact matching with Ag_{0.5}Zn_{1.5} hexagonal phase of P6₃/mmc space group (CSD: 58386(ICSD), No: 01-072-5198).

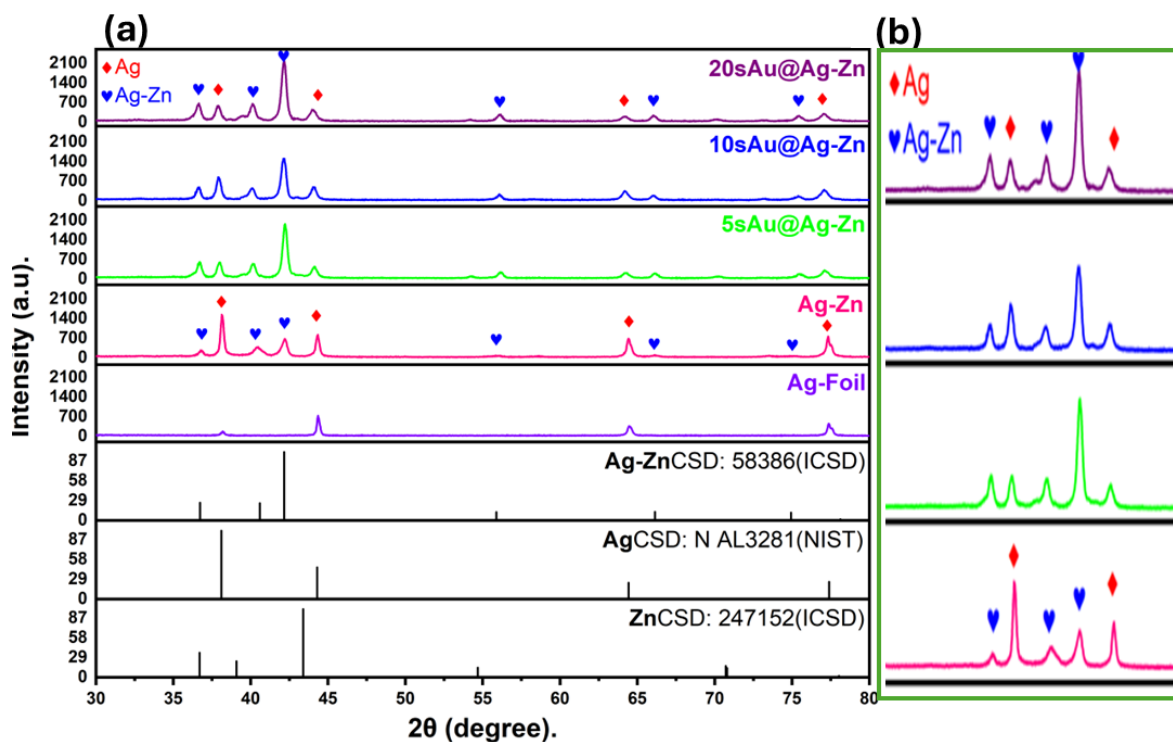


Figure 25. XRD spectra of Ag-Zn, 5Au@Ag-Zn, 10sAu@Ag-Zn and 20sAu@Ag-Zn before ECO₂RR compared with standards.

Among all the Au@Ag-Zn phase diffractions the peak belongs to (1 0 1) plane showed the highest intensity, highlighting preferential (1 0 1) orientation of Ag-Zn phase crystallites.

The other set of peaks in XRD spectra at $2\theta = 38.14^\circ, 44.36^\circ, 64.44^\circ, 77.34^\circ$ indexed as (111), (200), (220), (311) crystal planes of pure Ag (CSD: N AL3281(NIST) No: 03-065-2871). The broadening and change in intensity of Ag peaks relative to the Ag foil substrate, indicates the diffraction signals originates from catalyst layer not solely from the substrate due to not mainly small amount of Au at the surface of the Ag-Zn, instead high dispersion of Au as small nanoparticles by sputter coating, which results in poor crystallinity/amorphous structure of Au [160][161]. This was confirmed by 20s Au coating on glass substrate where no Au XRD signals was detected as in Fig. 25.

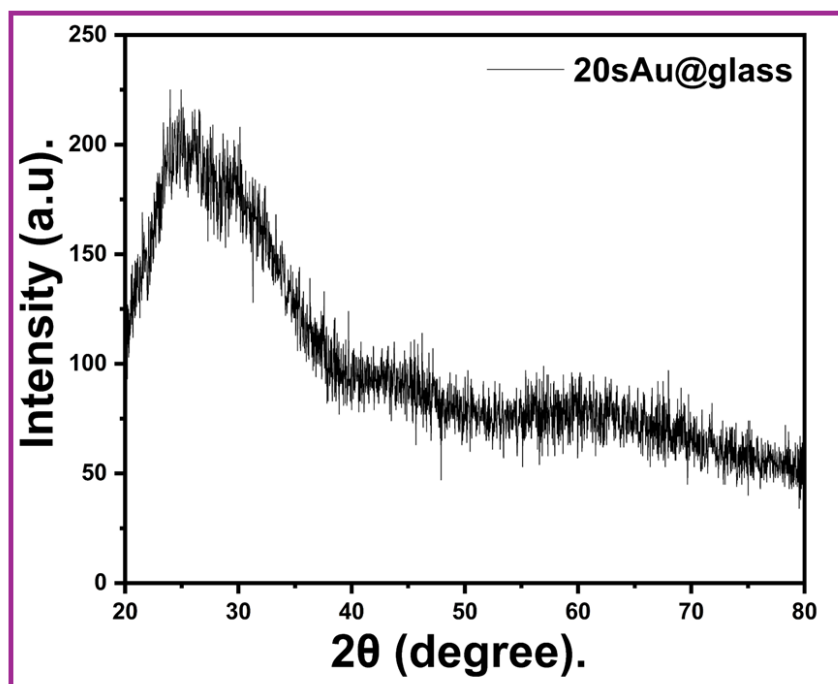


Figure 26. XRD spectra of 20s Au sputter coated on glass substrate

4.4. X-ray Photoelectron Spectroscopy

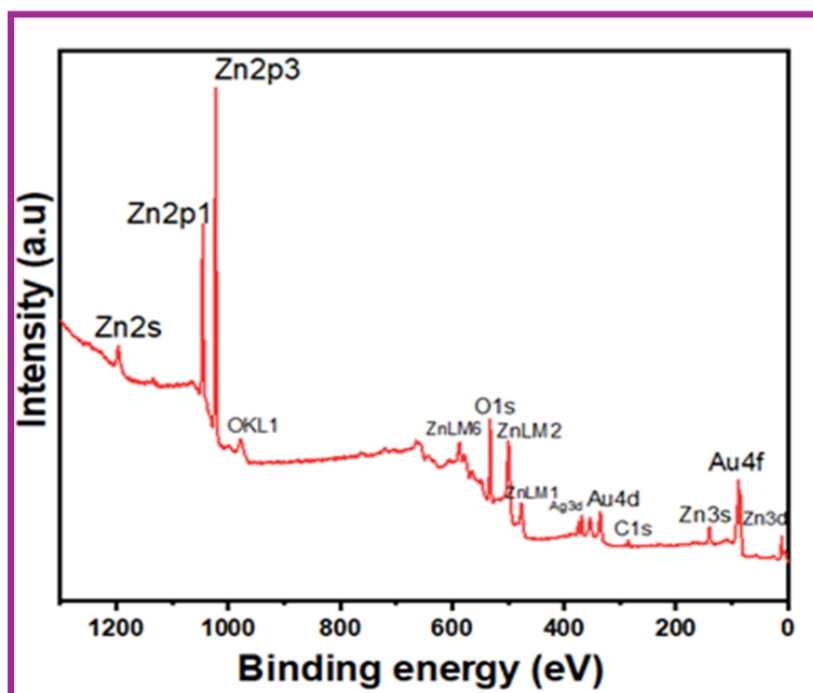


Figure 27. Survey scan spectra of 10sAu@Ag-Zn catalyst

The surface and near surface compositions and chemical states of the 10sAu@Ag-Zn catalyst was explored by X-ray Photoelectron Spectroscopy (XPS) analysis. The XPS survey scan shown in Fig. 26 represents Au deposited on the Ag-Zn surface, different from the XRD analysis where no obvious reflection of Au was detected. The prominent peaks of Au4f, Zn2p and Ag3d in XPS survey binding energy range 100-1300 eV revealed the presence of Au, Zn and Ag at the exposed surface of the catalyst where the surface coating of Au on Ag-Zn does not cover the complete Ag-Zn surface, in line with the EDS observations.

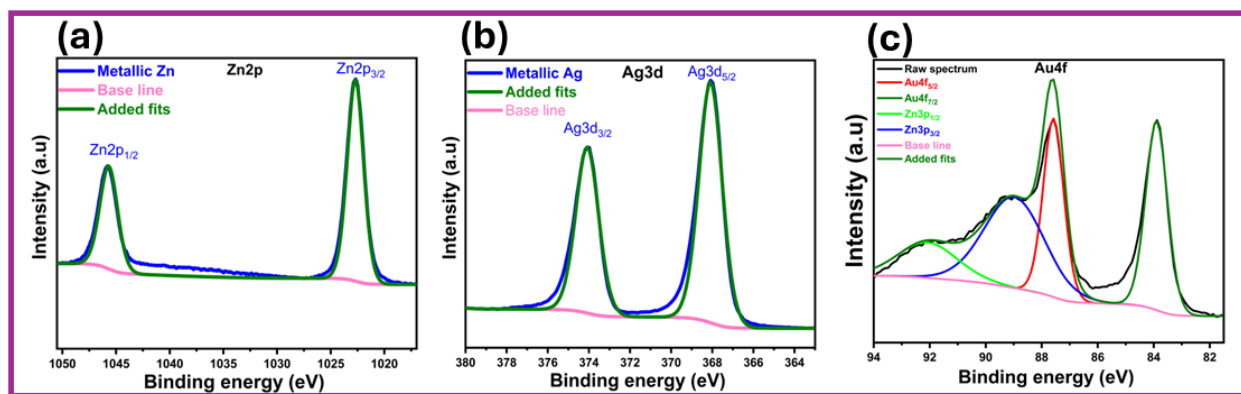


Figure 28. The high resolution XPS spectra of; (a) Zn2p, (b) Ag3d, (c) Au4f, of 10sAu@Ag-Zn catalyst

The high resolution XPS Zn2p doublet spectrum shown in Fig. 27(a), with Zn2p_{3/2} and Zn2p_{1/2} at 1021.7 eV and 1044.7 eV respectively. Here it is difficult to distinguish between Zn and ZnO because of their identical peak shape, position and Full width half maximum FWHM as well as Binding energy [162][163][164]. However, the presence of Zn²⁺ ions is still detectable in the present Zn2p high resolution photoemission from Fig. 28(a). Further, the photoemission reflection belongs to O1s shown in Fig. 28(b) conceivably deconvoluted into two individual peaks with the peak position at 530.7 eV and 532.9 eV specified to O²⁻ and due to O-metal bonding and adsorbed -OH species on the catalyst surface respectively [165].

To get insight into the bulk composition the surface of catalyst was etched few nanometers by Ar ions sputtering for 20 seconds during XPS analysis. The well identified binding energy of metallic Zn2P_{1/2}, Zn2P_{3/2}, and Ag3d_{3/2}, Ag3d_{5/2} is reported to be 1021.7 eV, 1044.7 eV and 374.5 eV, 368.5 eV respectively [162][166]. The depth profile high resolution XPS spectra of Zn2p and Ag3d after fitting charge shift taking C1s standard at 284.6eV shown in Fig. 27(a,b) reveals that a slight peak shift in Ag3d towards lower binding energy and of Zn2p towards the higher binding energy due to the transfer of electrons from Zn to Ag in Ag-Zn alloyed phase. The electronic interactions between Ag and Zn in bulk catalyst also indicates the formation of Ag-Zn alloy [9]. The Au4f high resolution spectra shown in Fig. 27(c). The Au 4f_{5/2} and Au4f_{7/2} peak at 83.9 eV and 87.9 eV respectively, belongs to metallic Au on the catalyst surface. Whereas the deconvolution of Au4f_{5/2} peak further into 3 identical peaks because of overlapping of binding energy between Au4f and Zn3p [167].

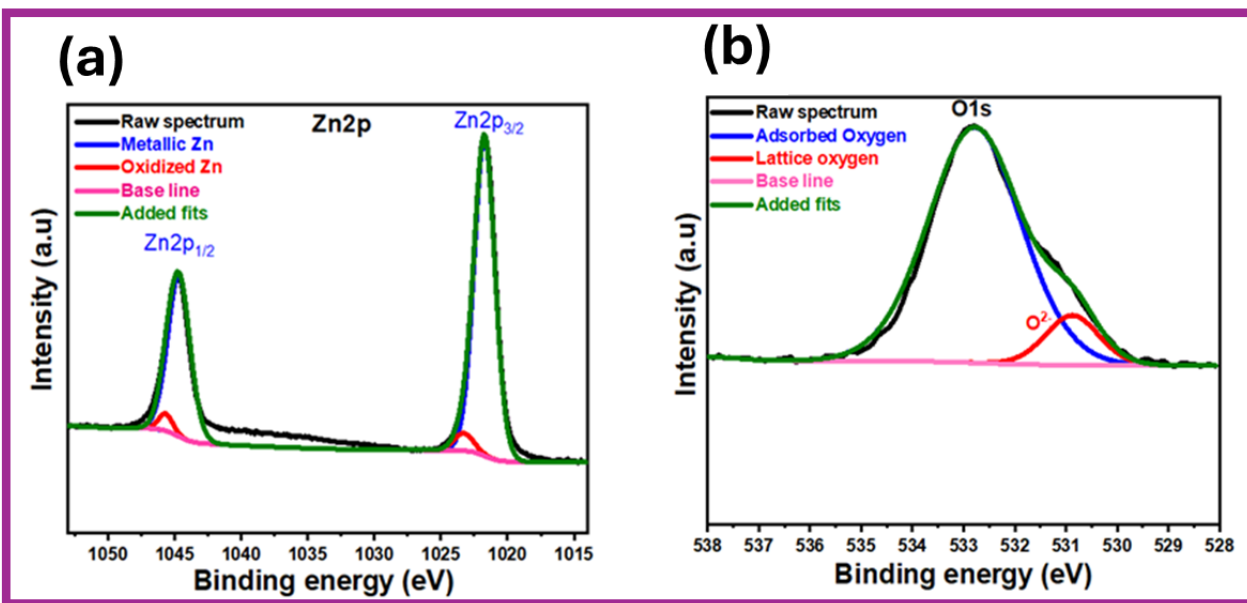


Figure 29. The high resolution XPS spectra of; (a) Zn2p spectrum of from catalyst surface (b) O1s spectrum of 10sAu@Ag-Zn catalyst

4.5. Transmission electron spectroscopy

Further to confirm the morphology at nanoscales of Ag-Zn thin films and Au decorated Ag-Zn electrocatalysts with the different concentration of Au deposition, transmission electron microscopy (TEM) analysis was performed for all the catalysts. Fig. 29-32 represents the TEM results, the morphology and the electron diffraction patterns of Ag-Zn, 5sAu@Ag-Zn, 10sAu@Ag-Zn and 20sAu@Ag-Zn respectively. The TEM results for all the catalysts confirms the formation of dendritic structure of at the nanoscale. The main focus of this analysis was to confirm the deposition of Au particles on the Ag-Zn surface. The selected area of the dendrite shown in Fig. 29-32(b), highlighted in green block was magnified upto 10nm resolution as shown in Fig. 29-32(c), and it there was not secondary atoms deposition was observed, only the single phase Ag-Zn dendritic structure exists in the catalyst.

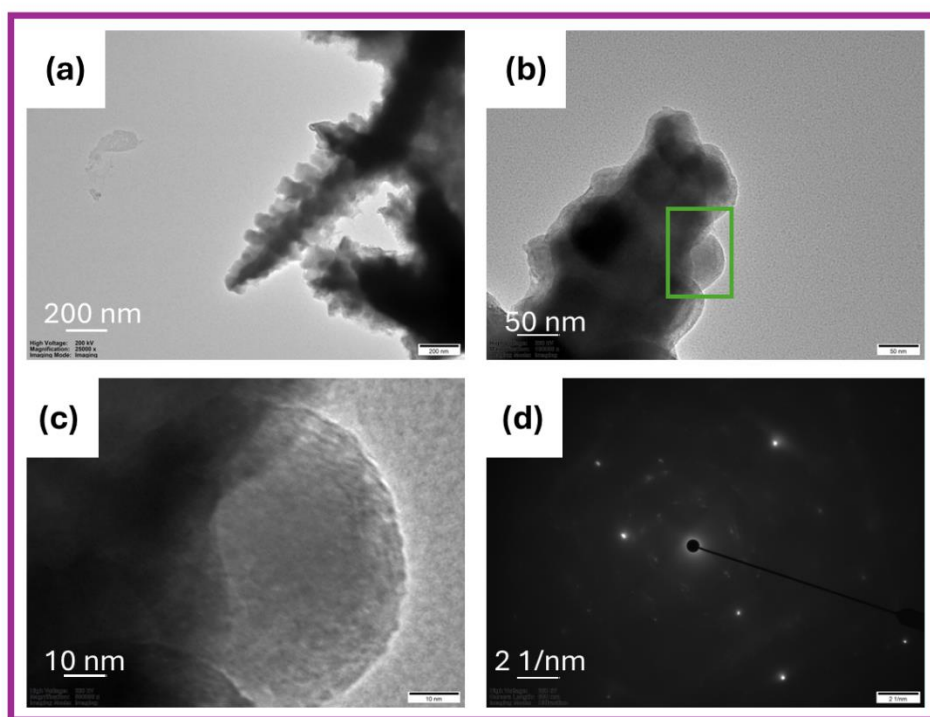


Figure 30. TEM images of Ag-Zn catalyst

However, in all the Au decorated Ag-Zn catalysts the Au particles was clearly observed as shown in Fig. 30(c), 31(c), 32(c), which confirms that successful deposition of Au particles by DC magnetron sputtering highlited in green circles on Ag-Zn catalyst surface. From the Fig. 30(c), 31(c), 32(c), it can be depicted that the concentration of Au on the catalyst surface increased with increasing the sputter deposition time which is in line with the results of EDS analysis. Combine TEM and EDS anylysis confirms the successful deposition of Au atoms on the Ag-Zn Dentrific structure and the concentration of Au incread from 4.3 wt% perecent to 9.7at% as shown in EDS- apctra in Fig. 20-23, with the increase Au sputter deposition time from 5s to 20s and the electron diffraction pattern of all the observed by TEM shows the polycrystalline naute of the catalyst

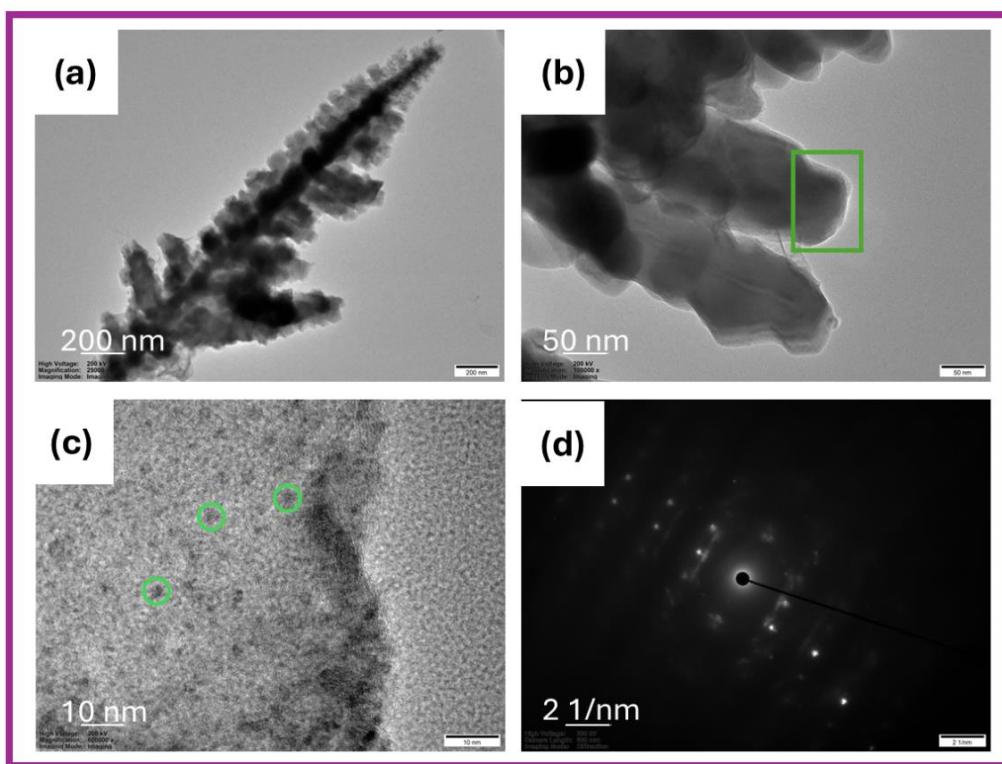


Figure 31. TEM images of 5sAu@Ag-Zn catalyst

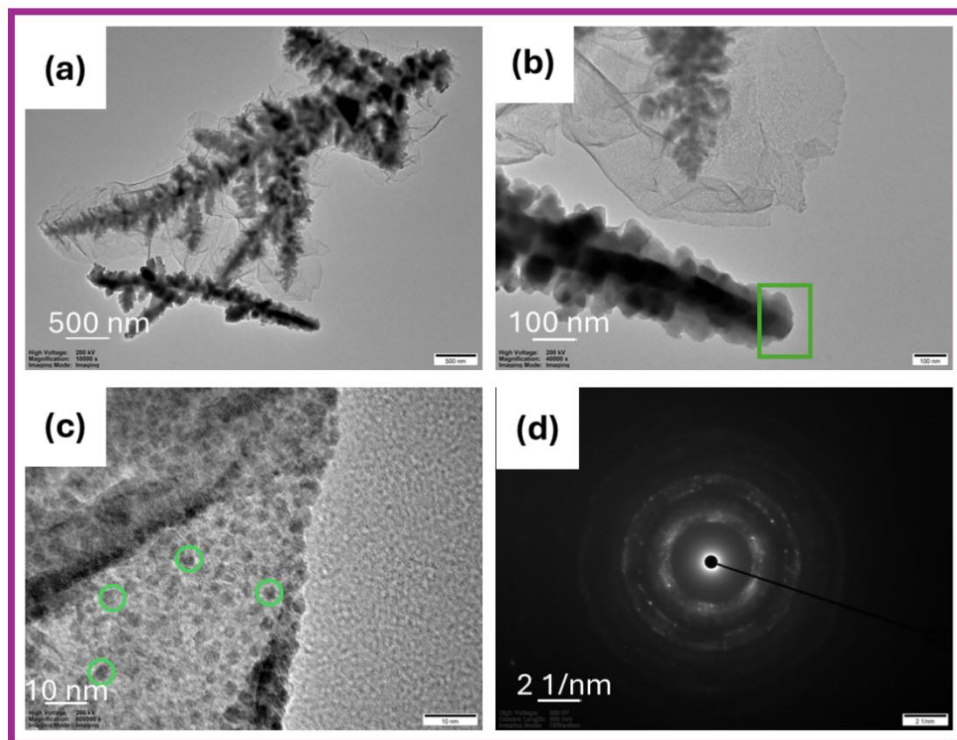


Figure 32. TEM images of 10sAu@Ag-Zn catalyst

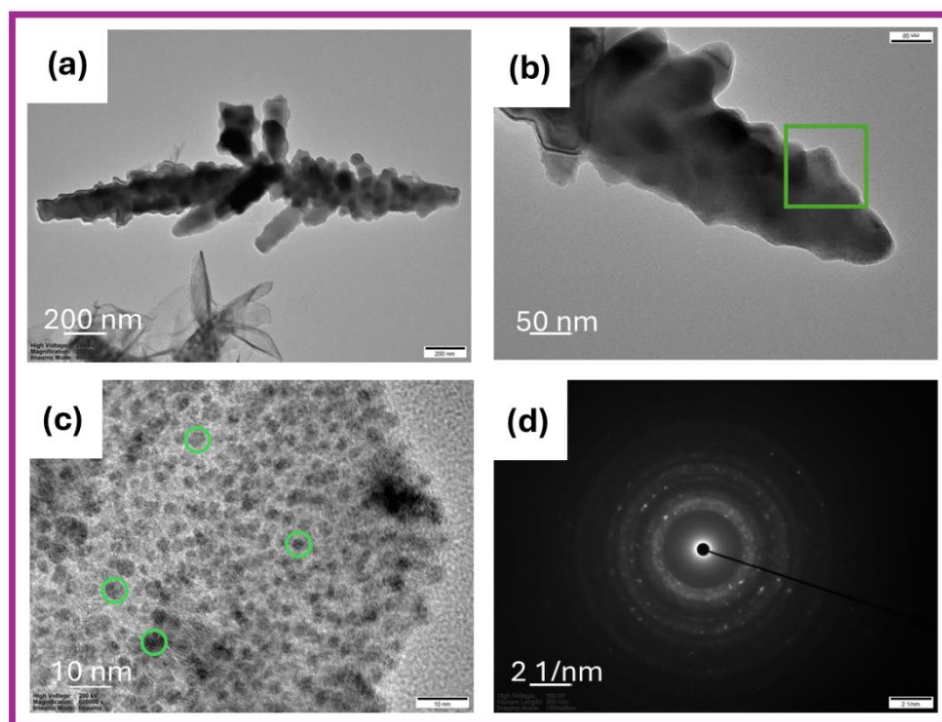


Figure 33. TEM images of 20sAu@Ag-Zn catalyst

4.6. Water contact angle measurements

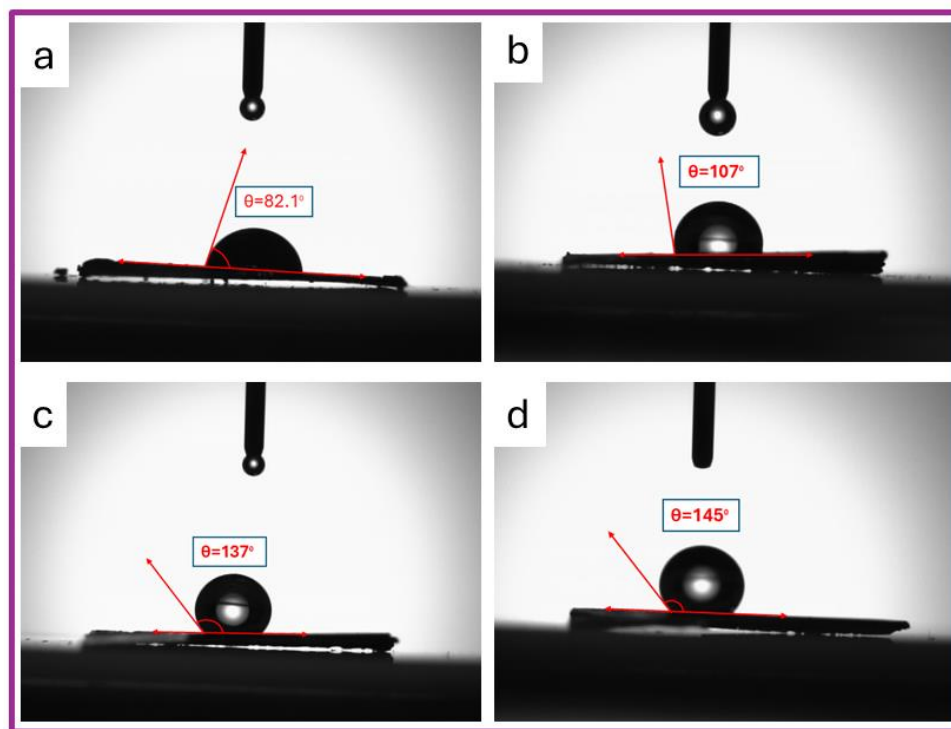


Figure 34. Wettability analysis of the catalysts; water contact angle measurements of (a) Ag-Zn, (b) 5sAu@Ag-Zn (c) 10sAu@Ag-Zn, (d) 20sAu@Ag-Zn catalyst.

CO₂ does not show remarkable solubility in aqueous media and excess availability of water molecules near electrocatalyst surface during CO₂RR favors the HER rather than CO₂ reduction. The hydrophobic nature of the electrocatalyst is a promising way for CO₂ to enrich local environment near catalyst surface to minimize the HER and efficiently reduce CO₂ [168]. Herein we tuned the Ag-Zn surface by sputtering Au on the Ag-Zn surface to obtain the hydrophobic nature of the catalyst in order enhance the CO₂ adsorption on the catalyst surface. To evaluate the wettability of Ag-Zn and Au coated Ag-Zn water contact angle (WCA) was measured. Fig. 33(a-d) highlights the WCA of Ag-Zn, 5sAu@Ag-Zn, 10sAu@Ag-Zn and 20sAu@Ag-Zn was 82.1°, 107°, 137°, and 145° respectively, reveals the hydrophilic nature of Ag-Zn binary catalyst and hydrophobic nature of Au deposited ternary catalysts where the 20s and 10s Au sputtered Ag-Zn

electrode exhibits maximum hydrophobic nature with the difference in WCA only 8°. The hydrophilic nature of the Ag-Zn is mainly due to Zn affinity to oxidize when exposed to the atmosphere. The formation of ZnO or Zn-OH on the catalyst face can attract water molecules. Whereas, after homogeneous distribution of Au atoms on the catalyst surface the major constituents exposed to the environment are Ag and Au forming hydrophobic porous environment at catalyst surface [169][170].

4.7. Electrochemical CO₂ reduction performance of the catalysts

All the electrochemical activities were performed in two compartment customized H-type cell shown in Fig. 34, equipped with Nafion-117 charge exchange membrane between cathodic and anodic chambers of the cell. To assess the electrochemical performance of Ag-Zn and Au decorated Ag-Zn catalysts, linear sweep voltammetry (LSV) analysis was performed from -0.2 to 1.4 V vs RHE, at a scan rate of 5mVs⁻¹ in 0.1M KHCO₃ electrolyte, saturated with Ar and CO₂. All the potential reported in this study was converted from Ag/AgCl into RHE.

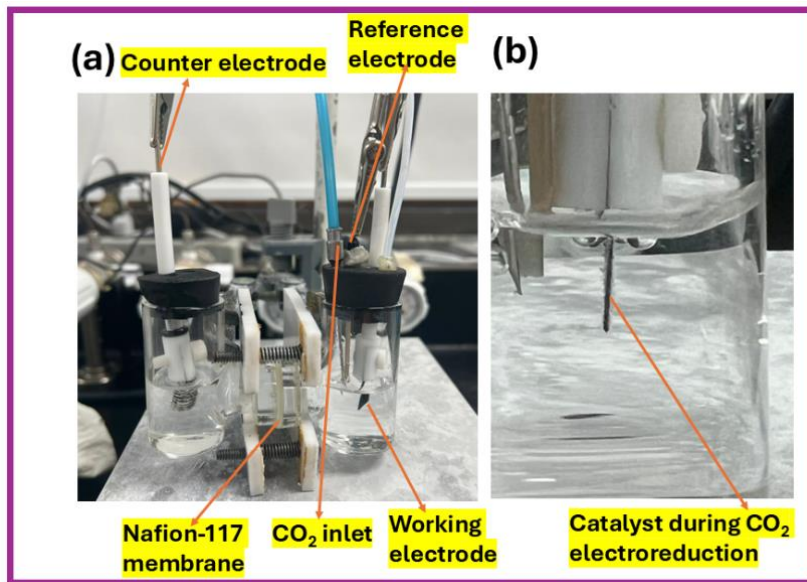


Figure 35. (a) Two compartment customized H-type cell, (b) photograph of the electrode dipped in 0.1M KHCO₃ taken during CO₂ electroreduction.

Each catalyst exhibits an increase in current density in CO₂ saturated solutions as compared to Ar atmosphere shown in Fig. 36(a) and Fig. 35(a-c) evidencing their catalytic activity towards ECO₂RR. The trend of increase in current density with the increase in onset potential was observed in all Ag alloyed Zn and Au coated Ag-Zn electrodes, till -1.3V vs. RHE and then become constant which is due to low solubility and mass transfer limitations of CO₂ in aqueous electrolyte [171]. Fig. 36(b) presents the current densities of all the electrodes at different potentials. However, the maximum total current density (j_{total}) at Ag-Zn electrode was achieved 25.85 mA cm⁻² at -1.2 V vs RHE.

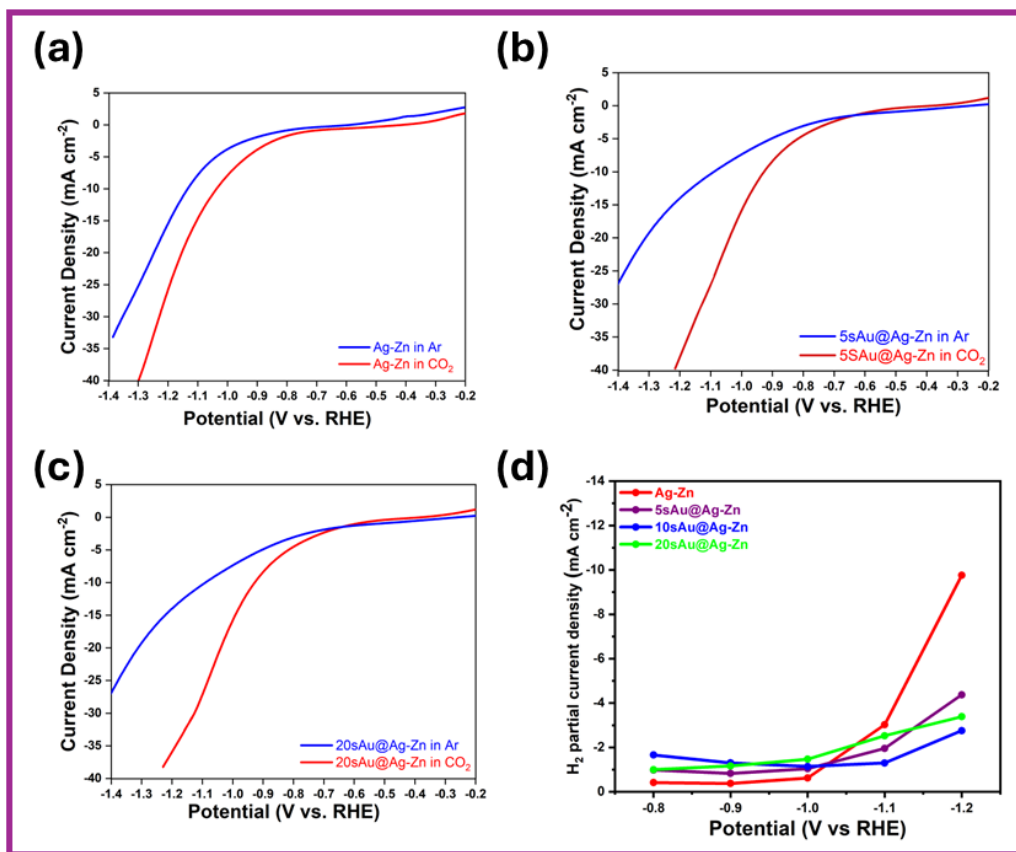


Figure 36. LSV curves of (a) Ag-Zn catalyst (b) 5sAu@Ag-Zn catalyst (c) 20sAu@Ag-Zn catalyst (d) H₂ partial current density of all the electrodes at different potentials.

In the potential range -0.8 V to -1.2V vs. RHE 10sAu@Ag-Zn electrode exhibits highest total and CO partial current density among all the electrodes reaching $-21.51 \text{ mA cm}^{-2}$ at -1 V vs RHE which further reached around -40 mA cm^{-2} at -1.3 V. Among all the catalysts 10sAu@Ag-Zn also exhibited the lowest onset reduction potential as depicted from in Fig. 36(a) and highest CO partial current density (j_{co}) from -0.8V to -1.2V vs. RHE can be depicted from Fig. 36(c) indicating that 10sAu@Ag-Zn can be the most efficient catalyst for CO₂ reduction in the potential range of -0.8 to -1.2V vs RHE.

Further to the ECO₂R performance of all the synthesized catalysts was evaluated in 0.1M KHCO₃ primarily saturated with CO₂ for 30 minutes with a constant flow rate 30ml/minute by applying constant potential pyrolysis. At lower potentials -0.5 to -0.7V vs. RHE the F.E towards CO remains less than 50 percent with the dominance of HER during the reduction process. Interestingly, at -0.8V the total F.E of all the electrodes was observed >90% with the major products formed CO and H₂. The maximum F.E_{CO} at -0.8V was achieved 79.5% at 10sAu@Ag-Zn electrode as shown in Fig. 36(d) whereas, Ag-Zn catalyst exhibited the minimum F.E_{CO} 73% at the same potential. To explore the optimum reduction potential for CO electroreduction, all electrodes were tested in potential window of -0.8 to -1.2V under same electrolytic and environmental conditions. Fig. 36(d) shows the FE of CO and H₂ at different potentials and trace amount of formic acid and acetic acid was observed only beyond -1V vs. RHE at 10sAu@Ag-Zn and the maximum F.E was achieved at -1V vs. RHE. A similar trend was observed as shown in Fig. 37(a-d), -1V vs. RHE to be the optimum potential towards CO production for Ag-Zn and Au decorated Ag-Zn catalysts. At more negative potentials H₂ evolution and formation of other trace products such as formate and Acetic acid becomes the major contribution of total current density which results in less selective CO production. For example, in Ag-Zn catalyst at -1V, F.E_{CO} and

$F.E_{H_2}$ were 90.4% and 7.8% respectively whereas, at -1.2V $F.E_{CO}$ reduced to 59.2% and H_2 increased to 20.8%, highlighting the less CO selectivity beyond -1V. The CO partial current density (j_{CO}) of all the catalysts at different potentials is represented graphically in Fig. 36(c). At the potential -1V vs RHE 10sAu@Ag-Zn catalysts showed the highest j_{CO} -20.26 mA cm⁻² and $F.E_{CO}$ 94.2% proved to be the best among all the fabricated electrodes for ECO₂R.

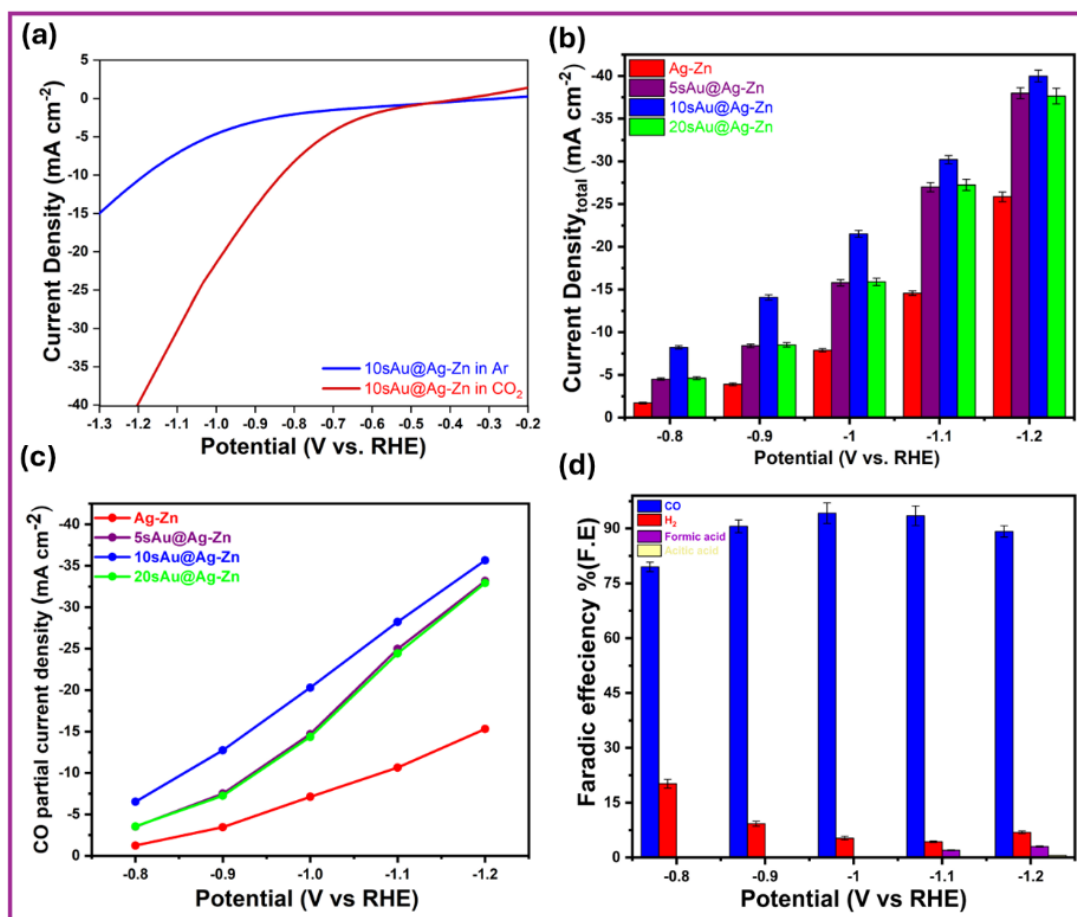


Figure 37. Electrochemical performance; (a) LSV of 10sAu@Ag-Zn catalyst in Ar and CO₂ saturated 0.1M KHCO₃, (b) Total current density, (c) CO partial current density of the Ag-Zn, 5sAu@Ag-Zn, 10sAu@Ag-Zn, and 20sAu@Ag-Zn electrodes at different potentials (d) F.E of all the products of 10sAu@Ag-Zn at different potentials.

Although 20sAu@Ag-Zn catalysts showed high total current densities at more negative potentials but the formation of formic acid and HER at high potentials results in less selectivity of

CO at 20sAu@Ag-Zn catalysts. As shown in Fig. 37(d), the combined F.E of HCOOH and H₂ for 20sAu@Ag-Zn is the highest at -1.2V vs. RHE among all the electrodes, and F.E_{CO} could be lower if a significant fraction of its current is going to other products. The 10s Au deposition, by contrast, appears to provide an optimal surface environment that specifically favors the CO pathway, thereby elevating CO share of the total current.

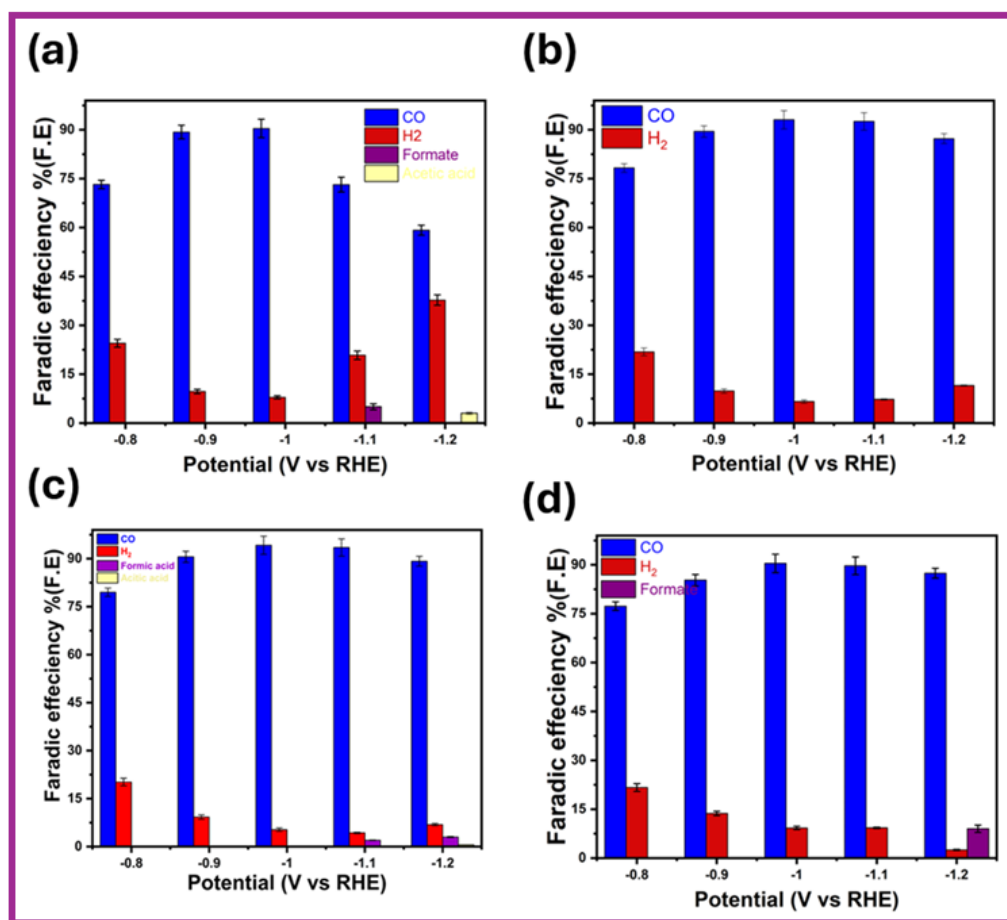


Figure 38. Faradic efficiency of all the products achieved by (a) Ag-Zn (b) 5sAu@Ag-Zn (c) 10sAu@Ag-Zn (d) 20sAu@Ag-Zn

Previously our group studied the Zn nanosheets for ECO₂R, and the maximum j_{co} was achieved -6.7mA cm⁻² with F.E_{CO} 89% at -1V vs RHE [172]. The Alloying of Ag with Zn is advantageous to improve the current density and CO selectivity. Alloying Ag with Zn and the

formation of dendritic like morphology of Ag-Zn and 10sAu@Ag-Zn catalysts surpassed the catalytic performance of Zn NS owing to the cooperative interplay between silver (Ag) and zinc (Zn), as observed in XPS analysis and high surface area and active sites available for CO₂ adsorption. From the XRD results, it can be depicted that the lowest intensity of (002) plane which is favorable site for H₂ evolution whereas, the preferential growth of (101) rough plane in all the Au decorated Ag-Zn electrodes can effectively stabilize *CO intermediates after protonation to produce CO, which is a rate limiting step for CO₂ to CO conversion [173]. Furthermore, the increase in the hydrophobicity by incorporation of Au on Ag-Zn surface indicates the increase in surface roughness of the catalysts. The increase in hydrophobicity without using PTFE or another hydrophobic agent is beneficial to expose the maximum intrinsic active sites during the reduction reaction. The Au decorated Ag-Zn catalysts hydrophobic nature and porous environment lead to increase in local PH and formation of three-phase interface which further favors the CO₂ reduction and minimizes H₂ evolution by suppressing the CO₂ mass transportation limitations [174].

In order to get insights into the catalytic properties of Ag-Zn and Au decorated Ag-Zn catalysts the double layer capacitance (CDL) was measured by the Cyclic voltammetry (CV) at different scan rates in non-faradic potential window as shown in Fig. 38(a,b) and Fig. 39(a,b). From the CDL measurement in the Fig. 39(c) it can be observed that all Au decorated Ag-Zn catalysts exhibit higher ECSA than bare Ag-Zn. The 10sAu@Ag-Zn electrode exhibits highest ECSA, around 2 folds higher value (5.28 mF cm⁻²) than Ag-Zn (2.57 mF cm⁻²), 1.9 and 1.3 folds higher than 5sAu@Ag-Zn and 20sAu@Ag-Zn respectively, in 0.1M KHCO₃, indicating a much higher electrochemical surface area (ECSA) and availability more active sites for CO₂ catalytic reduction, thereby improving catalytic activity by incorporation of Au on Ag-Zn surface [175].

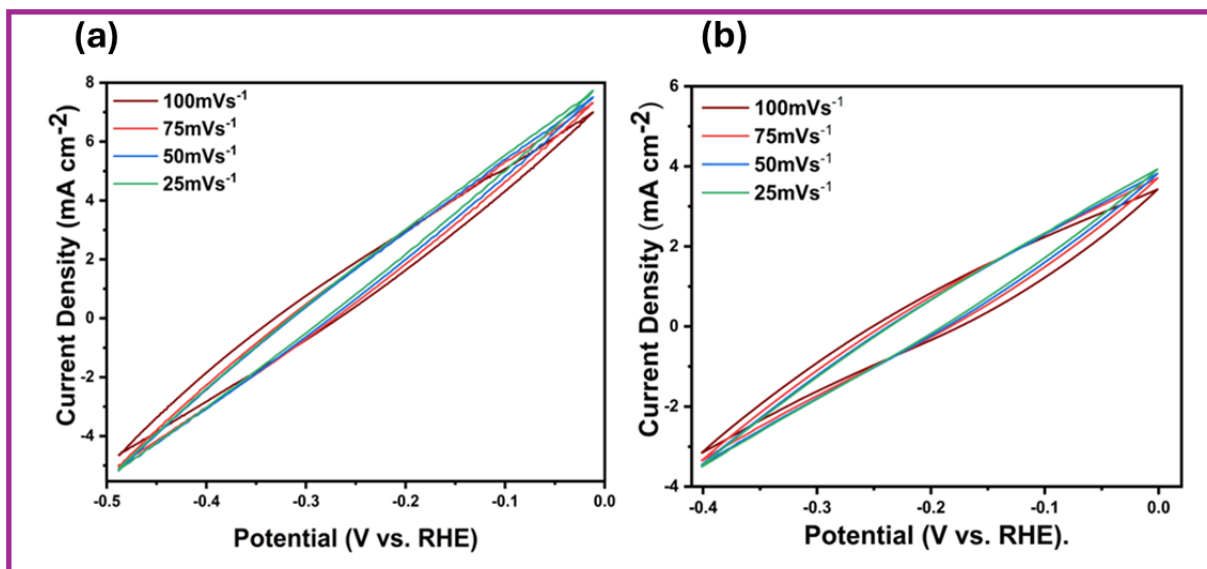


Figure 39. ECSA measurements; (a) CV curves of 5sAu@Ag-Zn; (b) CV curves of 20sAu@Ag-Zn in N₂ saturated 0.1M KHCO₃ in non-faradic potential regions at different scan rates.

Further, to verify the advantages of Au coating the charge transfer resistance of Ag-Zn and Au decorated Ag-Zn catalysts was determined by EIS analysis. The Nyquist plots of Ag-Zn and 10sAu@Ag-Zn electrodes is shown in Fig. 39(d), an equivalent electric-circuit was fitted by using Bio-logic EC Lab software which contains electrolyte resistance (R_s), double layer capacitance (C_{dl}), charge transfer resistance (R_{ct}), and Warburg impedance (Z_w) during reaction [176].

From the EIS observations it was confirmed that 10sAu@Ag-Zn exhibits much lower charger transfer resistance in comparison to Ag-Zn catalyst which indicates the fast charge transfer and high kinetics on 10sAu@Ag-Zn electrodes. Both the high availability of active sites and rapid kinetics to produce reaction intermediate by incorporation of Au reveals high intrinsic activity of 10sAu@Ag-Zn catalyst. These above findings suggest that the partial coverage of Au on Ag-Zn surface can provide more active sites and stabilize the key intermediates on the catalyst surface which leads to superior CO selectivity.

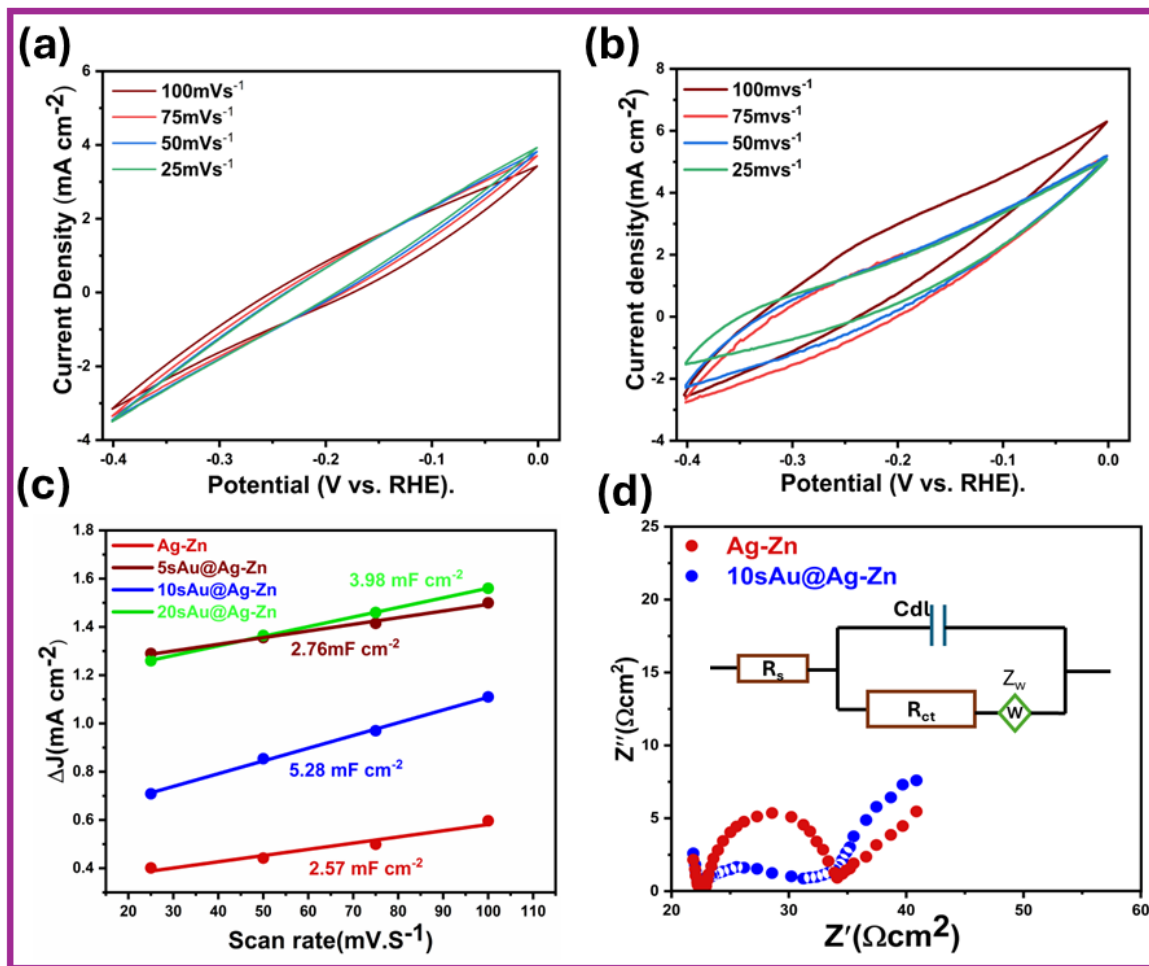
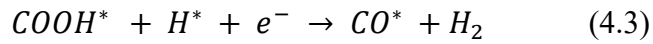
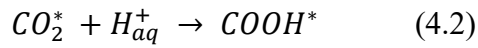
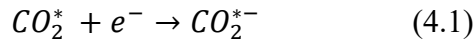


Figure 40. ECSA and EIS measurements; (a) CV curves of Ag-Zn; (b) CV curves of 10sAu@Ag-Zn in N₂ saturated 0.1M KHCO₃ in non-faradic potential regions at different scan rats, (c) ECSA measurements of Ag-Zn, 5sAu@Ag-Zn, 10sAu@Ag-Zn and 20sAu@Ag-Zn (d) EIS of Ag-Zn and 10sAu@Ag-Zn at -1V vs RHE.

4.7.1. CO₂ to CO reduction mechanism and catalyst stability

Since the CO₂ to CO conversion is two electron transfer process, the reaction intermediates formed after CO₂ protonation on catalyst surface highly depends on the catalyst nature, structure and chemical states of the elements present in the catalyst [177][178][179]. Tafel slope assists in determining the rate limiting step during CO₂ reduction to intermediates and finally into desired

product. To explore the underlying reaction mechanism and CO₂ reduction pathway we calculated the Tafel slopes of Ag-Zn and Au coated Ag-Zn catalysts represented in Fig. 40(d). The Tafel slope of 10sAu@Ag-Zn has the value of 274 mv/dec, which is very close to the theoretical 270 mv/dec [180], highlighting the conversion of CO₂ to CO* intermediate is a rate limiting step for 10sAu@Ag-Zn catalyst as shown in equation (4.1). However, the slope value in case of Ag-Zn is much higher than 10sAu@Ag-Zn, indicating that a small amount of Au on Ag-Zn surface can effectively improve the reaction rates for CO production, which is in-line with the ECSA and EIS analysis. The high value of Tafel slopes appears due to the requirement of high reduction potential for Zn-based catalysts to produce adequate amount of CO from CO₂ for plotting the Tafel slope [181]. As a result, the reaction pathway for CO₂ to CO conversion on Ag-Zn and 10sAu@Ag-Zn catalyst can be suggested as follows.



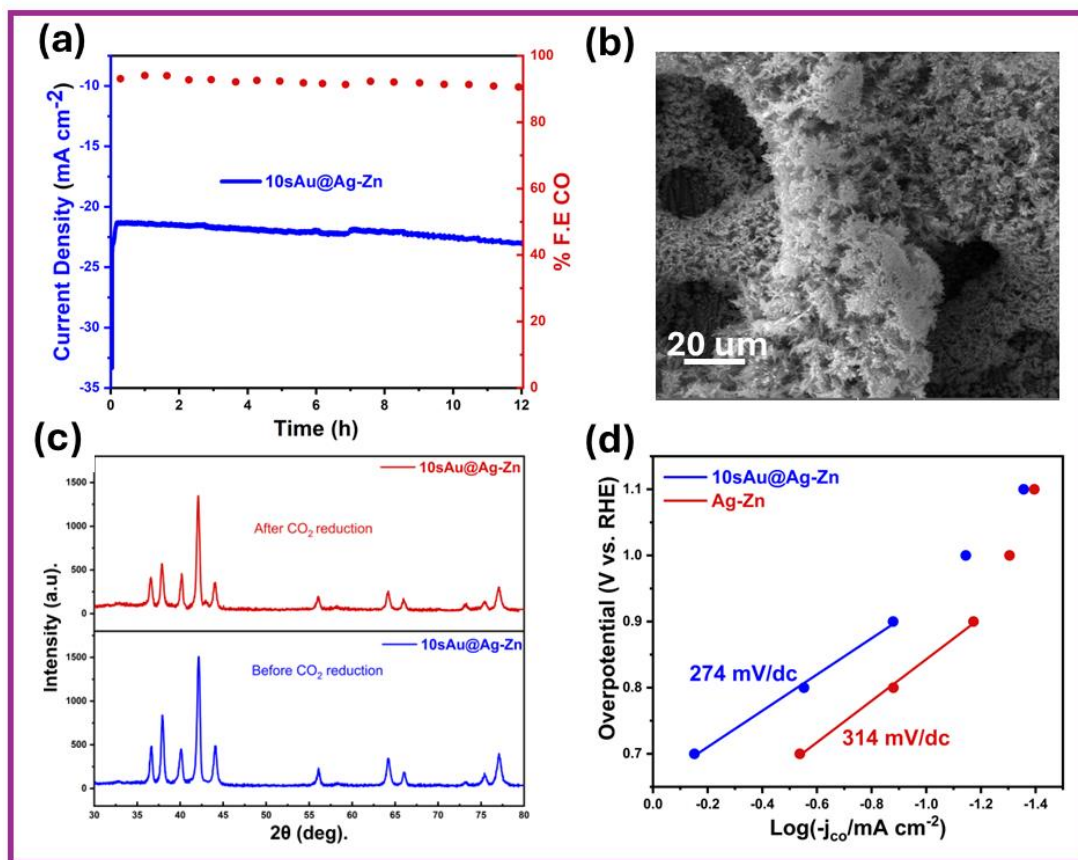


Figure 41. (a) Long-term stability test of 10sAu@Ag-Zn, (b) FE-SEM of 10sAu@Ag-Zn after ECO₂R, (c) XRD spectra of 10sAu@Ag-Zn before and after electrolysis, (d) Tafel slopes of Ag-Zn and 10sAu@Ag-Zn catalysts.

Additionally, the chronoamperometry results of 5sAu@Ag-Zn and 20sAu@Ag-Zn obtained during 1h CO₂ electrolysis at different potentials as shown in Fig. 41 which indicates the stable CO₂ reduction on Au decorated Ag-Zn catalysts in the potential window of -0.8V to -1.2V vs. RHE, as both the 5sAu@Ag-Zn and 20sAu@Ag-Zn does not exhibit noticeable variations in current density during CO₂ electrolysis.

Owing to the significance of the long-term stability the continuous electrolysis of Ag-Zn and 10sAu@Ag-Zn electrodes was analyzed by the chronoamperometry at -0.1V vs RHE. Ag-Zn samples remained stable without noticeable decrease in current density for 5h, after that the current

density and CO FE start decreasing continuously with time and maintained above 79% in 5h stability analysis as shown in Fig. 42.

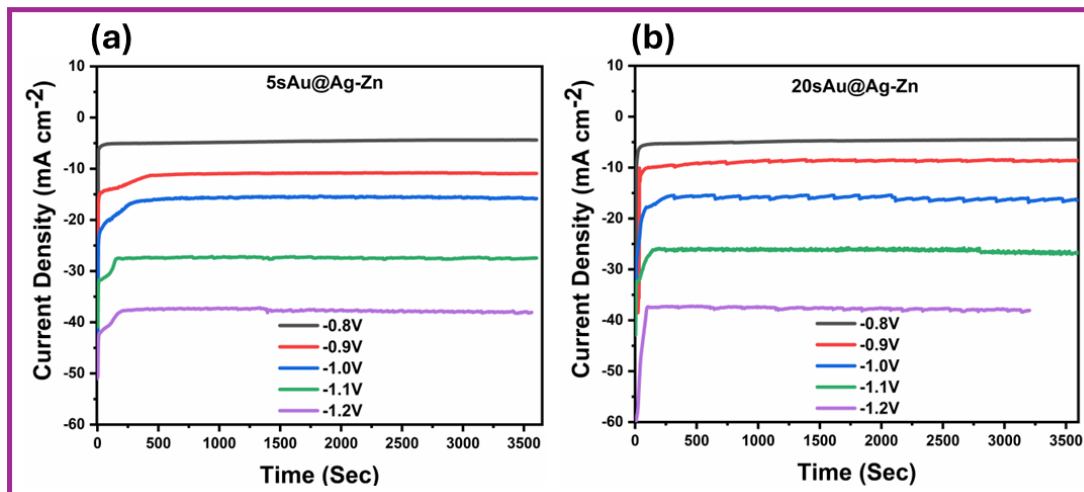


Figure 42. Chronoamperometry of (a) 5sAu@Ag-Zn and of (b) 20sAu@Ag-Zn catalysts during CO₂ electrolysis.

The current density of the 10sAu@Ag-Zn remained stable more than 12h during continuous electrolysis as shown in Fig. 40(a), which is 2.4 folds higher than Ag-Zn electrodes, with a remarkable F.E_{CO} maintained above 90%. The minor variations in the current density were observed during stability analysis which might be due to the continuous bubbles built-up on the catalyst surface as shown in Fig. 34(b). The remarkable increase in stability of 10sAu@Ag-Zn clearly due to the incorporation of Au which modifies the electronic structure on Ag-Zn surface and prevents the Zn dissolution and redeposition on the catalyst surface. XRD and SEM characterization of 10sAu@Ag-Zn after ECO₂RR shown in Fig. 40(b,c). The existence of the same phases with insignificant changes in morphology and composition after CO₂ reduction unveils the excellent stability of Au coated Ag-Zn catalysts.

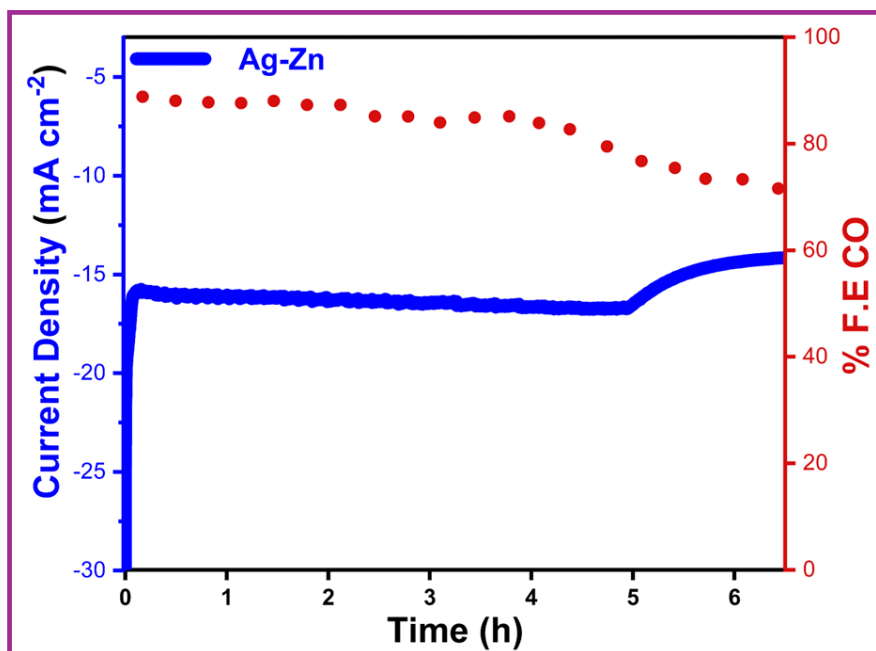


Figure 43. Long-term stability analysis of Ag-Zn catalyst.

In alloyed nanostructures atomic migrations can take place during ECO₂RR, which result in complicated element redistributions by alloying, dealloying and agglomeration of atoms at nanoscale depending on the elements type, atomic concentrations and reaction conditions. The atomic migrations are dependent on the intrinsic features of the elements. The dynamic evolutions of noble metals such as Au are relatively moderate than the active materials such as Zn due to the formation of energy barriers in noble metal lattices. As for Zn, the structure reconstruction occurs frequently during catalysis. Furthermore, the high curvature morphology of the catalysts possesses high surface energy is relatively vulnerable during ECO₂RR which leads to deformation high surface morphology, such as smoothening of high curvature sites by aggregation of particles. These structure evolutions in the catalysts e.g. surface energy, porosity, charge transfer, conductivity and adsorption energy alter the catalytic intrinsic properties, ultimately affecting the catalyst activity, selectivity and stability [182][183].

4.7.2. Insight to relative lower stability of Ag-Zn than 10sAu@Ag-Zn catalyst

Further to inspect the relative lower Ag-Zn activity and stability than 10sAu@Ag-Zn, XRD, SEM and EDS analysis of Ag-Zn catalyst after ECO₂RR was performed to observe structural and morphological changes as shown in Fig. 44(a-f). The appearance of Zn peaks along Ag-Zn phase in XRD spectrum in Fig. 44(a), demonstrates the dealloying behavior of Zn due to the atomic migrations of Zn from Ag-Zn alloyed phase during ECO₂RR. Furthermore, the SEM image as shown in Fig. 44(b), highlights the smoothening of high curvature Ag-Zn dendrites during the reduction reaction, which leads to deformation of high surface Ag-Zn morphology. These structural and morphological evolutions of Ag-Zn electrodes alter the catalytic intrinsic properties such as surface energy, porosity, charge transfer, conductivity and adsorption energy, ultimately affecting the catalyst activity and stability. No impurities detection in EDS mapping shown in Fig. 44(c-f) confirms that the low stability and activity of Ag-Zn electrodes are mainly due to structure and morphological evolutions during CO₂ electroreduction.

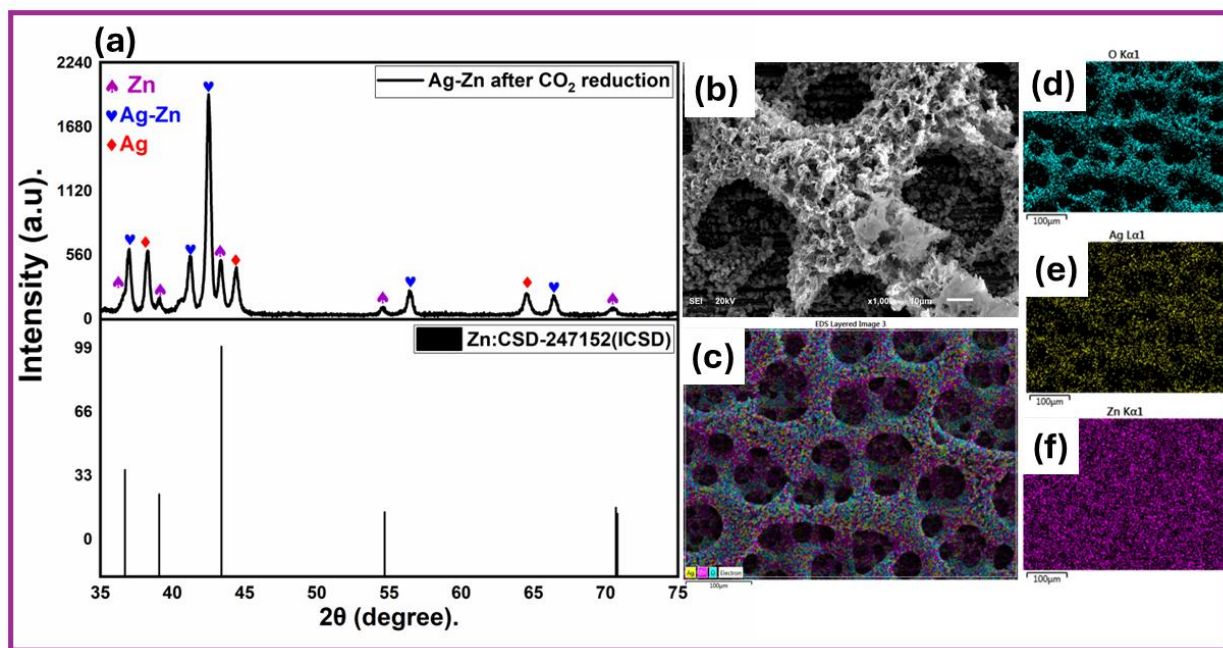


Figure 44. Ag-Zn catalyst analysis after CO₂ reduction (a)XRD spectrum, (b) SEM image and, (c-f) EDS mapping.

Table 6. Previously reported similar catalysts for electrochemical CO₂ reduction.

Catalyst	Cell type	Reduction potential	F.E CO	Stability	References
Porous Zn	H-cell	-1.66V vs. Ag/AgCl	80 %	-	[184]
ZnO	H-cell	-2.4V vs. Ag/AgCl	90%	5 h	[185]
Nanostructured Zn	H-cell	-1.1V vs. RHE	80%	12 h	[186]
ZnO nanoparticles	Flow-cell	-	80%	10 h	[187]
Zn foam	Flow-cell	-	80%	10 h	[188]
ZnO	H-cell	-0.8V vs. RHE	-	2 h	[189]
ZnAg foam	microchannel electrolyzer	-	92.1%	10 h	[190]
Zn-nanosheets	H-cell	-1V vs. RHE	89.5	10 h	[191]
Zn-Ag	H-cell	-1V vs. RHE	70%	-	[192]
(ZnO) ₃ @Ag	H-cell	-1.1V vs. RHE	84.6%	8 h	[193]
AgZn	H-cell	-1.0 V vs. RHE	84.2%	9 h	[194]
Ag-Zn	H-cell	-1V vs. RHE	90%	>5 h	This study
Au@Ag-Zn	H-cell	-1V vs. RHE	94.2%	>12 h	This study

CHAPTER 5

RESULTS AND DISCUSSION

Project 2

Chapter 5. Synthesis and characterization of sputtered modified Bi@Ag-Zn thin films for electrochemical CO₂ reduction

Bi is an earth abundant non-toxic and cheap material as compared to Au which can be used to modify the Ag-Zn alloyed catalysts to improve catalytic performance. The focus of the study is to further reduce the cost of Ag-Zn based catalysts using a non-noble metal to modify the catalysts properties. The Bi@Ag-Zn catalysts was fabricated via two-step synthesis strategy, electrodeposition followed by magnetron sputtering technique. The Ag-Zn thin films was fabricated by constant current electrodeposition using ZnSO₄·7H₂O and AgNO₃ metallic salt solutions as a source of Zn and Ag respectively. The Bi@Ag-Zn catalysts was prepared by Bi sputter coating on electrodeposited Ag-Zn thin films. Many physical and electrochemical characterization techniques were used to study the properties and electrochemical performance of the fabricated catalysts. In the present study we synthesized porous Bi decorated Ag-Zn catalysts, where the concentration of Bi (6-21 wt%) is incorporated by magnetron sputtering in co-electrodeposited Zn-Ag alloy to explore the effect of Bi on the activity and efficiency of bimetallic Zn-Ag electrodes towards CO selective reduction of CO₂. In our study we designed catalysts, keeping Zn as major constituent alloyed with Ag whereas, Bi (7.6 wt%) on the Ag-Zn surface further improved CO selectivity 93.5% F_{ECO} and j_{co} -68.2mA cm⁻² in Nafion-117 separated two compartment H-type cells. These findings indicate the potential of Bi decorated Ag-Zn thin films as promising catalyst for sustainable CO production.

5.1. Field Emission Scanning Electron Microscopy

Field Emission Scanning Electron Microscopy (FE-SEM), was used to morphological properties of the Ag-Zn and Bi decorated Ag-Zn catalysts. Fig. 45(a-h), represent the morphology of Ag-Zn, 30sBi@Ag-Zn, 1mBi@Ag-Zn and 2mBi@Ag-Zn electrodes, obtained by FE-SEM at different magnifications.

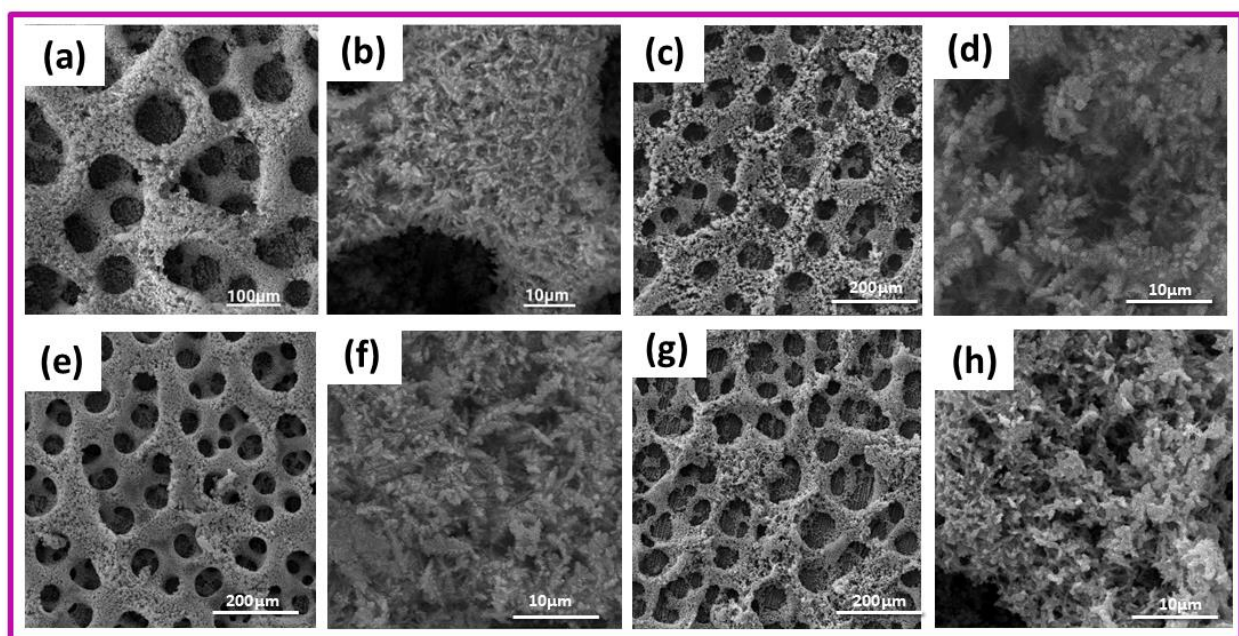


Figure 45. FE-SEM analysis of Bi@Ag-Zn catalysts at different magnification, (a,b) Ag-Zn, (c,d) 30sBi@Ag-Zn, (e,f) 1mBi@Ag-Zn, (g,h) 2mBi@Ag-Zn catalysts morphology

SEM analysis demonstrates the successful synthesis of highly porous Bi@Ag-Zn catalysts, having a foam like morphology similar as was observed in Au modified Ag-Zn catalysts. These morphology was achieved by co-electrodeposition of Ag and Zn followed by DC magnetron sputter deposition of Bi onto the Ag-Zn thin films surface. During electrodeposition, along with the metal ions reduction constant evolution of hydrogen bubbles at the cathode surface, results in the pores formation in the thin films of the catalysts [156].

The highly porous Ag-Zn foam with the preferential growth of Ag-Zn dendrites surrounding the micropores provides high surface area and active sites for ECO₂R. Moreover, Ag-Zn structure remained intact with the homogeneous distribution of Bi sputtered atoms at the surface. The dendritic Ag-Zn structure observed around the micropores further favors the catalytic efficiency. These dendrites not only increase the surface roughness but also facilitate effective mass transport of CO₂ and electron transfers during ECO₂RR.

5.2. Energy-dispersive x-ray spectroscopy

Quantitative analysis from the EDS data reveals the weight percentage composition of Zn is a significant portion of the catalyst. The presence of Oxygen in the EDS spectrum indicates that surface oxidation process converts the exposed zinc into a thin layer of ZnO. This is attributed to the inherently high sensitivity and reactivity of metallic Zn toward environmental oxygen especially when it is exposed to atmospheric conditions during the characterization and transportation of the samples after synthesis process. This spontaneous Zn oxidation leads to the formation of a thin native oxide layer on the catalyst surface which was confirmed by the appearance of a distinct oxygen peak in the EDS composition [157].

It is important to highlight that the surface oxide layer in the electrodes does not affect the performance of the catalysts in ECO₂RR. It has been reported that the native oxide layer of Zn rapidly reduced to metallic Zn under the reducing conditions that are applied during the CO₂ electroreduction which helps to study the intrinsic activity of pure metallic Zn based electrodes. Furthermore, the Au is highly active material towards CO₂ to CO reduction, and a small amount of it can not only improve catalytic efficiency but also helps to improve the charge transfer properties and prevents the further undesired oxidation during the long-term reaction conditions. Furthermore the EDS spectrum of the Bi decorated Ag-Zn thin films highlights that the

concentration of Bi in the catalysts is proportionally increasing with the sputtering time as shown in Fig. 46(a-f). The amount of Bi was detected 6.25 wt% in 30sBi@Ag-Zn which increased 7.64 wt% in 1mBi@Ag-Zn and 20.7 wt% in 2mBi@Ag-Zncatalyst.

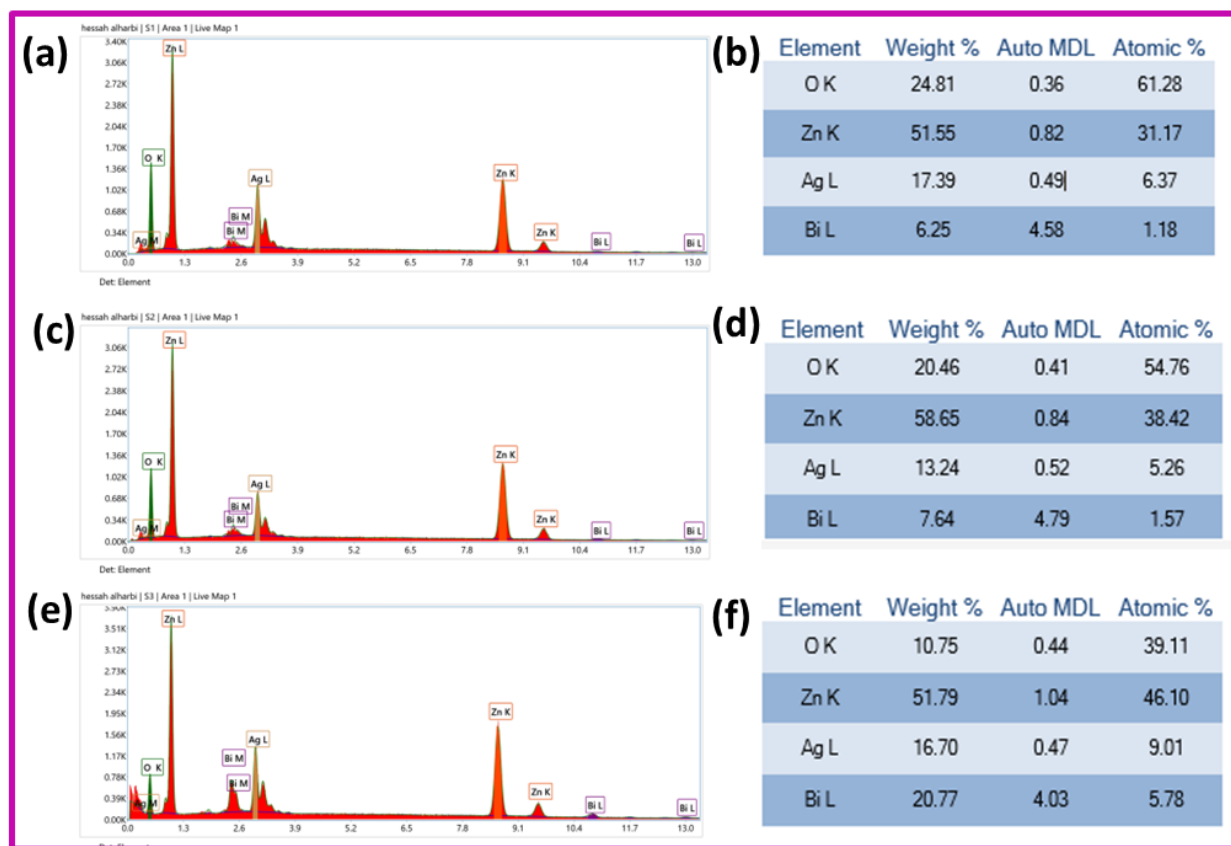


Figure 46. EDS spectra and elemental composition of (a, b) 30sBi@Ag-Zn, (c, d) 1mBi@Ag-Zn and (e, f) 2mBi@Ag-Zn

5.3. X-ray Diffraction analysis

The XRD spectra of Ag-Zn and Bi coated Ag-Zn thin film electrodes compared with the standard patterns shown in Fig. 47, which confirms the alloyed nature of catalysts. The characteristic diffractions signals from Ag-Zn and all the Au@Ag-Zn electrodes at $2\theta = 36.78^\circ$, 40.48° , 42.2° , 56.18° , 66.14° , 75.34° corresponding to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) crystal planes showed exact matching with $\text{Ag}_{0.5}\text{Zn}_{1.5}$ hexagonal phase of P63/mmc space group (CSD: 58386(ICSD), No: 01-072-5198).

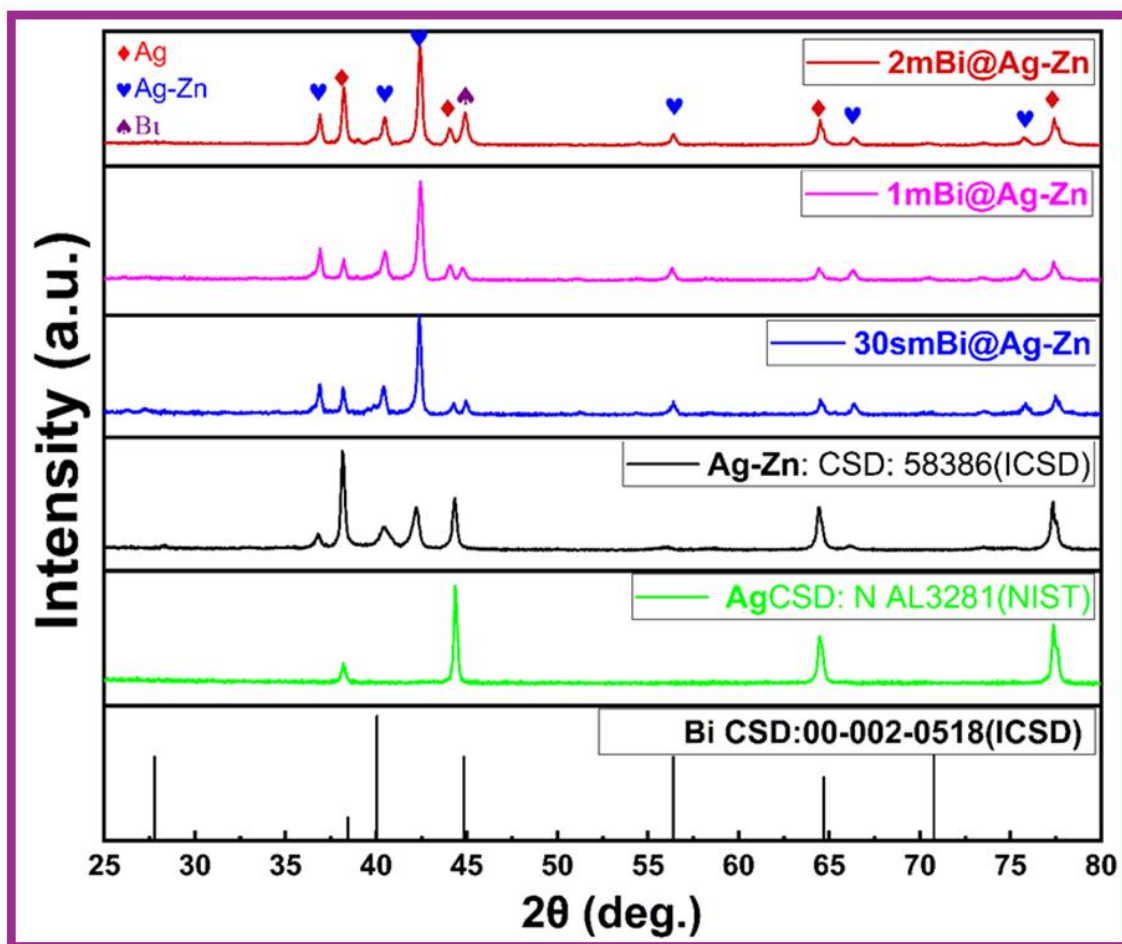


Figure 47. XRD spectra of Ag-Zn, 30sBi@Ag-Zn, 1mBi@Ag-Zn and 2mBi@Ag-Zn compared with standards.

Among all the Bi@Ag-Zn phase diffractions the peak belongs to (101) plane showed the highest intensity, highlighting preferential (101) orientation of Ag-Zn phase crystallites. The other set of peaks in XRD spectra at $2\theta = 38.14^\circ, 44.36^\circ, 64.44^\circ, 77.34^\circ$ indexed as (111), (200), (220), (311) crystal planes of pure Ag (CSD: N AL3281(NIST) No: 03-065-2871). The characteristic peak in Bi sputter coated samples appeared around 44.89° and the intensity of the Bi peak increased with increasing the concentration of Bi by increasing the sputtering time.

5.4. Water contact angle measurements

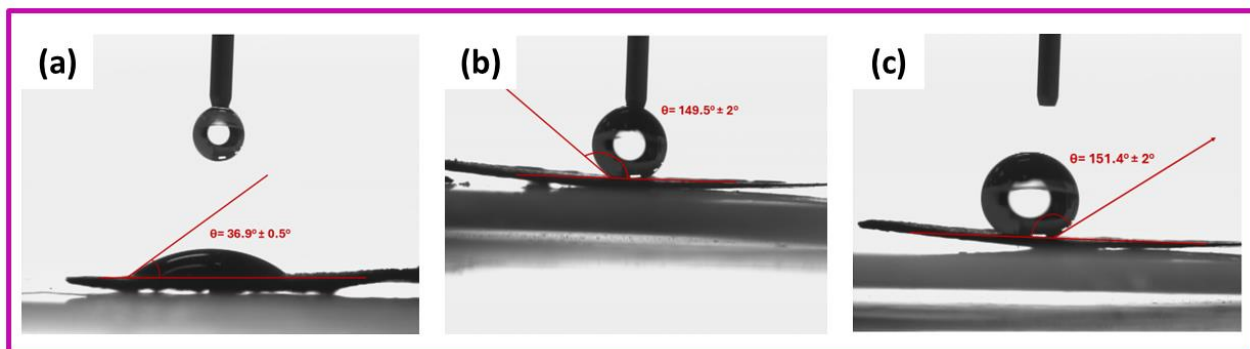


Figure 48. Wettability analysis of the catalysts; water contact angle measurements of (a) 30sBi@Ag-Zn (b) 1mABi@Ag-Zn, (d) 2mBi@Ag-Zn catalyst.

As mentioned earlier CO_2 does not show remarkable solubility in aqueous media and excess availability of water molecules near electrocatalyst surface during CO_2RR favors the HER rather than CO_2 reduction. The hydrophobic nature of the electrocatalyst is a promising way for CO_2 to enrich local environment near catalyst surface to minimize the HER and efficiently reduce CO_2 [168]. Herein, we tuned the Ag-Zn surface by sputtering Bi on the Ag-Zn surface to obtain the hydrophobic nature of the catalyst in order enhance the CO_2 adsorption on the catalyst surface. To evaluate the wettability of Ag-Zn and Bi coated Ag-Zn WCA was measured. Fig. 48(a-c) highlights the WCA of 30sBi@Ag-Zn, 1mBi@Ag-Zn and 2mBi@Ag-Zn was 36.9° , 149.5° , and 151.4° respectively, reveals the hydrophilic nature of Ag-Zn binary catalyst and hydrophobic nature of 7.67 wt% and 20.77 wt% Bi coated ternary catalysts where the 1m and 2m Bi sputtered Ag-Zn electrode exhibits maximum hydrophobic nature. The hydrophilic nature of the Ag-Zn and 30sBi@Ag-Zn is mainly due to Zn affinity to oxidize when exposed to the atmosphere. The formation of ZnO or Zn-OH on the catalyst face can attract water molecules. Whereas, after homogeneous distribution of Bi atoms on the catalyst surface the major constituents exposed to the environment are Ag and Bi forming hydrophobic porous environment at catalyst surface [169][170].

5.5. Electrochemical performance of the catalysts.

All the electrochemical tests were performed in similar conditions as mentioned in section 4.7, except the concentration of KHCO_3 of electrolyte was increased from 0.1 M to 0.5 M KHCO_3 to improve the current density and ionic conductivity of the electrolyte. The LSV analysis of Bi sputtered coated Ag-Zn electrodes shown in Fig. 49, which highlights that all the catalysts show high current densities in CO_2 saturated electrolyte in comparison to the Ar saturated electrolyte. The increase in the current density in CO_2 saturated electrolyte was observed due to the current density contributing to CO_2 reduction reaction which confirms that the Bi modified Ag-Zn thin film electrodes are active towards electrochemical CO_2 reduction reactions.

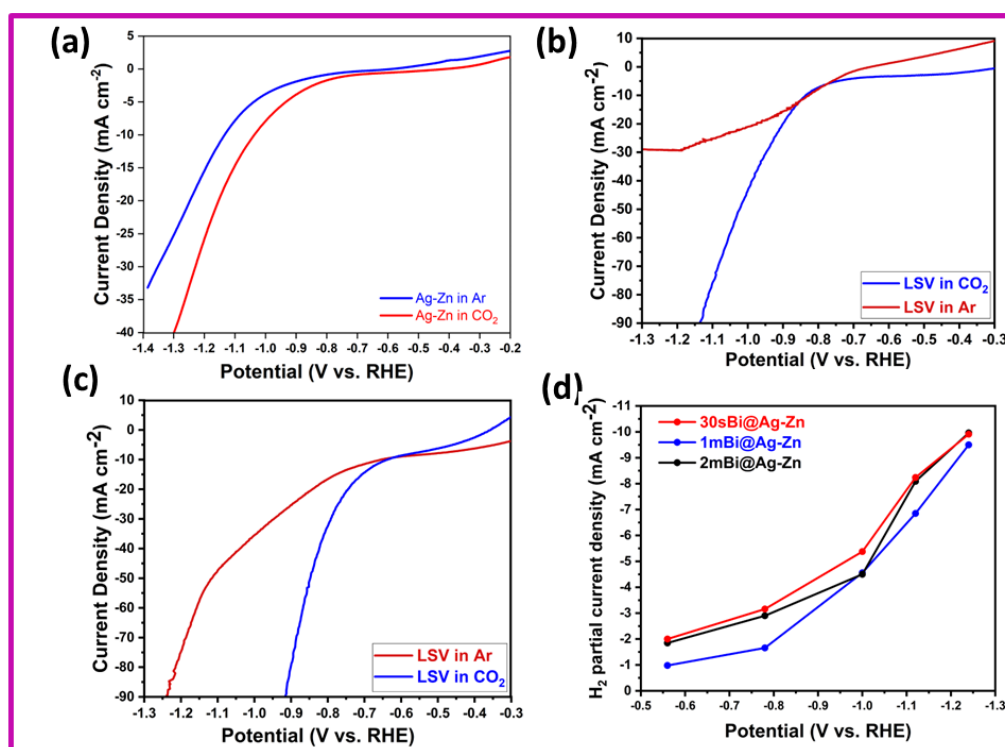


Figure 49. LSV curves of (a) Ag-Zn catalyst (b) 30sBi@Ag-Zn catalyst (c) 2mBi@Ag-Zn catalyst (d) H_2 partial current density of all the electrodes at different potentials.

The trend of increase in current density with the increase in onset potential was observed in all Ag alloyed Zn and Bi coated Ag-Zn electrodes, till -1.3 V vs. RHE and then become constant which is

due to low solubility and mass transfer limitations of CO₂ in aqueous electrolyte [171]. Fig. 50(b) presents the current densities of all the electrodes at different potentials.

In the potential all potential window 1mBi@Ag-Zn electrode exhibits highest total and CO partial current density among all the electrodes reaching 68.2 mA cm⁻² at -1 V vs RHE which further reached around 98.93 mA cm⁻² at -1.3 V. Among all the catalysts 1mBi@Ag-Zn also exhibited the lowest onset reduction potential as depicted from in Fig. 50(a) and highest CO partial current density (j_{CO}) from -0.6 V to -1.2V vs. RHE can be depicted from Fig. 50(c) indicating that 1mBi@Ag-Zn can be the most efficient catalyst for CO₂ reduction in the potential range of -0.6 to -1.2V vs RHE.

The maximum F.E_{CO} at -0.8V was achieved 74% at 1mBi@Ag-Zn electrode as shown in Fig. 50(d) whereas, Ag-Zn catalyst exhibited the minimum F.E_{CO} 73% at the same potential. To explore the optimum reduction potential for CO electroreduction, all electrodes were tested in potential window of -0.6 to -1.2V under same electrolytic and environmental conditions. Fig. 50(d) shows the FE of CO and H₂ at different potentials. The potential window of -1 to -1.1 V vs. RHE was observed to be the optimum reduction potential where, the maximum selectivity and minimum H₂ evolution was observed on all the Bi modified Ag-Zn electrodes. At more negative potentials H₂ evolution increased and became the major contribution of total current density which results in less selective CO production. At the potential -1V vs RHE 1mBi@Ag-Zn catalysts showed the highest j_{CO} 68.2 mA cm⁻² and F.E_{CO} 93.5% proved to be the best among all the fabricated electrodes for ECO₂R. The increase in hydrophobicity by incorporation of Bi on Ag-Zn surface indicates the increase in surface roughness of the catalysts. The Bi decorated Ag-Zn catalysts hydrophobic nature and porous environment lead to increase in local PH and formation of three-phase interface

which further favors the CO₂ reduction and minimizes H₂ evolution by suppressing the CO₂ mass transportation limitations [174].

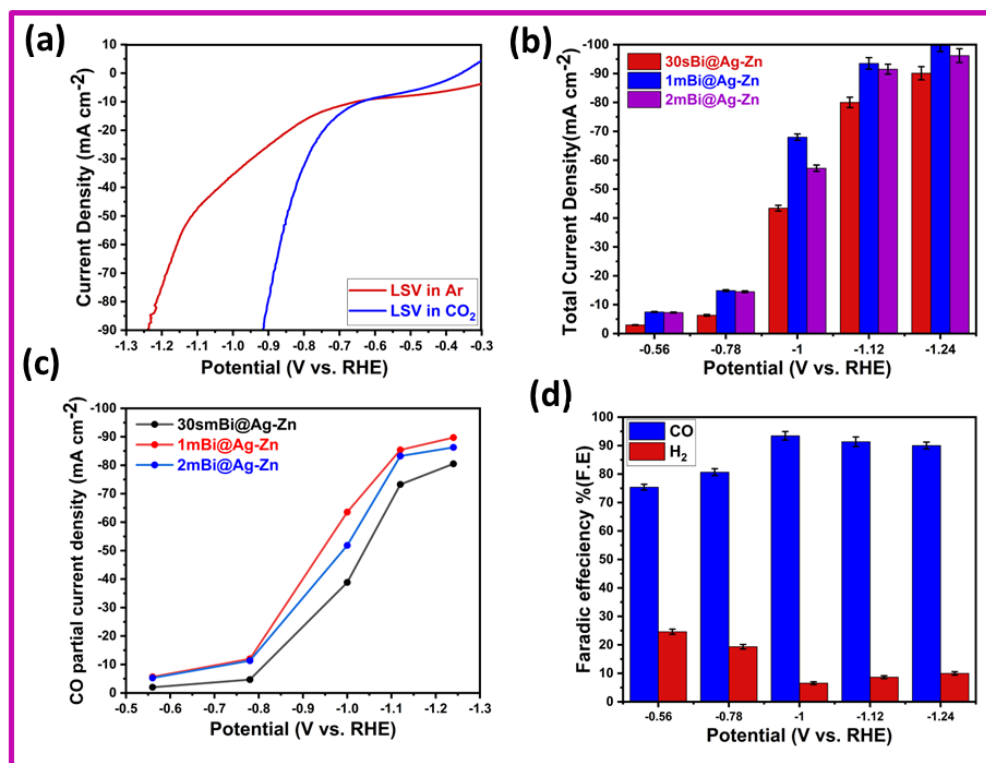


Figure 50. Electrochemical performance; (a) LSV of 1mBi@Ag-Zn catalyst in Ar and CO₂ saturated 0.5M KHCO₃, (b) Total current density, (c) CO partial current density of the Ag-Zn, 30sBi@Ag-Zn, 1mBi@Ag-Zn, and 2mBi@Ag-Zn electrodes at different potentials (d) F.E of all the products of 1mBi@Ag-Zn at different potentials.

In order to get insights into the catalytic properties of Bi decorated Ag-Zn catalysts the double layer capacitance (CDL) was measured by the Cyclic voltammetry (CV) at different scan rates in non-faradic potential window as shown in Fig. 51(a-c).

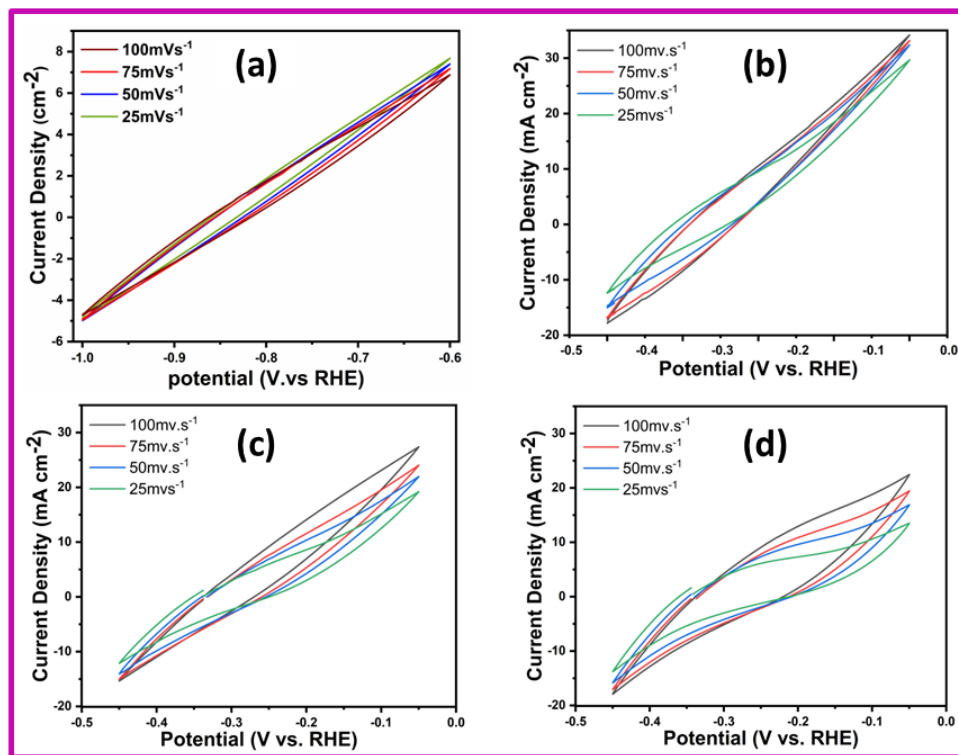


Figure 51. (a) CV curves of Ag-Zn; (b) CV curves of 30sBi@Ag-Zn, (c) CV curves of 2mBi@Ag-Zn (d) CV curves of 1mBi@Ag-Zn in N₂ saturated 0.5M KHCO₃ in non-faradic potential regions at different scan rats

From the CDL measurement in the Fig. 39(c) it can be observed that all Bi decorated Ag-Zn catalysts exhibit higher CDL than bare Ag-Zn. The 1mBi@Ag-Zn electrode exhibits highest ECSA (18.92 mF cm⁻²) in 0.5M KHCO₃ as shown in Fig 52(a), indicating a much higher electrochemical surface area (ECSA) and availability more active sites for CO₂ catalytic reduction, thereby improving catalytic activity by incorporation of Au on Ag-Zn surface [175].

Further, to confirm the advantages of Bi coating the charge transfer resistance of Ag-Zn and Bi decorated Ag-Zn catalysts was determined by EIS analysis. The Nyquist plots of 30sBi@Ag-Zn, 1mBi@Ag-Zn and 2mBi@Ag-Zn electrodes is shown in Fig. 52(b), an equivalent electric-circuit was fitted by using Bio-logic EC Lab software which contains electrolyte resistance

(R_s), double layer capacitance (C_{dl}), charge transfer resistance (R_{ct}), and Warburg impedance (Z_w) during reaction [176].

From the EIS observations it was confirmed that 1mBi@Ag-Zn exhibits much lower charger transfer resistance in comparison to Ag-Zn catalyst which indicates the fast charge transfer and high kinetics on 1mBi@Ag-Zn electrodes. Both the high availability of active sites and rapid kinetics to produce reaction intermediate by incorporation of Au reveals high intrinsic activity of 1mBi@Ag-Zn catalyst. These above findings suggest that the partial coverage of Bi on Ag-Zn surface can provide more active sites and stabilize the key intermediates on the catalyst surface which leads to superior CO selectivity.

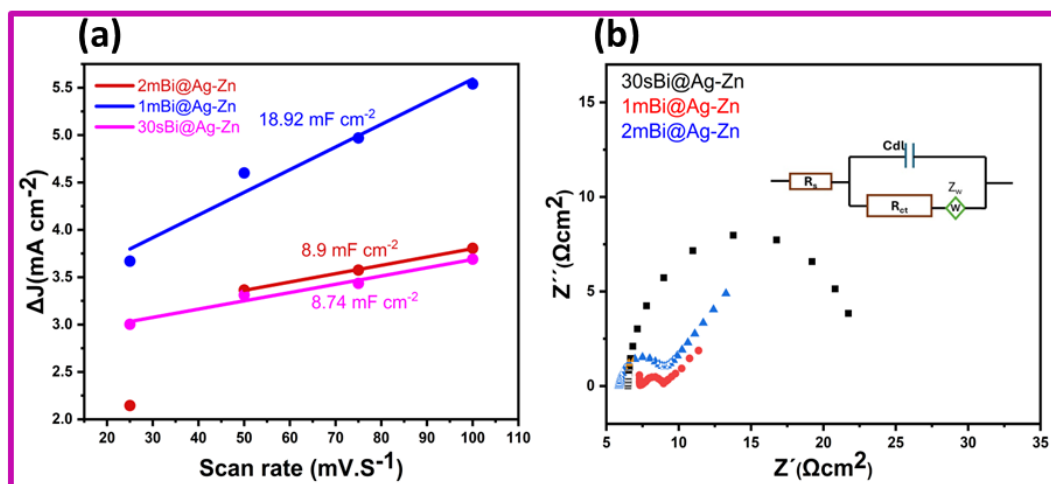


Figure 52. (a) CDL measurements of Bi decorated Ag-Zn catalysts, (b) EIS measurements of Bi decorated Ag-Zn catalysts.

To explore the underlying reaction mechanism and CO_2 reduction pathway we calculated the Tafel slopes 1mBi-Ag-Zn catalysts represented in Fig. 53(a). The Tafel slope of 1mBi@Ag-Zn has the value of 269 mV/dec , which is very close to the theoretical 270 mV/dec [180], highlighting the conversion of CO_2 to CO^* intermediate is a rate limiting step for 1mBi@Ag-Zn catalyst as shown in Fig. 53(b) which is much lower than the Ag-Zn catalysts due to high charge transfer ability in

Bi modified Ag-Zn catalysts which was confirmed by EIS and less CO₂ mass transport limitations which was due to hydrophobic nature of the 1mBi@Ag-Zn catalyst.

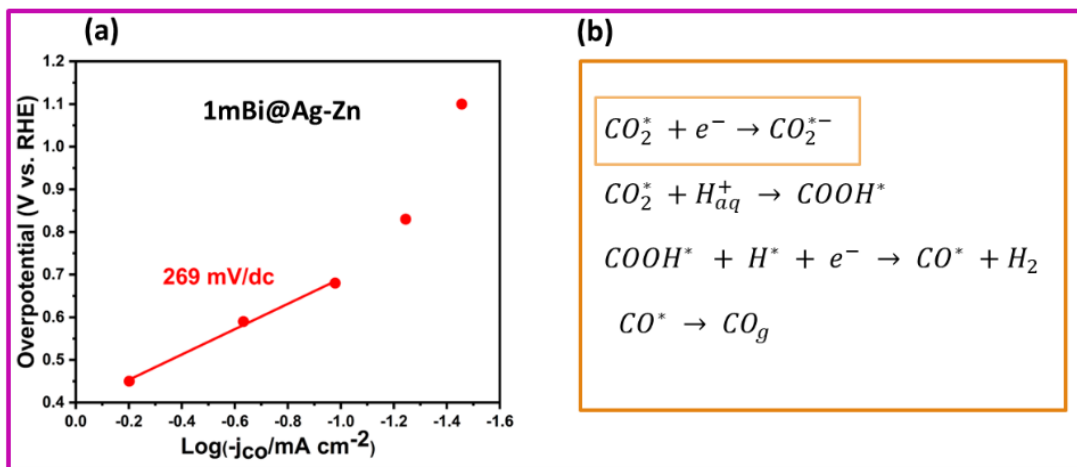


Figure 53. (a) Tafel slope of 1mBi@Ag-Zn catalyst, (b) Reaction steps for ECO₂RR on 1mBi@Ag-Zn

Furthermore, the chronoamperometry analysis of all the Bi decorated Ag-Zn catalyst was collected during 1h CO₂ electrolysis process at each potential as shown in Fig. 54 (a-c). No reasonable current density deviations during the ECO₂RR in all the catalysts at different potentials confirms that the catalysts remained stable for effective reduction of CO₂ to CO without losing their original efficiency in 1h electrolysis process.

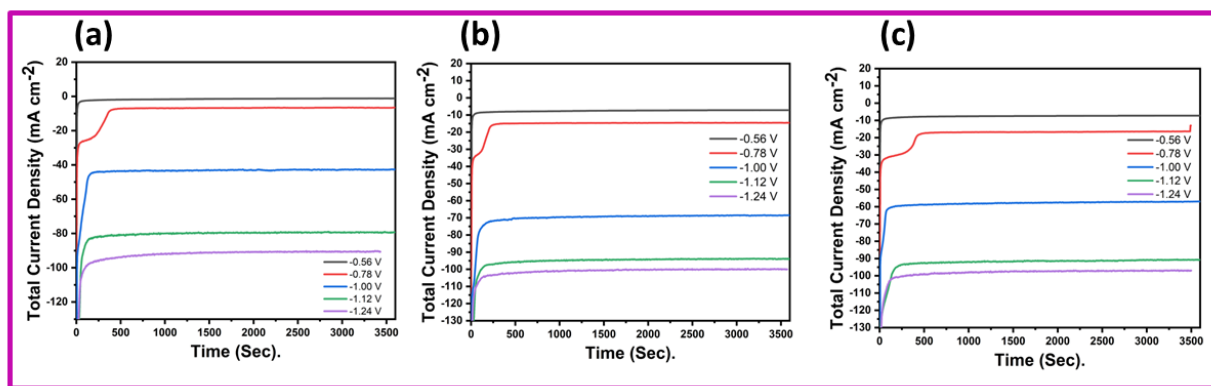


Figure 54. Chronoamperometry analysis (a) 30sBi@Ag-Zn, (b) 1mBi@Ag-Zn, (c) 2mBi@Ag-Zn in 0.5 M KHCO₃ at different potentials.

CHAPTER 6

CONCLUSION AND FUTURE WORK

Chapter 6. Conclusion and Future work.

In this work, we have developed and systematically evaluated a series of Ag-Zn, Au decorated Ag-Zn and Bi decorated Ag-Zn thin film electrocatalysts for the selective electrochemical reduction of CO₂ to CO. These catalysts were fabricated by straightforward two-step process, (i) co-electrodeposition of Ag and Zn to form a highly porous, dendritic Ag-Zn structure on Ag foil substrates, and (ii) subsequent DC magnetron sputtering of Au for 5s, 10s, and 20s, yielding Au loadings of 4.3, 5.7, and 9.7 wt%, respectively denoted as 5sAu@Ag-Zn, 10sAu@Ag-Zn, and 20sAu@Ag-Zn in the study. Whereas the Bi decorated catalysts were synthesized by using the Bi target in sputtering step. DC magnetron sputtering of Bi for 30s, 1m and 2m yield Bi loading of 6.25, 7.64 and 20.77 wt%, respectively named as 30sBi@Ag-Zn, 1mBi@Ag-Zn, and 2mBi@Ag-Zn. Through comprehensive physical characterizations such as XRD, FE-SEM, EDS, XPS, WCA and electrochemical tests. We have identified that the 10s Au (10sAu@Ag-Zn) and 1m Bi (1mBi@Ag-Zn) are the optimal composition to achieve a high Faradaic efficiency toward CO. The 10s Au sputtering catalyst exhibited F.E_{CO} of 94.2% and a CO partial current density of -20.26 mA cm⁻² at -1.0 V versus RHE in a conventional type H-cell and 1m Bi sputter coated Ag-Zn catalysts exhibited F.E_{CO} 93.5% at CO partial current density -68.2 mA/cm² in 0.5 M KHCO₃ at -1V in H-cell. All catalysts exhibited catalytic activity for ECO₂RR however, the 10sAu@Ag-Zn and 1mBi@Ag-Zn electrode outperformed both the parent Ag-Zn catalysts. At -1.0 V vs. RHE, the pure Ag-Zn catalyst displayed an F.E_{CO} of 90.4 % and a j_{CO} of 15.9 mA/cm², whereas 10sAu@Ag-Zn reached 94.2 % F.E_{CO} and j_{CO} -20.26 mA cm⁻² which reflects remarkable improvement in CO production rates. Similarly, the 1mBi@Ag-Zn catalysts also exhibited remarkable current density and F.E towards CO. This enhancement can be attributed to three synergistic effects imparted by the Au and Bi decoration: (i) electronic modulation of the

Ag-Zn surface (d-band center tuning) that accelerates the rate-determining $\ast\text{CO}_2 \rightarrow \ast\text{CO}/\ast\text{COOH}$ step which is evidenced by the reduced Tafel slope of 274 mV dec⁻¹ in Au modified and 269 mV dec⁻¹ in Bi modified electrodes versus 314 mV dec⁻¹ for Ag-Zn, (ii) increased electrochemical surface area (ECSA), as shown by a 2.7 fold rise in double layer capacitance (5.28 vs. 1.95 mF cm⁻²), and (iii) surface hydrophobicity, which fosters a localized three-phase (gas/liquid/solid) interface that enriches CO₂ near active sites and suppresses competitive H₂ evolution.

In long-term chronoamperometry at -1.0 V vs. RHE, the bare Ag-Zn catalyst maintained $\geq 79\%$ of its initial j_{CO} for 5 h, whereas the 10sAu@Ag-Zn electrode retained $>90\%$ of its activity and FE_{CO} for over 12 h which is 2.4 times the durability of Ag-Zn electrode. Post electrolysis XRD and SEM analyses confirmed that the Au layer acts as a protective island that inhibits Zn dissolution and structural collapse of the dendritic network, preserving active morphology and catalytic function under constant reductive bias. FE-SEM and TEM images taken before and after Au sputtering, and following extended ECO₂RR, reveal that the underlying Ag-Zn dendritic framework remains intact after Au deposit and prolonged operation. The conformal adhesion of Au and Bi nano islands along Ag-Zn dendrites does not obstruct pore networks or blunt active edge sites. This structural preservation ensures continuous mass transport channels, maximizes active site exposure, and underpins both the high ECSA and long-term stability.

Water contact-angle measurements show a progressive increase in hydrophobicity with Au and Bi loading without the need for PTFE or other additives. In our H-cell configuration, where bulk CO₂ supply is generally sufficient, this surface hydrophobicity nonetheless enhances the CO₂ concentration directly at the catalyst–electrolyte interface which lessens the electrolyte coverage,

and suppresses H₂ evolution, eventually contributes to the overall enhancement in CO₂ mass transportation on the catalyst surface and CO selectivity.

Future Work

- Test the prepared catalysts for CO₂ electroreduction in the Flow cell system.
- Expand this study to target C₂ products by exploring various metals and alloy compositions.
- Investigate the reaction mechanism to gain a deeper understanding of the factors driving the optimized catalyst's exceptional performance.
- DFT Modeling to design catalysts and predict the catalysts properties before experimental work.

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Journal Publications:

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2. Farid, A., Mahyoub, S.A., Kotoba, E. and Drmosh, Q.A., 2025. Au@ Ag-Zn Thin Films Catalysts for Selective and Stable CO₂ Electroreduction. *Journal of Environmental Chemical Engineering*, p.117430. <https://doi.org/10.1016/j.jece.2025.117430>