

**Synthesis and application of metal-based electrocatalysts for
CO₂ reduction to value added chemicals.**

BY

Mustapha Umar

A Dissertation Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY

In

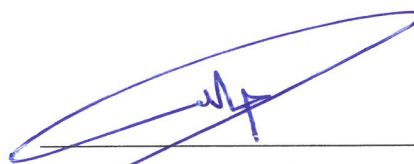
CHEMISTRY

December 2023

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

DEANSHIP OF GRADUATE STUDIES

This thesis, written by **Mustapha Umar** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY IN CHEMISTRY**.



Dr. Khalid Alhooshani
(Advisor)



Dr. Jameel Al-Tagfi
Department Chairman



Dr. Ali Shaikh Asrof
(Member)



Dr. Suliman Saleh Al-Homidan
Dean of Graduate Studies

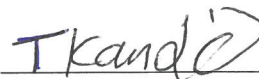


Dr. Abdulaziz Al-Saadi
(Member)

Date



Dr. Saheed A. Ganiyu
(Member)



Dr. Tarek Kandiel
(Member)

© Mustapha Umar

2023

|Allahu Subhanahu Wa Ta'ala (SWT) |

ACKNOWLEDGMENTS

I extend my heartfelt gratitude to the Almighty Allah for His boundless mercy and guidance throughout my academic journey at KFUPM. While it is impossible to individually acknowledge everyone who contributed to my stay, I want to express my sincere thanks to all those who supported me intellectually and materially, shaping this research work.

My family, especially my parents, aunts, brothers, grandmothers, uncles, sisters, and friends, deserve special mention for their unwavering moral and financial support. I am deeply indebted to my institution, King Fahd University of Petroleum Minerals (KFUPM), for providing me with a nurturing environment for both moral and academic growth.

I am profoundly grateful to my supervisor, Dr. Khalid R. Alhooshani, and my committee members, Dr. Ali Shaikh Asrof, Dr. Abdulaziz Al-Saadi, Dr. Saheed Adewale Ganiyu, and Dr. Tarek Kandial. Their insightful reviews, meticulous probing for weaknesses, error corrections, and overall guidance significantly enhanced the quality of this work. Their generosity in sharing their extensive knowledge and expertise in the field of Chemistry has been invaluable.

Special thanks are due to the faculty and staff of the Chemistry Department, with a particular mention to Dr. Jameel Al-Thagfi, the Chairman, whose mentorship was pivotal to my studies. The support from the University's Library Service and Research Institute, which facilitated access to essential instruments, reference sources, and books, played a crucial role in my research.

Lastly, I express my gratitude to my university colleagues, regardless of their departments and academic levels. Their willingness to share knowledge, ideas, and experiences, along with their valuable suggestions, greatly enriched my academic journey.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
TABLE OF CONTENTS.....	VII
LIST OF TABLES.....	X
LIST OF FIGURES.....	XI
ABSTRACT	XV
ملخص الرسالة	XVII
 CHAPTER 1 INTRODUCTION	 19
1.1 Background Information	19
1.2 Statement of the Problem.....	25
1.3 Research Objectives	26
1.4 Organization of the thesis	27
 CHAPTER 2 LITERATURE REVIEW.....	 29
2.1 Introduction.....	30
2.1.1 Transition metals-based electrocatalysts for CO ₂ reduction	39
2.2 First row of <i>d</i> -block transition metals	43
2.2.1 Vanadium (V) and Manganese (Mn) based Electrocatalysts	43
2.2.2 Iron (Fe) based Electrocatalysts	47
2.2.3 Iron (Fe) based Electrocatalysts	49
2.2.4 Iron (Fe) based Electrocatalysts	53
2.2.5 Copper (Cu) based Electrocatalysts	60
2.2.6 Zinc (Zn) based Electrocatalysts	66

2.3	Second row of d-block transition metals.....	68
2.3.1	Pd-based Electrocatalysts.....	68
2.3.2	Ag-based Electrocatalysts	72
2.4	Third row of d-block transition metal	76
2.4.1	Rhenium (Re) based Electrocatalyst	76
2.4.2	Tungsten (W) and Lanthanum (La) based Electrocatalyst	77
2.5	Challenges and future perspectives	78
CHAPTER 3 RESULTS AND CONCLUSION		80
3.1	Introduction	81
3.2	Experimental section	83
3.2.1	Material and Chemicals.....	83
3.2.2	Synthesis of ZnO nanoneedle and nanorod	83
3.2.3	Characterization.....	84
3.2.4	Electrochemical evaluation	85
3.3	Result and discussion.....	87
3.3.1	Characterization of ZnO nanoneedle and nanorod.....	87
3.3.2	Electrochemical performance of ZnO nanoneedle and nanorod.....	89
3.4	Conclusion	94
CHAPTER 4.....		96
4.1	Introduction	97
4.2	Materials	99
4.3	Synthesis of ZIF-zni	99
4.3.1	Synthesis of Ce _x -ZIF-zni-X	100
4.4	Characterization of ZIF-zni and Ce _x -ZIF-zni-X.....	101

4.5	Results and discussion	102
4.5.1	XRD pattern.....	102
4.5.2	Morphology of the catalysts	103
4.5.3	XPS Analysis of the synthesized catalysts	104
4.5.4	Electrochemical measurements.....	106
4.6	Conclusion	112
CHAPTER 5.....		114
5.1	Introduction.....	115
5.2	Experimental.....	117
5.2.1	Reagents and chemicals	117
5.2.2	Electrode preparation and characterization	117
5.3	Electrochemical measurements	118
5.4	Computational method.....	120
5.5	Results and discussion	121
5.6	<i>Ex-situ</i> SEM and XRD	130
5.7	Conclusions.....	133
CHAPTER 6 CONCLUSION AND RECOMMENDATIONS.....		135
6.1	Conclusions.....	135
6.2	Recommendations	135
REFERENCES.....		137
VITAE.....		8

LIST OF TABLES

Table 1. Summary of electro-catalyst with their corresponding morphology and FE (%)	57
Table 2. Correlation between electro-catalyst's morphologies and their corresponding and FE	59

LIST OF FIGURES

Figure 1. Electrochemical CO ₂ reduction	21
Figure 2. Schematic diagram of CO ₂ utilization and chemical conversion to useful products.....	32
Figure 3. Different studies published in the past ten years over the CO ₂ electrocatalytic reduction on Scopus, October 25, 2022, under the keyword “CO ₂ electrocatalytic reduction”.....	35
Figure 4. CO ₂ RR to CO reaction pathway and the estimated value of the Tafel slope for each possible rate-limiting step. Reprinted with permission from Gu et al. [157].	38
Figure 5. Proposed a CO ₂ RR pathway for the formation of methane (4a), ethane, and methanol (4b). Reprinted with permission from Ren et al. [164].	39
Figure 6. Illustrations of transition metals in the periodic table.	43
Figure 7. (a) Schematic illustration of the synthesis of M–N–C catalysts. The HAADF-STEM images of (b–e) Fe–N–C and (f–i) Co–N–C catalysts. Reprinted with permission from Pan et al., [193].	48
Figure 8. SEM images of Co-PAN nanofibers before annealing (a and b); after annealing at 550 °C for 30 min in the air (c and d). Reprinted with permission from Aljabour et al., [202], and after electrochemical investigations and (g) Photos of a piece of flexible CoSA/HCNFs membrane ; (h–j) FE-SEM, and (d) HR-TEM. Reprinted with permission from Yang et al., [204].	51
Figure 9. (a) the formation process of Co-N ₄ and Co-N ₂ (b) SEM and (c) TEM images of Co-N ₂ . (d) Examination of the corresponding EDS mapping reveals the homogeneous distribution of Co and N on the carbon support. Reprinted with permission from Wang et al., [205].	52
Figure 10. The synthesis procedure of Ni-N/C-x., TEM images of (a) Ni-N/C-3/2, and (b) Ni-N/C-1/4 (scale bars is 50 nm in inset images); (c) SEM images of Ni-N/C-3/2, and (d) Ni-N/C-1. Reprinted with permission from Ma <i>et al.</i> [217].	56
Figure 11. CuO microboxes (a). SEM images (b) and (c), TEM images (d) and (e), HRTEM image (f), and EDX mapping (g) of CuO microboxes. Scale bars, 300 nm in (b), 150 nm in (c), 200 nm in (d), 20 nm in (e), 2 nm in (f). Reprinted with permission from Tan et al., [238]. SEM and TEM images of different synthesized Cu ₂ O catalysts: (g & k) Cu ₂ O-c, (h & l) Cu ₂ O-o, (I & m) Cu ₂ O-t, and (j & n). Reprinted with permission from Liu et al., [240].	61
Figure 12. Representation of low- and high-magnification OD-Cu NAs SEM images of (a) as-synthesized CuOx NAs, (b) thermally reduced CuOx NAs-42 C/cm ² , and (c) OD-Cu NAs generated from CuOx NAs-42 C/cm ² . Reprinted with permission from Wang et al., [241]. And SEM images of (d) one fiber of carbon paper, (e) electrodeposited ZnO on carbon paper, (f) ZnO/GO, and (g) RZnO/rGO. Scale bar, 5 μm. (h) Visualization showing the detailed structure of R-ZnO/rGO electrodes. Reprinted with permission from Le Tri Nguyen et al., [248].	63

Figure 13. Design concept and structural characterizations of (a) Schematic of the “two ships in a bottle” design. (b) SEM image, (c) TEM image, (d) HRTEM image, and corresponding FFT diffraction patterns for (e) Ag(111) and (f) ZnO(101), (g) HAADF-STEM image (inset: size distribution histogram), (h) HAADF-STEM image, and (i-n) corresponding EDS element mapping of individual twinned ZnO-Ag nanoparticle accommodated within carbon pores of ZnO-Ag@UC. Reprinted with permission from Zhang et al., [263].....	68
Figure 14. SEM images of nanocrystalline Pd electrocatalyst: (a) Cubes, (b) Rhombic dodecahedra, (c) and Branched nanoparticles, (d) Nanoparticles with mixed low-index facets, and (e) Pd black. Reprinted with permission from Klinkova et al [250] at potentials between 0.5 to 0.9 V versus RHE, the octahedra produced an FE greater than 80 percent for CO generation across potentials ranging from 0.5 to 0.9 V vs RHE. Noticeably, at 0.9 V versus RHE, the CO partial current density of the octahedra was three times that of the cubes [251]. The performance differences can be linked to a more facile reaction pathway for CO production on PdH(111) surface.	70
Figure 15. SEM images of nanostructured Ag from various studies. (a) Nanoporous Ag nanowires Reprinted with permission from Park <i>et al.</i> [258] (b) Vertical nanowires. Reprinted with permission from Ge <i>et al.</i> [303] and (c) Anodic-etched Ag. Reprinted with permission from Ma et al. [307]	76
Figure 16. FE-SEM micrographs for a WO ₃ -NR/FTO electrode (a) before and (b) after electrolysis in acetonitrile. Reprinted with permission from Mendieta-Reyes et al [246].	77
Figure 17. Scheme hydrothermal synthesis of ZnO in CTAB and PVP, resulting in nanorod and nanoneedle like structures	84
Figure 18. XRD pattern of ZnO-NN and ZnO-NR.....	87
Figure 19. SEM analysis of (a) ZnO-NN and (b) ZnO-NR.	88
Figure 20. XPS spectra of ZnO-NN (a) Zn 2p and (b) O 1s and ZnO-NR (c) Zn 2p and (d) O 1s.....	89
Figure 21. Electrochemical measurements of ZnO-NN and ZnO-NR (a) LSV graphs in a 0.5 M KHCO ₃ electrolyte solution saturated with CO ₂ and Ar and (b) FE _{CO} of the ZnO-NN and ZnO-NR samples.	90
Figure 22. (a) showcases the long-term stability test of the sample, while (b) presents Operando Raman spectra of the same sample taken at various time intervals during the pre-reduction at -0.88 and -0.98 V vs RHE. All Raman spectra were obtained in a CO ₂ -saturated 0.5 M KHCO ₃ environment.	92
Figure 23. Electrochemical characteristics of ZnO-NN and ZnO-NR (a) Electrochemical impedance spectroscopy (EIS) curves (b) Tafel slope and (c) Double-layer capacitance (Cdl) measurement, half of charging current density differences ($\Delta j/2$) plotted against scan rates in CO ₂ -saturated 0.5 KHCO ₃ electrolyte solution.	94
Figure 24. Schematic reflux synthesis of ZIF-zni.....	100

Figure 25. Image of (a) XRD pattern of Simulated ZIF-zni, experimental ZIF-zni and cerium in cooperated ZIF-zni using Chemical vapor deposition (CVD) and excess solvent deposition. (b) FTIR spectra of ZIF-zni and cerium incorporated	103
Figure 26. SEM analysis of (a) ZIF-zni, (b) Ce _{0.23} -ZIF-zni (c) Ce _{0.23} -ZIF-zni-CVD and TEM analysis of (d) Showing rod like morphology of the ZIF-zni, (e) Ce _{0.23} -ZIF-zni and (f) Ce _{0.23} -ZIF-zni-CVD	104
Figure 27. High-resolution XPS spectra of Ce 3d of (a) Ce _{0.23} -ZIF-zni (c) Ce _{0.23} -ZIF-zni-CVD and O 1s of (b) Ce _{0.23} -ZIF-zni (d) Ce _{0.23} -ZIF-zni-CVD.....	106
Figure 28. Electrochemical measurements of ZIF-zni and Ce _x -ZIF-zni-X (a) LSV curves in CO ₂ and Ar saturated 0.5 KHCO ₃ electrolyte solution. (b and c) Cyclic voltammograms of ZIF-zni and Ce _{0.23} -ZIF-zni-CVD at several scan rates in the region of 0.0 to 0.5 V vs RHE. (d) ECSA measurement, half of charging current density differences (Dj/2) plotted against scan rates.	108
Figure 29. (a) Faradaic efficiencies (%) of ZIF-zni and Cex-ZIF-zni-X (b) FECO at different applied potential and (c) Tafel plots for ZIF-zni and Cex-ZIF-zni-X	110
Figure 30. DFT calculations of the optimized structures for the main intermediates of the electrochemical CO ₂ reduction reaction on Ce _x O _y -ZIF-zni surface.	111
Figure 31. DFT calculations of electrochemical CO ₂ reduction reaction on ZIF-zni and Ce _x O _y -ZIF-zni surface.....	112
Figure 32. Schematic illustration of the preparation of Pb electrode using commercial sheets.	118
Figure 33. Reactor setup of electrochemical cell for Pb electrode.	120
Figure 34. FESEM micrographs of (a) pristine and ORC-treated Pb electrodes at (b) 5 cycles, (c) 10 cycles, (d) 20 cycles, (e) 50 cycles. The expanded view of the 50 cycles-treated electrode is shown in (f). The EDX spectrum of the 50 cycle ORC-treated electrode is shown in (g). The elemental distribution on the surface of the electrode is shown in (h).	122
Figure 35. Optical 3D profiler topography of (a) pristine Pb electrode, and the (b) 50 cycles ORC-treated, in 0.3 M KCl electrolyte solution.	123
Figure 36. X-ray diffraction patterns of (a) pristine Pb electrode, and the (b) 5 cycles ORC-treated, (c) 10 cycles treated, (d) 20 cycles treated and (e) 50 cycles treated electrodes in 0.3 M KCl electrolyte solution	124
Figure 37. (a) CV curves corresponding to 50 ORC treatment on Pb electrode, (b) Nyquist plots of the pristine and ORC-treated electrodes in 5.0 mM K ₃ [Fe(CN) ₆] containing 1.0 M KCl as supporting electrolyte, (c) LSV curves of the treated electrodes in CO ₂ -saturated 0.5 M KHCO ₃ , and (d) LSV curves of the 50 cycles treated electrode in CO ₂ - and Ar-saturated electrolyte	126
Figure 38. (a) CO Faradaic efficiencies plots and (b) Tafel plots of CO production for pristine and ORC-treated electrodes at different applied potentials in CO ₂ saturated 0.5 M KHCO ₃ electrolyte.	128

Figure 39. CVs of (a) Pristine Pb and (b) 50 cycles treated electrode with various scan rates (10–100 mV s ⁻¹) in the region of 0.125 to 0.425 V vs. RHE. (c) The capacitance double layer (Cdl) as a function of scan rates.	129
Figure 40. (a) Long term stability test of 50 ORC treatment on Pb electrode during the 24 h continuous electrolysis. (b) Production rate of all products on pristine Pb and ORC-treated electrodes.	130
Figure 41. Ex-situ FESEM micrograms of (a) pristine and ORC-treated Pb electrodes at (b) 5 cycles, (c) 10 cycles, (d) 20 cycles, (e) 50 cycles and the elemental distribution on the surface of the electrode is shown in (f). After 1h electrolysis in CO ₂ -saturated 0	131
Figure 42. Ex-situ XRD patterns of (a) pristine Pb electrode, and the (b) 5 cycles ORC-treated, (c) 10 cycles treated, (d) 20 cycles treated and (e) 50 cycles treated electrodes. After 1h electrolysis in CO ₂ -saturated 0.5M KHCO ₃	132
Figure 43. DFT calculated reaction pathways and free energy diagram.	133

ABSTRACT

Full Name : [Mustapha Umar]

Thesis Title : [Synthesis and application of metal-based electrocatalysts for CO₂ reduction to value added chemicals]

Major Field : [Chemistry]

Date of Degree : [12/2023]

In this comprehensive study, the urgent need to mitigate rising atmospheric carbon dioxide (CO₂) levels is addressed through electrochemical CO₂ reduction reactions (CO₂RR) aimed at producing valuable chemicals. The research focuses on enhancing the efficiency and selectivity of CO₂RR by engineering electrocatalytic systems, particularly through the control of catalyst morphology. Firstly, a review article explores recent advancements in the rational design of electrocatalysts, primarily within the first three rows of the d-block metal catalysts. The emphasis is placed on the influence of various morphologies on CO₂RR, highlighting the significance of understanding the morphology–performance relationship. The study delves into the molecular-level insights concerning activity, selectivity, and stability during CO₂ electrolysis, stressing the importance of comprehensive discussions on the morphologies of single metals and heterostructures for CO₂ conversion.

The subsequent experimental work involves the synthesis of zinc (Zn) catalysts with distinct morphologies (ZnO-Nano-needle (ZnO-NN) and ZnO-Nano-rod (ZnO-NR) through hydrothermal methods. These catalysts exhibited significant electro-reconstruction, forming hexagonal metallic Zn crystals during CO₂-to-CO conversion. The ZnO-NN catalysts displayed remarkable stability and selectivity, achieving over 90% CO

selectivity and maintaining high performance for more than 17 hours. Conversely, ZnO-NR catalysts exhibited a slightly lower CO selectivity but demonstrated stability for 14 hours, emphasizing the importance of morphology in influencing electrocatalytic outcomes.

Furthermore, the research focuses on the synthesis and electrocatalytic evaluation of a Ce_xO_y and ZIF-zinc ion (ZIF-zni) interface for CO_2 reduction, achieving excellent selectivity to CO and high FE. DFT calculations elucidate the synergistic interaction between oxygen from Ce_xO_y and the Zn ion of ZIF-zni, exposing cerium as the active site for CO_2 activation. This interaction stabilizes the crucial $^*\text{COOH}$ intermediate, facilitating the electrochemical CO_2 reduction reaction.

Additionally, the study presents a strategy for adjusting the selectivity of Pb electrodes through electrochemical roughening in a KCl electrolyte. By subjecting the Pb electrodes to multiple oxidation-reduction cycles (ORC), a rough surface with stacked layers and Pb particle valleys was created. This treatment significantly improved electrocatalytic performance, achieving a maximum current density of 80 mA cm^{-2} and remarkable CO selectivity of 89%. DFT calculations supported these findings, indicating enhanced adsorption behavior of $^*\text{COOH}$ intermediate on ORC-treated electrodes, thereby enhancing CO product selectivity. These findings collectively provide crucial insights into enhancing the electrocatalytic conversion of CO_2 into valuable chemicals, contributing significantly to sustainable energy technologies and addressing environmental challenges associated with rising CO_2 levels. |

ملخص الرسالة

الاسم الكامل: مصطفى عمر

عنوان الرسالة: تصنيع وتطبيق المحفزات الكهربائية ذات الأساس المعدني لتخفيض ثاني أكسيد الكربون إلى المواد الكيميائية ذات القيمة المضافة

التخصص: كيمياء

تاريخ الدرجة العلمية: ديسمبر/ ٢٠٢٣

في هذه الدراسة الشاملة، تتم معالجة الحاجة الملحة للتخفيف من ارتفاع مستويات ثاني أكسيد الكربون في الغلاف الجوي (CO_2) من خلال تفاعلات تخفيض ثاني أكسيد الكربون الكهروكيميائية (CO_2RR) التي تهدف إلى إنتاج مواد كيميائية قيمة. يركز البحث على تعزيز كفاءة وانتقائية ثاني أكسيد الكربون من خلال هندسة أنظمة التحفيز الكهربائي، لا سيما من خلال التحكم في مورفولوجيا المحفز. أولاً، تستكشف مقالة المراجعة التطورات الحديثة في التصميم العقلاني للمحفزات الكهربائية، بشكل أساسي داخل الصفوف الثلاثة الأولى من المحفزات المعدنية ذات الكتلة d . يتم التركيز على تأثير الأشكال المختلفة على ثاني أكسيد الكربون، مع تسليط الضوء على أهمية فهم العلاقة بين الشكل والأداء. تتعمق الدراسة في الأفكار على المستوى الجزيئي فيما يتعلق بالنشاط والانتقائية والاستقرار أثناء التحليل الكهربائي لثاني أكسيد الكربون، مع التركيز على أهمية المناقشات الشاملة حول أشكال المعادن المفردة والهياكل المتغايرة لتحويل ثاني أكسيد الكربون.

يتضمن العمل التجريبي اللاحق تخليق محفزات الزنك (Zn) ذات أشكال مورفولوجية متميزة (ZnO - و $ZnO-NN$) من خلال الطرق الحرارية المائية. أظهرت هذه المحفزات إعادة بناء كهربائية كبيرة، وشكلت بلورات الزنك المعدنية السداسية أثناء تحويل ثاني أكسيد الكربون إلى ثاني أكسيد الكربون. أظهرت محفزات $ZnO-NN$ ثباتاً وانتقائية ملحوظين، حيث حققت انتقائية لثاني أكسيد الكربون بنسبة تزيد عن 90% وحافظت على الأداء العالي لأكثر من 17 ساعة. على العكس من ذلك، أظهرت محفزات $ZnO-NR$ انتقائية أقل قليلاً لثاني أكسيد الكربون ولكنها أظهرت ثباتاً لمدة 14 ساعة، مما يؤكد على أهمية التشكل في التأثير على نتائج التحفيز الكهربائي.

علاوة على ذلك، يركز البحث على التوليف وتقييم التحفيز الكهربائي لواجهة Ce_xO_y و ZIF-zni لتقليل ثاني أكسيد الكربون، وتحقيق انتقائية ممتازة لثاني أكسيد الكربون و FE العالي. توضح حسابات DFT التفاعل التآزري بين الأكسجين من Ce_xO_y وأيون Zn من ZIF-zni، مما يكشف عن السيريوم كموقع نشط لتنشيط ثاني أكسيد الكربون. يعمل هذا التفاعل على تثبيت وسيط COOH^* المهم، مما يسهل تفاعل تقليل ثاني أكسيد الكربون الكهروكيميائي. بالإضافة إلى ذلك، تقدم الدراسة استراتيجية لضبط انتقائية أقطاب الرصاص Pb من خلال التخشين الكهروكيميائي في المنحل بالكهرباء KCl. من خلال إخضاع أقطاب الرصاص إلى دورات متعددة من الأكسدة والاختزال (ORC)، تم إنشاء سطح خشن بطبقات مكسدة ووديان جسيمات الرصاص. أدى هذا العلاج إلى تحسين أداء التحفيز الكهربائي بشكل كبير، حيث حقق أقصى كثافة تيار تبلغ 80 مللي أمبير سم⁻² وانتقائية رائعة لثاني أكسيد الكربون بنسبة 89%. دعمت حسابات DFT هذه النتائج، مما يشير إلى سلوك الامتزاز المعزز لـ COOH^* الوسيط على الأقطاب الكهربائية المعالجة بـ ORC، وبالتالي تعزيز انتقائية منتج ثاني أكسيد الكربون. توفر هذه النتائج مجتمعة رؤية مهمة لتعزيز التحويل التحفيزي الكهربائي لثاني أكسيد الكربون إلى مواد كيميائية قيمة، مما يساهم بشكل كبير في تقنيات الطاقة المستدامة ومعالجة التحديات البيئية المرتبطة بارتفاع مستويات ثاني أكسيد الكربون.

CHAPTER 1

INTRODUCTION

1.1 Background Information

The continuous increase in the demand for sustainable energy is significantly attracting global attention. Combustion of fossil fuels, the commonly source of energy for industries and humans, induces excessive discharge of greenhouse gases (e.g., CO₂, NO and CH₄) and thus fast-tracks climate change[1], [2]. In order to accomplish the global temperature of 1.5 °C as advocated by the Intergovernmental Panel on Climate Change (IPCC) and the 2016 Paris conference Agreement on Climate Change [3], [4], extensive research attempts have been made to resourcefully convert the excess CO₂ into high value-added chemicals and fuels. This essential and effective approach, well-known as carbon capture and utilization technology, can result to recycling of carbon into sustainable value added products [5]. Along with various existing technologies, adsorption has been regarded as the most promising approach with large scale potentials in industries due to enormous economic likelihood. Nevertheless, the shortcoming related to this technology are far reaching and include high capital requirement due to large energy costs and regeneration problems, fears of harmfulness and further contamination evolving from most of the present common solvents employed. On the other hand, adsorption, a surface chemistry process, has been established to be valuable means of separating gaseous mixtures in an industrial process due to its benefits such as precursor availability, effortlessness of management in rejuvenation and low cost [6]. Despite these benefits, the triumph of this technique is a function of developing a best adsorbent with extraordinary analytes uptake, excellent selectivity, rapid kinetics, low-cost, high-accessibility,

cyclic stability, mechanical and chemical strength, and an easy regeneration regime [7]–[9]. Ultimately, electro-chemical reduction of CO₂ stands as one of the promising approaches for a robust sustainable chemical production and energy storage infrastructure. For the hands-on execution of a significant proficiency conversion system, control of products selectivity, enhancement of conversion rate, and minimal needed over potential yet continue to be the key tasks[2], [10], [11]. Typically, this process comprises of numerous proton and electron transfers, producing various products each with several likely reaction intermediates. This associated complexity, presents significant challenges in the characterization of molecular-level reaction mechanisms, which are demanding in designing efficient, selective, electrodes and stable electro-catalysts [11].

Given CO₂ electro-reduction's enormous economic and environmental prospective, the technology has remained the focus of considerable research activity within the past periods [12]. On the contrary, highest difficulties of converting CO₂ in an electrochemical cell, is overwhelming the enormous energy barrier essential to accomplish that; in the likes of formate the energy-storing reaction for CO₂ conversion to formate involved two electrons transfer process [13]. The sole electron reduction of CO₂ to CO₂^{•-}, a simple stage in numerous CO₂ reduction process, involves a utilized potential of –1.97 V measured versus standard hydrogen electrode (SHE) [12], [14]. Thus, selective production of formate at low over-potential and high current is of great concern. Furthermore, other causes, such as low selectivity and current density, complexity of the final reduction products, have mostly narrowed the useful applications of CO₂ electrochemical reduction [15]. More so, the huge energy barrier required to adsorb and activate CO₂ likewise have essential impact on CO₂ electrochemical reduction [16], [17]. To this end, it is important to design promising electro-catalysts that can efficiently adsorb, activate and convert CO₂ into value-added products [18]. In pursuit of these goals, and in addition to a suitable electrodes, a diverse of experimental methods have been adopted to

investigate the reaction routes and mechanisms of EC conversion of greenhouse gases in particular CO_2 , from feeding supposed intermediate species as reactants to employing spectroscopic techniques to examine reaction intermediates each with their own advantages and limitations [11].

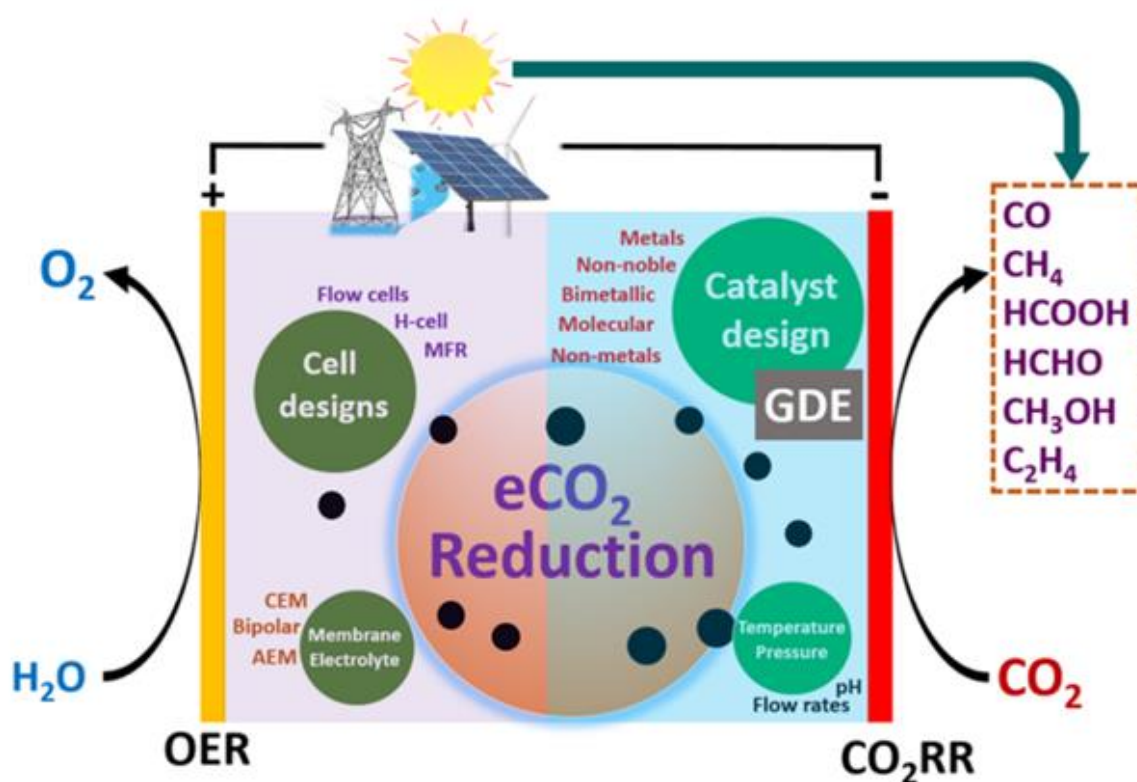


Figure 1. Electrochemical CO_2 reduction

In general, materials employed in electrochemical analysis should be available in large scale with high-efficiency while still maintaining low-enough costs to ensure their economic viability. In addition, meeting industrial challenges requires innovation in design to suit desired application, enhance sensitive, stability and selectivity in less time. Presently, the benchmark electrocatalysts for CO_2 reduction reactions comprises of the expensive precious metals [19]–[24]. Thus, different electrodes material and design have been investigated for electrochemical reduction of CO_2 to valuable added chemicals. Examples are, metal nanostructure such as; Cu,

Au, Pt and Ag, metal alloys which includes; Cu–Ag, Cu–Pd, Cu–Sn, Cu–Zn, and Cu–Ni, metal oxide namely; CuOx, CeO₂ and SnO₂, chalcogenides; WS₂ MoS₂, and metal-free electrodes; C and Si. Over all, the design (shape and size) of these electrodes greatly affect their electrochemical behavior towards CO₂ reduction[2], [25]–[27]. To date, Au is most frequently used electrodes due to its ability to convert CO₂ into other added value chemicals with high selectivity and efficiency. Nevertheless, its biggest hindrance to industrial application is its relative scarcity and high cost [2]. Lately, scientists have focused their attention on nanostructured (NS) Au based catalysts, which have demonstrated improved catalytic activity and greater conversion efficiency relative to polycrystalline or single crystalline surfaces. For instance, different shapes (spherical and nanowires) and sizes (4, 6, 8, and 10 nm) of Au nanocrystals were studied as electro-catalysts for CO₂ reduction to CO. This was achieved by depositing Au nanocrystals on carbon black and annealing to remove ligands at 165 °C for 12h, followed by the preparation of a paste made of the C-Au, PVDF (polyvinylidene fluoride), and NMP (N-methyl-2-pyrrolidone) before depositing the slurry on carbon paper [26]–[27]. It was also observed that size-dependent proportion of surface corner, facets and edges of Au NPs (nanoparticles) plays an important role in faradic efficiency and selectivity which is also supported by DFT models [2]. Furthermore, Cu is amongst the most studied electrodes, and its catalytic activity have been enhanced by fabricating distinct types of Cu NS, comprising of NPs of (0)-dimensional (0-D), 1D, and 2D over layers and 3D foams [2]. And their influence on CO₂ electro-chemical reduction have been examined thoroughly. The Cu NPs revealed a considerably greater catalytic activity in comparison with Cu foil. Without the addition of carbon particles or binders different spherical Cu NCs (Nano cubes) were synthesized by simply deposition of NCs on glassy carbon. Similarly, ultrathin fivefold twinned Cu NWs (Nano wires) loaded on glassy carbon were synthesized [2]–[25]. In another development, the selectivity of ethylene over methane during the electrochemical CO₂ reduction on single crystal

Cu NCs were examined. Nilsson and co-workers demonstrated that Cu NCs grown electrochemically from copper foil decrease the onset potential for ethylene production [28]. Additionally, variation in size (tunable sizes; 24, 44, and 63 nm) of Cu NCs synthesized by simply spin-coating the NCs on a glassy carbon plate to exclude any possible interference of binders on the intrinsic activity influence selectivity towards ethylene [25]. Another metal of interest is Ag and its composites, and it has been reported to play a significant part in electrochemical reduction of CO₂ as a result of many merits associated to its electrodes. Ag nanostructures co-catalyzed by ionic liquids can convert CO₂ to CO with excellent FE (faradaic efficiency (%)) at lower over potential. The limitations of this method, however, are its water susceptibility and the extraordinary price of ionic liquids, which would thwart the industrial feasibility of the catalysts [2]. For Ag NPs electrodes, it was proven that the size impacts the catalytic activity of Ag NPs. By reducing the size, the activity is enhanced, however this occurs to some degree at sizes of approximately below 5 nm, where this tendency is transformed greatly. In comparison with bulk Ag, the degree of CO₂ conversion is 10 times more than 5 nm Ag NPs. The writers attributed that to smaller nature of particles which exhibit additional binding energies in contrast to the bulk Ag, as the intermediates produced exhibit greater stability to be further reduced. Nevertheless, once the particle size turns out to be very trivial, the intermediates attached very intensely to the surface, triggering product discharge to be very challenging. Therefore, in a perfect situation, the electro-catalyst ought to demonstrate a suitable intermediate binding energies, not highly strong or highly weak [29]. Accordingly, Lu *et al.*, fabricated an Ag nanoporous electrode by using the de-alloying arc melting approach. The developed electrodes revealed an improved electro-chemical surface area with a superior amount of active surface sites in contrast to polycrystalline Ag. As results of these excellent features, Ag nanoporous electrodes can produce CO with a high FE [30]. Also, recently, a 3D nanoporous Ag electrode named Ag foam fabricated by adopting an easy electrodeposition

technique was investigated. Ag foam demonstrated capability toward the selective conversion of CO₂ to CO with a great FE [31].

To overcome the challenges of fabricating electrode-catalyst exhibiting high activity and selectivity towards CO₂ reduction at low-cost, recently metal alloys have attracted considerable attention because they can enhance the electro-catalytic activity of metallic catalysts [25][2]. Cu is believed to be one of the best candidates for conversion of CO₂. Yet, the yields selectivity and robustness notwithstanding require to be enhanced. Alloying or bimetallic are good method to improve the both yield selectivity and the FE and to reduce the over potential [32][25]. Zhao *et al.*, made-up alloy consisting of Au₃Cu NCs by means of a level stabilization approach, which displayed improved catalytic selectivity and activity to CO₂ electro-chemical conversion in contrast to nanocrystals of monometallic Au. The writers suggested that this approach of synthesizing alloys may perhaps offer an added suitable pathway to acquiring diverse alloy NCs [33]. Similarly, by means of colloidal chemistry to tune the composition while keeping the other parameters, such as the size and the shape, constant. A highly monodisperse 10 nm spherical NCs were synthesized with the composition ranging from Au, Au₃Cu, AuCu, and AuCu₃ to Cu and assembled as a monolayer on glassy carbon. 10 nm Au NCs produce CO and H₂ and spherical Cu NCs mostly hydrogen, similarly to previous studies. When comparing the different compositions at the lowest potential, interestingly, Au₃Cu is the catalyst with the highest activity toward CO [34][35]. In recent times, Cu–Pt based monodispersed NCs with various molar proportions were synthesized by Guo and coworkers, and it was observed that variation in the molar concentration of the individual precursor of Cu and Pt had no visible impact on the shape of the Cu–Pt NCs. The writers notice that the composition-dependent activity of Cu–Pt NCs with growing the Cu content in the Cu–Pt NCs aided the conversion of CO₂, resulting to improved catalytic activity [36]. Just as with metallic electrodes, diverse types of metal-oxides, for example Co₃O₄, FeOx, Ga₂O₃, TiO₂, CeO₂, Cu₂O, and SnO₂, , have been

explored as prospective electro-catalysts for conversion of CO₂ [2]. SnO₂ has been reported by literatures to be an active electro-catalyst for CO₂ reduction. Meyer *et al.*, synthesized NPs of SnO₂ with a 5 nm average length employing a hydrothermal technique. To enhance the surface area and simplify the CO₂ reduction process, the NPs were incorporated into graphene and carbon black [37]. The SnO₂ NPs with carbon black revealed a great selectivity for formate. Other transition metals oxide such as, MoO₂, Ga₂O₃, and Cu₂O have also attracted attention of researchers in the field of electro-chemical reduction of CO₂ [2]. Also, doping has been established to contribute to changes in electronic structure and, thus, expected to modify the catalytic activity. Sargent showed that Cu₂S core with a vacancy-rich copper shell NCs, fabricated by partially reducing colloidal vacancy-enriched Cu₂S NCs, modulates the reaction pathway at the branching point between ethylene and ethanol to favor the production of alcohols [38].

While these catalysts have shown superior electro-catalytic performance towards CO₂ reduction due to the tendency to control their crystal morphology, manipulate their composition and tune their selectivity, the cost of implementing these catalysts on large-scale electrolyzers makes it impractical. Thus, low-cost, non-precious earth-abundant metals are currently being explored.

1.2 Statement of the Problem

The electrochemical reduction of carbon dioxide (CO₂) represents a critical area of research due to the pressing global challenges associated with climate change and the increasing levels of atmospheric CO₂. Addressing this problem is essential as CO₂ is a major greenhouse gas contributing significantly to global warming. Traditional methods of reducing CO₂ emissions, though important, are insufficient to mitigate the environmental impact effectively. Electrochemical CO₂ reduction offers a promising avenue to convert CO₂ into valuable

chemicals and fuels, thereby mitigating environmental pollution and advancing sustainable energy solutions [3], [4], [39].

However, the electrochemical CO₂ reduction reaction faces several complex challenges. Firstly, the reaction requires efficient catalysts to facilitate the conversion of CO₂ molecules into useful products, such as carbon monoxide (CO) or methane (CH₄). Designing catalysts that are both highly selective and active is a substantial challenge. Secondly, the reaction pathways and mechanisms involved in electrochemical CO₂ reduction are intricate and not yet fully understood. Unraveling these mechanisms is crucial for enhancing the efficiency and selectivity of the process. Additionally, the stability and durability of electrocatalysts under the harsh conditions of CO₂ reduction reactions pose a significant problem. Developing catalysts that maintain their activity over extended periods is vital for practical applications [7]–[9].

Furthermore, the electrochemical CO₂ reduction reaction is influenced by factors such as electrode surface modifications, reaction kinetics, and mass transport phenomena. Understanding and optimizing these factors are essential to achieve high conversion rates and selectivity. Moreover, the integration of renewable energy sources, such as solar and wind power, into the electrochemical CO₂ reduction process adds another layer of complexity. Efficient coupling of renewable energy systems with CO₂ reduction technologies is necessary to create sustainable and economically viable solutions [39].

1.3 Research Objectives

The main research objective is to design, synthesize, characterize and evaluate a series of metal-based electro-catalysts for CO₂ reduction to value added chemicals. The specific objectives are as follows;

1. The design and synthesis of transitional metal based electro-catalyst

2. The electrocatalytic evaluation of the synthesized catalysts for CO₂ reduction
3. The evaluation of the catalyst's stability, deactivation and regeneration and the economic viability assessment for practical applications.

1.4 Organization of the thesis

This PhD thesis follows a manuscript-style structure designed to enhance readability and comprehension. Chapter 1 serves as the introduction to the thesis, providing an overview of the research. Chapter 2 delves into literature reviews on electrochemical CO₂ reduction reactions, exploring various transition metal-based catalysts and their morphological impacts on electrocatalytic reactions.

Chapter 3 focuses on the investigation of electrochemical CO₂ reduction using zinc (Zn) catalysts prepared through hydrothermal methods, employing polyvinylpyrrolidone (PVP) or Cetyltrimethylammonium bromide (CTAB) as stabilizing agents. This chapter explores the electrocatalyst reconstruction process, leading to the formation of hexagonal metallic Zn crystals, irrespective of their initial characteristics.

In Chapter 4, the research investigates the synthesis of ZIF-zni and incorporates Cerium through excess solvent deposition and chemical vapor depositions for electrochemical CO₂ reduction. The synergistic effect of Ce_xO_y and Zn ions within the ZIF-zni framework is examined for enhanced electrocatalytic CO₂ reduction. Detailed Density Functional Theory (DFT) calculations are performed to comprehend the mechanistic reaction pathway.

Chapter 5 explores the impact of electrochemical surface roughening on Pb-based electrodes for the electrocatalytic reduction of CO₂ to CO. The study investigates the effects of oxidation-reduction cycles on the characteristics of the Pb surface. DFT calculations are utilized to gain insights into the mechanistic reaction pathway.

Throughout the thesis, the catalysts' structure-performance characteristics are analyzed using various physio-chemical and electrochemical characterization techniques. Chapter 6 summarizes the overall conclusions drawn from the research and provides recommendations. The thesis concludes with references, appendices, and the author's resume.

CHAPTER 2

LITERATURE REVIEW

The role of morphology on the electrochemical CO₂ reduction performance of transition metal-based catalysts

Abstract

The continued increase in population and the industrial revolution have led to an increase in atmospheric carbon dioxide (CO₂) concentration. Consequently, developing and implementing effective solutions to reduce CO₂ emissions is a global priority. The electrochemical CO₂ reduction reaction (CO₂RR) is strongly believed to be a promising alternative to fossil fuel-based technologies for the production of value-added chemicals. So far, the implementation of CO₂RR is hindered by associated electrochemical reactions, such as low selectivity, hydrogen evolution reaction (HER), and in some cases induced additional overpotential. As a result, it is necessary to conduct a timely evaluation of the state-of-the-art strategies in CO₂RR, with a focus on the engineering of the electrocatalytic systems. Catalyst morphology is one factor that plays a critical role in overcoming these drawbacks and significantly contributes to enhancing product selectivity and Faradaic efficiency (FE). This review article summarizes the recent advances in the rational design of electrocatalysts with various morphologies and the influence of these morphologies on CO₂RR. To compare literature findings in a meaningful way, the article focuses on results reported under a well-defined period and considered the first three (3) rows of the d-block metal catalysts. The discussion typically covers the design of nanostructured catalysts and the molecular-level understanding of morphology–performance relationship, in terms of activity, selectivity, and stability during CO₂ electrolysis. Among others, it would be convenient to recommend a comprehensive discussion on the morphologies

of single metals and heterostructures with a detailed emphasis on their impact on CO₂ conversion.

Keywords: CO₂ electroreduction; electrochemical reduction of CO₂; Morphology; Catalysts; *d*-block metals catalysts; Faradaic efficiency; Selectivity.

2.1 Introduction

The burning of fossil fuels like coal, petroleum materials, and natural gas has constituted the means of generating greenhouse gas (GHG) largely due to the high energy demand and has been relied upon by the global communities [40]–[42]. A GHG known as CO₂, is a foremost byproduct of this combustion process. The unabated release of this greenhouse gas has resulted in the release of huge quantities of the gas into the atmosphere. It has unwantedly encouraged the warming of the globe, ocean bodies' acidification, unfavorable weather conditions, and the extreme annihilation of important natural species [43]–[46]. Within the last two decades, global warming and the shortage of energy and other natural resources, have triggered collective global concerns [40], [41], [47]–[51]. Within the same period, the atmospheric CO₂ concentration has swiftly and unceasingly surged from about 280 ppm in the last 1800s [52] to beyond 389 ppm and 400 ppm in 2019 and 2020, respectively [53]. Unfortunately, this menace has received minimal mitigative attentiveness. As reported by the International Panel on Climate Change (IPCC), the concentration of atmospheric CO₂ is projected to reach as much as 950 ppm by 2100, triggering a 1.9 °C average rise in atmospheric temperature [54]–[56]. Consequently, regulating the release and the concentration of the GHG released is as crucial now as never been felt for years back and deserves unwavering attention. Apparently, fossil fuels will linger to be global major sources of energy for a reasonable extent of time, thus decreasing the anthropogenic emissions of CO₂ via capturing at their point of source, will be an approach of great benefit. To actualize this impressive scheme, efficient

carbon capturing, storage, and utilization technologies may be employed. To capture and store CO₂, various materials of adsorption have been developed however, the majority of these materials need elevated temperatures and most critically, suffer from inadequate adsorption capacities which hinder their improvement for carbon capture and storage [57]–[59].

The past decade has witnessed significant research and advancement of CO₂-capturing materials like covalent organic frameworks (COFs), organic polymers, zeolitic materials, metal-organic frameworks (MOFs), and ionic liquids (ILs) [60]–[68]. The CO₂-capture and utilization (CCU) methods provide an economic approach to obtaining commercial use of CO₂ reduction through the production of value-added products commensurate to the expenses of handling CO₂ as shown in **Figure 2**. The conversion and the subsequent utilization of CO₂ require different forms of energy to overcome the kinetic inertia and the thermodynamic energy barrier. Methods such as the Fischer-Tropsch [69], [70], mineralization of CO₂ [71], and catalytic hydrogenation [72], [73], are a few of the industrially adopted methods.

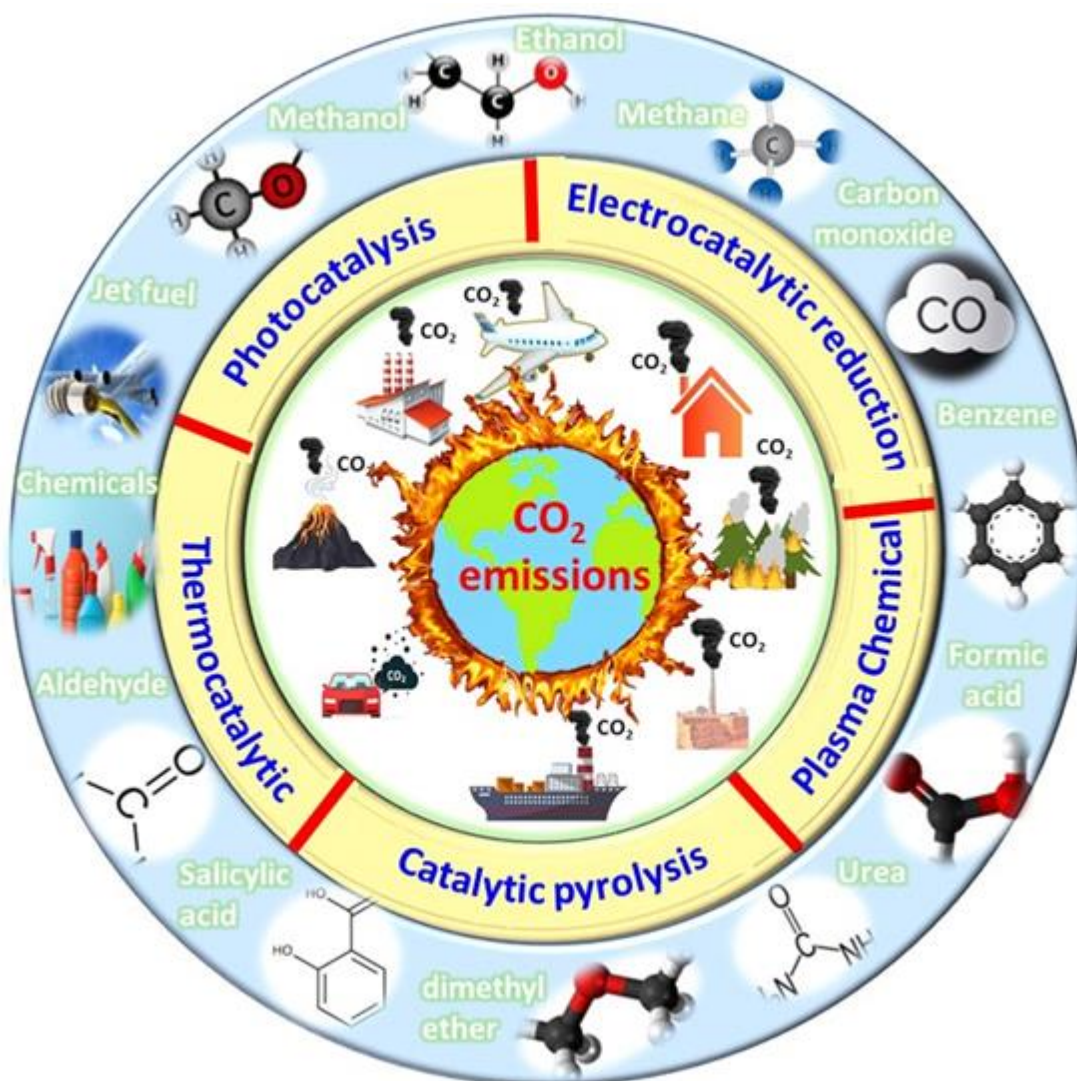


Figure 2. Schematic diagram of CO₂ utilization and chemical conversion to useful products.

Despite the obvious contributions of these conventional methods toward CO₂ conversion/utilization, their limitations cannot be over-emphasized. For instance, the process of these conventional methods requires catalytic materials and elevated temperatures due to the remarkable stability of CO₂, which renders the process non-efficient and/or economically appealing. However, techniques with novel alternatives such as biochemical [74]–[76] photochemical [77], [78], plasma-based technology [79], [80], and electrochemical [81]–[84], are presently being exploitatively expanded.

Electrochemical CO₂ reduction has significantly improved in recent years. The industrial commercialization of this technology largely relies on the activities, selectivity, and robustness of numerous multiproton and multielectron chemical processes [85]–[87]. Though the techno-economic viability of CO₂ electrochemical reduction extremely depends on the end-product such as methanol and ethanol, these productivity yardsticks are driving this technological strategy toward a viable option. This is most obvious owing to the rapid development of the renewable energy infrastructure [88]. More precisely, the electrochemical generation of ethanol has attained an extraordinary 91% FE at -0.7V vs reversible hydrogen electrode (RHE) [89]. Almost all laboratory-scale electrochemical CO₂ reduction processes have made use of high-purity CO₂ gas cylinders to standardize catalyst and/or device performance and also to get rid of the dilute or impure source of carbon. The function of the source of CO₂ and its utilization efficiency towards the process of electrochemical conversion hasn't been thoroughly investigated partly because of the relatively modest technical readiness and know-how of this growing technology.

The electrochemical method of CO₂ conversion has shown strong competitiveness against other conversion methods/techniques. For instance, the technique can be controlled by a handful of parameters like temperature and electrode potentials [81], [90]–[93]. More so, a wide variety of value-added chemical products can be obtained either in a mixture state or in their pure state or forms. For instance, aside from the direct electrochemical CO₂ reduction to CH₃OH, it is also achievable to generate CO and H₂ at the cathode in an H₂/CO ratio close to 2, while at the anode, a valuable stream of pure oxygen is produced [90]. Lastly, the electrochemical reaction systems are modular, compact, on-demand, and hence easy to employ in small or large scale-up applications [90]. To present, the accomplishments of the CO₂ electrochemical reduction technique have been appealing and fascinating with numerous potential rewards. However, some underlying drawbacks of the technique cannot easily be

ignored. This may include but is not restricted to a) high overpotential and low CO₂ solubility in the aqueous solution [94]–[97], b) formation of mixtures of product, thus requiring expensive separation steps [95], c) fouling and catalytic deactivation of the electrodes by impurities, reaction intermediates and by-products [94], [95], [98] and electrode material instability [98].

Recycling CO₂ to produce value-added products such as formic acid, carbon monoxide, ethanol, and ethylene, especially through electrochemical reduction of CO₂, contributes to the reduction of atmospheric greenhouse gases. It also contributes to the production of important industrial chemicals and carbon-neutral fuels [99], [100]. Unfortunately, a major drawback of this electroreduction of CO₂ is the development of catalysts possessing high activities and selectivity [101], [102]. So far, different classes of electrocatalytic materials have been investigated including metals [103]–[105], metal chalcogenides [106], [107], molecular metal complexes [108], [109], carbon materials [110], [111], and metallic oxides [112]–[114]. In early 2000, Hori et al. pioneered the investigation of the majority of the bimetallic and metallic bulk electrodes [115], [116]. A few years later, it was observed that the electrocatalytic selectivity and activity can be improved by controlling the size, crystal facet, and morphology of the material [117]–[120]. Among the d-block metals utilized as electrochemical catalytic electrodes thus far, copper, Cu has reported the most significant yield [121]–[124]. Metal-based catalysts like ZnO, RuO, Co₃O₄, PbO, Ag₂O, TiO₂, Cu₂O, and SnO_x, have proven to be effective in the electrocatalytic reduction of CO₂ to value-added chemicals with appealing activity and selectivity [91], [125]–[134]. Therefore, to engineer excellent electrocatalytic materials for the reduction of CO₂, materials with several components or structural complexities, ought to be investigated. The number of publications on electrocatalytic reduction of CO₂ over the last decade is evidence of the growing interest in this field as shown in **Figure 3**.

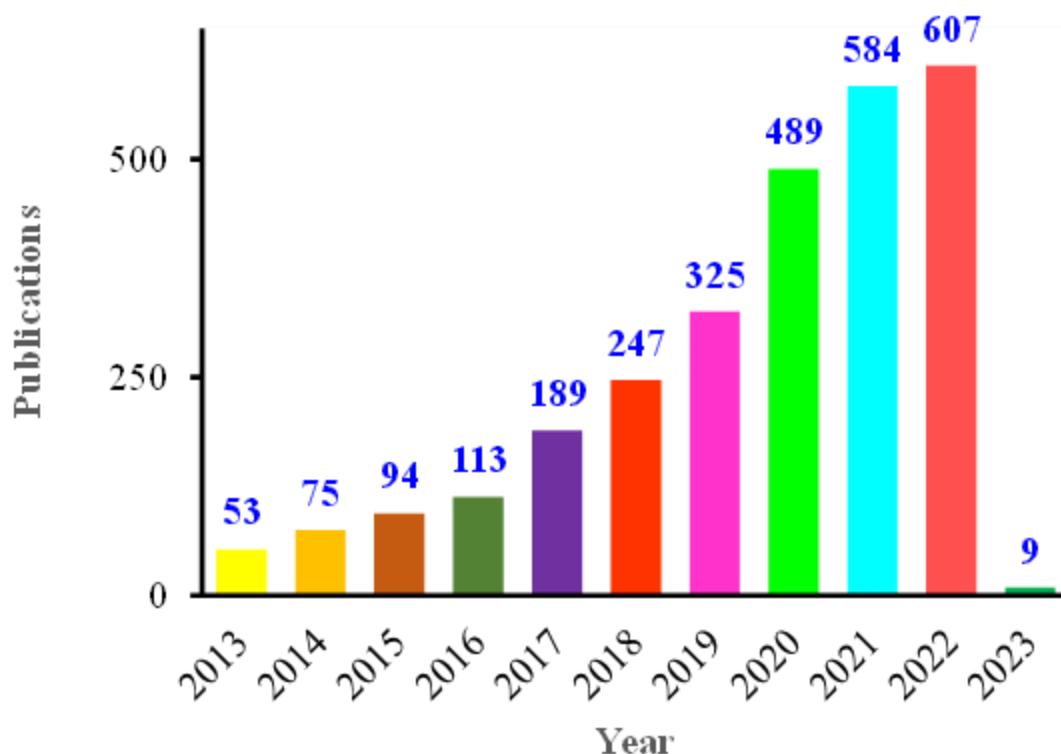


Figure 3. Different studies published in the past ten years over the CO₂ electrocatalytic reduction on Scopus, October 25, 2022, under the keyword “CO₂ electrocatalytic reduction”

An effective approach toward creating new avenues for achieving excellent electrocatalysis is by adopting metal and/or metal oxide heterostructures. Effective and efficient interactions of “metal-based catalysts” systems have widely been used to enhance the chemical kinetics of catalysis in the gaseous phase [135], [136]. However, similar ideas are under-investigated for electrocatalysis in the liquified phase [137], [138]. In the area of electrocatalytic CO₂ reduction, fewer than less have been utilized. According to Xie *et al.*, a stable and selective reduction of CO₂ to formate was achieved with a 2D atomic-layered Co/Co₃O₄ catalyst [139]. Similarly, Pérez-Ramírez *et al.* reported Cu/In(OH)₃ and Ag/In(OH)₃ electrocatalysts for CO₂ electrochemical reduction to carbon monoxide with a modest FE [140], [141]. Shu *et al.* investigated a dual-electrode on Ag-Cu sequential electroreduction of CO₂ towards hydrocarbon products [142]. Most recently, Honghui *et al.* studied a multi-layer SnO_x electrocatalyst structure for excellent selectivity and electroreduction of CO₂ to formate with

as high as 93.22% FE and with over 40 h electrocatalysis for a minimum of 5 cycles [134]. These and other research findings [143]–[146] have indicated that the interfaces of metal/metal(hydro) or metal/metal oxide if appropriately engineered, would certainly impact the kinetics of the electrocatalytic reduction of CO₂.

Recently, the electrocatalytic CO₂RR has become the most promising approach due to its advantageous properties: 1) the electrical energy that drives the reduction of CO₂ to several value-added products can be sourced from renewably intermittent energy sources such as geothermal power, solar, tidal, and wind energies; 2) valuable chemical and/or fuel products such as acetate, alcohols (methanol, n-propanol, ethanol, etc.), carbon monoxide, hydrocarbons (methane, ethane, ethene, etc.), and formate acid, are important products of electrocatalytic CO₂RR that fit properly into the existing industries and vehicles; 3) mild reaction conditions and processes that are controllable; 4) the simplicity of the electrocatalytic systems and ease with which they can be scaled up. However, the processes of CO₂RR extensively rely on the electrocatalysts involved which improve the product selectivity, lower the overpotential, and speed up the rates of the reaction [147]. The electrocatalyst of CO₂RR was investigated and reported in different literature including but not limited to metal-organic complexes [148], [149] materials of metal-free carbon-based [150], and metal-based materials [55], [151]

A lot of reputable research have been performed on the reaction mechanism of CO₂RR some of which are based on the single-atom catalysts (SACs). For example, while Cheng et al. developed supported SACs for CO₂RR, Yang et al. put together a list of different CO₂RR catalysts containing M-N_x sites [152], [153]. Similarly, Varela et al. provided a comprehensive review of the CO₂RR catalytic materials containing N, C, and non-costly metals and evaluated the active sites of these catalysts and their reaction mechanism [154]. Due to the excellent activity and selectivity of SACs, they have been studied extensively for CO₂RR to CO with a large chunk of these catalysts performing comparably to the traditional metal catalysts like Ag

and Au. According to Li et al., [155], CO₂RR to CO mechanism involves the steps shown in equations 1-3 and depicted in **Figure 4**. Where * is the active site on the surface of the catalyst



The first step involves the CO₂RR to CO through the *COOH (carboxyl) intermediate pathway as shown in equation 1a, which is widely acceptable. This mechanism of coupled proton-electron transfer (CPET) is where a concerted protonation and electron transfer result in the formation of *COOH from CO₂. Then the *COOH intermediate converts to *CO through another proton-electron transfer. Lastly, the dissociation of weakly bonded *CO to generate the CO product takes place. On the other hand, a proton decoupled electron transfer mechanism takes place during which *COOH formation proceeds via two distinct steps, namely: the adsorption of CO₂ through one-electron transfer mechanism to form CO₂^{•-} adsorbed (Equation 1b), and the protonation of the adsorbed CO₂^{•-} intermediate to produce *COOH (Equation 1c) [154], [155]. The direction of these mechanisms relies on whether *COOH intermediate forms directly through a coupled proton-electron transfer or the formation of CO₂^{•-} intermediate through an electron as shown in **Figure 3**. These steps are consistent with both experimental and DFT studies and showed that the reduction pathway of CO₂ is also related to the nature of the metal center which improves its activity and selectivity [156].

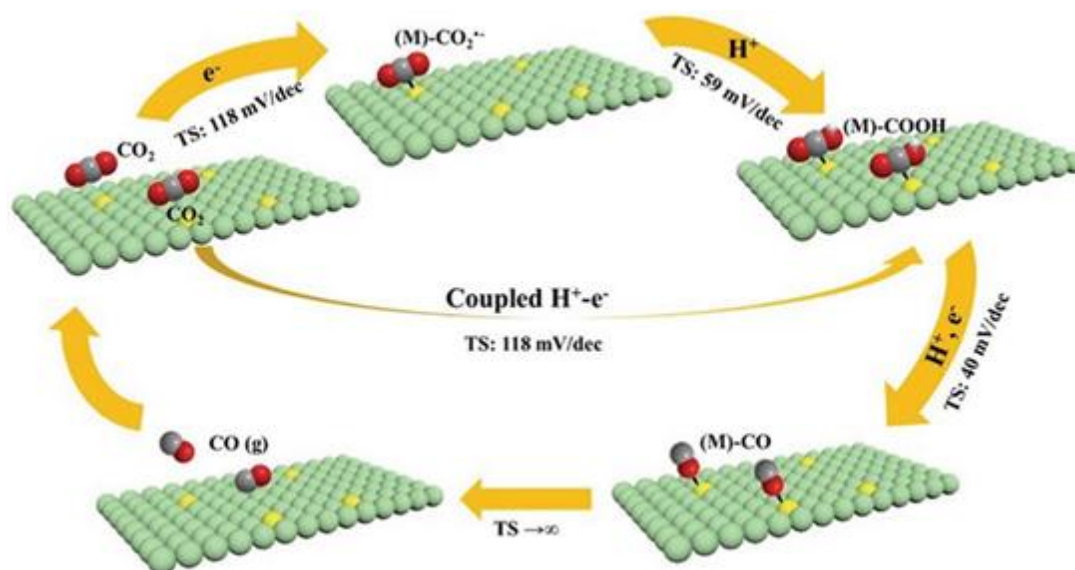


Figure 4. CO₂RR to CO reaction pathway and the estimated value of the Tafel slope for each possible rate-limiting step. Reprinted with permission from Gu et al. [157].

The development and improvement of methods of characterization such as the operando spectroscopic techniques, have made the experimental investigation of the CO₂RR mechanism feasible [158], [159]. These techniques make it easy to detect the key intermediate like *CO, *COOH, and *CHO which are detected by in situ attenuated total reflection infrared (ATR-IR) spectroscopy [160], [161]. The CO₂ activation on the metal site can be confirmed by x-ray photoelectron spectroscopy (XPS) and operando x-ray absorption spectroscopy (XAS) [162]. While the identification of the CO₂⁻ intermediate can be achieved through in situ FTIR [163]. **Figure 5** shows the proposed CO₂RR pathway for the formation of methane, ethane, and methanol by Ren et al. [164]. Lastly, the coordination environment around the metal center such as the M-N_x moieties is also believed to play a crucial role in the activity and selectivity of CO₂RR to CO mechanism

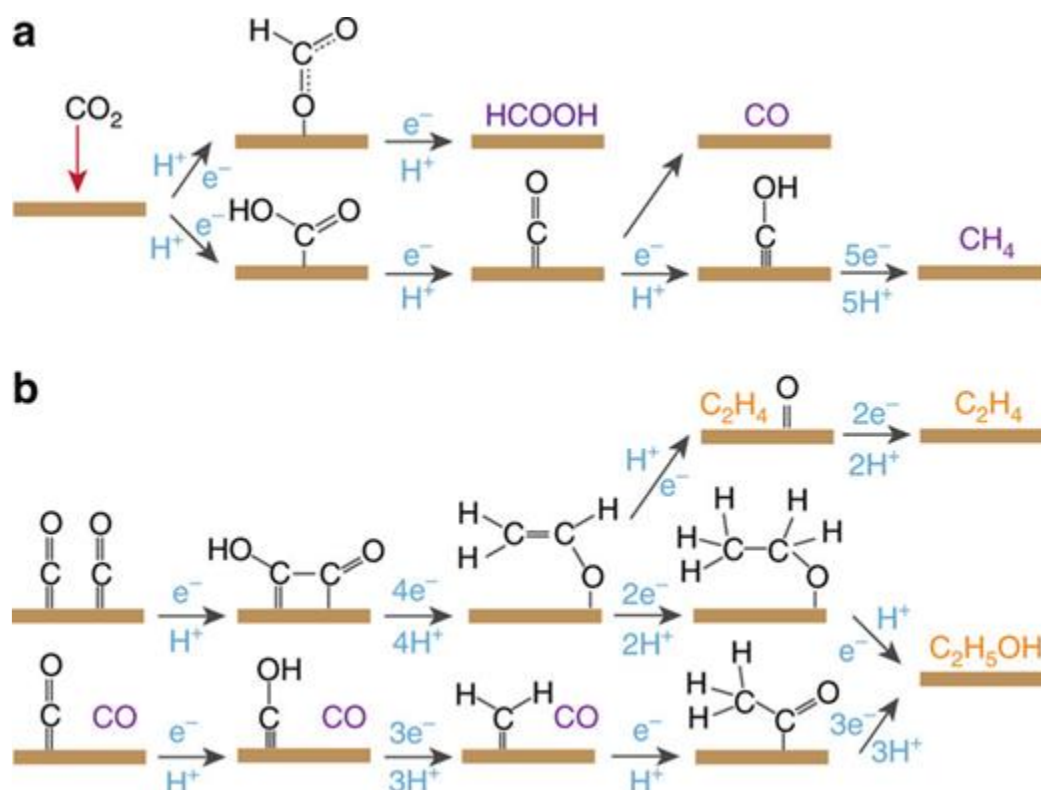


Figure 5. Proposed a CO₂RR pathway for the formation of methane (4a), ethane, and methanol (4b). Reprinted with permission from Ren et al. [164].

Although extensive progress has been made, systematic investigations on metal -based catalysts catalytic heterostructures such as the effect of the catalytic properties (product selectivity) on the composition of the material are still not duly attended to. Hence, this review reports the influence of the morphology of the transition metals-based catalysts (singly or heterostructures) of first-third rows d-blocks on the product selectivity, activity, FE, and the current density of the electrocatalytic reduction of CO₂. The synthesis route, morphology analysis, and comparison of the transition metal-based catalysts catalytic electrodes and their derivatives are also reported. Electrochemical parameters such as electrochemical surface area (ECSA), stability, electrochemical impedance spectroscopy (EIS), etc., are critically discussed.

2.1.1 Transition metals-based electrocatalysts for CO₂ reduction

The transition metals, especially those in the first and second series have been extensively employed as efficient electrocatalysts for CO₂ reduction (Figure 3) [165]. .

Regardless of the metal in question, morphological control has generally been well thought-out as an effective approach to enhance the electrocatalytic activity of materials. The design of nanostructures with many dimensions such as zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) nanostructures, does not only significantly surge the amount and exposes the active sites of catalysts but also efficiently control the mass diffusion in the catalytic process [166].

The shape and composition of nanocrystals (NCs) are significant factors that impact the characteristics of these structures and, as a result, their applications in several fields, such as catalysis. Understanding this information is crucial for numerous research fields, and it is particularly significant in comprehending catalytic activity. A considerable effort has been devoted to having in-depth catalysis processes that are influenced by morphology. However, evaluating this dependency is not a simple task because the actual atom arrangement in shaped NCs is more intricate than what the conventional model of polyhedral crystals had proposed [167].

The CO₂RR process is highly sensitive to local factors such as CO₂ concentration/pH and mass transportation of CO₂/intermediates/products near the gas-solid-liquid three-phase interface. Consequently, the regulation of the CO₂RR shows great potential through the engineering of catalysts' morphological and interfacial properties. By altering the morphology and interface properties of the electrode catalysts, it is possible to adjust several important factors such as product selectivity, overpotential, current density, productivity, charge transfer resistance, mass transportation, reaction kinetics, and stability. This can be achieved even though the atomic and/or nano-level electronic structure remains unchanged across various morphologies [168], [169]. Through extensive investigations into the mechanisms of CO₂RR, it has been discovered that the process is heavily influenced by various factors including the electronic structure, local morphology, interfacial properties, and reaction conditions of the electrode

materials. Among these factors, significant attention has been given to manipulating the electronic structure of active sites as a means to adjust CO₂RR [170]. The underlying principle is that CO₂RR primarily involves the adsorption of intermediates on the catalyst surface. Consequently, by modifying the atomic and/or nano-scale electronic properties of nanocubes, nanosphere, polyhedral, nanotubes, nanorods, and nanowires, such as introducing defects, doping, alloying, strain, faceting, grain boundaries, atom locations (edges, corners, and terraces), and surface distortion or by introducing porosity, it becomes possible to modulate the binding strength between intermediates and active sites. This, in turn, affects the adsorption/desorption of intermediates, ultimately influencing the distribution and generation rate of products [167]–[169], [171], [172]. For instance, in two separate studies conducted by Sun et al. and Manthiram et al., the performance of spherical gold and copper NCs of various sizes as electrocatalysts for CO₂ reduction was investigated. The density of adsorption sites (corner and edge) was analyzed as a function of size for both the gold and copper NCs. Sun et al. observed that the highest FE was achieved with gold NCs that had a near-optimal number of edge sites (with a coordination number of 7) and minimized corner sites (with a coordination number of 5) that are selective for the HER. This was attributed to the superior catalytic activity of the edges toward CO. As the diameter of the gold particles increased, the reactivity shifted to the dominance of the (111) facets, which required higher energy for the formation of the key intermediate COOH* compared to the stepped (211) surfaces [173].

On the other hand, Manthiram et al. found that the enhanced methane generation in their study was associated with the exposure of active sites, specifically the (210) planes when the copper NCs were isolated from each other at low catalyst loading. However, these active sites were no longer accessible in continuous films as the copper NCs came into closer proximity to one another [174]. Furthermore, the impact of nanowire (NW) length and ultrathin fivefold twinned copper NWs on CO₂RR performance was investigated by Sun et al. and Yang et al.,

respectively. Yang et al.'s study attributed selectivity to low-coordinated edge sites and concluded that the morphological features of copper NWs greatly influence product selectivity [175]. Meanwhile, Sun et al. demonstrated that the most favorable performance in terms of CO production was achieved due to a higher ratio of edge/corner atoms on the surface. Computational calculations revealed that both COOH* and CO* preferred binding to the bridge site on the Au NW edge. Notably, COOH* binding was slightly stronger on the Au (211) edge compared to the Au NW edge, while CO* binding was slightly weaker than observed on Au₁₃ clusters. Essentially, the surfaces of the NWs possessed an optimal configuration for activating CO₂ to COOH* while facilitating CO desorption. These scenarios highlight the importance of stabilizing the key intermediate COOH* at a favorable binding site, particularly the edge site in the case of Au NCs, for efficient and selective electrocatalytic CO₂ reduction to CO [27]. Also, in their study, Loiudice et al. synthesized copper nanocubes with adjustable sizes, including 24 nm, 44 nm, and 63 nm. Interestingly, the nanocubes with a 44 nm edge length exhibited the highest selectivity for CO₂RR and achieved the highest FE for ethylene production. Statistical analysis of the surface atom density highlighted the significant role played by the edge sites in CO₂RR. The analysis of the lattice plane composition revealed that each nanocube had {100} facets, along with {110} edges and {111} corners. The presence of {111} corners had minimal impact on the catalytic behavior since Cu {111} primarily leads to the generation of methane, which is not the primary product from these nanocubes. Initial theoretical results and degradation studies provided evidence that the catalytic sites favoring C-C coupling were located at the intersection between the {110} edges and {100} facets. As the size of the nanocubes increased, the {110}/ {100} ratio decreased. Consequently, the 44 nm nanocubes possessed a nearly optimal ratio for maximizing the rate-determining step in ethylene production [34]. In another development, by utilizing Pd as seeds and employing selective chemical etching, Wang et al. successfully achieved surface enrichment of high-

energy Cu (110) facets. Among various shapes, the rhombic dodecahedrons demonstrated superior activity and selectivity for CO₂RR, which can be attributed to the exposure of high-energy surfaces characterized by a high coordination number [176].

The image shows a periodic table with a red circle highlighting the transition metals (d-block). The elements are color-coded: purple for alkali and alkaline earth metals, blue for transition metals, green for post-transition metals, yellow for metalloids, and orange for noble gases. The transition metals are labeled 'Transition metals' in red text above the d-block.

Figure 6. Illustrations of transition metals in the periodic table.

2.2 First row of *d*-block transition metals

2.2.1 Vanadium (V) and Manganese (Mn) based Electrocatalysts.

First row of *d*-block transition metal, including vanadium, which is an essential element capable of oxidation states of +2, +3, +4, and +5, and considered among the subfamilies with high adsorption affinity for hydrogen protons, a prospective approach to facilitate the formation of critical intermediates and the resultant products such as alcohol [177]. However, the studies of V-based electrocatalysts for CO₂RR have been rarely reported, because the catalytic performance is far inferior to that of other metal counterparts. For instance, Cu-based catalysts are famous to exhibit many product distributions, therefore Yang *et al.*, studied the integration of vanadium oxides (VO₂) into cubic copper morphology by a one-step chemical de-alloying

approach to enhance the selectivity of CO₂RR towards predominant products. This approach according to the authors offers a large specific surface area, bimodal porous structure, and excellent electrochemical stability, leading to remarkable CO₂RR performance and long-term catalytic lifetime. The developed catalysts exhibit selectivity towards ethanol with 4-fold FE and an ethanol partial current density of 16 mA cm⁻² at -0.62 V versus the RHE compared to bare nanoporous Cu. More so, it delivers an ethanol partial current density that exceeds 39 mA cm⁻² at -0.8 V vs [178]. The remarkable performance can be ascribed to the convergence between the edges and facets of the nanocube.

Manganese oxide, one significant transition metal oxide with advantages of extraordinary redox potential, eco-friendly, and rich reserves, holds unlimited potential for widespread use as electrocatalysts. As the third most abundant transition metal in Earth's crust, Mn-based materials, including Mn oxides, Mn complexes, Mn single-atom catalysts (SACs) have been reported as catalysts for the CO₂RR [179]. Despite its numerous merits, its application to the electrochemical CO₂RR has been rarely reported. Oxygen vacancies in metallic oxide catalysts are suggested to improve adsorption capability and aid the activation of CO₂ molecules by controlling the surface electronic structure thus enhancing electrocatalytic CO₂RR activity and selectivity in heterogeneous catalysis [180]. For example, Han and co-workers recently developed a class of oxygen vacancies amorphous MnO_x by employing Ar plasma treatment. The flower-like aggregated MnO_x platelet morphology with greater distribution of oxygen vacancy on the catalyst surface, selectively converts CO₂ to CO with a superior FE of 94.8% and a partial current density of 10.4 mA cm⁻² at a comparatively inferior over-potential of 510 mV. The high activity and selectivity towards CO production achieved were attributed to the distribution of oxygen vacancies across the flower-like morphologies because both the low, pristine, and high oxygen vacancies disclosed relatively very similar ECSA [181]. The fascinating aspect is that the MnO_x platelet catalyst with a flower-like structure showcases

multiple crystal facets, plentiful corners and ridges, and well-defined grain boundaries, which may account for its exceptional performance.

For the first time Peng *et al.* obtained interconnected 3D uniform MnO₂ nanosheet arrays supported on nickel foam by binder-free one-step hydrothermal method. The well-distributed MnO₂ nanosheet arrays aid in selectively catalyzing CO₂ reduction to CO with a large current density of 14.1 mA cm⁻², excellent FE of 71%, and great electrochemical stability of 10 h. Also, the MnO₂ nanosheet arrays catalyst exhibited significantly higher ECSA than the commercial MnO₂ mainly due to the direct growth of MnO₂ nanosheet arrays on the nickel foam [182]. The presence of a substantial surface area and a porous structure is likely to have promotes the accessibility of additional active sites and facilitate the swift transport of species relevant to CO₂RR

SACs have demonstrated efficient electrocatalysts for CO₂RR with unlimited significance. Studies have shown that SACs for CO₂RR application are synthesized commonly via two approaches, high-temperature pyrolysis of the organometallic precursor such as MOFs or by direct incorporation of metal precursor onto the support surface, followed by heat and acids treatment to remove excess nanoparticles [183]. For instance, Feng *et al.* reported the preparation of Mn SAC with an Mn–N₃ site embedded in graphitic carbon nitride (g-C₃N₄) on carbon nanotubes (CNTs) morphology for efficient CO₂RR. The prepared catalyst achieved significant selectivity towards CO with 98.8% FE and j_{CO} of 14.0 mA cm⁻² at a low over-potential of -0.44 V in aqueous electrolyte, and remarkable outclassing all Mn SACs reported in the literature. The authors ascribed the activity and selectivity to the enormous electrochemical active surface area (ECSA) of the catalyst and the rapid interfacial charge transfer process during the CO₂ reaction process than the other catalysts, which could improve the reaction activity [179]. Due to the prevalence of edge lattice over corner lattice in the nanotube, the exceptional outcomes can be attributed to the existence of unsaturated Mn–N₃

species firmly attached to the nanotube's edge, which creates a favorable environment for CO₂ activation and facilitates the desorption of CO molecules. Similarly, using a hydrothermal approach Wang *et al.*, synthesized MnO nanoparticles on 3D N-doped graphene aerogels. The obtained interconnected 3D graphene network with a continuous macropore architecture exhibit a chiffon shape morphology and crumpled texture analogous to those of graphene. The catalyst demonstrates a FE of 86% for CO at a potential of -0.82 V vs RHE and better stability over 10 h. The excellent CO₂RR performance can be attributed to the large specific area of the unique 3D crumpled porous nanostructure as well as, the synergistic effect of the the edges of diamond-like MnO particles, which exhibit a broad size range, uniformly anchored on both sides of the porous graphene aerogels sheet, contributes to the outstanding results.[184].

Kossmann and co-workers prepared a sub-nanometric Mn active site over colloidal N-doped carbonaceous material through condensation of uracil at elevated temperature (800 °C) in an N₂ atmosphere. The colloidal structure of uracil and its morphology stayed unaffected upon increasing Mn loading. The morphology of the support did not only encourage robust stabilization of the Mn(II) sites but also simultaneously improved its stability against oxidation and provides a suitable coordination environment of Mn(II) sites enabling 60% FE of CO, 2% FE of HCOOH and 23% FE for CH₃COOH production from electrochemical CO₂ reduction [185]. In another development, Zhang *et al.*, obtained a graphitic carbon layer catalyst, with a lateral size of ~3µm and thickness of ~1.1 nm through two-step single pot synthesis. The halogen and N dual-coordination aid to control the electronic structure of the Mn atom, hence significantly improving the electro-catalytic performance of Mn-based heterogeneous catalysts. The graphitic carbon layer morphology reduced CO₂ to CO with a maximum FE of 97% and a high current density of 10 mA cm⁻² at a low over-potential of -0.49 V. More so, the ECSA of the halogen and N dual-coordination is approximately 29 and 58 times higher than those of the halogen free catalysts [186].

2.2.2 Iron (Fe) based Electrocatalysts

In recent years, the utilization of Fe has seen widespread application, particularly in the field of catalysis and other areas. The availability of Fe in large quantities and at a low cost has rendered Fe-based electrocatalysts highly promising substitutes for costly noble metals. [187]. However, these catalysts usually show high activities for hydrogen evolution reaction which competes against CO₂ reduction [188]. In addition, the activity of Fe monatomic catalysts is influenced by various factors, yet understanding their structure-property relationship remains a significant challenge. Recent research on Fe monatomic catalysts indicates that the active sites are intricately linked to the local environment of Fe atoms, including the coordination number and electronegativity of neighboring atoms [189]. The remarkable electronic structure of active sites in SACs, which maximizes atomic efficiency, makes them highly promising electrocatalysts for the CO₂RR [163]. Latterly, Fe embedded into N-doped carbon frameworks is also an alternative for non-precious metals for CO₂RR catalysts. Due to their cost-effectiveness and impressive CO₂RR activities and selectivity, coupled with a higher CO production yield compared to precious metals catalysts, SACs have gained significant attention. The N-coordinated metal moieties have been identified as prospective catalytic sites due to their optimal binding affinity with the chemical species involved in the CO₂RR. [190]–[200]. For instance, Fe–N–C catalysts were synthesized by Wang et al., Sun et al., and Pan et al., through the encapsulation or doping of Fe into ZIF-8 as a precursor, followed by pyrolysis. The resulting catalysts exhibited atomically dispersed Fe sites with a rhombic-dodecahedron morphology (see **Figure 7**) and demonstrated high catalytic activity in the conversion of CO₂ to CO reaching FE of 94, 85, and 93% and delivering a reduction current density of 5 mA cm⁻² and at -0.47 V, 3.7 mA cm⁻² at -0.73V and 2.8 mA cm⁻² at -0.47V RHE respectively. Wang et al. and Pan et al. attributed the active sites for CO₂RR to the edge Fe–N_x active site and edge-

hosted $M-N_{2+2}-C_8$ moieties that bridge adjacent armchair-like graphitic layers respectively, benefiting from the increased number of N-coordinated and atomically accessible Fe sites in the rhombic-dodecahedron morphology. In contrast, the inferior performance observed by Sun et al. might be attributed to the competing activity of Z-N_x and mesoNC-Fe active sites within the rhombic-dodecahedron structure. Furthermore, according to the authors, the rhombic-dodecahedron electrocatalysts exhibited excellent long-term stability during CO₂RR in aqueous media [193], [195], [196].

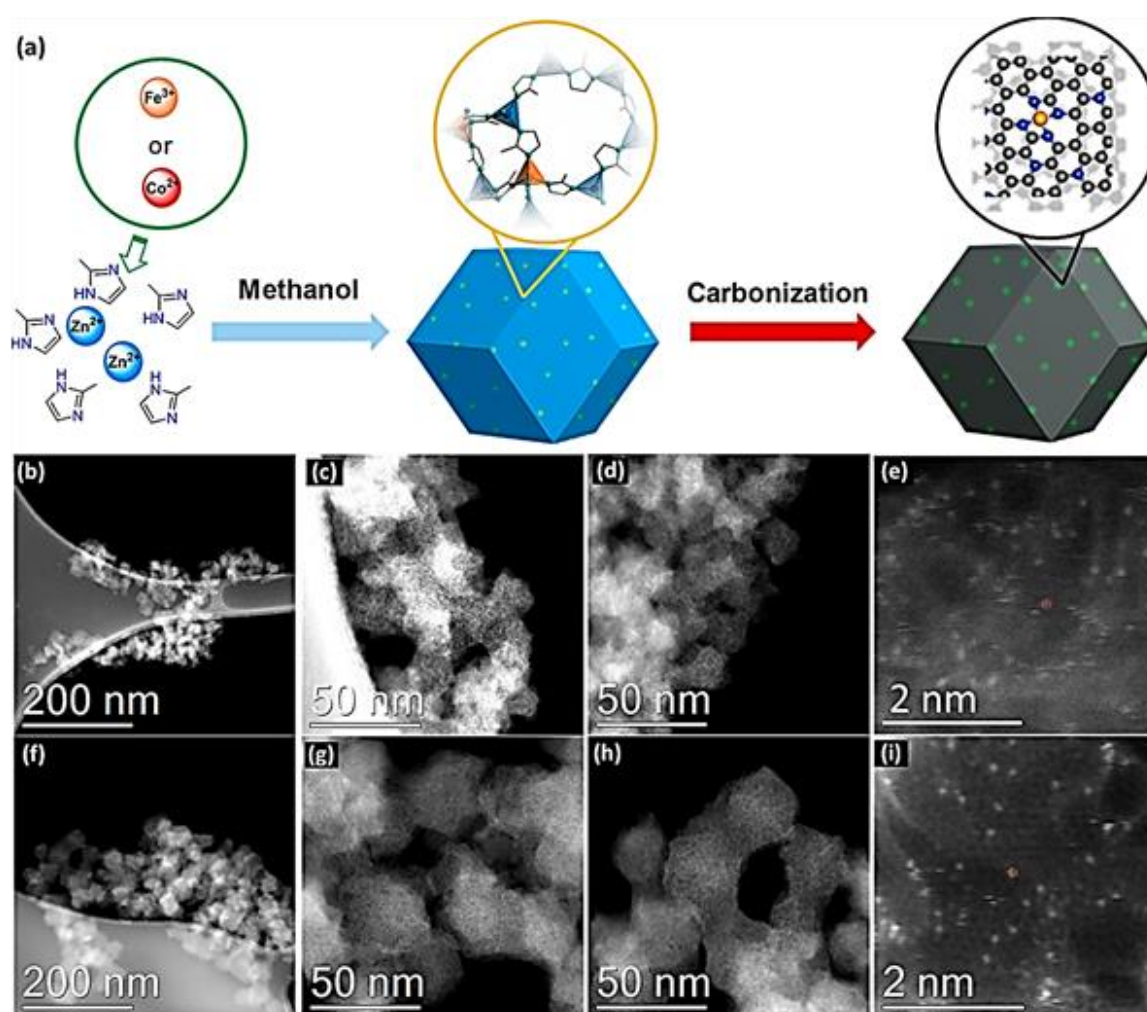


Figure 7. (a) Schematic illustration of the synthesis of M-N-C catalysts. The HAADF-STEM images of (b-e) Fe-N-C and (f-i) Co-N-C catalysts. Reprinted with permission from Pan et al., [193].

Similarly, Zhang and co-workers, deposited Fe nanoparticles on the surface of g-C₃N₄ nano-sheets morphology via single pot synthesis. The catalysts convert CO₂ to CO with 88% FE at -

0.38 V vs RHE and attain 23 mA cm⁻² current density. More so, the synergic effects between the nanosheet-like morphology and the highly active Fe nanoparticles provided large amounts of exposed ECAS sites during the CO₂RR process and demonstrated stability measurement for about 5 h [198]. Furthermore, Genovese *et al.*, synthesized nanostructured Fe³⁺ oxyhydroxide on N-doped carbon. The thin layer Fe-phase morphology on fiber structure reduced CO₂ selectively to acetic acid with FE of 61% at 0.5V vs Ag/AgCl [194]. They relate the performance to the creation of N-coordinated Fe²⁺ sites at the boundary between FeO(OH) (oxyhydroxide) and the thin layer of N-doped carbon. Similarly, Zhang and co-workers reported a graphene layer morphology by extended thermal pyrolysis of hemin and melamine molecules on graphene. The Fe-N-C single atom morphology catalyzed CO₂ to CO with 97% FE at -0.46V corresponding to -0.35V vs RHE over-potential. The catalysts maintained a long-term durability test for about 24 h measurement [190]. The notable selectivity for the conversion to CO was ascribed to the existence of highly efficient singly dispersed Fe active sites on the N-doped graphene layer. On the other hand, Gang *et al.*, oxidized petroleum coke as a carbon source and doped Ni/Fe and N afterward, and the resultant catalysts demonstrate large sheet-like morphology. The sheet-like morphology achieved 90% CO FE at -0.7 V versus RHE, in addition, the bimetallic doping of Ni and Fe enhanced both the total current density and CO partial current density and long term stability for 24 h [192]. The exceptional performance metrics can be attributed to the distinctive structures of the nanosheet/nanolayer, which possess numerous edge and corner sites. These structures result in a strong local electric field, making them highly probable active sites for the CO₂RR.

2.2.3 Iron (Fe) based Electrocatalysts

Co catalysts have been widely employed as viable alternatives to noble metals electrocatalysts due to their remarkable activity and stability [183], [201]. Unfortunately, high

overpotentials and low FE of target products have hampered the practical applications of Co-based catalysts. Co-based systems enjoy multiple alternatives for catalytic CO₂ conversion to hydrocarbons, while conversion to CO has been reported only in the presence of metal additives [202], [203]. For instance, Aljabour *et al.* utilized the electrospinning technique to obtain Co₃O₄ nanofiber morphologies (See **Figure 8a-f**) as an electrocatalyst for CO₂ reduction. The nanofibers exhibited high selectivity towards CO with a FE of 65%. Additionally, stability measurements indicated that the nanofibrous morphology electrodes remained intact for a duration of 8 h.[202]. Also, Yang *et al.* utilized a SA Co by fabricating an unsupported continuous porous structured membrane. The 3D cross-linked nanofibers morphologies (See **Figure 8g-j**) present enormous electrochemical active surface areas and ease reactant diffusion. The outcome of their findings reveals the conversion of CO₂ to CO with FE of 91% at -0.9V vs RHE and 67 mA cm⁻² current density. The long-term performance of the nanofibers evaluated for 50 h shows excellent stability [204]. In another outcome, Wang *et al.* prepared atomically dispersed Co atoms anchored on N-doped porous carbon by high-temperature pyrolysis and obtained a rhombic dodecahedron (polyhedra interlinked) morphology (See **Figure 9**) analogous to the parent ZIF-67 morphology. The findings show high selectivity towards CO with a performance of about 94% FE and a current density of 18.1 mA cm⁻² at an over-potential of 520 mV. The authors establish a correlation between the outcome to the lower Co-N coordination number. This lower coordination number facilitates the activation of CO₂ to form the CO²⁻ intermediate, thereby enhancing the electroreduction activity of CO₂. Furthermore, stability measurement for 60 h reveals insignificant deterioration in current density and virtually constant CO FE [205].

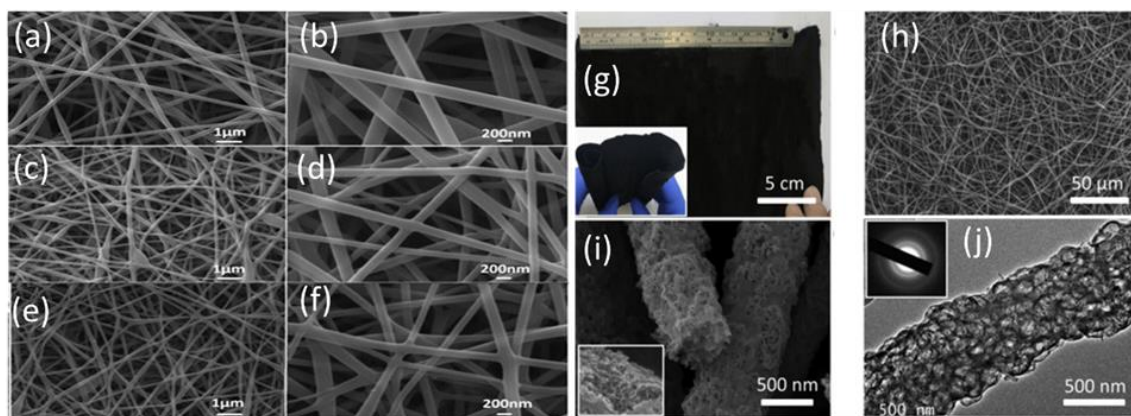


Figure 8. SEM images of Co-PAN nanofibers before annealing (a and b); after annealing at 550 °C for 30 min in the air (c and d). Reprinted with permission from Aljabour et al., [202], and after electrochemical investigations and (g) Photos of a piece of flexible CoSA/HCNFs membrane ; (h-j) FE-SEM, and (d) HR-TEM. Reprinted with permission from Yang et al., [204].

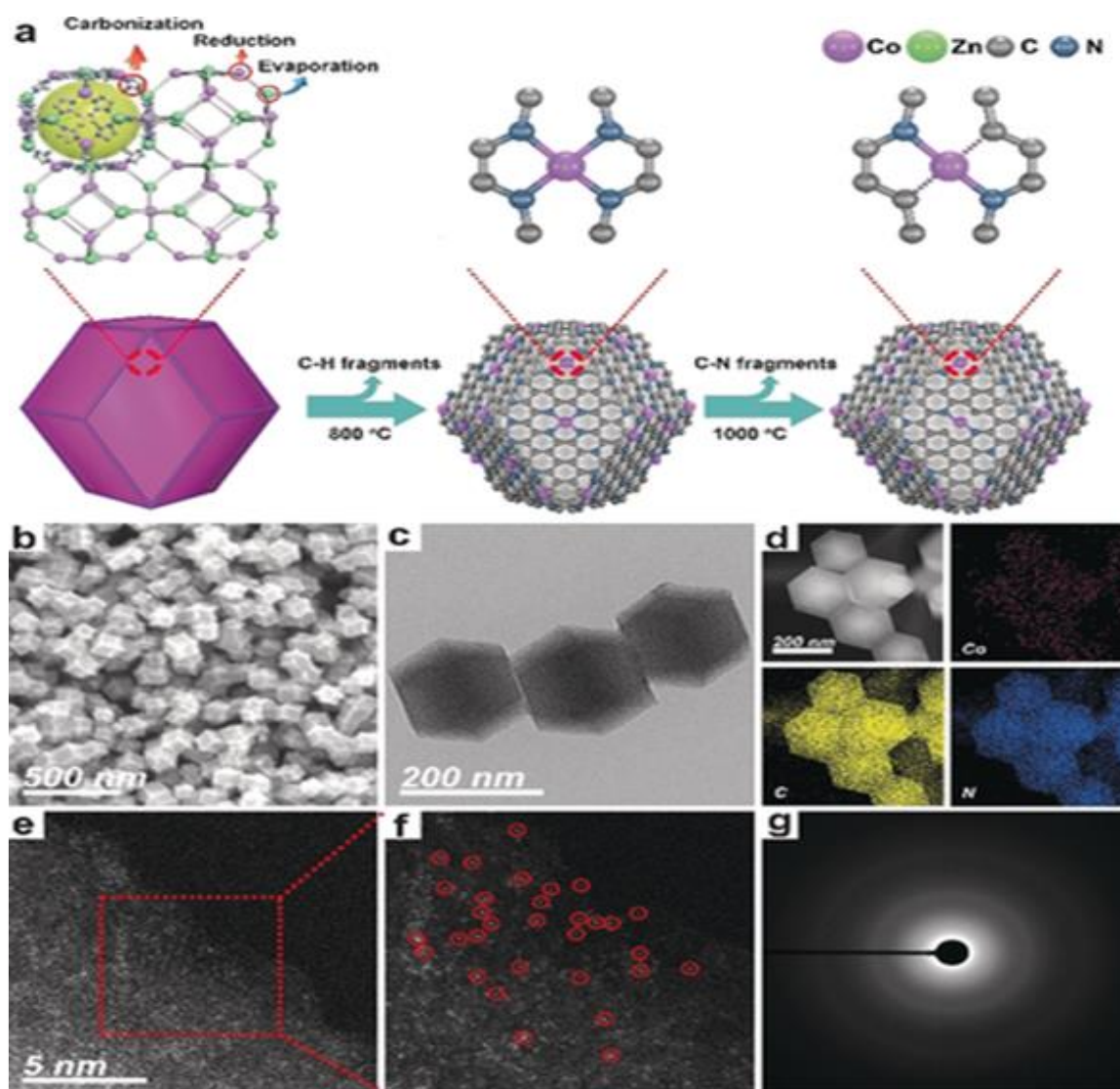


Figure 9. (a) the formation process of Co-N₄ and Co-N₂ (b) SEM and (c) TEM images of Co-N₂. (d) Examination of the corresponding EDS mapping reveals the homogeneous distribution of Co and N on the carbon support. Reprinted with permission from Wang et al., [205].

Also, Song and co-workers pyrolyzed ZnO@ZIF and obtained Co single atoms and N functional groups. The irregular carbon sphere morphologies with a rugged surface and an average diameter of approximately 200 nm convert CO₂ to CO with approximately 100% FE. The 3D hollow structure and sponge-like thin shell carbon with hierarchical porous coordination simplified mass diffusion and utmost revelation of active sites. Further analysis of the stability test demonstrates the irregular carbon spheres morphologies to endure long term durability, and slight degradation of current density after constant electrolysis for 24 h [206].

Cheng *et al.*, dispersed atomic Co on N-doped carbon nanotube using first of its kind multiple step pyrolysis technique. Although the Co-based electrocatalyst demonstrates activity toward CO, however inferior selectivity (around 20% FE) was achieved compared to its corresponding metal-based counterpart [207]. On the other hand, Huang *et al.*, synthesized moderately oxidized Co nanoparticles dispersed on single-layer N-doped graphene by a simple one-pot synthesis method. The ultrathin sheet-like morphology electrocatalyst demonstrates high selectivity for methanol with FE of 71.4% at -0.90V vs saturated calomel electrode (SCE). Remarkably, the catalyst possessed high stability after 10 h CO₂RR, and the ultrathin sheet-like morphologies, particle size, structure, and element contents of the catalyst almost remain stable [201]. Furthermore, the roughness observed in the sheetlike morphology, resulting from the presence of numerous crinkled structures, can be attributed to the formation of defective structures and nitrogen doping. These factors contribute to the catalytic activity of the material. Lin and co-workers anchored Fe-N with Co-phthalocyanine using successive pyrolysis and post-loading approach to enhance CO₂RR. The rhombic-dodecahedron morphologies aid to transform CO₂ to CO with FE greater than 90% over a wide range of -0.13 to -0.84 V potential vs RHE. The results simultaneously reveal high current density and stability at low overpotentials [208]. This is largely due to suppression of the competitive HER at Fe-N sites, as a result signifying an unprecedented synergistic catalysis effect toward CO₂RR. Equally, Nazir *et al.*, synthesized a hybrid structure of Co₃O₄ and CuO NSs by solution combustion synthesis. The porous fibrous morphologies aid to catalyze CO₂ to formate with an increase in current density to about 0.6 folds than the corresponding individual oxides [203]. The authors observed the activity of the mixed oxide to supersede the individual oxide nanoparticles.

2.2.4 Iron (Fe) based Electrocatalysts

Nickel (Ni) is an abundant transition metal, with broad applications in catalysis. Nevertheless, its electrocatalytic CO₂ RR in an aqueous medium is significantly limited as a

result of contending HER and surface poisoning by intermediates such as CO among others [209]–[216]. Consequently, several strategies have been employed to fine-tune its catalytic performance in the direction of CO₂RR. The commonly adopted approach is the coordination of Ni with N-doped carbon. For example, Daiyan *et al.* developed Ni-coordinated graphitic carbon shell morphologies via pyrolysis. In addition to improved electronic structure, this approach not only enhanced the stability of the Ni-coordinated graphitic carbon shells for 50 hrs but also prevents poisoning of the catalysts. The findings demonstrate an FE of 96% for CO and a partial current density of 17 mA cm⁻² at -1.0 V vs RHE. Additionally, the Ni-coordinated graphitic carbon shells revealed very similar EIS, ECSA, and electro-kinetics for CO₂RR [213]. Also, Jia *et al.*, investigated carbon-coated Ni nanoparticles supported on N-doped carbon through pyrolysis and obtained carbon shell morphologies. Their findings reveal suppression of HER and CO₂ conversion to CO with a FE of 94% at -0.59V over-potential, reaching a partial current density of 22.7 mA cm⁻² [209]. The selectivity was achieved by fine-tuning the support surface through control of the MOF to tailor the properties of the Ni nanoparticles. The authors observed lattice fringes within the Ni nanoparticle, specifically corresponding to Ni(111) facets, which were suggested to be the catalytic active sites. Additionally, through high-angle annular dark-field imaging, the absence of edges typically observed in works related to single atoms was noted in Ni@NC, indicating the absence of isolated Ni single atoms within the structure. In contrast, high-angle annular dark-field images of Ni-N-C showed numerous bright atomic spots dispersed throughout the carbon matrix, suggesting the presence of Ni single atoms within the catalyst. Similarly, Tan *et al.*, studied N-carbon layer coated Ni nanoparticles by employing a chemical method. Their findings disclosed a sea cucumbers morphology like Ni electrocatalyst with high FE 97.5% for CO reaching a current density of 43.8 mA cm⁻² at a fairly potential of -0.61 V. Furthermore, the sea cucumbers-like morphology provides a larger ECSA, stability for 36 h of electrolysis and

efficiently circumvent catalyst poisoning by eliminating CO from catalyst surface and overpowering the competing HER [210]. The authors suggest Ni(111) facet to serve as the active site for CO₂RR based on the observation that it exhibits the most intense diffraction peak in XRD analysis. This indicates that the Ni(111) facet is highly exposed and likely plays a crucial role in the catalytic activity for the CO₂ reduction reaction. Liu and co-workers incorporated NiO nanoparticles on a mesoporous graphene sheet by employing low-intensity pulsed laser irradiation and pyrolysis treatments. The outcome of the results reveals a FE of 87.5% for CO at -0.74V vs RHE and a high current density of 35 mA cm⁻² with stability exceeding 12 h [212]. The authors observed pyridinic N coordinated to Ni to be responsible for improved CO₂RR reduction instead of pyrrolic N. Likewise, Ma *et al.*, reported the synthesis of innovative Ni single atom catalysts embedded in N-doped hollow carbon spheres morphologies (See **Figure 10**) through thermal treatment. The results disclose 80% FE of CO at -0.78 V potential vs RHE which could be ascribed to the Ni ions coordinated to N thus acting as the active site to catalyze CO₂RR. Furthermore, excellent stability during 4.5 h of CO₂ reduction electrolysis [217]. But in contrast to the report by Liu *et al.*, the syngenic effect between pyrrolic-N and Ni ions contributed to the higher performance recorded. Li *et al.* reported various sizes of Ni single atoms distributed through N-doped carbon by chemical approach followed by calcination at elevated temperatures. The results indicate that the catalysts maintain the rhombic dodecahedron morphologies of the substrate (ZIF-8). The rhombic dodecahedron morphology catalyst aid to transform CO₂ achieving the highest CO FE of 97% at -0.8V vs RHE, a current density of greater than 10 mA cm⁻² and withstand long term stability after 24 h of nonstop electrolysis [211]. Analysis of the Gibbs free energy for the rate-determining step, specifically the formation of *COOH, provides significant evidence that smaller-sized Ni NPs exhibit a lower energy barrier compared to larger-sized Ni NPs. This finding is consistent with the experimental results. The lower energy barrier observed in

smaller particles indicates that they have a higher number of active sites available for binding with CO₂ conversion intermediate species. This suggests that smaller particles have a greater propensity for catalytic activity in the CO₂ conversion process. In another development, Cheng *et al.*, reported an atomically dispersed Ni, NiCo, and NiPt on nitrogen-doped carbon nanotubes using several stage pyrolysis processes. In comparison, Ni-based exhibited excellent performance and selectivity among its prepared counterpart catalysts accomplishing a FE of 89% and 91% at -0.55 V and -0.7 V vs RHE [207]. **Table 1 and 2.** below summaries some catalysts' morphology and their corresponding activity and selectivity in CO₂RR.

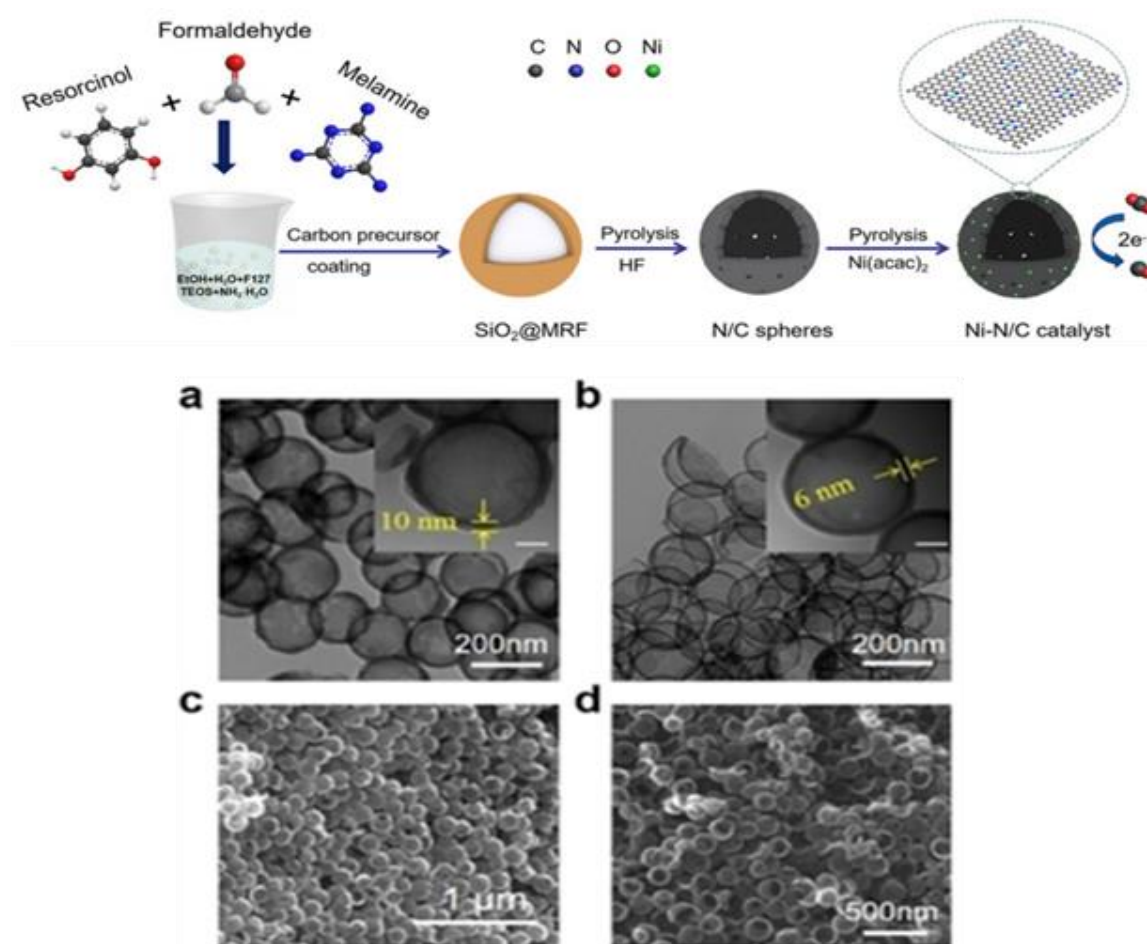


Figure 10. The synthesis procedure of Ni-N/C-x., TEM images of (a) Ni-N/C-3/2, and (b) Ni-N/C-1/4 (scale bars is 50 nm in inset images); (c) SEM images of Ni-N/C-3/2, and (d) Ni-N/C-1. Reprinted with permission from Ma *et al.* [217]

Table 1. Summary of electro-catalyst with their corresponding morphology and FE (%)

Catalysts	Morphology	FE (%)	Products	Over-potential (V)	Ref
Ni-based catalyst					
Ni SAs -dispersed N-doped carbon	Carbon nanotubes	97	CO	0.90 vs RHE	[218]
Atomically dispersed Ni(i) N-doped carbon array	Carbon nanotubes	97	CO	0.62 vs RHE	[219]
Ni SAs on N-doped graphene oxide	Graphene oxide sheet	97	CO	0.80 vs RHE	[220]
Ni SACs dispersed N-doped carbon	Carbon nanotubes	91.3	CO	0.70 vs RHE	[207]
Ni SACs dispersed N-doped carbon	Tubular	99.4	CO	0.24 vs RHE	[221]
Ni SACs dispersed N-doped carbon tubes	Carbon nanotubes	99	CO	0.60 vs RHE	[222]
Ni SAs on N-doped graphene	Graphene sheets	97	CO	0.61 vs RHE	[223]
Ni-N-C	Rhombic dodecahedron	96	CO	0.57 vs RHE	[224]
Ni-N-C	Rhombic dodecahedron	99	CO	0.68 vs RHE	[225]
Ni-N-C	Hallow carbon spheres	97	CO	0.8 vs RHE	[226]
Ni N-modified porous carbon	Carbon Nanotube	94	CO	0.66 vs RHE	[227]
Ni Nitride on multiwalled	Carbon Nanotube	89	CO	0.73 vs RHE	[228]

Ni and N co-doped Carbon	Nanosheet/Nanotube	91	CO	0.74 vs RHE	[229]
Ni, Fe, and N co-doped carbon	Sheets-like	97	CO	0.80 vs RHE	[192]
Ni nanoclusters supported on N-doped carbon	Rod-like	98.7	CO	0.88 vs RHE	[230]
Ni-doped indium oxide	Nanofibers	90	HCOO ⁻	0.80 vs RHE	[231]
Ni-N-C	Ball like	97	CO	0.80 vs RHE	[232]
Ni-N-C-rGO	Nanosheet	85	CO	0.87 vs RHE	[233]

Cu-based catalysts

Cu ₂ O	Quasi-spherical	78.5	C ₂	1.1 vs RHE	[234]
Copper oxide	Nanowire (2.3 μm)	63	CO	0.69 vs RHE	[235]
Copper oxide	Nanowire (2.7 μm)	52	HCOO ⁻	0.69 vs RHE	[235]
	Rhombic dodecahedral				
Cu-doped ZIF-8	cubic	35.2	CH ₄	-	[236]
Cu ₆₈ Ag ₃₂	Nanowires	60	CH ₄	0.85 vs RHE	[237]
CuO	Nanosheet	56.2	C ₂ H ₄	0.87 vs RHE	[83]

Table 2. Correlation between electro-catalyst's morphologies and their corresponding and FE

Oxide-based catalysts				
Catalysts	Morphologies	Products	FE (%)	Ref.
Mn-based	Flower-like (platelet)	CO	94.8	[181]
	Nanosheets		71	[182]
Co-based	Nanofibers		65	[202]
Cu-based	Cubic	C ₂ H ₄	51.3	[238]
			57.3	[239]
	Truncated octahedron	Alcohols (CH ₄ O, C ₂ H ₆ O and C ₃ H ₈ O)	26.2	[240]
	Urchin-like		10.7	
	Octahedron		25	
	Nanowires	CO	55.4	
			41	[241]
			77.4	[242]
Zn-based	Dendritic	CO	34.1	[243]
WO ₃	Nanorod		68	[244]
			86	[245]
			42	[246]
Nanoparticles (NPs)				
MnO diamond	chiffon shape	CO	86	[184]
Fe NPs	g-C ₃ N ₄ nanosheets		88	[198]
Co NPs	g-C ₃ N ₄ nanosheet	CH ₃ OH	71.4	[201]
Ni sea cucumbers NPs	g-C ₃ N ₄ nanosheets	CO	87.5	[212]
Cu NPs	N-doped nanodiamonds	C ₂ H ₆ O and C ₂ H ₃ O ₂ ⁻	63	[247]
Zn cylindrical NPs	g-C ₃ N ₄ nanolayer	CO	94	[248]
Pd NPs	Nanocube	HCOO ⁻	90-100	[249]
	Rhombic-dodecahedron		95	[250]
	Branched		97	
	low-index facets		95	
	Cube		90	[251]
	Rhombic-dodecahedron		50-80	
	Nanosheets		>80	
Ag NPs	Microrod array	CO	93	[252]
	Flat		70	[253]
	Nanocubes		90	[254]
			93	[255]
	octahedra		62.7	[256]
	Nanosheets		48.1	[257]
	Nanowires		95	
	microspheres		98.7	
			94	[259]
Heterostructure				
Fe/Ni-N-PC	Sheet-like	CO	90	[192]
Fe-N/CoPc	Rhombic-dodecahedron		90	[208]
Cu-Bi	Dendritic	HCOO ⁻	94.7	[260]
Cu-Sn			91	[261]

Cu-Sn	Flat	CO	73.9	[262]
	Rod		65	
	3D hierarchical		98.6	
Zn-Ag-O	Spherical	CO	94.1	[263]
AuNP-in-PdNS	Egg-waffle-like	HCOO ⁻	>97.8	[264]
Pd-PdO	Nanowires	CO	94	[265]
Single-atom-based catalysts (SACs)				
Mn–N ₃ SACs	Nanotube	CO	98.8	[179]
	Nanolayer		97	[186]
Fe-N-C SAC	Rhombic-dodecahedron		94	[205]
			85	[195]
	g-C ₃ N ₄ layer		93	[193]
Co-N-C SAC	Nanofibers		97	[190]
	Rhombic-dodecahedron		91	[204]
	Sphere		94	[205]
	Nanotube		100	[206]
Ni-N-C SAC	Carbon shell		20	[207]
			96	[213]
	Hollow carbon spheres		94	[209]
	Rhombic-dodecahedron		80	[266]
	Carbon nanotubes		97	[211]
	Sea cucumbers		89	[207]
		97.5	[210]	

2.2.5 Copper (Cu) based Electrocatalysts.

Cu-based electrocatalysts have attracted considerable attention for CO₂RR with enormous, reported work, because of their uniqueness and ability to catalyze the electrochemical conversion of CO₂ to value-added chemicals. Besides, a Cu-based electrocatalyst is unarguably the most extraordinary catalyst for converting CO₂ to several forms of liquids and gas products [243], [267]–[276]. Consequently, considerable research attention is focused on improving the distribution of the product (selectivity) through systematically adjusting its physical structures [83], [277]–[280]. For example, Tan *et al.* reported multi-shelled CuO microboxes (See **Figure 11a-f**) obtained through a chemical method for selective conversion of CO₂ to ethylene with 51.3% FE. Their findings reveal a high current density of 61.9 mA cm⁻², large ECSA, and

stability for 10 h under the electrolysis process [238]. Furthermore, the cubic morphology aids the ease of access of active sites, increase adsorption of CO (as intermediate), prevents the distribution of formed OH^- , and facilitates C–C coupling reaction. Based on their findings, the authors conclude that the unsaturated coordination structure of the multishelled CuO microboxes provides a higher number of active sites. These active sites are beneficial for enhancing the catalytic efficiency of the material in the context of CO_2RR .

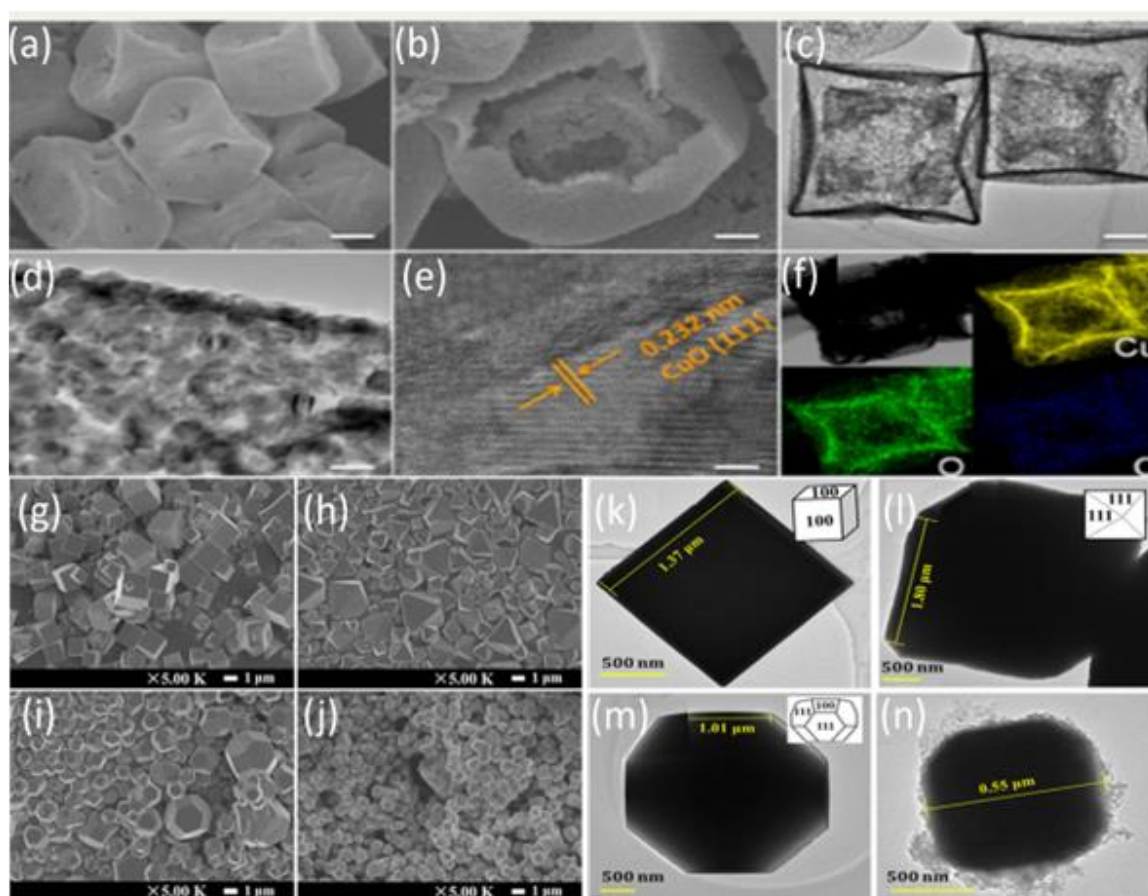


Figure 11. CuO microboxes (a). SEM images (b) and (c), TEM images (d) and (e), HRTEM image (f), and EDX mapping (g) of CuO microboxes. Scale bars, 300 nm in (b), 150 nm in (c), 200 nm in (d), 20 nm in (e), 2 nm in (f). Reprinted with permission from Tan et al., [238]. SEM and TEM images of different synthesized Cu_2O catalysts: (g & k) Cu_2O -c, (h & l) Cu_2O -o, (i & m) Cu_2O -t, and (j & n). Reprinted with permission from Liu et al., [240].

Similarly, Jung and co-workers synthesized a cubic Cu_2O morphology by a one-pot approach. The results demonstrate large ECSA and selectivity towards ethylene reaching a 57.3% FE with a decrease in nanoparticle size [239]. The amplified ethylene conversion activity was

correlated to the morphological alteration over reaction time. In which the crystal plane deformed, beginning from the surface of the aggregated nanoparticles, which subsequently fragment into 2-4 nm Cu-based particles on the carbon support. These particles come into contact with each other, resulting in the formation of numerous boundaries. Also, Liu *et al.* synthesized diverse Cu₂O nanostructure morphologies for CO₂RR via a hydrothermal approach and obtained cubic, octahedrons (See **Figure 11g-n**), truncated octahedrons, and urchin-like structures. The electrochemical CO₂ reduction reveals the activity-to-alcohols, such as methanol, ethanol, and isopropanol as the major products. More so, the octahedron morphology demonstrated great and continuous ECSA for more than 6 h and best FE of 35.4% comprising of 4.9%, 17.9%, and 12.6% corresponding to methanol, ethanol, and isopropanol respectively at 0.51 mA cm⁻² partial current density [240]. In addition to the facet's dependent effects, the efficiency of the CO₂RR was likewise related to the surface reconstruction of Cu₂O which includes different concentrations of oxygen-vacancy defects and the distinct lengths of Cu-O bonds across different crystal facets. In another development, Wang *et al.*, synthesized Cu nanowire arrays morphology (**Figure 12a-c**) by thermal oxidation developed on Cu mesh. Thermal and electrochemical reduction were employed to reduce copper oxide to Cu while preserving the morphology of nanowires. The outcome of the work reveals H₂ and CO (FE 41%) from a 1:2 to 3:1 ratio and high current density at 0.5V vs RHE [241]. The activity and selectivity of the catalysts were found to be influenced by the initial thickness of the Cu₂O layer, with the enhanced catalytic performance attributed to the presence of grain boundaries. It has been demonstrated that the surface terminations at grain boundaries are active for CO₂ reduction, and the lattice strain induced by these grain boundaries can tune the binding energies of CO₂ reduction intermediates, thereby reducing the activation barriers for CO₂ activation

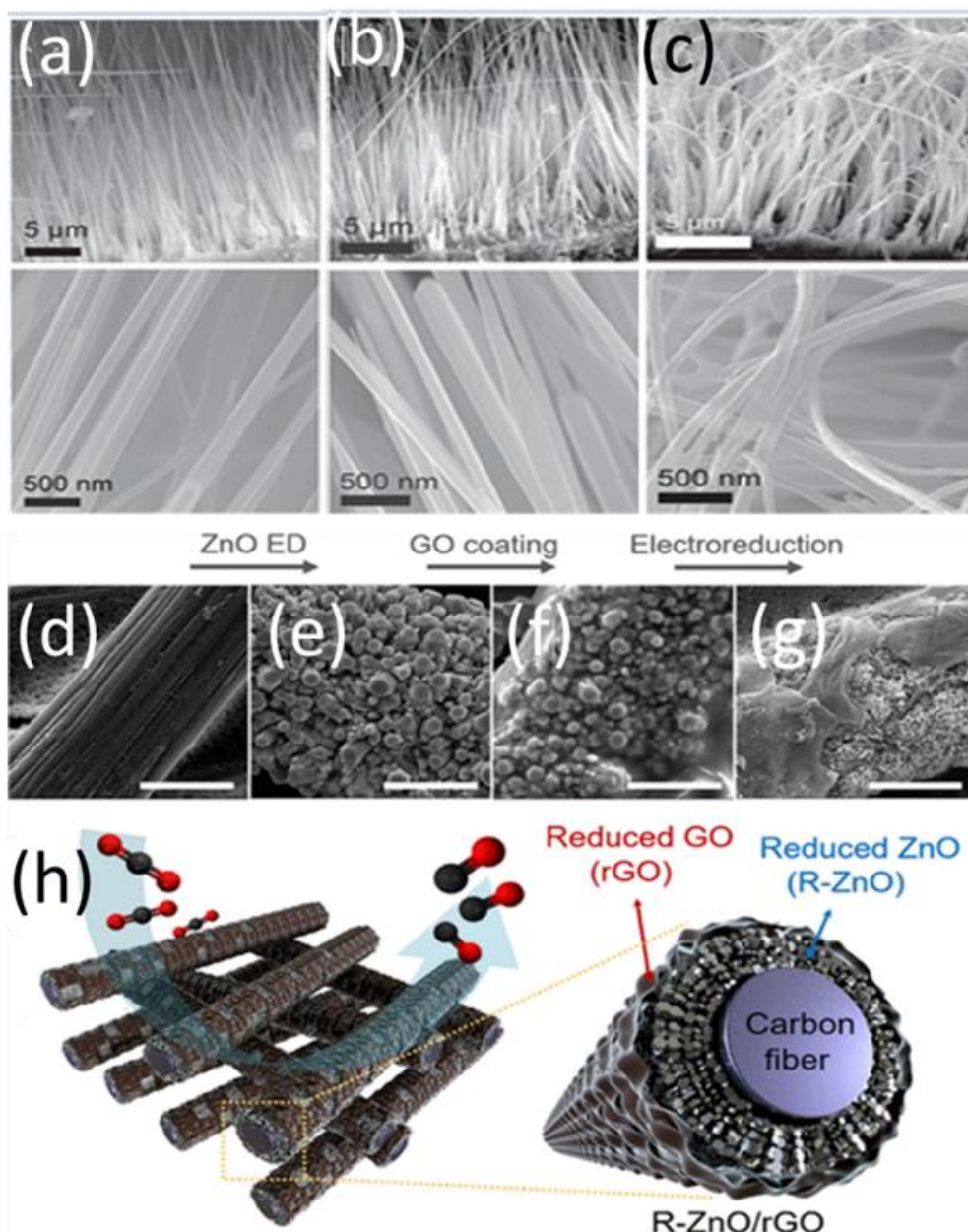


Figure 12. Representation of low- and high-magnification OD-Cu NAs SEM mages of (a) as-synthesized CuOx NAs, (b) thermally reduced CuOx NAs-42 C/cm², and (c) OD-Cu NAs generated from CuOx NAs-42 C/cm². Reprinted with permission from Wang et al., [241]. And SEM images of (d) one fiber of carbon paper, (e) electrodeposited ZnO on carbon paper, (f) ZnO/GO, and (g) RZnO/rGO. Scale bar, 5 μm. (h) Visualization showing the detailed structure of R-ZnO/rGO electrodes. Reprinted with permission from Le Tri Nguyen et al., [248].

Also, Choi *et al.* prepared Cu nanowires through in situ electrochemical activations of pre-grown Cu nanowires. The Cu nanowire morphologies catalyzed CO₂ to ethylene with 77.4% FE at 17.3 mA cm⁻² partial current density and demonstrated stability for 200 h [281]. The

higher ethylene production is credited to the exceptional surface structure of the Cu nanowires having ample stepped sites. Computational studies have shown that under operating conditions, these steps are thermodynamically more favorable compared to the Cu(100) surface. Additionally, the stepped surface promotes the formation of C₂ products by suppressing the C₁ pathway and hydrogen production. Equally, Wen and co-workers reported Cu nanowires-like morphologies obtained via the potential cycling of copper oxides synthesized through hydrothermal treatment. The synthesized nanowires-like morphology catalyzed CO₂ selectively to C₂ with 34.1% and 80 mA cm⁻² partial current density at -0.8V vs RHE [243]. The authors attributed the performance to the improved surface defects formed on the Cu catalysts in the course of potential cycling. Ebaid *et al.*, studied regular octahedron mesoporous metallic Cu catalyst synthesized by electrochemical reduction of thermally nitride Cu foil. The regular octahedron morphologies exhibited a total of 68% FE for ethylene, methanol, and propanol with predominant oxygenated products and a current density of 18.5 mA cm⁻² at -1.0V vs RHE [244]. The performance recorded was considerably due to the extreme roughness of the mesoporous regular octahedron morphologies which leads to a higher exposure of under-coordinated Cu surface sites. These sites have a strong affinity for adsorbed CO compared to low-index Cu facets such as Cu(111) and Cu(100). Consequently, the reduction of adsorbed CO is promoted rather than its desorption. The presence of square sites adjacent to steps further stabilizes intermediates, such as OC-CO and OC-CHO, which play a crucial role in the formation of C₂ products like C₂H₄ and C₂H₅OH. Moreover, the higher concentration of surface sites exhibiting strong CO binding suppresses the competitive adsorption of hydrogen, resulting in an increased ratio of oxygenates to hydrocarbons. This phenomenon leads to a higher yield of oxygen-containing compounds compared to purely hydrocarbon products. To fine-tune the Cu electronic properties and enhanced its selective, Wang *et al.*, reported N-doped nanodiamonds structure and Cu nanoparticles using microwave plasma-assisted chemical

vapor deposition. The nanodiamond structure catalyzed CO₂ to C₂ oxygenates with 63% FE at -0.5 V vs RHE and is stable for 120 h [247]. They attributed the selectivity of C₂ oxygenate as a result of conversion that ensues at the interface and the advantage from the synergy of the two components. Bimetallic electrocatalysts recently have demonstrated excellent CO₂ reduction performance and efficiency [269]. For instance, Xiong *et al.*, synthesized Cu-Bi for CO₂RR by electrodeposition technique and obtained dendritic morphologies. The catalysts aid in catalyzing CO₂RR to formate with FE of 94.7% at -1.0 V vs RHE and display long-term stability [260]. The higher activity and selectivity recorded largely were ascribed to many available reaction sites naturally from the irregular atomic structures on the amorphous dendritic Cu-Bi electrocatalysts. More so, the morphology aids in fast-tracking charge transfer and enables the formation of adsorbed intermediates such as CO₂ (ads) anion. In the same way, Ju and co-workers achieved dendritic morphologies upon decorating Sn on Cu in two steps; electroplating of Cu followed by decoration of Sn. The findings reveal 91% FE for CO at 10 mA cm⁻² and -0.7 V vs RHE [261]. The authors attribute the enhanced performance of the catalyst to the local electric field induced by sharp morphological features. Sharp dendritic electrodes, for example, have the ability to nucleate and release gas bubbles at smaller sizes. This phenomenon improves the effective mass transport through convective flow, especially at higher current densities (>10 mA·cm⁻²). Both the convective flow and the dendrite morphology contribute to an increase in the local reagent concentration. As a result, there is an enhanced selectivity for the CO₂RR towards the production of CO rather than HER. The increased local reagent concentration and improved mass transport in the dendritic structure plays a crucial role in achieving this enhanced selectivity. Besides, investigation into the effect of morphologies on performance and products desirability suggests dendrite morphology favors great CO₂ absorption at the electrode surface and upholds an extraordinary CO FE over a wide-range potential than less sharp and rounder morphologies. Also, Yoo *et al.* investigated the

correlation between compositions and geometry of Cu-Sn through the construction of 3D hierarchical (3D-h) Cu nanostructure and chemical-based coating of Sn nanoparticles (NPs) and obtained flat, rod-like, and 3D-h Cu-Sn morphologies. The resulting CO₂RR to CO shows FE of 73.9% associated with flat morphology at -0.95 V vs RHE, 65% FE for rod at 0.9 V vs RHE, and 98.6% FE for 3D-h at -0.45 V vs RHE. Additionally, 3D-h presents the highest partial current density of 9.6 mA cm⁻², good stability for 10 h, and an incredible over-potential of 0.25 less than the corresponding morphologies [262]. 3D finite-element-based solver with COMSOL Multiphysics analysis demonstrates Cu rod, electric field to intensify at the edges of the rod. However, in the case of 3D-h Cu, a strong electric field is localized at the tip of the branches. Additionally, the hierarchical nanoscale geometry of the catalyst generates a strong localized electric field, leading to the accumulation of K⁺ ions near the catalyst's surfaces. These cations can alter the free-energy landscape for the CO₂ to CO reaction and facilitate the charge transfer between the catalyst and the reactant. The authors concluded that the activity and selectivity of CO were improved as the geometric configuration turned out to be complex in favor of flat, rods, and 3D-h Cu-Sn.

2.2.6 Zinc (Zn) based Electrocatalysts

Zn-based catalysts are among the non-precious metals reported as an electrocatalyst for the CO₂RR to value added chemicals. However, this abundant Earth-metal suffers from low selectivity as a result of competing for hydrogen evolution reaction (HER) [282], [283]. Consequently, one strategy employed to enhance its electro-catalytic application is the design and fabrication of nanostructure [284], [285]. For example, Nguyen *et al.* reported a cylindrical pack of porous Zn NPs wrapped in thin rGO layers (**Figure 12d-h**) synthesized via a chemical method. The outcome of the work reveals FE of 94% for CO at 1.0 V RHE, partial current density greater than 7 mA cm⁻², and long-term stability for 21 h under electrolysis [248]. The

studies reveal graphene oxide layers act as geometric barriers for the mass diffusion networks of reactants instead of altering the chemical states of the Zn-based electrocatalysts.

Kang *et al.* obtained a porous dendritic oxide derived from Zn via in situ electrolytic transformations of ZnO. The report demonstrates CO FE of 86% at -0.95 V RHE and a partial current density of 266 mA cm⁻² [245]. They observed the under-coordinated sites of the oxide derive Zn to contribute to the efficient CO₂RR performance than electrodeposited Zn metal. Besides, computational studies have shown that the formation of oxygen vacancies is energetically more favorable on step edges compared to terraces. Lourenco and co-workers pyrolyzed two different sources of carbon and achieved a hexagonal wurtzite structure and a 3D flower-like with nanoflakes architecture conforming to pristine biochar and ZnO. The study shows selectivity towards CO with FE of 85.8% at -1.1 V vs RHE and good long-term durability under CO₂ electrolysis [286]. The research findings demonstrate that catalysts incorporating both pyridinic and pyridine nitrogen within their framework exhibit superior performance compared to catalysts with a carbon matrix for ZnO particles. Another approach used in improving the electro-catalytic selectivity of Zn is the introduction of secondary metal to form a bimetallic structure [287]. For example, Zhang *et al.* reported Zn-Ag-O with spherical morphology (**Figure 13**) prepared through hydrothermal-assisted synthesis. Their work efficiently and selectively converts CO₂ to CO at 94.1% FE and is stable for over 150 h [263]. The finding demonstrates regulation of not only nanoparticle size but also gives extraordinarily high surface-to-volume ratio thus making active sites accessible which significantly aids CO₂RR activity.

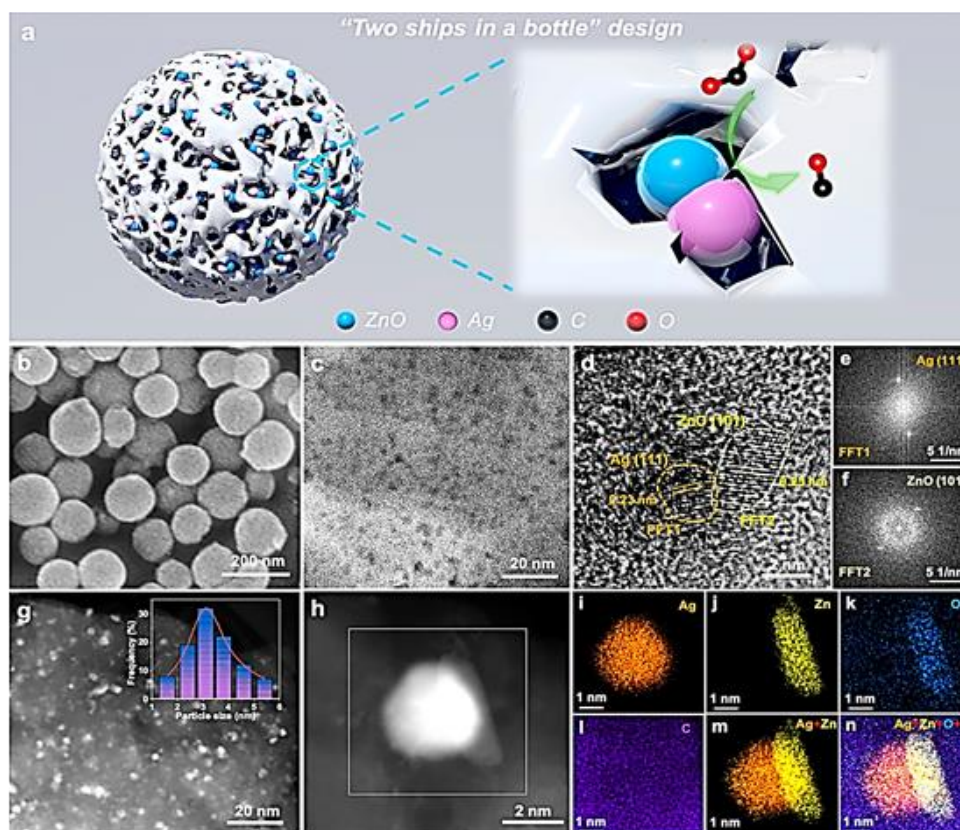


Figure 13. Design concept and structural characterizations of (a) Schematic of the “two ships in a bottle” design. (b) SEM image, (c) TEM image, (d) HRTEM image, and corresponding FFT diffraction patterns for (e) Ag(111) and (f) ZnO(101), (g) HAADF-STEM image (inset: size distribution histogram), (h) HAADF-STEM image, and (i-n) corresponding EDS element mapping of individual twinned ZnO-Ag nanoparticle accommodated within carbon pores of ZnO-Ag@UC. Reprinted with permission from Zhang et al., [263].

2.3 Second row of d-block transition metals

2.3.1 Pd-based Electrocatalysts

Palladium (Pd)-based catalysts have been widely recognized as possible candidates for a variety of electrochemical reactions including CO₂ reduction [288]. The major attraction for this type of material is that, unlike non-noble metals, they can selectively catalyze the reduction of CO₂ to formate at a very low overpotential. However, the traditional Pd electrocatalysts generally suffer from low activity and are vulnerable to CO poisoning. To this end, various structural and electronic modification strategies have been employed to realize highly stable and active Pd-based electrocatalysts. For instance, engineering the Pd surface morphology

using a variety of synthesis methods can be used to dramatically amplify the electrocatalytic performance [289]. Recently, Lv *et al.* fabricated mesoporous, cube-shaped Pd and Pd alloy NCs through a facile solution protocol by reducing PdCl_4^{2-} with L-ascorbic acid in the presence of cetyltrimethylammonium chloride (CTAC) as surfactant and Cl ions [249]. From these nanocubic morphologies, they achieved great selectivity (90-100%) and stability toward formate production from electrochemical CO_2 reduction. This enhancement might be attributed to the abundance of undercoordinated reaction sites as well as the large surface area provided by the mesoporous and nanocubic catalyst structure. Similarly, Klinkova *et al.* employed cetyltrimethylammonium bromide as a surfactant to prepare nanocrystalline shapes including cubes, rhombic dodecahedra, and branched NPs catalysts for formic acid electrosynthesis [250]. Their findings revealed that branched Pd NPs with abundant high-index facets inhibit CO poisoning while concurrently displaying a record geometric current density of 22 mA cm^{-2} at a low overpotential of -0.2 V and impressive FE of 97%. SEM image depicting the geometry of this study as shown in **Figure 14**. As a further example, Tackett *et al.* synthesized nanosized palladium cube and octahedron having preferentially exposed Pd(100) and (111) facets, respectively, as electrocatalysts for CO_2 conversion to syn gas. The authors noticed that the CO_2 reduction performances of the variously shaped Pd particles were evidently different. In comparison to Pd cubes, which yield FE in the range of 50 and 80 percent

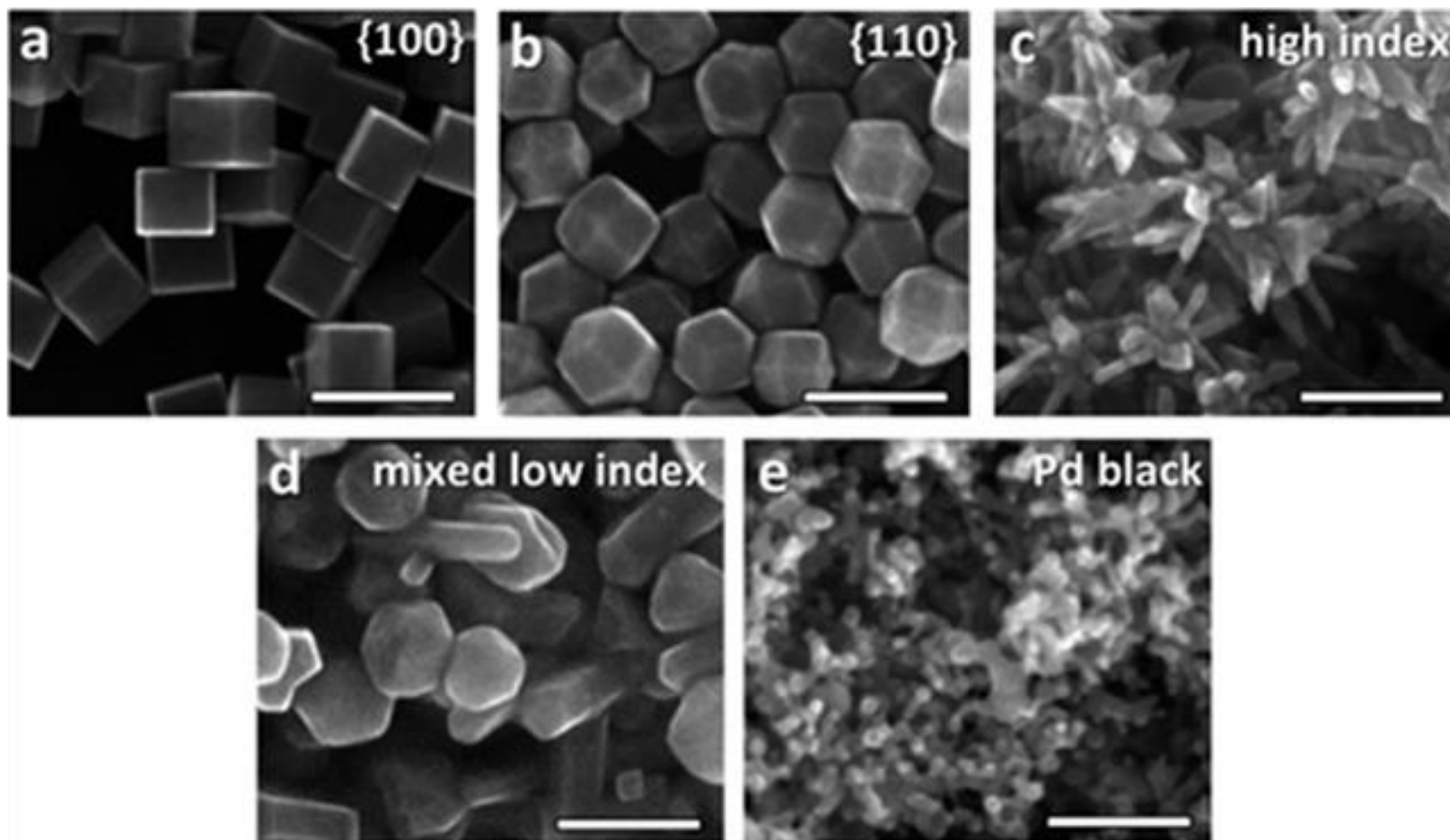


Figure 14. SEM images of nanocrystalline Pd electrocatalyst: (a) Cubes, (b) Rhombic dodecahedra, (c) and Branched nanoparticles, (d) Nanoparticles with mixed low-index facets, and (e) Pd black. Reprinted with permission from Klinkova et al [250] at potentials between 0.5 to 0.9 V versus RHE, the octahedra produced an FE greater than 80 percent for CO generation across potentials ranging from 0.5 to 0.9 V vs RHE. Noticeably, at 0.9 V versus RHE, the CO partial current density of the octahedra was three times that of the cubes [251]. The performance differences can be linked to a more facile reaction pathway for CO production on PdH(111) surface.

Benefiting from the electronic and architectural merits, 2D and 3D Pd-based nanomaterials have shown improved electrocatalytic performance when compared to bulk counterparts [290]. Gao *et al.* prepared Au nanoparticles intercalated in 2D Pd nanosheets (AuNP-in-PdNS) with egg-waffle-like morphology via a one-step chemical approach [264]. The authors employed this AuNP-in-PdNS to catalyze CO₂ conversion reaction and observed that it exhibited excellent selectivity (>97.8%) for formate generation at an applied potential of -0.6 V vs RHE. This outstanding selectivity for formate generation was ascribed to the regulation of local electronic structure after the intercalation of Au nanoparticles in the Pd nanosheet leading to the elimination of CO poisoning on the Pd surface. Wang *et al.* directly synthesized unique 3D porous Pd NPs ensembles via chemical reduction of Na₂PdCl₄ with NaBH₄ and employed them as the catalyst for electrochemical CO₂ conversion to syngas [291]. At the potential of -0.8 V vs RHE, these catalysts achieved higher CO selectivity (90%) and FE of CO and H₂ reaches up to 90%.

Lately, DFT calculations and experimental studies have revealed that modification of Pd nanostructures through the inclusion of foreign atoms (non-metal atomic doping) has a remarkable influence on their electronic and morphological features, and therefore triggers research in the fabrication of non-metal doped Pd nanomaterials for electrocatalytic applications [288]. Tao and co-workers reported the synthesis of Pd NCs doped with tellurium (PdTe), loaded on the surface of graphene through ultrasonication-assisted reduction of a mixture of PdCl₂ and TeCl₄ [292]. The maximum FE_{CO} of the doped Pd electrocatalyst was reported to be 90% at -0.8 V vs RHE, which was significantly higher than the undoped Pd catalyst counterpart. In another study, He *et al.* synthesized carbon-supported nitrogen-doped palladium (Pd-NC) single-atom electrocatalyst [293]. When evaluating CO₂ reduction activities, the authors observed that the Pd-NC catalyst displayed enhanced selectivity and exhibits higher activity toward CO generation (FE = 55% at -0.5 V vs RHE) than its Pd nanoparticle equivalent.

Metal–metal oxide heterostructures have recently attracted a lot of attention as efficient electrocatalysts for CO₂ reduction due to their superior catalytic characteristics compared to lone metal or metal oxide [294]. In a recent study, Wang *et al.* synthesized Pd-PdO heterostructured nanowires via a simple Pd(II) complex pyrolysis protocol and reported its enhanced CO₂ reduction performance (FE_{CO} = 94% at potential -0.8 V) over commercial Pd catalyst [265]. The unique architectural features of the prepared catalyst including Pd-PdO heterostructure and abundant defect sites were observed to induce enhancement of CO₂ adsorption and convert it selectively to the final CO product.

A crucial factor to consider when examining the influence of morphology is stability, both in terms of activity and maintaining the synthesized shape during the reduction reaction [267]. Nanostructured Pd like other transition metal-metal-based nanostructures may be prone to structural alterations during electrocatalytic CO₂ reduction, which in turn remarkably changes the catalytic performance. For instance, Zhao *et al.* reported dramatic changes in the morphology of ultrathin palladium nanosheets during CO₂ electroreduction [252]. The authors observed that within an hour of electrolysis, ultrathin hexagonal nanosheets with prominent (111) facets convert into randomly crumpled structures with enhanced exposure of (100) facets. Furthermore, they observed that this structural change dramatically enhances the density of active sites on Pd surfaces while lowering CO binding strength and boosting CO₂-to-CO conversion. At -0.7 V vs. RHE, the reconstructed Pd nanosheets achieved a high CO selectivity of 93%.

2.3.2 Ag-based Electrocatalysts

Silver is regarded as a good candidate for scalable CO₂ conversion to valuable products since it is efficient, selective, and cost-effective compared to other noble metals counterparts [295]. However, Ag has relatively not been widely investigated because the needed overpotential is large. The morphology of Ag catalyst can have a profound influence on the electrocatalytic activities in the reduction reaction of CO₂ by reducing the overpotential, prompting the development of

modified Ag catalysts [21], [296]. Nanostructuring the surface has been widely recognized as a viable protocol to enhance the selectivity of Ag catalyst for electrochemical CO₂ reduction at reduced overpotentials. For instance, Yu et al. employed a facile plasma activation procedure to produce different Ag microstructures consisting of reactive nanoparticles [253]. The authors were able to tune the silver morphology and optimize the catalytic performance by changing the oxygen plasma conditions. The optimized Ag morphology (microrod array) displayed outstanding CO₂ electroreduction activity to CO (CO partial current density $\sim 10 \text{ mA cm}^{-2}$ at -0.5 V vs. RHE) with remarkably high selectivity over a broad potential range (>70% between -0.35 V to -0.7 V vs. RHE). Similarly, with nanostructured Ag catalyst made by low-pressure plasma treatments, Mistry and coworkers achieved greater than 90% FE_{CO} at -0.6 V vs RHE, an extraordinary improvement in comparison with a flat Ag surface which needs greater than -0.9 V vs RHE to convert CO₂ [254]. In another study, Ma et al. demonstrated that nanostructured Ag catalysts derived via the reduction of Ag₂CO₃ exhibited high activity with 92% FE_{CO} at a very low overpotential of 290 mV, which outcompetes other reported Ag catalysts under similar reaction conditions [297]. SEM image depicting the geometry of this study is shown in **Figure 15a**. Furthermore, Chen et. al demonstrated that thiol-capped Ag nanostructures supported on carbon display high CO₂ to CO conversion activity (86.7%) when compared to bare Ag nanoparticles [298].

To make the synthesis of morphology-controlled Ag NCs more scalable, a novel synthesis procedure is required. Fan and co-workers developed a novel electrochemically driven approach to synthesize Ag nanocubes having uniform sponge-like morphology (SPC-Ag) for the electroreduction of CO₂ to CO [255]. The SPC-Ag demonstrated outstanding activity for CO₂ reduction with a maximum FE_{CO} of 93% at -0.9 vs RHE. Yang *et al.* also demonstrated the shape-dependent electrocatalytic CO₂ reduction activity of Ag cubes and octahedra fabricated via a morphology-preserved reduction of Ag₂O [256]. The authors reported that the Ag cubes show higher electrocatalytic performance than Ag octahedra, which was attributed to exposed facets. Chloride-derived Ag nanosheets fabricated using a facial electrochemical redox method showed

higher selectivity (~95% at a low overpotential of 0.29 V) for CO₂ electroreduction to CO compared to Ag foil, which is owed to their open structure and high surface area [257]. In addition, self-supported preferentially oriented nanoparticles were synthesized through a simple and scalable two-step anodization approach that oxidizes the Ag electrode to Ag₂CO₃ in the initial stage followed by fast electroreduction back to crystalline metallic AgNPs [299]. The catalyst displayed superior performance with high partial current density (4.4 mA cm⁻²) and FE_{CO} of 96.7% (0.69 V vs RHE), which is much greater than FE_{CO} of 60% (at an operating potential of 0.87 vs RHE) for polycrystalline Ag. As a further example, Luo and the group observed that in comparison with bulk Ag and comparable-sized nanoplates, triangular Ag nanoplates fabricated via shape-controlled synthesis showed the best CO₂ reduction activity toward CO production at very low overpotential (96 mV) and attains a maximum FE_{CO} of 96.8% at -0.855 V vs RHE [300].

Porous 3D Ag structures are also capable of effectively converting CO₂ to useful chemicals since they have high surface atom density. In a recent study, self-supported nanoporous Ag nanowires with a 3D network and enlarged surface area were fabricated by electrochemical reduction of AgCl nanowires, and the SEM image is shown in (**Figure 15b**) [258]. Obviously, the Ag nanowires demonstrate high selectivity with 98.7% FE_{CO} and 3.16 mA cm⁻² partial current density, which is much greater than that of Ag foil (FE= 15.1%). Daiyan and co-workers fabricated a novel 3D, porous Ag foam catalyst via an electrodeposition method, which exhibited remarkably enhanced accessible pores, and a high surface area with abundant active sites for a CO₂ reduction reaction to occur [31]. As a result, the AgFoam displayed high catalytic performance with 94.7% FE_{CO} and 10.80 mA cm⁻² current density at a potential of -0.99 V vs RHE. Similarly, Wei *et al* employed the electrodeposition technique to synthesize 3D porous Ag nanofoam with predominantly curved surfaces modified by thiocyanate ligands [301]. The authors observed that when utilized as a catalyst for the electro-conversion of CO₂, the Ag nanofoam can sustain an excellent CO selectivity (FE > 90%) in a broad operation range (-0.5 to -1.2 V vs RHE) and demonstrates a maximum mass activity of 23.5 A g_{Ag}⁻¹, which is much greater than those of Ag

nanoparticles and Ag foil. In another study, nanoporous Ag microspheres with uniform spherical morphology were synthesized using a template-assisted method for the selective electroreduction of CO₂ to CO [259]. The porous Ag catalysts exhibit excellent selectivity and achieve 94% FE_{CO} at an overpotential of -0.735 V, which is much greater than solid Ag (63.5%). The high performance of porous Ag was ascribed to the unique hollow structure and high density of exposed active sites.

Core-shell nanowires (CSNW) arrays have also attracted attention in electroreduction reactions because of their outstanding activity arising from effective charge transport and large ECSA [302]. Ge *et al.* reported the synthesis of vertical Ag@AgCl_x core-shell nanowire array via direct imprinting of the nanowire array on silver foil substrate [303]. The authors observed that in comparison to the Ag foil, the Ag@AgCl_x nanowire array has a significantly greater CO₂ electroreduction activity (103 times higher). They attributed the record-high activity of the CSNW to a large surface area and strong coupling between support (AgCl_x) and the active catalyst (Ag core). SEM image depicting the geometry of this study is shown in (**Figure 15c**). Lately, attention has also been devoted to nanoclusters which provide vastly improved catalytic performance because of their unique structures and size effects [304], [305]. Wang *et al.* reported that hydrophobically modified Ag nanoclusters deposited on carbon black exhibited high electrocatalytic performance in CO₂ reduction and repulsed water for the undesirable reaction. At -1.4 V vs RHE, the Ag nanoclusters achieved high mass activity ($\sim 10200 \text{ A cm}^{-2} \text{ g}^{-1}$) for CO generation, which is much higher than the nanoparticles counterpart [306].

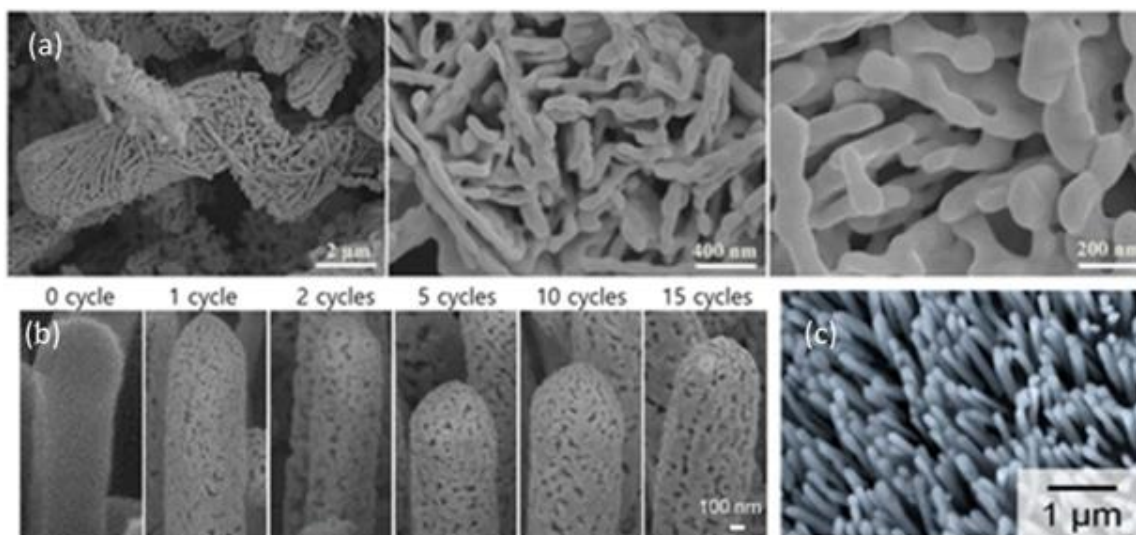


Figure 15. SEM images of nanostructured Ag from various studies. (a) Nanoporous Ag nanowires Reprinted with permission from Park *et al.* [258] (b) Vertical nanowires. Reprinted with permission from Ge *et al.* [303] and (c) Anodic-etched Ag. Reprinted with permission from Ma *et al.* [307]

2.4 Third row of d-block transition metal

The development of cost-effective electrocatalysts that can effectively reduce CO_2 with tunable selectivity and long-term stability is one of the primary impediments to accomplishing this goal. Numerous research has been carried out in this field to address this challenge and several electrocatalysts have been developed which has shown applauding efficiency both at the laboratory and industrial level. All the same, there are limited reported literature employing the third-row transition metal-based electrocatalysts for the reduction of CO_2 to useful products. The key reason for the limited use of these noble metals (Re, Au, Pt, Os, and Ir) is their absolute expensiveness and abundance.

2.4.1 Rhenium (Re) based Electrocatalyst.

Of all the known molecular catalysts for CO_2RR , the rhenium bipyridine-based complexes in general are deemed to be captivating due to their high performance toward offering high activity and selectivity for CO production [308], [309]. For instance, the works of Orchanian and his colleagues reported the surface functionalization of graphite rods to generate surface-immobilized

conjugated polymers incorporated rhenium bipyridine motifs via the electropolymerization approach for CO₂RR. Although the complexes were tested under high overpotential conditions (-2.25 V) the modified rhenium complex exhibited excellent performance up to 99% FE [309].

2.4.2 Tungsten (W) and Lanthanum (La) based Electrocatalyst.

Tungsten also a subclass of transition metal, in its diverse forms, has been reported to exhibit valuable properties for different catalytic applications [310]–[313]. Although, different W compounds for CO₂ electrochemical reduction either as complexes, carbide, nitride, or oxide have been examined with a promising outcome and enhanced ability [314]–[316]. Recently, a nanorod film morphology-like WO₃ nanoparticulate was synthesized by the solvothermal approach and tested in two different environments, dry and humid, for CO₂RR. The results reveal the conversion of CO₂ to CO with 42% FE. Nevertheless, a drastic change in the density of the smaller diameter nanorods (See **Figure 16**) was observed upon electrolysis [246].

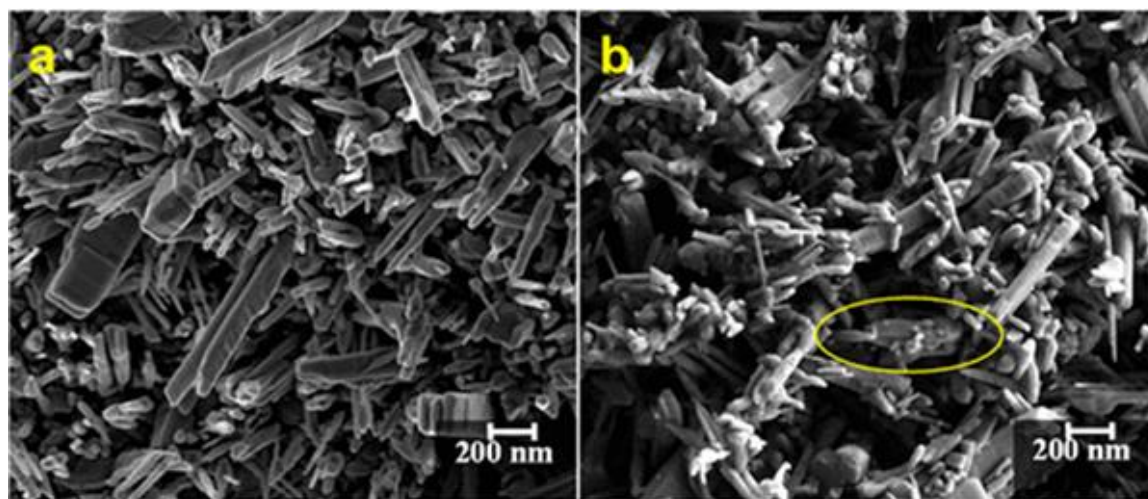


Figure 16. FE-SEM micrographs for a WO₃–NR/FTO electrode (a) before and (b) after electrolysis in acetonitrile. Reprinted with permission from Mendieta-Reyes et al [246].

Rare earth elements such as La play significant roles in several fields because of their special electronic structure. La-based perovskites such as lanthanum strontium cobalt ferrite (LSCF) or

lanthanum strontium ferrite (LSF), have gained much attention nowadays due to their mixed electronic and ionic conductivities. Also, a couple of studies have been carried out on La-doped form, however, the effectiveness of some parameters such as temperature or the current density in the material was well-thought-out [317]–[319]. For instance, the Ni-doped $\text{La}_{0.7}\text{Sr}_{0.2}\text{Ni}_{0.2}\text{Fe}_{0.8}\text{O}_3$ cathode in which the nanoparticles incorporated into the Perovskite through in situ exsolution resulted in enhanced performance from 65% to 80% CO FE. The growth of the Ni particles were observed to increase with an increase in temperature at the tetragonal perovskite layer [320]. In another development, thinly rolled nanosheets of Zn and La showed an epic performance with 25.99% and 54% FE yield for CO and H_2 and reached a current density of 2.5 mA cm^{-2} [321].

2.5 Challenges and future perspectives

In summary, this review centers on the recently reported nanostructure-based catalysts for CO_2RR , exclusively the morphology performance correlation. Even though activity, product selectivity, and FE are affected by several factors such as crystals facet and composition, as shown in Table 2. the morphology plays a key role in dictating the overall electrocatalytic activity and product selectivity of various transition-based electrocatalysts. An appropriate modification and engineering of different catalysts allow the binding of the catalysts to various intermediates to different extents, which leads to different products via control of the catalyst design. Although extensive experimental and limited computational studies have been repeatedly conducted over the past few years to accelerate the development of electrocatalysis for CO_2RR and understand the morphology–performance relationships, it is very challenging to efficiently reduce CO_2 to desirable products with maximum selectivity. This hinders the commercialization of electrocatalysis on an industrial scale. This part should be strengthened based on the general overview of the impact of morphology on the 1st–3rd rows. The big question would be "what are the impacts of heterostructures on the morphology and overall efficiency of the CO_2RR ?". It would be convenient to suggest a separate discussion of the morphologies of single metals and

heterostructures with a detailed emphasis. In general, an informative review would be strengthened if techno-economy feasibility can be added. Regardless of the tremendous progress achieved so far, this article would recommend the exhaustive investigation of the following key ideas as they will improve the research area:

- Theoretical studies: To strengthen the experimental findings, the CO₂ electro-reduction studies can be combined with simulation models to predict the impact of catalysts' morphology on effective CO₂RR. This will further guide and enhanced better catalyst development for efficient CO₂RR.
- Techno-economy feasibilities: In-depth techno-economic studies on the impact of catalysts' morphology are highly recommended to correlate the cost and energy needed to achieve high selectivity and better FE.
- Comparison between single metal atom and heterostructures.
- The use of complexes: Fundamentally, electrochemical CO₂RR involves electron transfer. Thus, the employment of organometallic complexes is desirable to rise the conjugation of the materials to overwhelm the conductivity challenge of CO₂RR for products involving a >8 electron system.

CHAPTER 3

RESULTS AND CONCLUSION

Modulating the electrocatalytic reduction of CO₂ to CO via surface reconstruction of ZnO nanoshapes

The electrocatalytic conversion of carbon dioxide (CO₂) into valuable chemicals presents a promising strategy for closing the carbon cycle. In this study, we synthesized zinc (Zn) catalysts through hydrothermal methods using either polyvinylpyrrolidone (PVP) or Cetyltrimethylammonium bromide (CTAB) as stabilizing agents. These catalysts proved highly efficient in converting CO₂ into carbon monoxide (CO). Our findings reveal that ZnO, synthesized with different morphologies—namely, nanoneedles (ZnO-NN) and nanorods (ZnO-NR)—underwent significant electro-reconstruction, ultimately leading to the formation of hexagonal metallic Zn crystals, regardless of their initial characteristics. Utilizing ex-situ operando techniques, we elucidated that metallic Zn serves as the active phase for the CO₂-to-CO conversion process. In a comparison, ZnO-NN catalysts demonstrated superior selectivity and stability, achieving over 90% CO selectivity at a potential of -0.88 V vs RHE (Reversible Hydrogen Electrode). Remarkably, these catalysts maintained this level of performance for more than 17 hours. Conversely, ZnO-NR catalysts exhibited a lower CO selectivity of 62.5% at a relatively higher potential of -0.98 V vs RHE.

Keywords: Electrochemical CO₂ reduction; surface reconstruction; ZnO, ex-situ operando Raman; PVP and CTAB

3.1 Introduction

The rise in global climate crisis attributed to the increasing accumulation of carbon dioxide (CO₂) in the Earth's atmosphere, primarily caused by human actions such as the combustion of fossil fuels, deforestation, and industrial processes. As a consequence, there is an urgent need for sustainable and efficient strategies to mitigate the impacts of increasing CO₂ levels [39]. Electrochemical CO₂ reduction has emerged as a promising and environmentally benign approach to convert CO₂ into valuable chemical feedstocks, thereby offering a potential pathway for the reduction of greenhouse gas emissions while simultaneously producing valuable products [322], [323], depending on the catalyst and reaction conditions, including, CO, CH₄, HCOOH/HCOO⁻, and C₂H₄ [324]. Among these products, CO has attracted substantial interest because of its versatile applications as a chemical feedstock in various industries [284]. Lately, there has been an increasing interest in metal oxide catalysts due to their remarkable potential for enhancing the electrochemical conversion of CO₂ into various valuable products, notably carbon monoxide (CO) [325]. Our recent findings have highlighted the significance of shape and composition of nanocrystals (NCs) in influencing the characteristics of these materials, thereby impacting their applications in diverse fields, including catalysis. This knowledge is of paramount importance across multiple research domains and holds particular significance in the context of understanding catalytic activity [39].

Among these catalysts, zinc oxide (ZnO) has emerged as a highly promising candidate due to its unique properties, which can be finely tuned to optimize its performance in CO₂ reduction [323]. ZnO possesses several key advantages, including remarkable stability, low cost, and abundance in the Earth's crust, making it an appealing catalyst for large-scale industrial applications. However, the efficiency of the electrochemical CO₂ reduction process significantly depends on the morphology of the ZnO catalysts. Morphology plays a crucial role in determining the catalyst's surface area, active sites, and electronic structure, which directly impact its catalytic activity and

selectivity towards CO₂ reduction [284], [326]–[331]. Tailoring the morphology of ZnO allows for the control of various surface properties, such as exposed crystal facets, defects, and particle size, all of which can influence the catalyst's performance [39]. For instance, defects such as oxygen vacancies can act as active sites for CO₂ adsorption and subsequent reduction to CO. The exposed crystal facets, such as (0001) and (10-10), exhibit different catalytic activities, and tuning the surface orientation can enhance the selectivity towards CO production [330], [331].

Extensive research has been directed towards comprehending the intricate catalytic processes influenced by morphology. Yet, assessing this dependence is a complex endeavor, primarily because the actual atomic arrangement within shaped nanocrystals is far more intricate than what is outlined in the traditional model of polyhedral crystals [39]. In this study, nanostructures of ZnO with different morphologies were synthesized, namely ZnO nanoneedles (ZnO-NN) and ZnO nanorods (ZnO-NR), to examine the influence of morphology on enhancing the efficiency of the CO₂ reduction process. Exceptional electrolysis durability exceeding 17 hours, coupled with remarkable selectivity (91%) towards CO production, was accomplished at a potential of -0.99 V vs. the reversible hydrogen electrode (RHE).

3.2 Experimental section

3.2.1 Material and Chemicals

All the chemicals and solvents were readily accessible commercially and used directly without requiring additional purification. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, sodium hydroxide (NaOH), polyvinylpyrrolidone (PVP), Cetyltrimethylammonium bromide (CTAB) and methanol were purchased from SigmaAldrich. While Nafion D520 and carbon paper were purchased from Fuel cell store.

3.2.2 Synthesis of ZnO nanoneedle and nanorod

Typically the ZnO nanostructures were synthesized through a process involving the dissolution of 1.189 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 20 ml of deionized water. Subsequently, 1g of either PVP or CTAB was introduced into the solution, followed by vigorous stirring. The pH of the solution was then raised to 13 using NaOH. After achieving a uniform solution, it was transferred into a Teflon-lined stainless-steel autoclave. These autoclaves were then introduced into a furnace, where the temperature was carefully held at 100°C for a period of 24 hours. This controlled environment facilitated the successful execution of the hydrothermal process. Finally, the resulting samples were washed and dried at a temperature of 60°C.

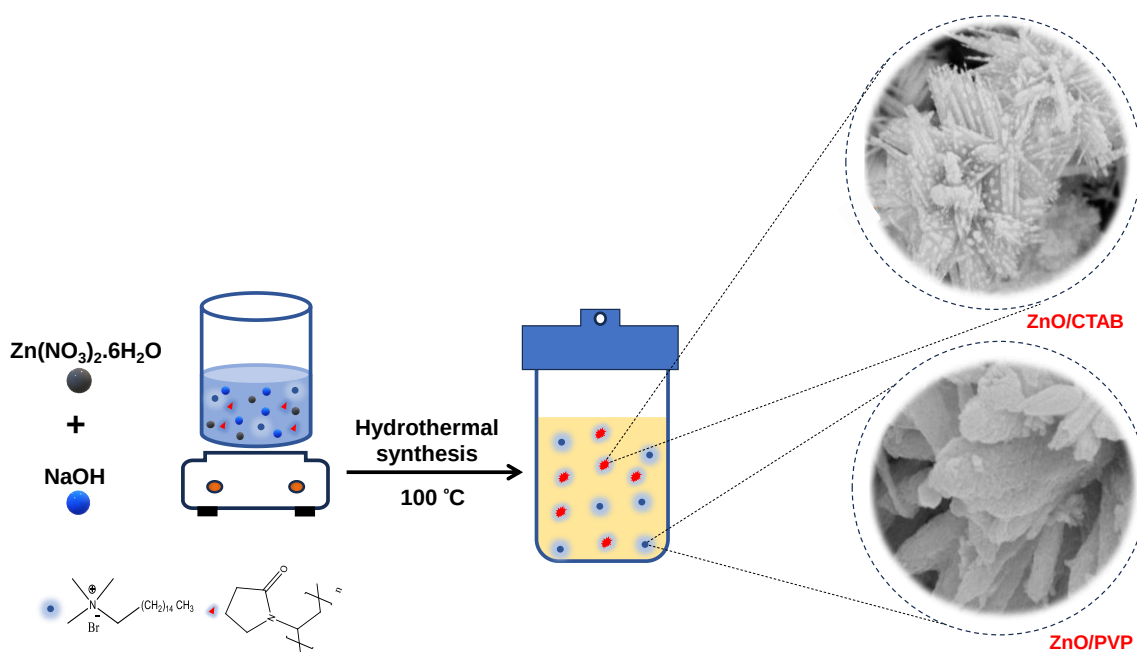


Figure 17. Scheme hydrothermal synthesis of ZnO in CTAB and PVP, resulting in nanorod and nanoneedle like structures.

3.2.3 Characterization

The physical and structural properties of both ZnO-NN and ZnO-NR were thoroughly examined to establish a comprehensive understanding of their characteristics. This in-depth characterization process offers valuable insights into the diverse structural and chemical behaviors exhibited by the catalysts, ultimately facilitating a more profound comprehension of the relationships between their structures, properties, and performance. The phases of ZnO-NN and ZnO-NR were identified through X-ray diffraction (XRD), employing a scan range spanning from 30° to 70° 2θ . The XRD analysis was conducted using a Rigaku Ultima IV X-ray diffractometer, operating at a scanning speed of $5^\circ/\text{min}$ and X-ray energy of 40 kV and 40 mA. To attain high-resolution microscopic images, the Zeiss Laser-Crossbeam 550 scanning electron microscope (SEM) at CIPR-KFUPM was employed. An Oxford EDS detector, integrated into the instrument, was utilized to collect compositional data from the samples. This collected data provided insight into the elemental composition at various marked positions on the samples. At least three elemental spectra were obtained from these designated locations, and subsequently processed using the proprietary INCA

software package. Furthermore, the chemical states of the catalysts were elucidated using X-ray photoelectron spectroscopy (XPS) with the PHI 5000 Versa Probe II, a spectroscope from ULVAC-PHI Inc. Prior to XPS analysis, the pelletized disc samples underwent a high vacuum treatment.

3.2.4 Electrochemical evaluation

For the electrocatalytic reduction experiments, controlled potential coulometry was performed in a sealed two-compartment H-type cell configuration, with a Nafion-117 proton exchange membrane separating the compartments. This setup utilized a three-electrode system, including a platinum wire as the counter electrode, an Ag/AgCl as the reference electrode, and the synthesized electrocatalyst as the working electrode. To prepare the working electrode, a catalyst amounting to 5 mg was mixed with 4 mL of methanol, followed by the addition of 2 μ L of Nafion solution (5 wt%). The resulting mixture or ink was subjected to sonication for 15 minutes. Subsequently, 50 μ L of this catalyst ink was deposited onto a 1 cm $\times$ 1 cm carbon paper and allowed to air dry overnight at room temperature. The assembled electrode configuration consisted of the aforementioned working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. In this setup, both the anode and cathode electrolytes were 0.5 M KHCO₃. Prior to the electrolysis, highly pure CO₂ (99.999%) was introduced into the electrolyte for 30 minutes at a flow rate of 50 standard cubic centimeters per minute (sccm), which was then maintained at 5 sccm throughout the electrolysis. This procedure ensured the removal of residual air and continuous CO₂ supply. Gas products generated during the electrolysis were continuously monitored and analyzed using a Clarus 580 gas chromatograph (Perkin Elmer). The GC is equipped with Hayesep and Molecular sieve columns, as well as thermal conductivity (TCD) and flame ionization (FID) detectors, respectively. Additionally, the headspace products were intermittently injected into the gas chromatograph at 20-minute intervals. At the conclusion of a 1-hour electrolysis period, the

electrolyte solution was collected and subjected to analysis to identify and quantify liquid products by ^1H NMR.

The faradaic efficiency (FE) of the products were estimated using the eq [31]:

$$FE = \left(\frac{Z * C * F}{Q} \right) * 100 \dots \dots \dots$$

Where, Z represents the number of transferred electrons during the electrolysis, C is the molar concentration of the products (mol/L) as detected on GC, F is the Faraday constant (96485 C mol⁻¹ of electrons), and Q is the overall charge over the period of 1 h electrolysis.

Unless where stated, all of the potentials reported in this study were converted to the reversible hydrogen electrode, RHE using the eq:

$$E_{RHE} = E_{(Ag/AgCl)} + E_{\left(\frac{Ag}{AgCl}\right)}^0 + 0.059 * pH \dots \dots \dots$$

Where, $E^0_{(Ag/AgCl)}$ was taken as 0.1976 V, and the pH of CO₂-saturated 0.5 M KHCO₃ was measured as 7.2.

The electrodes were characterized through Linear Sweep Voltammetry (LSV) measurements spanning a potential range of 0 to -1.6 V versus Ag/AgCl, employing a scan rate of 50 mV s⁻¹. The LSV plots were presented without employing iR correction. The Electrochemical surface area (ECSA) was determined by calculating the electrical double layer capacitance (Cdl). Additionally, Cyclic Voltammetry (CV) measurements were conducted by assessing Cdl across a variety of scan rates within a non-Faradaic potential range versus RHE. Furthermore, potentiostatic Electrochemical Impedance Spectroscopy (EIS) measurements were performed in an electrolyte containing 0.5 M KHCO₃ saturated with CO₂. The impedance spectra were recorded across a frequency span from 100 kHz to 100 mHz, while applying an amplitude of 10 mV root mean square (r.m.s.).

3.3 Result and discussion

3.3.1 Characterization of ZnO nanoneedle and nanorod

The powder X-ray diffraction (PXRD) method was utilized to firstly examine the crystallinity of the prepared ZnO-NN and ZnO-NR electrocatalysts. The diffraction pattern, as illustrated in **Figure 18**, clearly confirmed the significant crystalline quality of the ZnO catalysts produced in this research. The distinct and accurately aligned diffraction peaks in the pattern closely corresponded to the established hexagonal wurtzite structure of ZnO, as indicated by the matching with the standard JCPDS No. 36-1451 reference pattern [332].

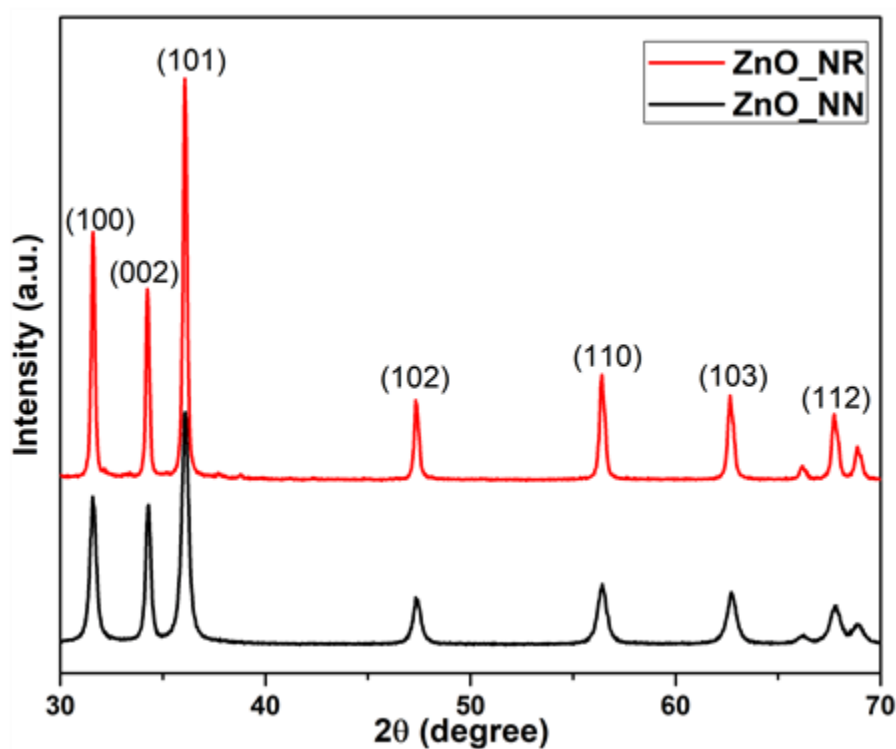


Figure 18. XRD pattern of ZnO-NN and ZnO-NR

The scanning electron microscope (SEM) images illustrate that the ZnO-NN sample, depicted in **Figure 19a** displays uniformly coverage of nanoneedle arrays, characterized by a typical length of 102 μm and a tip diameter of 4 μm , which corresponds to findings reported in the literature [333].

In contrast, the ZnO-NR sample (**Figure 19b**) exhibits arrays of nanorods with an typical length of 142 μm and a diameter of 24 μm , aligning with previous observations of ZnO nanorod synthesis in PVP [334], [335]. Likewise, the EDS elemental analysis and mapping provide a clear representation of the distribution, highlighting a notably high concentration of zinc, particularly in the ZnO-NN sample (see **Figure SI1-SI4** and **Table SI1** and **SI2** in appendix).

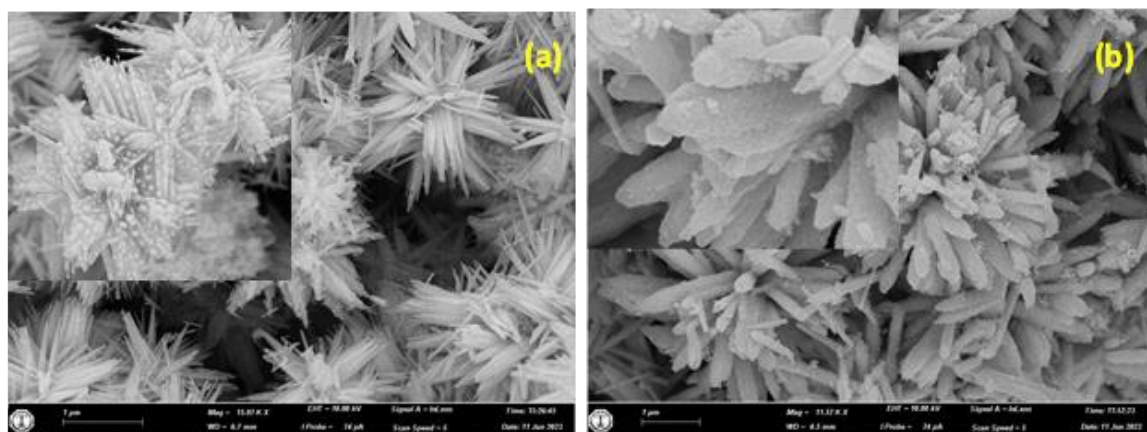


Figure 19. SEM analysis of (a) ZnO-NN and (b) ZnO-NR.

Furthermore, XPS analysis was conducted to explore the electronic structure of Zn and O, as illustrated in **Figure 20**. The confirmation of the presence of ZnO was achieved by examining core-level XPS lines, specifically focusing on Zn 2p and O 1s, which correspond to the elemental composition. In the Zn spectrum (see **Figure 20a** and **20c**), the apparent peaks at binding energies of 1044.4 and 1021.3 eV were assigned to Zn 2p_{1/2} and Zn 2p_{3/2} peaks, respectively, corresponding to Zn²⁺ states. In the O 1s spectrum depicted in **Figure 20b** and **20d**, the peaks at 532.4 and 530.5 eV were associated with OH⁻ and O²⁻ species, respectively. The peak at 530.5 eV indicates the presence of lattice oxygen bound with Zn, while the peak centered at 532.4 eV suggests the existence of surface hydroxyl groups.

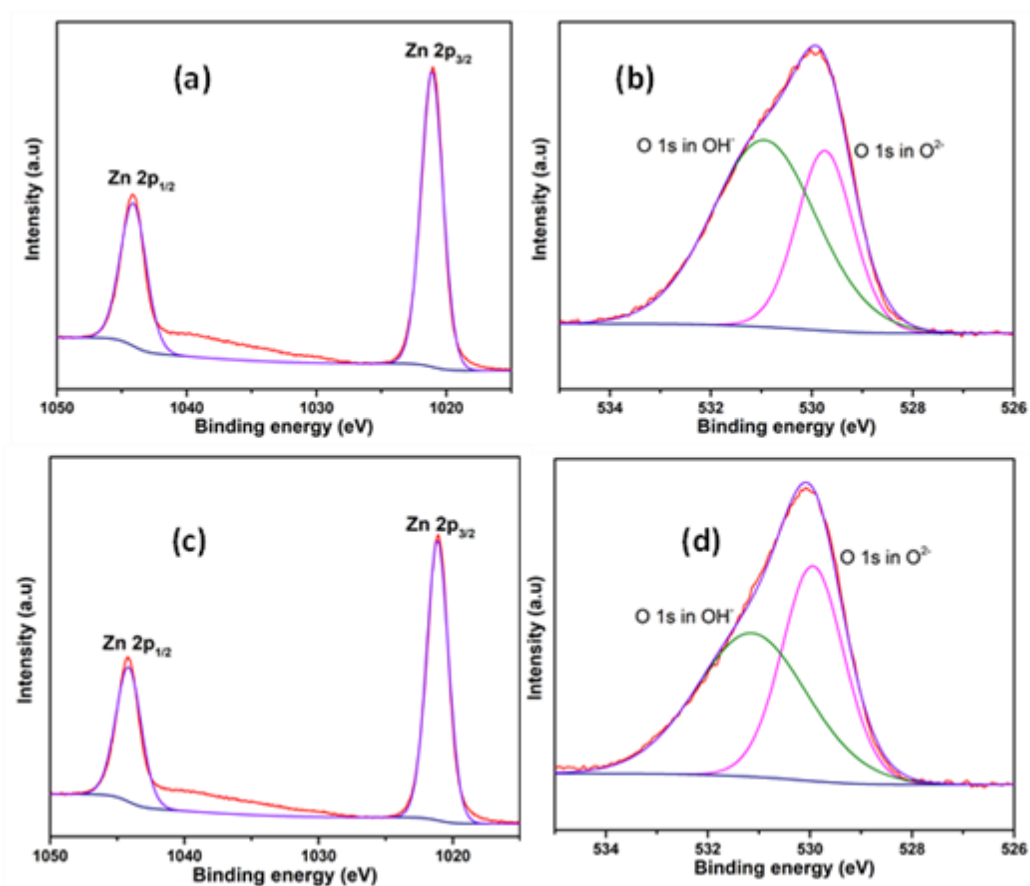


Figure 20. XPS spectra of ZnO-NN (a) Zn 2p and (b) O 1s and ZnO-NR (c) Zn 2p and (d) O 1s

3.3.2 Electrochemical performance of ZnO nanoneedle and nanorod

The electrochemical performance of the ZnO-NN and ZnO-NR catalysts in the reduction of CO_2 was assessed using a type H-cell. A solution of 0.5 M KHCO_3 saturated with either CO_2 or Ar served as the electrolyte. To assess the electrochemical performance of these catalysts, primary Linear Sweep Voltammetry (LSV) measurements were carried out in two distinct environments, as shown in **Figure 21a**, at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$. In both cases, the electrocatalysts exhibited similar curve shapes and relatively lower current densities when the electrolyte was saturated with Ar. However, a notable change occurred in CO_2 -saturated environment, in the presence of CO_2 , all tested samples displayed a substantial increase in current densities. This suggests their ability to facilitate the reduction of CO_2 , with ZnO-NR showing a slight enhancement in current density compared to the ZnO-NN catalyst.

The Faradaic efficiency (FE%) for each product generated by the ZnO-NN and ZnO-NR electrocatalysts during continuous operation was plotted against the applied potential in reverse hydrogen evolution (V vs RHE) as shown in **Figure 21b**. Two main products were observed: CO, resulting from the reduction of CO₂, and H₂, produced as a byproduct of the simultaneous proton reduction reaction. Quantitative analysis of the FE_{CO} for both ZnO-NN and ZnO-NR catalysts revealed FE values of 44.1%, 91.33%, and 62.1% for ZnO-NN, and 42.7%, 61.0%, and 62.5% for ZnO-NR at potential values of -0.78, -0.88 and -0.98 V vs RHE, respectively. Furthermore, an increase in the applied potential resulted in the suppression of the hydrogen evolution reaction (HER) and an enhancement in CO selectivity, albeit at the cost of higher partial current densities. Overall, the evaluation of FE indicated that ZnO-NN exhibited a notably higher FE_{CO} of 91.3% at a relatively lower potential of -0.88 V vs RHE, in contrast to a FE_{CO} of 62.5% at -0.98 V vs RHE.

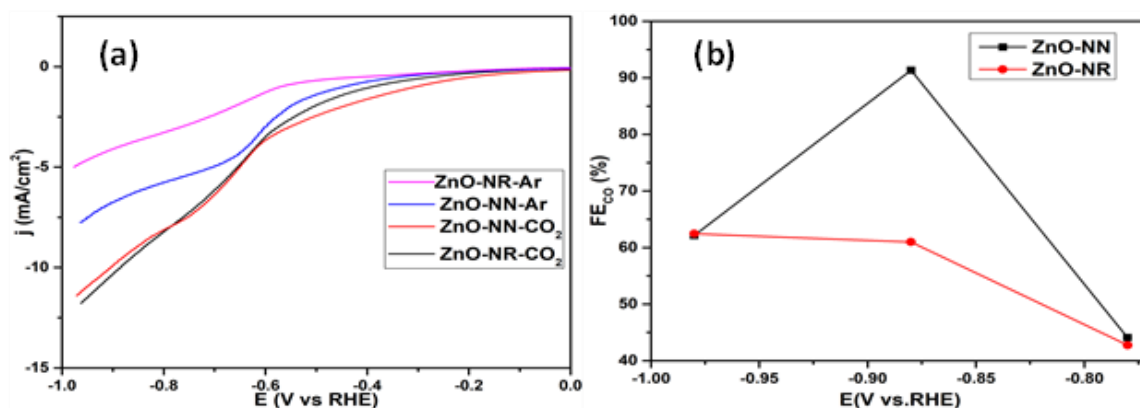


Figure 21. Electrochemical measurements of ZnO-NN and ZnO-NR (a) LSV graphs in a 0.5 M KHCO₃ electrolyte solution saturated with CO₂ and Ar and (b) FE_{CO} of the ZnO-NN and ZnO-NR samples.

Additionally, ZnO-NN and ZnO-NR demonstrated robust endurance, enduring continuous electrolysis for over 17 hours at -0.88 V vs RHE and 14 hours at -0.98 V vs RHE while maintaining a partial current density of 10.5 and 9.58 mA, respectively. Throughout the electrolysis process, the current density remained stable, and the final FE_{CO} values were consistent, with ZnO-NN at 91.3% and ZnO-NR at 62.5% (see **Figure 22a**). It's worth noting that a slight degradation was observed in ZnO-NR after surpassing the 14-hour mark, reaffirming its impressive durability.

To gain instantaneous understandings into the reduction process of ZnO during the electroreduction of CO₂, we employed ex-situ operando Raman spectroscopy. **Figure 22b**, displays the Raman spectra for ZnO-NN and ZnO-NR samples, recorded during pre-reduction at applied voltages of -0.88 and -0.98 V vs RHE in a solution of 0.5 M KHCO₃ saturated with CO₂. Initially, at 0 minutes, we observed distinct Raman peaks at 99, 332, 380, and 437 cm⁻¹, characteristic of ZnO [323], [336], [337]. This outcome aligns closely with our XPS findings, which indicate that the chemical state of Zn on the surface of ZnO predominantly exists in the 2+ state. Over the first 10 minutes of reduction, these ZnO peaks gradually diminished in intensity, signifying the one-sided conversion of the uppermost layers of ZnO into metallic Zn. This observation implies that during the initial 10-minute reduction phase, significant structural changes occurred, preventing the complete coverage of the ZnO surface by reduced Zn crystals. After 20 minutes of reduction, no apparent ZnO peaks were present in the Raman ranges, signifying the complete reduction of surface ZnO to metallic Zn [338]. The featureless spectra observed after 20 minutes of reduction provide compelling evidence that Zn can maintain its metallic state under the applied CO₂ electrolysis potentials.

Collectively, these findings suggest that, in the electrochemical CO₂ reduction reaction, ZnO samples tend to undergo a transformation into hexagonal metallic Zn crystals, regardless of their primary shapes. This characteristic of restructuring underscores the significance of conducting comprehensive investigations of the ultimate states of nanostructured catalysts to establish precise relationships between their structure and performance. The consistent hexagonal crystal structure observed in the reduced Zn electrodes provides a foundation for identifying the critical features influencing catalytic activity, whereas its inherent energetic stability is crucial for maintaining a stable CO₂ reduction performance.

To gain insight into the morphological reconstruction, SEM images were captured for the ZnO-NN and ZnO-NR samples following a 20-minute electrochemical CO₂ reduction (**Figure 22c and**

22d). The images reveal a noteworthy transformation from the initial nanoneedles and nanorods into a sponge-like hexagonal crystal structure. This transformation is attributed to a dissolution-reduction-crystallization sequence in ZnO. Initially, ZnO dissolves, forming soluble $\text{Zn}(\text{OH})_4^{2-}$ ions [339], [340], which are then reduced to Zn, leading to the growth of Zn crystals. The specific crystal shape of the resulting Zn deposits is primarily influenced by the rates of dissolution and re-deposition [341]. In the context of CO_2 reduction, well-defined hexagonal crystals are favored due to the relatively gradual overall reduction rate, allowing the formation of a shape with minimal surface energy.

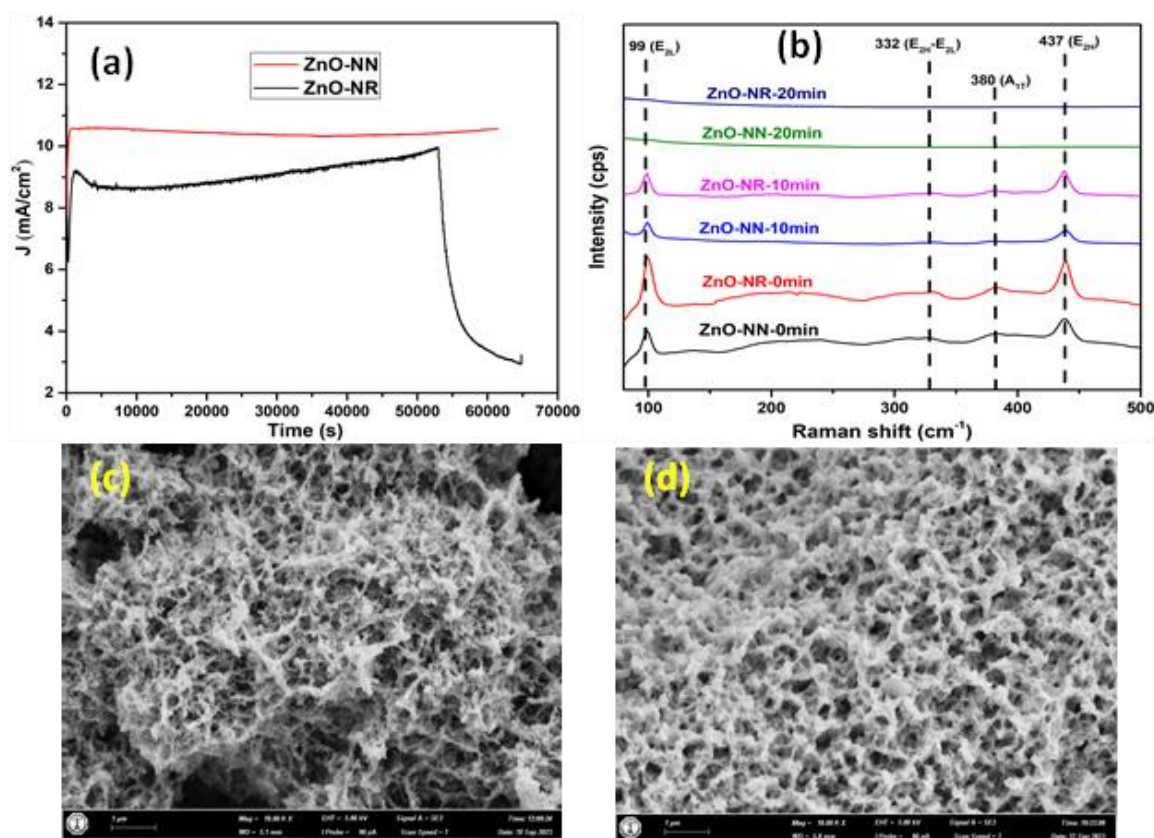


Figure 22. (a) showcases the long-term stability test of the sample, while (b) presents Operando Raman spectra of the same sample taken at various time intervals during the pre-reduction at -0.88 and -0.98 V vs RHE. All Raman spectra were obtained in a CO_2 -saturated 0.5 M KHCO_3 environment.

Moreover, we conducted an Electrochemical Impedance Spectroscopy (EIS) analysis to assess both the series resistance and charge transfer resistance of the electrode as illustrated in **Figure 23a** curves. According to the EIS measurements, the ZnO-NN electrocatalyst demonstrates the

most favorable charge transfer resistance at 10.9 Ω , surpassing the ZnO-NR electrocatalyst, which exhibited a resistance of 13.7 Ω . The lower charge transfer resistance signifies a swifter electron transfer process. In order to precisely assess the reaction kinetics at the surface level, we conducted an analysis of the Tafel slope. This involves examining the relationship between the overpotential and the logarithm of the current density, which can offer valuable mechanistic insights into the rate-determining step of the two-electron reduction of CO₂ to CO in ZnO-NN and ZnO-NR electrocatalysts. In theory, a Tafel slope of approximately 118 mV dec⁻¹ corresponds to the formation of one electron to create the crucial CO^{2*-} intermediate [326]. Notably, the ZnO-NN electrocatalyst exhibits a Tafel slope of 146.7 mV dec⁻¹, while the ZnO-NR displays a slightly higher Tafel slope of 149.3 mV dec⁻¹, as depicted in **Figure 23b**. The attained Tafel slope value for ZnO-NN is remarkably close to the theoretical value of 118 mV dec⁻¹, significantly smaller than the 149.3 mV dec⁻¹ observed for ZnO-NR. This observation suggests that ZnO-NN exhibits substantially higher intrinsic electrocatalytic activity. Moreover, it indicates that the rate-determining step involves the initial electron transfer to CO₂, leading to the formation of an adsorbed CO^{2*-} intermediate on the surface of ZnO-NN.

The electrochemical active surface area (ECSA) of the ZnO-NN and ZnO-NR electrocatalysts was determined through the measurement of cyclic voltammetry (CV) and double-layer capacitance (C_{dl}). A linear relationship between current density and scan rate can provide the C_{dl} value. In this study, a CV was conducted with scan rates ranging from 5 to 100 mV s⁻¹ (see **Figure SI5 in appendix**). Using the CV data, the C_{dl} values for ZnO-NN and ZnO-NR were calculated and are depicted in **Figure 23c**. The CV measurements reveal an expanding total activity area as the scan rate increases at a constant potential. Hence, ZnO-NN and ZnO-NR exhibited C_{dl} values of 7 and 3.3 mF cm⁻², respectively. These findings indicate that ZnO-NN possesses the highest ECSA among the two. These outcomes underscore the significant impact of distinct morphological

properties on reaction kinetics, ultimately leading to remarkable levels of activity and selectivity in electrochemical CO₂ reduction performance.

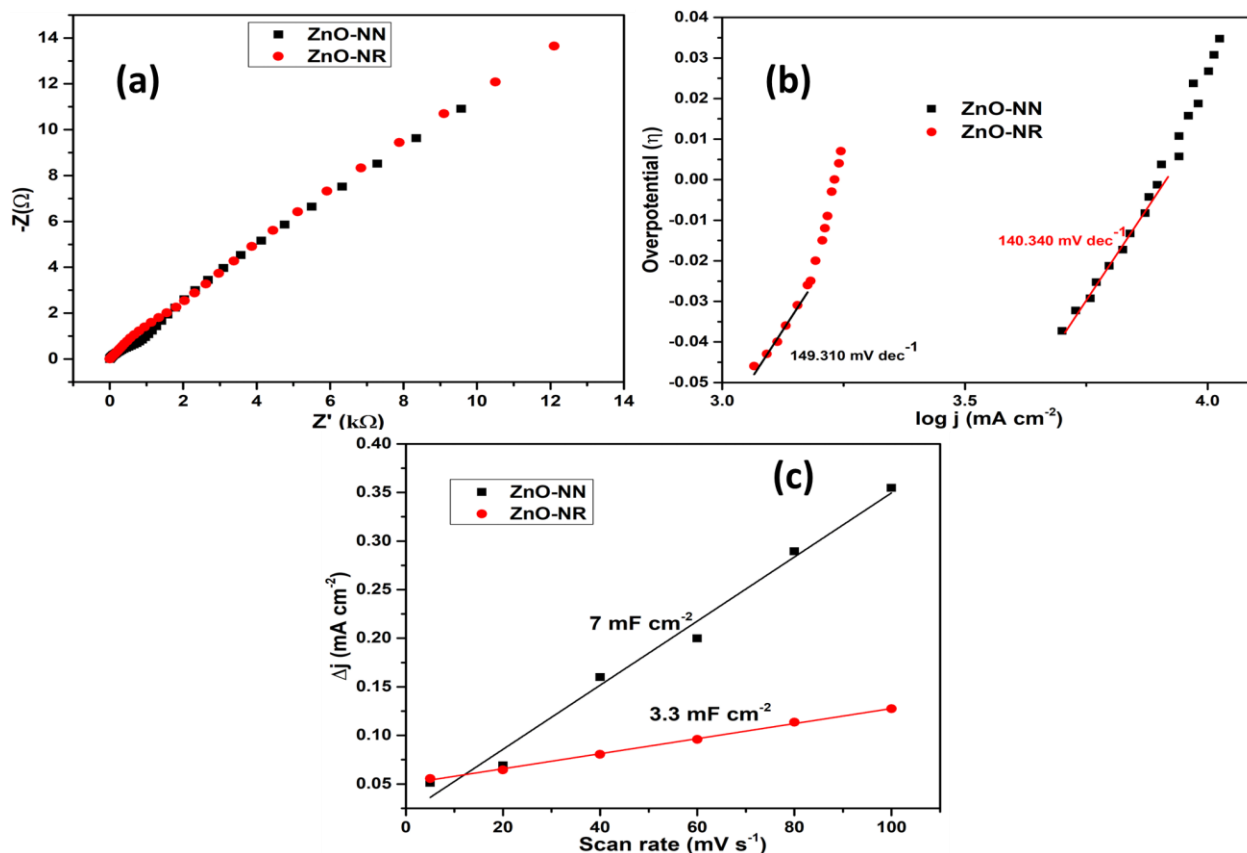


Figure 23. Electrochemical characteristics of ZnO-NN and ZnO-NR (a) Electrochemical impedance spectroscopy (EIS) curves (b) Tafel slope and (c) Double-layer capacitance (Cdl) measurement, half of charging current density differences ($\Delta j/2$) plotted against scan rates in CO₂-saturated 0.5 KHCO₃ electrolyte solution.

3.4 Conclusion

To summarize, we successfully synthesized ZnO with distinct morphologies, namely ZnO-NN (nanoneedles) and ZnO-NR (nanorods) catalysts, through hydrothermal synthesis using PVP or CTAB. These catalysts exhibited remarkable activity, selectivity, and stability in the electrochemical conversion of CO₂. ZnO-NN catalysts displayed exceptional performance with over 90% FE_{CO} selectivity at relatively modest overpotentials of 347.6 mV and sustained stability exceeding 17 hours. In contrast, ZnO-NR achieved over 60% FE_{CO} selectivity but required a relatively higher overpotential of 447.6 mV and exhibited stability for 14 hours.

Ex-situ Raman operando studies unveiled that both ZnO-NN and ZnO-NR electrodes experience a transformation into hexagonal metallic Zn crystals during the electrochemical CO₂ reduction process, irrespective of their primary shapes. Furthermore, electrochemical evaluation established that metallic Zn functions as the active site for the conversion of CO₂ to CO. These discoveries emphasize the need to establish relationships between structure and performance based on the final electrode states rather than the primary morphology, as the reduction and reconstruction processes have a significant impact on the overall performance.

Acknowledgments

The authors would like to express their gratitude to the Center for Refining and Advanced Chemicals, King Fahd University of Petroleum & Minerals (KFUPM), located in Dhahran, Saudi Arabia, for the support provided, under project INRC2216.

CHAPTER 4

Synergistic Effect of Ce_xO_y and Zn ion within the ZIF-zni Framework for Enhanced Electrocatalytic Reduction of CO_2

Abstract

In recent years, human activities have led to an unprecedented rise in atmospheric CO_2 levels, causing significant environmental challenges. To combat this issue, there's growing interest in the conversion of CO_2 into valuable chemicals. This study reports the synthesis and electrocatalytic evaluation of Ce_xO_y and ZIF-zni interface for CO_2 reduction. The catalyst exhibited remarkable selectivity to CO, achieving excellent Faradaic efficiency (FE) of 87.7% at an overpotential of 170 mV. The findings revealed that by adjusting the applied potential during electrolysis, it was possible to tune the catalyst's electronic properties. This resulted in a reduced overpotential and a lower CO onset potential of -300 mV. Density functional theory (DFT) calculations revealed that the synergistic interaction between the oxygen of Ce_xO_x and the Zn ion of the ZIF-zni, exposes cerium as the active site for CO_2 activation. This interaction also stabilizes the crucial $^*\text{COOH}$ intermediate, facilitating the electrochemical CO_2 reduction reaction.

Keywords: ZIF-zni, Electrochemical CO_2 reduction reaction, Cerium, Reflux assisted synthesis, synergetic effect.

4.1 Introduction

The continuing increase in the demand for sustainable energy is significantly attracting global attention. Burning of fossil fuels, the common source of energy for industries and humans, induces excessive discharge of greenhouse gases (e.g., CO₂, NO and CH₄) and thus stimulate climate change[1], [2], [39]. Yet, , the valorization of CO₂ through the electrocatalytic reduction to value added chemicals remain a viable option for environmental sustainability [342]. Given the CO₂ electrochemical reduction's enormous economic and environmental potential, it has garner the attention of researchers over the past decades [12]. For the practical execution of this technology, the control of products selectivity, the enhancement of products conversion rate, and the minimal needed overpotential makes the actualization of this technology very challenging [2], [10], [11], [13]. Typically, this process comprises of numerous proton and electron transfers, thus producing various products each with several likely reaction intermediates. This associated difficulty, poses significant drawbacks in the characterization of molecular-level reaction mechanisms, which are demanding in the design of selective, effective, electrodes and stable electrocatalysts [11]. To date, different electrode materials and designs have been investigated for the electrochemical reduction of CO₂. These include: metal nanostructures such as Cu, Au, Pt and Ag, metal alloys which includes Cu–Ni, Cu–Pd, Cu–Sn, Cu–Zn, Cu–Ag, and Cu–In, metal oxides namely; CuO_x, SnO₂ and CeO₂, chalcogenides; MoS₂, WS₂ and metal-free electrodes; C and Si. Overall, the design (shape and size) of these electrodes greatly affect their electrochemical behavior towards CO₂ reduction[2], [25]–[27].

To overcome these challenges, transition metal and N-C (co-doped) (M/N–C) class of materials have been studied as electro-catalysts for a range of electrochemical reactions including carbon dioxide reduction reaction (CO₂RR) [343]. Typically, these promising materials are synthesized via thermal decomposition of suitable C, M and N precursors under different temperature and in an inert atmosphere. Inorganic or organic compounds, metal-organic frameworks (MOFs),

biomass and organic polymers precursors have been utilized to obtain the structure, morphology, and microstructure of the ensuing M/N–C materials [343]. Amongst these class of materials, zeolitic imidazole frameworks (ZIFs) a subclass of MOFs comprising of M–Im–M (in which M denotes Zn, Co cation and Im as imidazolate linker) constitutes an attractive group of self-sacrificed support for very well effective M/N–C electrocatalysts due to their inherent benefits namely high surface area, tunable pores and structures, and expanded configurations [344][345]. These intrinsic characteristics have fascinated significant interest for possible industrial applications, namely adsorption and separation, drug delivery, sensing, and as catalysts or catalyst support [346]. Yet, substantial industrial scale application of ZIFs faces some challenges. In addition to the cost, the energy and time consumption during synthesis with the space–time yield normally below $300 \text{ kg m}^{-3} \text{ d}^{-1}$ has made this class of materials impractical for large scale applications. To address these challenges, several approaches have been proposed for the effective synthesis of ZIFs. These approaches nevertheless generally entail extreme energy intake and lengthy reaction times ($>24 \text{ h}$ with low production rates) [346].

Ceria an abundant Earth's ore, is a promising redox material exhibiting wide range of application in catalytic process owing to its capacity to demonstrate significant oxygen storage and discharge abilities to form Ce^{3+} , single phase stability at elevated temperatures [347]–[352]. Besides, it can further aid water separation to form adsorbed hydrogen (H^*) due to its strong binding affinity with H^* . Additionally, the effortlessly made frustrated-Lewis pairs in CeO_2 may perhaps encourage the simultaneous adsorption and activation of CO_2 through the oxygen lattice binding with carbon and the two nearby Ce^{3+} ions bonded to oxygen atoms of CO_2 as the Lewis basic site and Lewis acidic site respectively [352]. However, its direct application as electrocatalyst is limited as a result of its poor electron-ion conductivity. Recently, tuning its oxygen vacancies, chemical state and electronic structures through insertion of low oxidation metal cations or designing metal/oxide interfaces are some of the approaches employed to enhanced its catalytic processes [353]–[360].

Fundamentally, these concepts are employed to enhance electron-ion pairs, electronic-ion conductivity and above all to make available catalytic active sites essential for CO₂ adsorption [361]. More so, the relationship amongst the metal class and CeO₂ can as well promote charge transportation during the electro-catalytic processes and thus, enhance CO₂ electrolysis performance. Herein, we proposed a reflux-assisted facile synthesis of ZIF-zni at a very short time of 3 h. More specifically, the ZIF-zni framework is characterized by the chemical composition of [Zn(C₃H₃N₂)₂], consisting of both inorganic and organic building components that include the divalent Zn²⁺ metal cation and an unsubstituted imidazolate ligand [(C₃H₃N₂)₂]. Subsequently, cerium was incorporated into the as-synthesized ZIF-zni via excess solvent deposition (ESD) and chemical vapor deposition (CVD) approach and applied as a potential electrocatalyst for CO₂ reduction. Further insights from density functional theory (DFT) calculations highlight a synergistic interaction between cerium and zinc ions within the ZIF-zni framework.

4.2 Materials

Ce(NO₃)₃•6H₂O (AR, ≥99.0%), Zn(NO₃)₂•6H₂O (AR, ≥98.5%), and imidazole were purchased from Sigma-Aldrich while methanol (AR, ≥99.0%) was obtained from Acros Organics and all chemicals were used as received. High-purity deionized water (18 μS/cm) was produced and obtained in-house using a Thermo Scientific Barnstead Nanopure water purification system after distillation with a Labstrong FiSTREEM II 2S Glass Still distiller.

4.3 Synthesis of ZIF-zni

ZIF-zni was prepared by dissolving 0.06 mol of imidazole in 50 mL methanol, followed by addition of about 0.006 mol of Zn (NO₃)₂•6H₂O to the solution and vigorously stirred for 1 h at room temperature. The mixture was refluxed for about 3 h at 65 °C while stirring. The solid particles were collected by centrifuge and washed several times with methanol. The final whitish powder

was oven-dried under vacuum at 65 °C overnight. The ZIF-zni powder was finally activated in furnace at 200 °C under vacuum condition for 2 h prior to use.

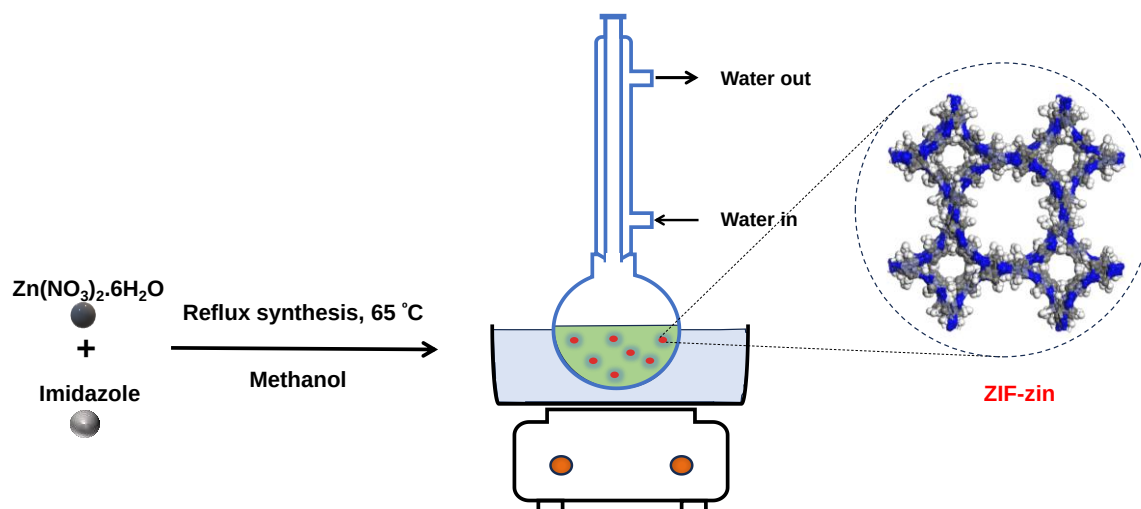


Figure 24. Schematic reflux synthesis of ZIF-zni

4.3.1 Synthesis of $\text{Ce}_x\text{-ZIF-zni-X}$

ZIF-zni supported Ce_xO_y nanoparticles ($\text{Ce}_x\text{-ZIF-zni-X}$) were first synthesized by dispersing ZIF-zni and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in methanol, as described herein. Typically, 1:1 ZIF-zni and Ce precursor were dispersed in 20 mL of methanol and sonicated for 0.5 h at room temperature, followed by drying at 60 °C in an oven for overnight. The final powdered products were activated at 150 °C and denoted as Ce-ZIF-zni. Furthermore, CVD method was explored for the effective synthesis of the catalyst. In a typical preparation, 1:1 ratio of ZIF-zni and Ce precursor were placed separately in two porcelain boats and heated in a tubular furnace to 200 °C for 2 h with a heating rate of 2 °C min^{-1} under Ar flow and the final products were denoted as Ce-ZIF-zni-CVD. The choice for 200 °C as the heating temperature, was due to the melting point of the cerium precursor. To determine the optimal ratio of Ce in $\text{Ce}_x\text{-ZIF-zni-X}$ (where X= is excess solvent (ESD) or CVD) for the electrochemical CO_2 reduction to CO, three different percentage of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were synthesized and denoted as $\text{Ce}_x\text{-ZIF-zni-X}$ (where x is the mol of Ce).

4.4 Characterization of ZIF-zni and Ce_x-ZIF-zni-X

The X-ray diffraction (XRD) patterns of the products were recorded using a Rigaku Ultima IV X-ray diffractometer, operating at a scanning speed of 5°/min with X-ray energy set at 40 kV and 40 mA. Fourier transform infrared (FT-IR) spectroscopy was conducted using a Thermo Scientific Nicolet 6,700 FTIR spectrometer across the mid-IR range (400 – 4000 cm⁻¹). Scanning electron microscopy (SEM) analysis was performed on a Hitachi S-4800 II field emission scanning electron microscope with an accelerating voltage of 20 kV, while the Zeiss Laser-Crossbeam 550 scanning electron microscope (SEM) at CIPR-KFUPM was employed. To gather elemental compositional data from the samples, an Oxford EDS detector integrated into the instrument was used, providing insight into the elemental composition at various marked positions on the samples. At least three elemental spectra were obtained from these designated locations and subsequently processed using the proprietary INCA software package. Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) analyses were carried out on a JEOL-JEM-2100 operating at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were recorded using the PHI 5000 Versa Probe II spectroscope from ULVAC-PHI Inc. Before XPS analysis, the pelletized disc samples underwent a high vacuum treatment. Gas products produced during electrolysis were analyzed in real-time using a Clarus 580 GC (Perkin Elmer) equipped with Hayesep and Molecular sieve columns and thermal conductivity (TCD) and flame ionization (FID) detectors, respectively. For the liquid products, the electrolyte solution collected after 1 hour of electrolysis was analyzed, and ¹H nuclear magnetic resonance (NMR) spectra were obtained using a Bruker Ascend spectrometer operating at 500 MHz.

4.5 Results and discussion

4.5.1 XRD pattern

The X-ray diffraction patterns obtained from the experimental analysis of ZIF-zni demonstrate a correlation with both reported experimental and simulated crystal data (**Figure 25a**) [362]. The presence of characteristic peaks at 15°, 17°, 18°, and 21° serves as clear evidence of the successful synthesis of ZIF-zni crystals, achieved through the use of a significantly reduced solvent volume and a notably shorter synthesis time [363].

Moreover, the X-ray diffraction analysis of the as-synthesized ZIF-zni samples revealed a minimal presence of extra diffraction peaks, indicating the absence of any unidentified phases within the materials. Notably, the incorporation of cerium into the ZIF-zni structure and the subsequent activation through heating did not result in any apparent alterations to the crystalline phase, except in cases of ESD and more prominently, at higher cerium loadings. Remarkably, the absence of distinctive diffraction peaks associated with cerium species in the CVD analysis suggests a controlled doping of cerium into the ZIF-zni crystal lattice or its uniform dispersion on the ZIF-zni surface. In contrast, a significant degree of crystal phase alteration, characterized by cerium agglomeration, was observed in instances of excess solvent loading.

Confirmation of the ZIF-zni formation was additionally validated through Fourier transform infrared spectroscopy (FTIR) **Figure 25b**. The FT-IR spectra of all the catalysts revealed absorption bands at around 2930, 1637, 1499 and 1300-480 cm^{-1} . These results are in good agreement with earlier reported results of ZIF-zni [364]. In comparison with ZIF-zni, the FT-IR spectra of all the catalysts do not depict additional absorption band. The bands around 900 cm^{-1} to 1400 cm^{-1} are characteristic peaks corresponding to the C–N bonds in the imidazole group, while 757 cm^{-1} , corresponds to the Zn–O bonds, and 668.4 cm^{-1} , attributed to Zn–N bonds, of the ZIF-zni structure [365], [366]. Furthermore the IR band corresponding to 500–700 cm^{-1} range can be ascribed to the Ce–O stretching vibration [367].

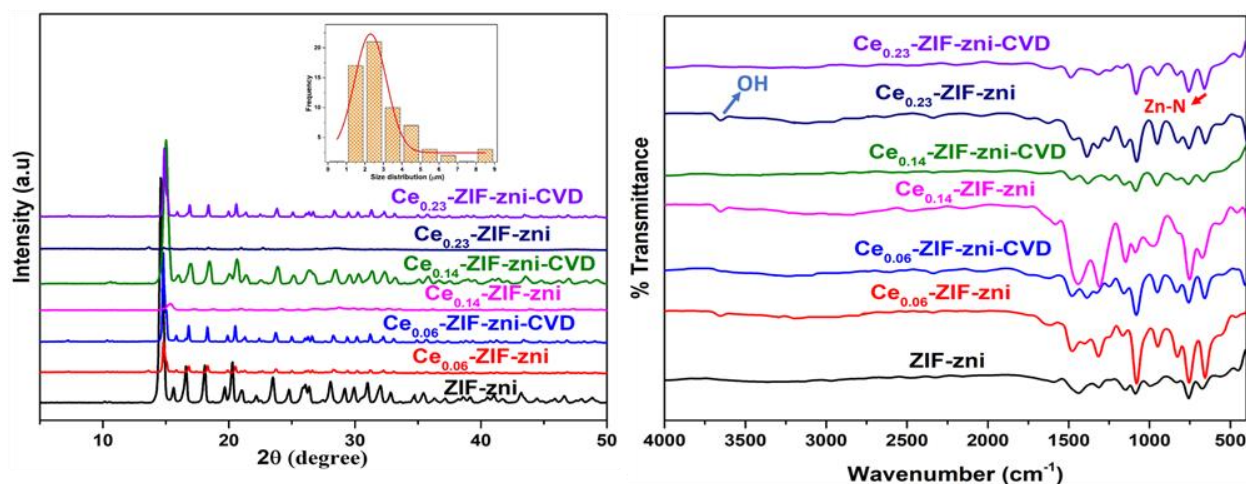


Figure 25. Image of (a) XRD pattern of Simulated ZIF-zni, experimental ZIF-zni and cerium in cooperated ZIF-zni using Chemical vapor deposition (CVD) and excess solvent deposition. (b) FTIR spectra of ZIF-zni and cerium incorporated

4.5.2 Morphology of the catalysts

The crystal morphologies of the synthesized catalysts were investigated using scanning electron microscopy (SEM). In **Figure 26a**, the SEM images of ZIF-zni revealed a well-defined, uniform nano-rod-like structure with distinct inter-particle voids, consistent with previous research findings [344], [364]. Particle size distribution analysis (**Figure SI6 in appendix**) indicates an average particle size of 4.3 μm for ZIF-zni, with a deviation of 1.5 μm. Similarly, the Ce_{0.23}-ZIF-zni-CVD catalyst maintains the uniform rod-like morphology observed in the parent ZIF-zni (**Figure 26a**), accompanied by clearly defined small inter-particle voids that confirm the even distribution of cerium, as indicated by XRD analysis. The particle size distribution (**Figure 25a inset**) shows an average particle size of 3.2 μm and a deviation of 1.8 μm. In contrast, the catalyst Ce_{0.23}-ZIF-zni, prepared using the ESD method (**Figure 26b**), aligns with the XRD pattern (**Figure 25**) and exhibits a flake-like structure with fewer and larger inter-particle voids, a characteristic of excess Ce in the structure lattice.

Interestingly the observed rod-like structure of the ZIF-zni in SEM could also be noticed with HRTEM analysis as depicted in **Figure 26d**. The HRTEM image of Ce_{0.23}-ZIF-zni-X showed the lattice interatomic spacing of around 0.28 nm corresponded to the (111) plane of CeO₂ in agreement with reported studies [361]. The oxygen free environment and the inherent pyrophoric of CeO₂

perhaps facilitated the development of Ce nanoparticles [342], [352]. The EDS mapping and elemental analysis of the catalyst illustrated in **(Figure SI7 in appendix)** further display the dispersion of cerium atoms on the surface of the support. The mapping revealed all $\text{Ce}_x\text{-ZIF-ZNI}$ catalysts to exhibit dense Ce content than the corresponding $\text{Ce}_x\text{-ZIF-ZNI-CVD}$ catalysts. This observation is anticipated considering the ESD approached used in $\text{Ce}_x\text{-ZIF-zni}$ synthesis. Nevertheless, $\text{Ce}_x\text{-ZIF-zni-CVD}$ based catalysts exhibit the lowest percent of oxygen in comparison with the other catalysts further signifying the oxygen free environment of CVD and incorporation of nano-cerium in contrast to ESD approach.

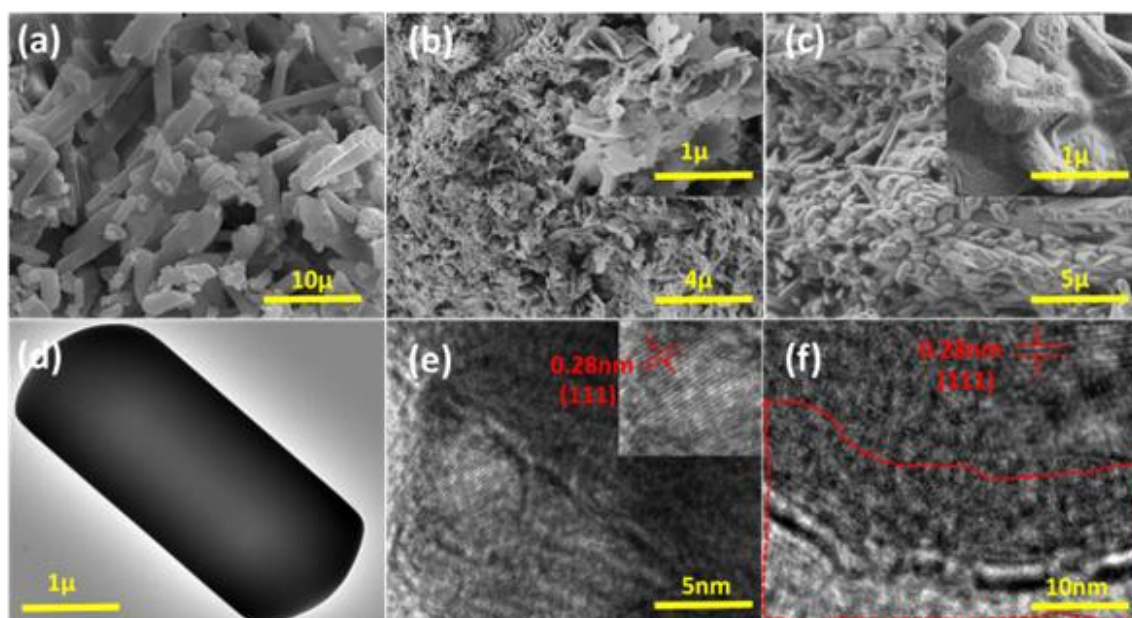


Figure 26. SEM analysis of (a) ZIF-zni, (b) $\text{Ce}_{0.23}\text{-ZIF-zni}$ (c) $\text{Ce}_{0.23}\text{-ZIF-zni-CVD}$ and TEM analysis of (d) Showing rod like morphology of the ZIF-zni, (e) $\text{Ce}_{0.23}\text{-ZIF-zni}$ and (f) $\text{Ce}_{0.23}\text{-ZIF-zni-CVD}$

4.5.3 XPS Analysis of the synthesized catalysts

The XPS analysis depicted in **Figure 27** explores the chemical and elemental states of ZIF-zni, as well as the synthesized catalysts $\text{Ce}_{0.23}\text{-ZIF-zni}$ and $\text{Ce}_{0.23}\text{-ZIF-zni-CVD}$. All spectra were normalized to the C 1s peak at 284.8 eV, representative of adventitious hydrocarbon. Evaluation of the survey spectrum of ZIF-zni and the synthesized catalysts ($\text{Ce}_{0.23}\text{-ZIF-zni}$ and $\text{Ce}_{0.23}\text{-ZIF-zni-CVD}$) revealed the presence of C 1s, O 1s, N 1s, Zn 2p, and Ce 3d (**Figure S8 and S9 in appendix**).

The detailed analysis of the high-resolution Ce 3d spectrum (**Figure 27a and 27c**) displayed eight peaks, which could be attributed to the spin-orbit splitting of Ce 3d_{3/2} and Ce 3d_{5/2} states, indicative of both Ce³⁺ and Ce⁴⁺ chemical states. This splitting of the spin doublet suggests the non-stoichiometric nature of Ce, with the existence of oxygen vacancies within the Ce lattice [368]. Upon investigating the Ce_{0.23}-ZIF-zni catalyst spectrum and evaluating the percentage elemental compositions, evidence of both +3 and +4 oxidation states was observed. Conversely, the percentage elemental compositions of the Ce_{0.23}-ZIF-zni-CVD catalyst primarily indicated the +4 chemical state of Ce in the sample due to the spin doublet splitting (**Table S4 and S5 in appendix**) [369]–[371]. Notably, the Ce 3d profile for the Ce_{0.23}-ZIF-zni-CVD catalyst exhibited a slight shift towards higher binding energy, suggesting an electronic structural modification likely stemming from metal-support interaction, potentially between Zn and the Ce surface.

Furthermore, only the Ce_{0.23}-ZIF-zni catalyst displayed distinct O 1s peaks associated with lattice oxygen, adsorbed oxygen, and oxygen in the carbonate at binding energies of 528.8, 531.2, and 532.2 eV, respectively (**Figure 27b**). In contrast, ZIF-zni and the synthesized catalyst Ce_{0.23}-ZIF-zni-CVD showed two separate peaks with shift in higher binding energy [368] .

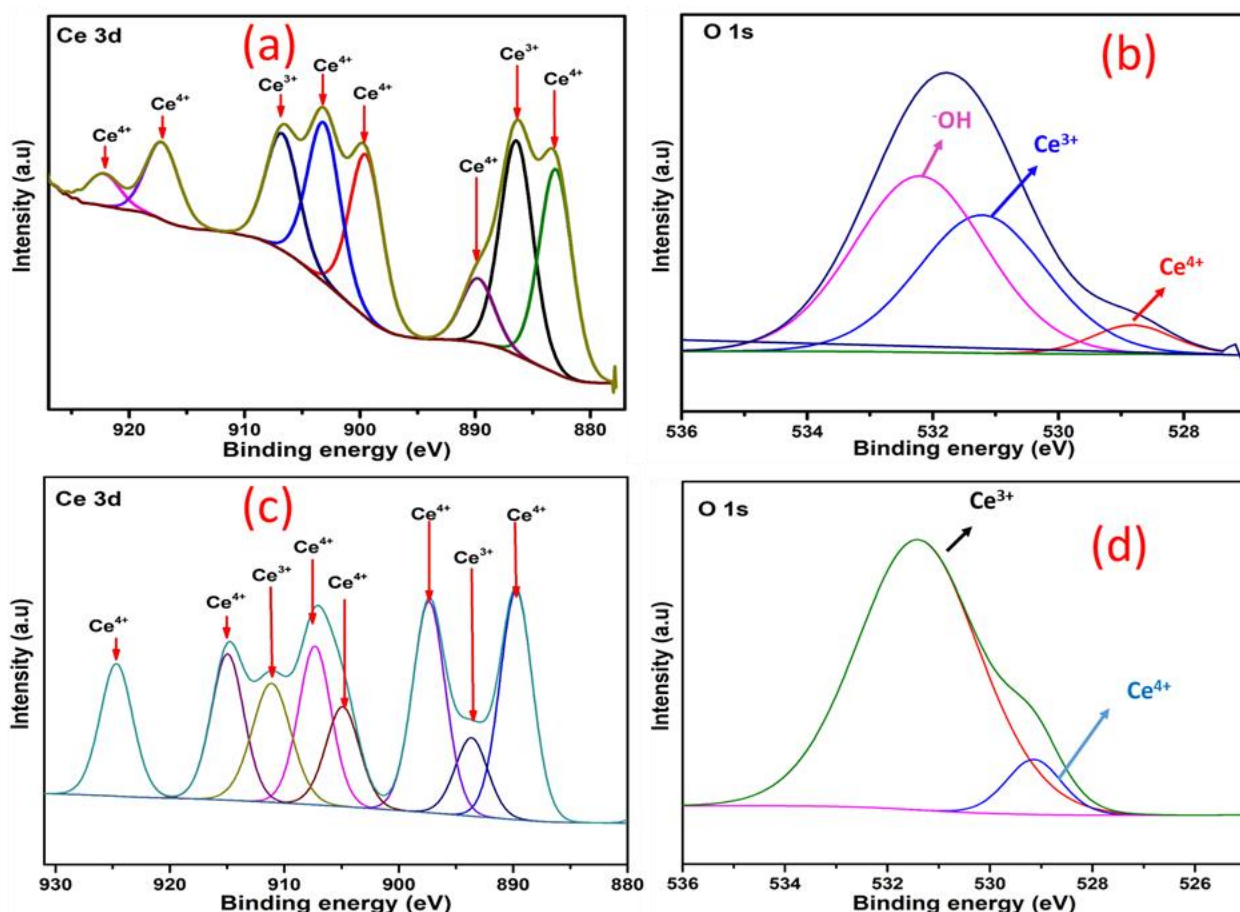


Figure 27. High-resolution XPS spectra of Ce 3d of (a) Ce_{0.23}-ZIF-zni (c) Ce_{0.23}-ZIF-zni-CVD and O 1s of (b) Ce_{0.23}-ZIF-zni (d) Ce_{0.23}-ZIF-zni-CVD

4.5.4 Electrochemical measurements

The electro-catalytic activity of CO₂ reduction on Ce_x-ZIF-zni-X catalysts were evaluated by linear sweep voltammetry measurements (LSV) in 0.5 M KHCO₃ solution saturated with CO₂ and Ar with parent ZIF-zni as the reference electro-catalyst. As presented in **Figure 28a**, Ce_{0.23}-ZIF-zni and Ce_{0.7}-ZIF-zni-CVD catalysts reveals inferior onset potential between -600 mV to -300 mV vs Ag/AgCl. The onset potential of Ce_{0.7}-ZIF-zni-CVD electro-catalysts was measured to be lower than the control sample (ZIF-zni) in 0.5 M KHCO₃ saturated environments. Essentially, Ce_{0.23}-ZIF-zni and Ce_{0.23}-ZIF-zni-CVD disclosed enhanced current densities in contrast to the pristine ZIF-zni in which Ce_{0.23}-ZIF-zni-CVD catalysts remarkably demonstrated 7.7 mA cm⁻², two times more than the current densities of the parent ZIF-zni. More so, the controlled potential electrolysis

conducted in saturated Ar to assess the reduction processes produced negligible current densities. The greater current densities witnessed in Ce_x-ZIF-zni-X electro-catalysts are obviously due to dissolved CO₂ whereas the inferior current densities for Ar saturated electrolytes an indicative of hydrogen evolution reaction shows fairly high over-potential on the Ce_x-ZIF-zni-X electrodes. Interestingly, the electro-catalytic activity of the Ce_x-ZIF-zni-X catalysts were improved upon the addition of elemental cerium to the parent ZIF-zni. The observed trend in current densities demonstrates a relationship with increasing cerium content and the onset potential for the most active electrode (Ce_{0.23}-ZIF-zni-CVD) is found to be effectively -300 mV vs CO₂/CO (**Figure 28a**—inset). The dormancy of the ZIF-zni electrode in CO₂ saturated electrolytes highlights the significance of cerium for the catalytic process.

The electrochemical active surface areas (ECSA) of the electro-catalysts ZIF-zni and Ce_x-ZIF-zni-X were measured from Cdl by analyzing the non-Faradaic region of CV plots at different scans rates ranging from 10-100 mVs⁻¹ rate in a CO₂-saturated 0.5 M KHCO₃ solution **Figure 28-c**. The ECSA **Figure 28d** of the parent ZIF-zni is observed to be 0.09 mFcm⁻², which is far less than the synthesized Ce_x-ZIF-zni-X electro-catalysts. Fascinatingly, since Cdl is directly related to ECSA, Ce_{0.23}-ZIF-zni-CVD exhibits a significantly increased electrochemical surface area of 1.81 mFcm⁻², showing a substantial 94.4% enhancement in ECSA compared to the parent ZIF-zni. The ECSA is observed to increases with increase in Ce content in consistent with obtained current densities. These results demonstrate a good relationship between ECSA and, the greater catalytic activity.

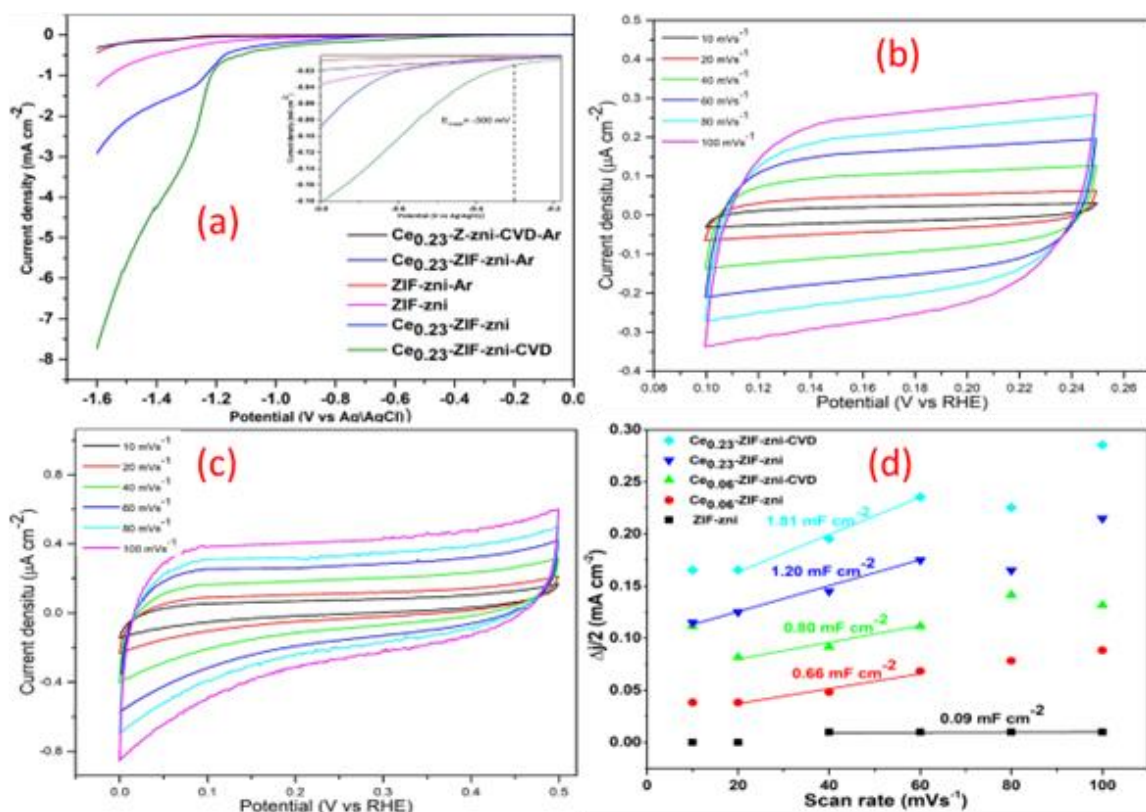


Figure 28. Electrochemical measurements of ZIF-zni and Ce_x-ZIF-zni-X (a) LSV curves in CO₂ and Ar saturated 0.5 KHCO₃ electrolyte solution. (b and c) Cyclic voltammograms of ZIF-zni and Ce_{0.23}-ZIF-zni-CVD at several scan rates in the region of 0.0 to 0.5 V vs RHE. (d) ECSA measurement, half of charging current density differences ($\Delta j/2$) plotted against scan rates.

The electro-catalytic activity of both the parent ZIF-zni and Ce_x-ZIF-zni-X for CO₂ electrochemical reduction reaction were investigated in 0.5 M KHCO₃ saturated CO₂ environment at -0.7 V to -1.0 V vs RHE. As presented in **Figure 29a**, irrespective of the applied potential, the major electrochemical CO₂ reduction products are CO with traced amount of H₂ as revealed by the online GC. The finding indicates Ce_x-ZIF-zni-X catalyst to exhibits a considerably greater selectivity for CO than the parent ZIF-. Remarkably, Ce_{0.23}-ZIF-zni-CVD electrode achieved 87.8% FE at -0.7 V vs RHE and at lower over-potential of CO₂ to CO (170 mV) than the parent ZIF-zni (270 mV). Furthermore, the inhibition of the competing hydrogen evolution reaction (HER) remains below 10% throughout the entire applied potential range. To facilitate a more meaningful comparison with prior research, we employed the commonly used KHCO₃ solution as the electrolyte in this study, along with a Ce electrode. Besides evaluating the selectivity of Ce_x-ZIF-zni-X, this research showcases significantly lower over-potential compared to previously

reported cerium-based electrocatalysts for the conversion of CO₂ to CO when assessed in a bicarbonate electrolyte **Table SI6 in appendix**.

To gain insights into the potential reaction mechanism, we investigated the electrochemical kinetics of the reaction process. As depicted in **Figure 29d**, the electrocatalysts Ce_x-ZIF-zni-X displayed enhanced reaction kinetics, evidenced by their lower Tafel slopes of 104.2 mV/dec and 109.7 mV/dec for Ce_{0.23}-ZIF-zni and Ce_{0.23}-ZIF-zni-CVD, respectively, in contrast to ZIF-zni, which exhibited a Tafel slope of 193.8 mV/dec. It is worth noting that studies have indicated that a Tafel slope approximately around 118 mV/dec suggests a likelihood of a single electron transfer step to CO₂ and is considered the rate-determining step.⁴⁶ Conversely, a slope exceeding this established value suggests slower kinetics in the context of the single electron transfer to CO₂. Therefore, the introduction of Ce into ZIF-zni (Ce_x-ZIF-zni-X electrocatalysts) may potentially enhance the reaction kinetics for the single electron transfer step to CO₂, while ZIF-zni exhibits slower kinetics in this regard. The superior catalytic performance of Ce_{0.23}-ZIF-zni-CVD, over Ce_{0.23}-ZIF-zni and ZIF-zni, was further confirmed through EIS. The Nyquist plots in reveal a significantly smaller impedance arc for Ce_{0.23}-ZIF-zni-CVD compared to Ce_{0.23}-ZIF-zni and ZIF-zni. This indicates that Ce_{0.23}-ZIF-zni-CVD exhibits a faster interfacial charge-transfer process during CO₂ reduction

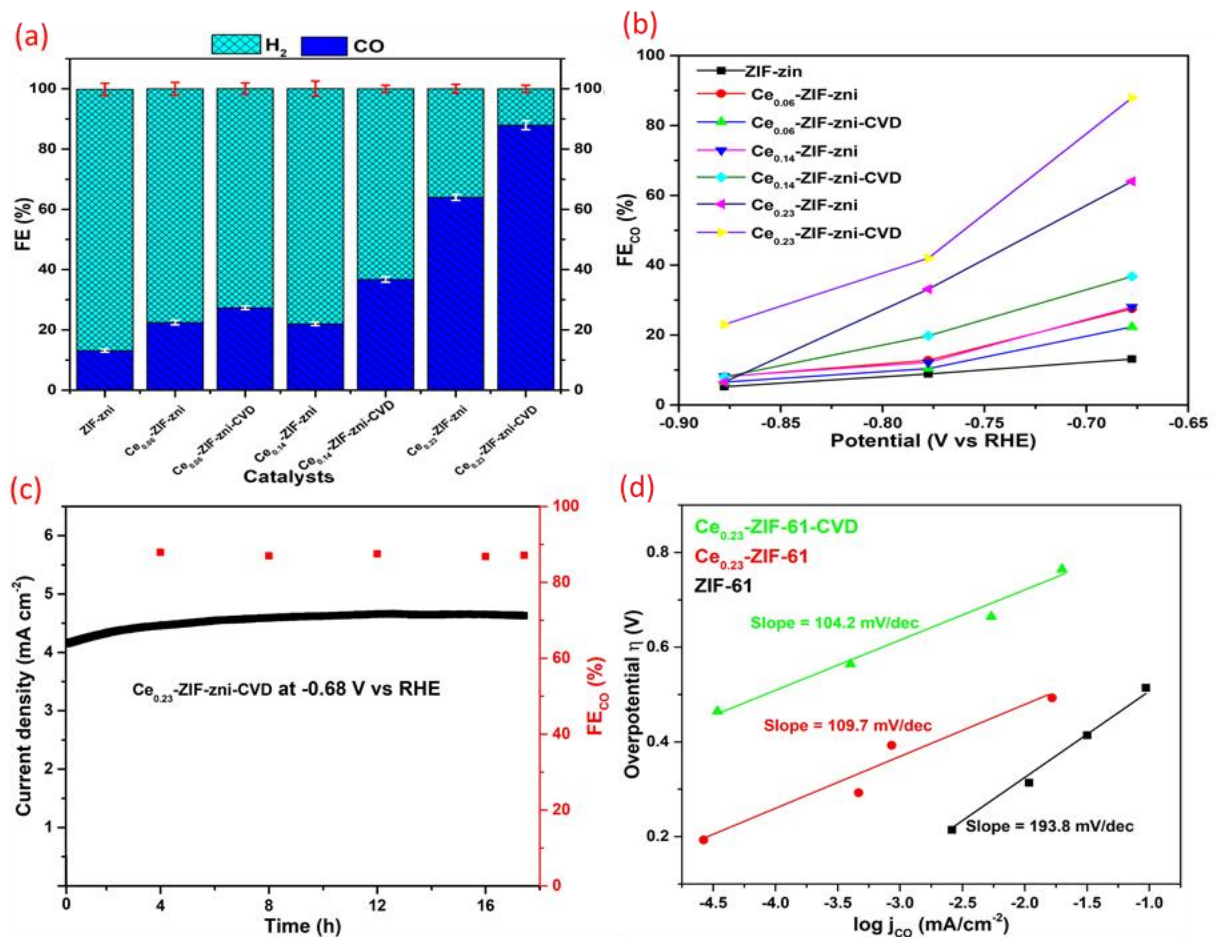
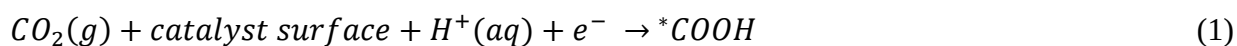


Figure 29. (a) Faradaic efficiencies (%) of ZIF-zni and Cex-ZIF-zni-X (b) FECO at different applied potential and (c) Tafel plots for ZIF-zni and Cex-ZIF-zni-X

In order to comprehend the reaction mechanism, we performed calculations using density functional theory (DFT) with Ce_x/ZIF-zni as the descriptor to elucidate the interface between Ce_xO_y and ZIF-zni. Furthermore, we accounted for the impact of the electrochemical environment on the electrochemical CO₂ reduction reaction by fully hydroxylating Ce_xO_y into Ce_xO_yH₂. This approach was based on the work outlined in a prior study **Figure 30** [368]. Drawing from earlier research into the electrochemical CO₂ reduction reaction yielding CO, we adopted the subsequent reaction mechanism.



When CO₂ encounters the ZIF-zni surface, the oxygen and carbon atoms of the CO₂ molecules arrange themselves around the Zn ion of the ZIF-zni located on the opposite side, maintaining an approximately uniform distance of about 2.1 **Figure SI10 in appendix**. This arrangement leads to the distortion of the ZIF-zni cavity. However, regardless of Ce specific chemical state, an intriguing synergistic effect emerges. In this scenario, the oxygen atoms associated with Ce orient themselves toward the Zn ion within the ZIF-zni structure, creating conditions conducive for the CO₂ to approach Ce atom from behind and this trend was maintained in all interaction **Figure SI11 in appendix**.

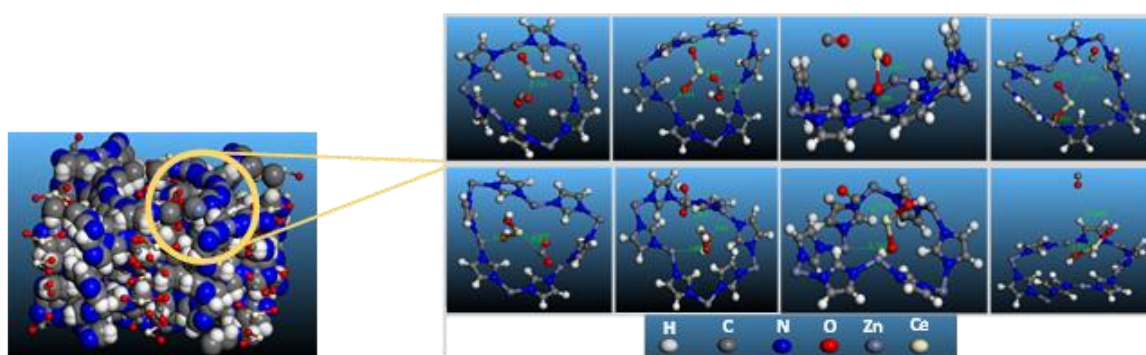


Figure 30. DFT calculations of the optimized structures for the main intermediates of the electrochemical CO₂ reduction reaction on Ce_xO_y-ZIF-zni surface.

Figure 31 illustrates the computed free energy diagram for the electrochemical CO₂ reduction reaction on both ZIF-zin and Ce_xO_yH₂/ZIF-zni. Our findings indicate that the rate-limiting step for both catalysts involves the formation of *COOH species through protonation, which aligns with previously reported research [368], [373]. Except for CeO₂-ZIF-zni, which demonstrates a higher energy cost compared to ZIF-zni, all other species exhibit lower energy requirements. As a result, the protonated decomposition of *COOH into *CO and the subsequent desorption of *CO are facilitated by the synergistic influence of Ce_xO_y and the Zn ion within the ZIF-zni framework.

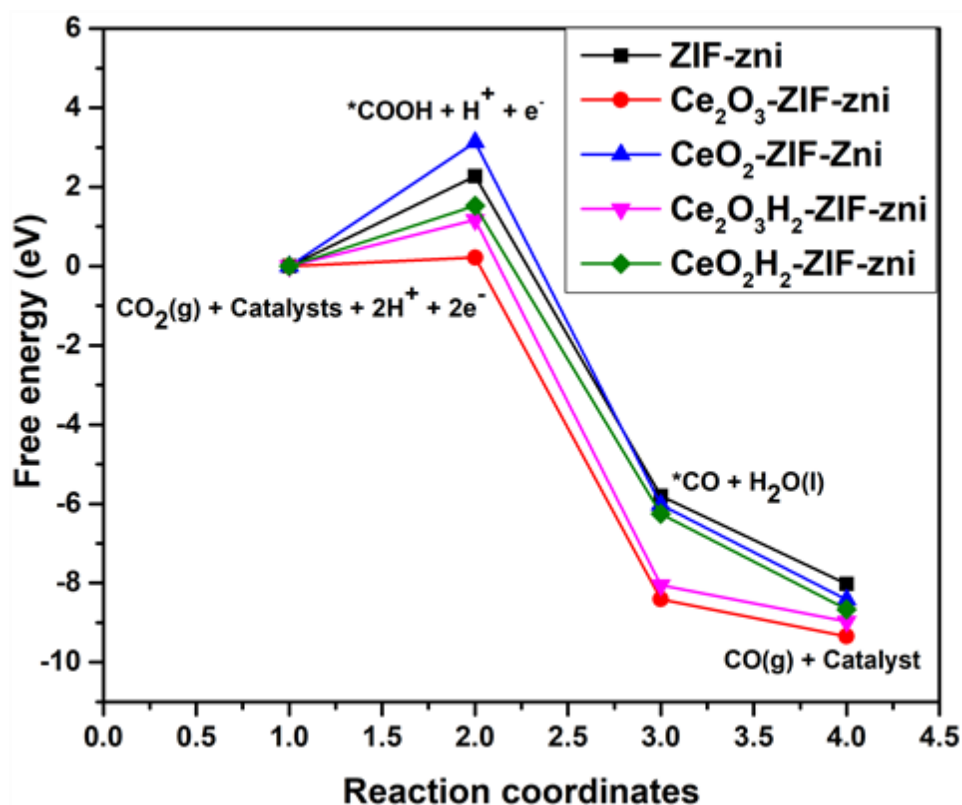


Figure 31. DFT calculations of electrochemical CO₂ reduction reaction on ZIF-zni and Ce_xO_y-ZIF-zni surface.

4.6 Conclusion

In summary, we proposed a novel and facile approach for synthesizing ZIF-zni with minimal solvent usage. The Ce_{0.23}-ZIF-zni-CVD catalysts show significant potential in the electrocatalytic conversion of CO₂ to CO, achieving an excellent Faradaic efficiency of up to 87.9% at an overpotential of 170 mV. This remarkable electrocatalytic performance can be attributed to the abundant catalytic Ce sites present on the catalysts which promoted the adsorption and activation of CO₂. DFT calculation reveals a synergetic interaction between the oxygen of the Ce_xO_y and Zn ion of the ZIF-zin within the framework. The formation of *COOH species is further found to be the rate-determining step. Consequently, by enhancing the adsorption of *COOH species at the active cerium site, the electrochemical reduction of CO₂ is significantly promoted. These findings underscore the potential of Ce_{0.23}-ZIF-zni-CVD in the conversion of CO₂ into valuable chemical products.

Acknowledgement

The authors would like to express their gratitude to the Center for Refining and Advanced Chemicals, King Fahd University of Petroleum & Minerals (KFUPM), located in Dhahran, Saudi Arabia, for the support provided, under project INRC2216.

CHAPTER 5

New insights into selectivity modulation of Pb-based electrode in electrocatalytic reduction of CO₂ to CO: Effect of electrochemical roughening

Abstract

As energy consumption and atmospheric CO₂ levels continue to rise, the electrochemical reduction of CO₂ (CO₂RR) presents a viable solution for converting CO₂ into valuable chemicals and achieving a carbon-neutral cycle. Although Pb-based electrocatalysts have exhibited exceptional performance in generating formate through CO₂RR, their ability to produce other value-added chemicals while maintaining selectivity remains a challenge. We present a simple method for adjusting the selectivity of Pb electrodes through electrochemical roughening in a 0.3 M KCl electrolyte. The pristine Pb electrodes achieved a maximum current density of 20 mA cm⁻² and a formate FE of 40%. By subjecting the Pb electrodes to multiple oxidation-reduction cycles (ORC), we were able to modify their selectivity. The SEM and 3D optical profilometer analysis unveiled the creation of a rough surface characterized by randomly stacked layers, which formed valleys consisting of Pb particles. This ORC-treatment exhibited a significantly improved electrocatalytic performance, achieving a maximum current density of 80 mA cm⁻². The treated electrodes displayed exceptional selectivity for CO, with an FE of 89%, and remarkable stability for up to 24 h of continuous electrolysis, producing CO at an average rate of 30 μmol cm⁻² hr⁻¹. These results highlight the importance of the Pb electrode's surface roughening in determining its CO selectivity. Evaluation of DFT calculation demonstrates *COOH intermediate as more likely to be generated and adsorb on ORC treated electrodes, verifying the charge acquisition of Pb²⁺ layer to enhance the activity and selectivity of CO product. The highly catalytic activity and selectivity of CO could be credited to the reduced formation energy barrier and enhanced adsorption behavior of *COOH intermediate.

Keywords: Electrochemical CO₂ reduction (CO₂RR); Morphology; Selectivity; Pb electrodes and Electrochemical surface roughening.

5.1 Introduction

The industrial revolution which took place in the nineteenth century brought to limelight several fossil fuels such as petroleum, coal and natural gas which serve as sources of energy for economic sustainability [374]. However, the extensive utilization of these fuels has continued to provoke global concerns due to the continued release of CO₂ into the atmosphere, which has negative climatic and environmental impacts [375], [376]. The present-day atmospheric CO₂ concentration has reached over 410 ppm and this has prompted the global researches into finding lasting solutions which addresses the negative effects of excessive CO₂ presence on the planet [377]. Electrocatalytic CO₂ conversion to value-added chemicals and fuels is a promising strategy for the mitigation of atmospheric CO₂ concentration as it is conducted at ambient conditions and can be driven by renewable energy sources such as solar and wind energies [39], [118], [378]–[380]. Furthermore, this technology offers an effective strategy towards energy storage in the form of fuels, chemicals and essential industrial feedstocks such as CH₄, CO, C₂H₄ and formate [381]. In spite of the numerous advantages of this technology, the lack of durable electrocatalysts, the poor selectivity of the existing catalysts and the competing hydrogen evolution reaction (HER) negates the practical implementations [382], [383]. A breakthrough in this technology would therefore be to design highly selective catalysts toward a particular product which are effective at low CO₂ activation overpotentials and eliminates the cost of product separation. Metal oxides-based electrocatalysts such as Pb, Sn, Ni, Cu and Pt have been reported for the reduction of CO₂ to formate, CO and alcohols [384]–[395]. A number of these catalysts have been synthesized through the deposition of metal nanoparticles on active supports [396], [397], the decomposition

of the metal precursors onto the catalysts support [398] or the use of solvent-assisted methods of synthesis [399], [400]. While the latter method often results in the design of morphology and size-controllable electrocatalysts, it generates large number of organic wastes making the whole process environmentally unsafe. An alternative to these synthetic methods is the microfabrication technique via electrochemical surface roughening of the metal plates which enables the formation of robust electroactive surfaces [401]. This often results in the formation of three-dimensional (3D) surfaces which exhibits high charge transfer characteristics and the effective distribution of electronic charges at the metal-CO₂ interface, lowering the energy of activation and promoting the adsorption and subsequent transformation of CO₂ molecules. Recently, the use of Pb-based electrocatalysts has been reported for the effective production of formate with high selectivity up to ~100% [374]. Lee and Kanan reported the synthesis of nanocrystalline Pb films by reducing PbO₂ precursors, which resulted in the suppression of H₂ evolution and promoted the effective reduction of CO₂ to formate [402]. Wang *et al.* demonstrated the synergy of Cu/Pb core/shell electrocatalysts for the production of C₂₊ liquid products, achieving the maximum current density of 196.8 mA cm⁻² and faradaic efficiency (FE) of 81.6% [403]. Zhao *et al.* reported the mechanistic study of CO₂ reduction to formate on Pb(111) surface using density functional theory and demonstrated the role of solvent and cations in tuning product selectivity [404]. He *et al.* reported the electrochemical roughening of Pb electrodes through oxidation-reduction cycling (ORC) which exhibited high activity towards CO₂ reduction to formate and achieving an FE of 89% [390].

In the present study, we report for the first time a facile method for tuning the selectivity of Pb electrodes by electrochemical roughening in 0.3 M KCl electrolyte. Compared to the pristine Pb which achieved a maximum current density of ~20 mAcm⁻² and an FE of formate ~40%, we demonstrated that by carrying out multiple oxidation-reduction cycling (ORC) on the Pb electrodes, it is possible to tune the selectivity. The ORC-treatment of the Pb electrodes resulted in the formation of randomly stacked layers forming valleys of Pb particles with a significantly enhanced electrocatalytic performance, reaching a maximum current density of ~80 mA cm⁻². The

treated electrode demonstrated very high selectivity to CO reaching an FE of 89%, and a very high stability within 24 hrs. of continuous electrolysis with an average CO production rate of $30 \mu\text{mol cm}^{-2} \text{ hr}^{-1}$ at an overpotential of 300 mV.

5.2 Experimental

5.2.1 Reagents and chemicals

All reagents and chemicals used were of high purity (> 99%) and used as-received without further purifications. These include: Potassium chloride, KCl and potassium bicarbonate, KHCO_3 (Fluka chemicals), sodium dihydrogen phosphate, NaH_2PO_4 and sodium hydrogen phosphate, Na_2HPO_4 (Fisher scientific), lead metal sheet 1/16" (technical grade, Fisher scientific), absolute ethanol (Merck) and 5 wt% Nafion D520 (Fuel cell store). Ultra-pure deionized water (DI) was used throughout the experiments.

5.2.2 Electrode preparation and characterization

Commercial Pb sheets were first cleaned with absolute ethanol followed by deionized water and then electrochemically roughened by carrying out multiple cycles (5, 10, 20, 50) of cyclic voltammetry (CV) in 0.3 M KCl electrolyte. The CV scans were conducted in the potential range -0.5 to -0.7 V (vs Ag/AgCl) at a scan rate of 20 mV/s. The roughened Pb sheets were rinsed several times with DI water and stored in a desiccator. A schematic diagram has been illustrated in in **Figure 32**. The morphology of the electrodes was examined using Quattro-S Ultra-versatile high-resolution field emission scanning electron microscope (FESEM) fitted with energy-dispersive x-ray spectrometer at an acceleration voltage of 15 kV (Thermo Scientific), whereas the x-ray diffraction patterns were recorded on Bruker-D2 Phaser bench-top x-ray diffractometer using $\text{CuK}\alpha$ radiation in the 2θ range of $10^\circ - 70^\circ$.

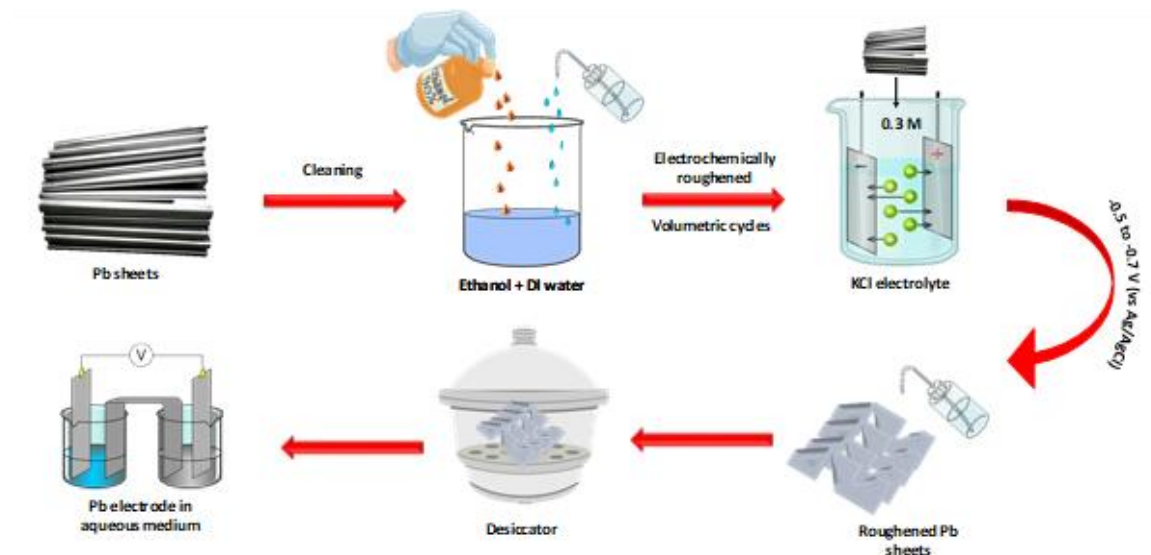


Figure 32. Schematic illustration of the preparation of Pb electrode using commercial sheets.

5.3 Electrochemical measurements

The electrodes were characterized by potentiostatic electrochemical impedance spectroscopy (EIS) measurements in 5 mM of the redox-active potassium ferricyanide, $K_3[Fe(CN)_6]$ containing 1.0 M KCl as supporting electrolyte. The impedance spectra were measured in the range of frequency 100 kHz to 100 mHz at an amplitude of 10 mV r.m.s. Electrocatalytic reduction experiments were conducted by controlled potential coulometry in a sealed two-compartment H-type electrochemical cell separated by Nafion-117 proton exchange membrane. A schematic diagram of experimental setup has been illustrated in **Figure 32**. The electrode assembly comprises of the lead sheet (1 cm $\times$ 1 cm $\times$ 0.2 mm) as the working electrode, platinum wire as the counter electrode and Ag/AgCl as the reference electrode. 0.5 M $KHCO_3$ served as the anode and cathode electrolyte, respectively. Prior to the electrolysis, high purity CO_2 (99.999%) was passed into the electrolyte for 30 min at a flow rate of 30 sccm, then maintained at 5 sccm during the electrolysis to remove residual air and ensure continuous CO_2 supply. The gas products were analyzed online on Clarus 580 GC (Perkin Elmer) equipped with Hayesep and Molecular sieve columns and thermal conductivity (TCD) and flame ionization (FID) detectors,

respectively. The headspace products were injected into the GC periodically at 20 min interval by an automated sampler. The electrolyte solution was collected at the end of 1 h electrolysis and analyzed for liquid products. Alcohols were analyzed on Agilent 7980A GC equipped with supelcowax 10 (60 m × 250 μm × 0.25 μm) column and an FID detector. Products were carried through the column at a flow rate of 1.2 mL/min. Formate was detected on Compact IC flex 930 ion-exchange chromatography (Metrohm instruments) equipped with Metrosep A 5 – 250 column (length 250 mm, ID 4mm) and Metrosep supp. 4/5 pre-column (length 5 mm, ID 4 mm). 3.2 mmol/L Na₂CO₃ and 1.0 mmol/L NaHCO₃ were used as eluents and 100 mmol/L H₂SO₄ as suppressant at a flow rate of 0.70 mL/min. 20 μL of the sample was injected each analysis time. The faradaic efficiency (FE) of the products were estimated using the Eq (1) [405]:

$$FE = \frac{Z \times c \times V \times F}{Q} \quad (1)$$

Where, Z represents the number of transferred electrons during the electrolysis, c is the molar concentration of the products (mol/L) as detected on GC or IC, V is the total volume of the gas or the liquid products (L), F is the Faraday constant (96485 C mol⁻¹ of electrons), and Q is the overall charge over the period of 1 h electrolysis. All of the potentials reported in this study were converted to the reversible hydrogen electrode, RHE using the Eq (2)

$$E_{RHE} = E_{Ag/AgCl} + E_{Ag/AgCl}^0 + 0.059pH \quad 2$$

Where, $E_{Ag/AgCl}^0$ was taken as 0.228 V, and the pH of CO₂-saturated 0.5 M KHCO₃ was measured as 7.47.

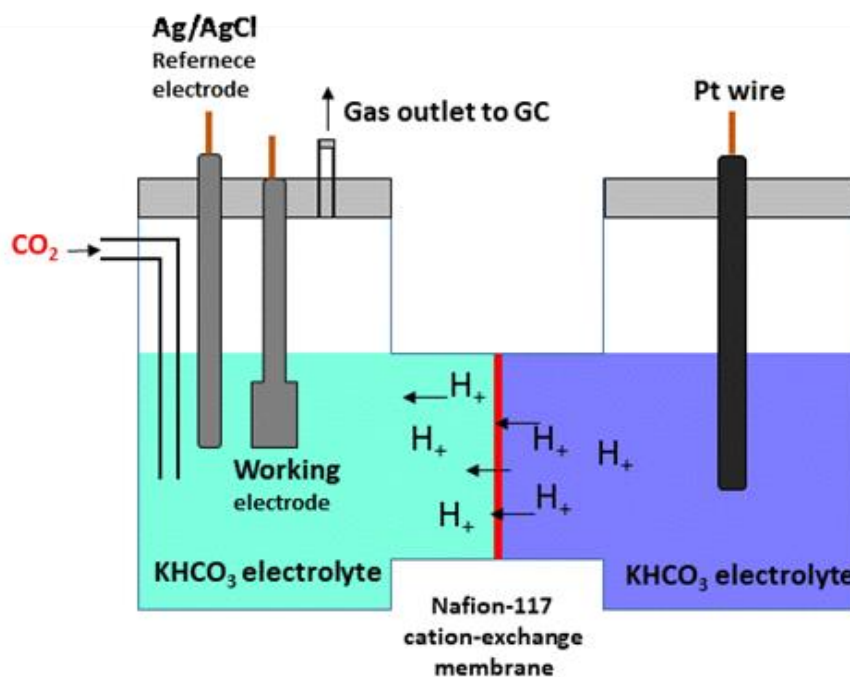


Figure 33. Reactor setup of electrochemical cell for Pb electrode.

5.4 Computational method

Density functional theory (DFT) calculations were conducted using the Pople's 6-311G* basis set for the non-metallic atoms, and the Stuttgart/Dresden (SDD) basis set for Pb atoms on Gaussian 09 [406]. The Grimme's dispersion correction (DFT-D3) was employed [407], [408] to account for the long-range Van der Waals interactions. A simple unit cell of PbO comprising of 4 atoms of Pb and 4 atoms of O was chosen to represent the catalyst surface [409]. Full geometry optimizations were carried out to the minima without imposing symmetry constraints on the potential energy surface. The self-consistent field convergence criterion was set to 1×10^{-8} Hartree during the optimizations, whereas the average root means square force on all atoms thresholds was set at 3.0×10^{-4} Hartree/Bohr. The adsorbed intermediates, HCOO* and *COOH pathways were considered, and the free energy changes at each step were computed. Adsorption of CO₂, the intermediates and the products (E_{ads}) were calculated using the Eq (3):

$$E_{ads} = E_T - (E_{PbO} + E_{mol}) \quad (3)$$

Where, E_T represent the free energy of the catalyst and the adsorbed reactants, intermediates or products, and E_{PbO} and E_{mol} represents the free energies of the isolated PbO catalyst and the isolated reactants, intermediates and products, respectively.

5.5 Results and discussion

Figure 34 presents the FESEM micrographs of the Pb electrodes before and after conducting multiple cycles of CV in 0.3 M KCl electrolyte solution. The pristine Pb electrode (**Figure 34a**) exhibits a smooth surface showing the grain boundaries in contrast to the roughened electrodes (**Figure 34b-e**) which depicts uniform randomly stacked layer of Pb particles having an average size of $\sim 1 \mu\text{m}$. **Figure 34e** and **f** show needle-like structures, of well-defined interconnection presents on the electrode surface to form a three-dimensional structure. The EDX spectrum (**Figure 34g**) and the elemental mapping data of the electrodes subjected to 50 cycles of treatment (**Figure 34h**) revealed the presence of Sn and Sb impurities, likely originating from the manufacturing process. Oxygen atoms, probably derived from metal oxides, were also detected. Furthermore, the EDX elemental analysis showed a significant decrease in the relative percentages of Sn and Sb, dropping from 13.2% and 11.45% in pristine Pb to 5.9% and 4.9% in the ORC treated electrode respectively. This highlights the importance of surface roughening, as illustrated in **Figure SI12 in appendix**. Similarly, we assessed the surface morphology and roughness parameters of the pristine Pb and ORC-treated Pb electrodes using 3D optical profilometer by acquiring 3D optical profiles in a random location on each type of electrocatalyst (**Figure 35a-b**). As shown in the 2D image of optical profiler surface scan (**Figure SI12 in appendix**) the ORC-treated Pb electrodes surface exhibits an arithmetic average roughness (S_a) and a root mean square roughness (S_q) in the 2.5–3.8 μm and 3.0–5.7 μm ranges, respectively. This roughness represents more than one order of magnitude higher than pristine Pb (S_a :1.4-1.9 μm , S_q :1.8-2.5 μm). The

significant difference in surface roughness mainly arises from the electrochemical surface roughness.

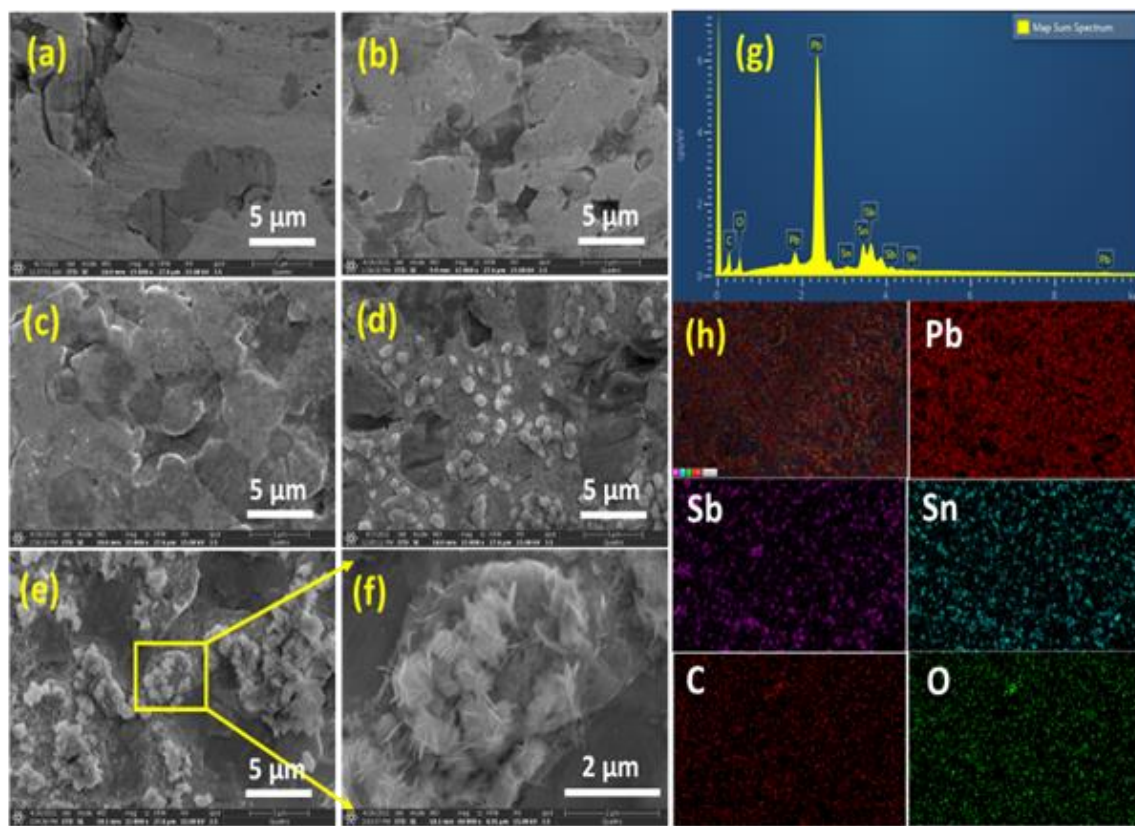


Figure 34. FESEM micrographs of (a) pristine and ORC-treated Pb electrodes at (b) 5 cycles, (c) 10 cycles, (d) 20 cycles, (e) 50 cycles. The expanded view of the 50 cycles-treated electrode is shown in (f). The EDX spectrum of the 50 cycle ORC-treated electrode is shown in (g). The elemental distribution on the surface of the electrode is shown in (h).

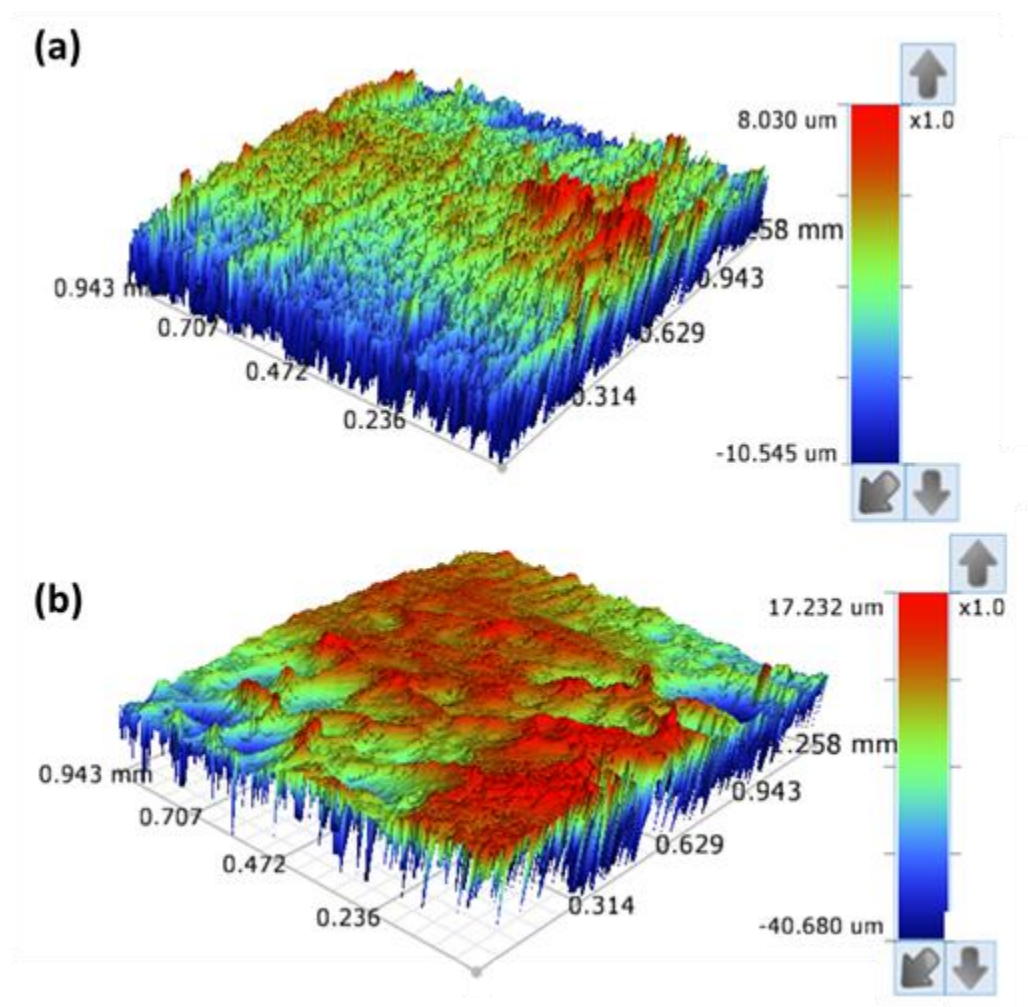


Figure 35. Optical 3D profiler topography of (a) pristine Pb electrode, and the (b) 50 cycles ORC-treated, in 0.3 M KCl electrolyte solution.

The x-ray diffraction patterns of the pristine and the ORC treated Pb electrodes are presented in **Figure 36**. The diffraction peaks observed for both the untreated and treated Pb electrodes closely aligned with the standard Pb diffraction peaks (JCPD No. 65-2873), indicating the presence of tetragonal PbO primarily on the pristine Pb surface and after the ORC treatment [19]. However, the diffraction pattern also revealed the presence of impurities such as hexagonal Sb and Sn [39], [40]. Remarkably, as the number of ORC cycles increased, the intensity of all diffraction patterns notably decreases aligning well with the findings from the EDX analysis. This reduction in peak intensity suggests the successful etching of the top pristine Pb layers and the effective roughening of the Pb electrode surface.

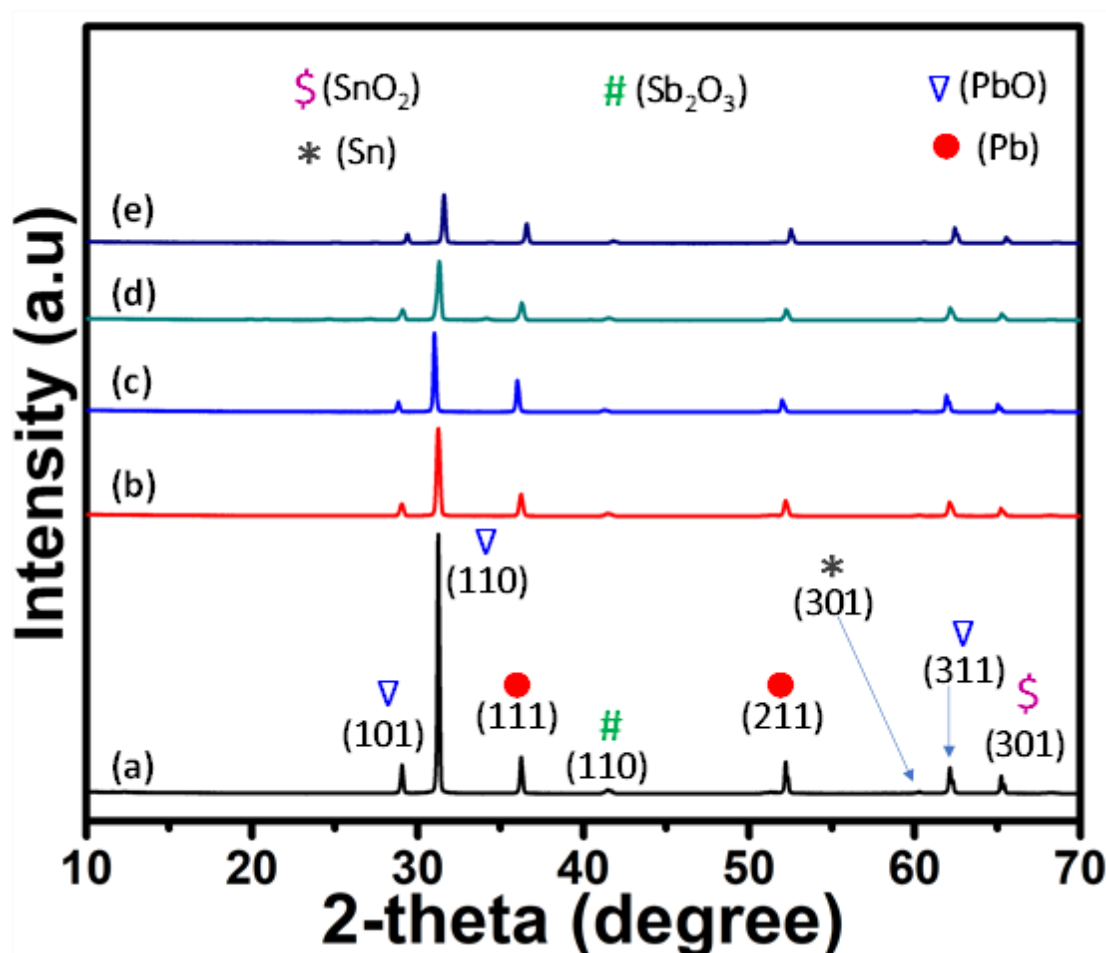


Figure 36. X-ray diffraction patterns of (a) pristine Pb electrode, and the (b) 5 cycles ORC-treated, (c) 10 cycles treated, (d) 20 cycles treated and (e) 50 cycles treated electrodes in 0.3 M KCl electrolyte solution

The CV plots corresponding to 50 ORC cycles on the Pb electrode is presented in **Figure 37a**. while other plots (5, 10 and 20 cycles) are presented in the supplementary information (**Figure SI13 in appendix**). The CV cycles depicts the roughening of the surface of the electrodes with strong reduction peak at -0.029 V vs RHE. Similarly, the redox couple ($E_{1/2}$) of the 50 ORC through CV reveals a $E_{1/2}$ of -0.014 V vs RHE in KHCO_3 corresponding to Pb/Pb^{2+} redox couple [410], [411]. Additionally, the Pb/Pb^{2+} redox event of ORC-treated electrodes at negative potential window renders a higher fraction of Pb^{2+} sites than in the pristine Pb, indicating that the active sites in ORC-treated electrodes would probably facilitate the generation of Pb^{2+} species generally considered as the active sites for reducing CO_2 . Meanwhile the charge transfer capacity of the roughened electrodes was significantly improved as depicted by the EIS Nyquist plots in **Figure**

37b. It is clearly evident that the ORC treatment resulted in the lowering of the charge transfer resistance, R_{ct} of the Pb electrodes which facilitates the effective mass transport of the electroactive species on the surface of the electrodes. The performance of the ORC-treated Pb electrodes on CO₂ electrocatalytic reduction was evaluated by linear sweep voltammetry (LSV) in a conventional three-electrode electrochemical cell (H-cell) containing CO₂-saturated 0.5 M KHCO₃ as electrolyte. As depicted by the LSV curves (**Figure 37c**), the ORC-treated electrodes exhibits strong reduction peak at ~ -0.3 V vs RHE corresponding to the reduction of Pb(II) species to Pb(0) [412]. On the contrary, when subjected to 5, 10, and 20 cycles, in addition to reduction of Pb(II) species to Pb(0), a distinct peak emerged at approximately +0.15 V vs RHE, indicating the oxidation of Sn(II) to Sn(IV) (see **Figure 37c**),. This phenomenon predominantly occurs due to the facile oxidation of Sn²⁺ to Sn⁴⁺ [44]. Meanwhile, the ORC-treated electrodes provided much higher current density compared to the pristine Pb electrode and the 50 cycle-treated electrode has the maximum current density of ~ 80 mA cm⁻². The 50 cycles-treated electrodes further demonstrate greater potential for CO₂ reduction as it yielded a significantly lower reduction current in Ar-saturated electrolyte (**Figure 37d**).

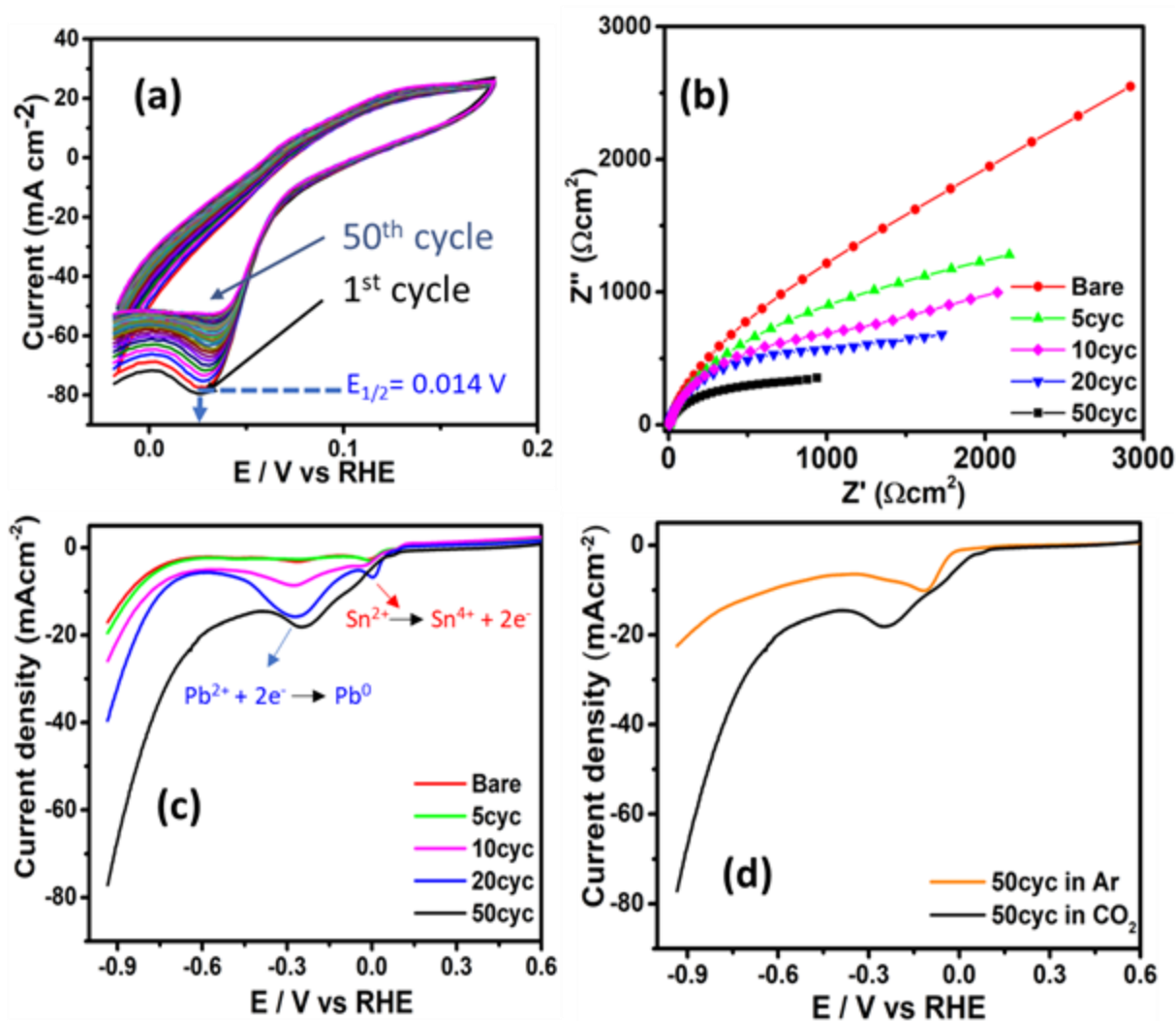


Figure 37. (a) CV curves corresponding to 50 ORC treatment on Pb electrode, (b) Nyquist plots of the pristine and ORC-treated electrodes in 5.0 mM $K_3[Fe(CN)_6]$ containing 1.0 M KCl as supporting electrolyte, (c) LSV curves of the treated electrodes in CO_2 -saturated 0.5 M $KHCO_3$, and (d) LSV curves of the 50 cycles treated electrode in CO_2 - and Ar-saturated electrolyte

The electrochemical reduction performance of the pristine Pb and ORC-treated electrodes was performed at different potentials to evaluate the FE values of CO_2 RR **Figure S14a in appendix** shows the time-dependent total catalytic current densities, all the current densities $\sim t$ plots remain stable for 3600 s suggesting robust short-term stability of the pristine Pb and ORC-treated electrodes. The results of gas chromatography reveal wide range of products such as ethanol, methanol, formate, CO and H_2 associated with all the catalysts (**Figure S114b-f in appendix**). The pristine Pb (**Figure S114b in appendix**) electrodes demonstrate activity towards H_2 with maximum FE of 78.2% at -0.6 V vs RHE but overall characterized with poor selectivity at higher applied potential. Meanwhile, a maximum of 53% FE of H_2 was detected with ORC-treated electrodes

with selectivity tuning towards CO. Remarkably, with increase in number of cycles the selectivity was enhanced with 50 cycles electrocatalyst achieving a maximum FE_{CO} of 89% at -0.8 V vs RHE (**Figure 38a**) and a FE of 5.6%, 3.8% and 1.5% corresponding to formate, ethanol, and methanol respectively (**Figure SI 15 in appendix**). Thus, highlighting the dominating role of the ORC-treatment for CO production. Furthermore, with the negative shift of working potential on the ORC-treated electrodes the FE_{CO} is observed to increase suggesting the suppression of the competing reaction of electrochemical hydrogen evolution at more negative working potential and overcoming limitation of CO_2 mass transfer in aqueous solution [402], [413]. To gain in-depth kinetics of the tuning and enhanced catalytic activity of CO_2 reduction to CO on ORC-treated electrodes from the electrochemical results, Tafel plots (over potential vs log of the partial current density) were studied and are shown in **Figure 38b**. The pristine Pb electrode revealed a Tafel slope of 216 mV dec^{-1} for CO production. However, the electrochemical surface roughening is observed to increase the Tafel slope from 216 mV dec^{-1} for pristine Pb to 343 mV dec^{-1} for 50 cycles. Analysis of the results revealed the values to be significantly higher than the established one electron transfer reaction as the rate determining step (120 mV dec^{-1}). This trend has in the past been reported for Pb based electrodes in alkaline solution at high current density. Despite the absence or insufficiency of explanations, research suggests that the steeper slopes can be ascribed to the presence of a thin, kinetically stable Pb oxide (or hydroxide) layer on the electrode surfaces. This passivating layer effectively hinders H_2 evolution in alkaline electrolytes, with H_2 evolution predominantly occurring at the remaining exposed Pb^0 on the electrode surface. The variance in activity between pristine Pb and ORC treated electrodes could probably be attributed to differences in the coverage of this passivating layer. In the case of pristine Pb, the oxide covers a substantial portion of the electrode surface, while in the case of ORC treated electrodes, it covers an even larger portion. [31].

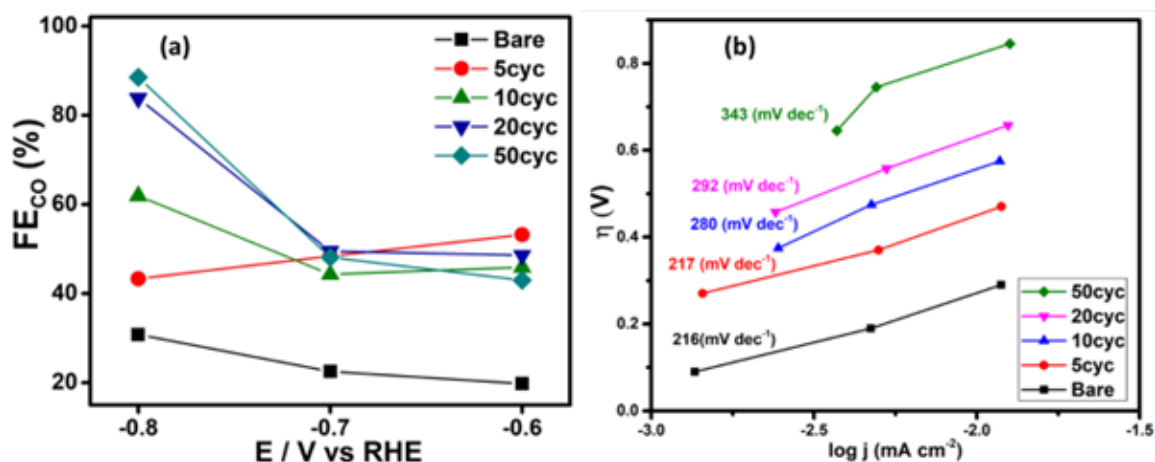


Figure 38. (a) CO Faradaic efficiencies plots and (b) Tafel plots of CO production for pristine and ORC-treated electrodes at different applied potentials in CO₂ saturated 0.5 M KHCO₃ electrolyte.

The enhanced activity can be attributed to the larger electrochemical active surface area (ECSA). One method to estimate ECSA is by measuring double layer capacitance (C_{dl}). Cyclic voltammograms (CVs) of the pristine Pb and 50 cycles treated electrode were obtained at scan rates of 10, 20, 40, 60, 80, and 100 mV s⁻¹, as shown in **Figure 39a** and **b**. It is evident that the C_{dl} of all ORC treated electrodes is significantly higher than that of pristine Pb (0.2 mF cm⁻²). This suggests a greater electrochemical active surface area and more exposed active sites for the ORC treated electrodes, which is advantageous for enhancing CO₂ reduction activity.

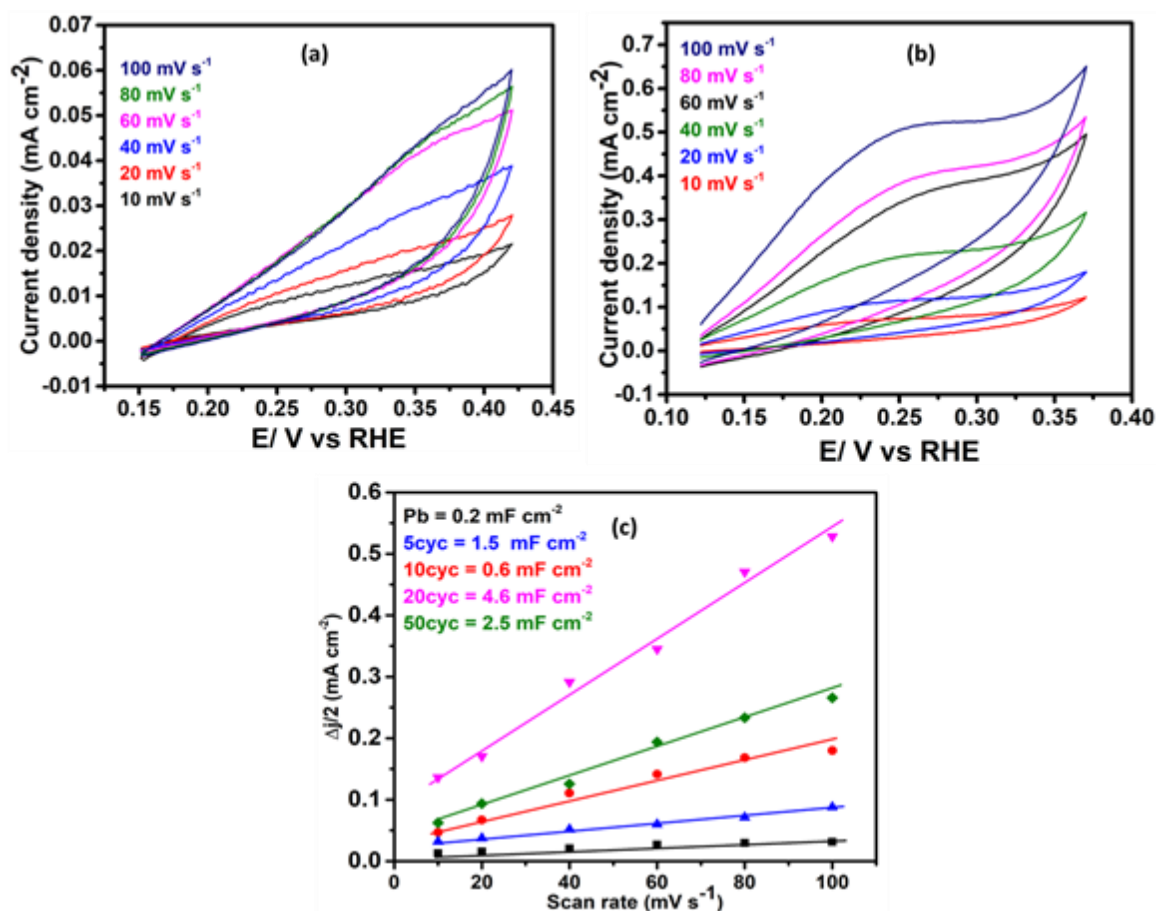


Figure 39. CVs of (a) Pristine Pb and (b) 50 cycles treated electrode with various scan rates (10–100 mV s⁻¹) in the region of 0.125 to 0.425 V vs. RHE. (c) The capacitance double layer (C_{dl}) as a function of scan rates.

We also demonstrate the long-term stability of our ORC-treated electrodes catalyst, for 24 h continuous and stable production of CO was achieved (**Figure 40a**). Despite an initial decrease in the current density to approximately 12 mA cm⁻² within the first 4 hours of electrolysis for the 50 cycles treated electrode, the CO selectivity remained relatively constant for 24h, consistently exceeding 80% at -0.8 V vs RHE. The evaluation of the production rates on ORC-treated electrodes demonstrated the production of CO to outshine other products in a wide potential range. Remarkably, at -0.8 V vs RHE, as shown in **Figure 41b** the CO production rate reaches an unprecedented value of 30.5 μmol h⁻¹ cm⁻². In the entire potential range, the ORC-treated electrode shows 81.6% order of magnitude higher in CO production rate than its analogous products. The

CO₂RR performance and CO selectivity of the ORC-treated electrodes could perhaps be attributed to the electrochemical roughening and the enhanced current density.

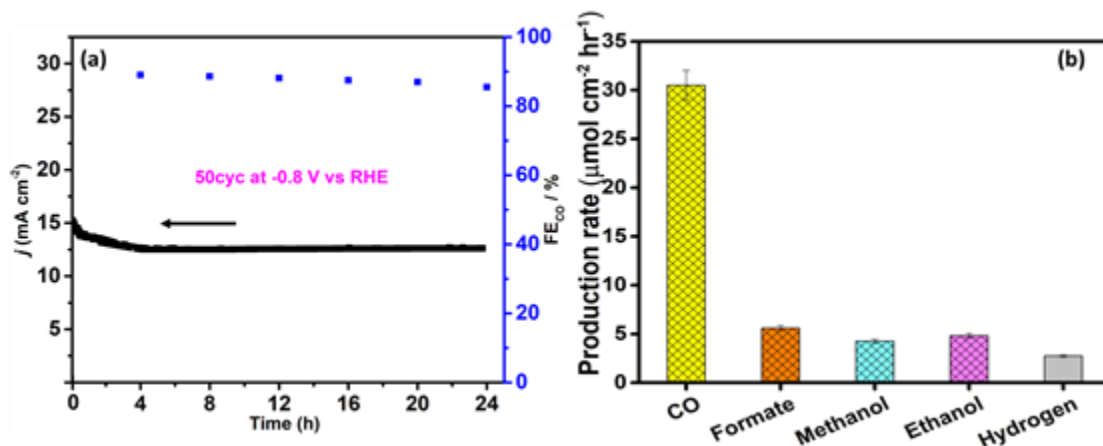


Figure 40. (a) Long term stability test of 50 ORC treatment on Pb electrode during the 24 h continuous electrolysis. (b) Production rate of all products on pristine Pb and ORC-treated electrodes.

5.6 Ex-situ SEM and XRD

To gain insights into potential changes in the surface morphology of both the pristine Pb and the ORC-treated electrodes, we conducted ex-situ scanning electron microscope (SEM) imaging. **Figure 42** showcases SEM images obtained after 1 hour of electrolysis in CO₂-saturated 0.5M KHCO₃. In **Figure 42a**, a smooth surface and clusters of hexagonal shapes are consistently observed with the pristine Pb after 1 hour of electrolysis. However, in addition to the hexagonal shapes seen in the pristine Pb, a roughened surface with variations in shapes are revealed, as depicted in **Figure 42b-e**. Notably, in contrast to the pristine Pb, all the ORC-treated electrodes exhibit pore-like features on the Pb surface, as illustrated in the inserts of **Figure 42b-e**. Additionally, the EDX mapping and elemental analysis depicted in **Figure 42f** reveal the presence of Pb, Sn, and Sb, along with potassium (K) and carbon (C) originating from the electrolytes. The elemental analysis presented illustrates that the electrode treated for 50 cycles is mainly composed of Pb with trace amounts of Sn and Sb. Similarly, the pristine Pb also exhibits a similar pattern but with a higher quantity of Sn. These findings further emphasize the significance of surface roughening.

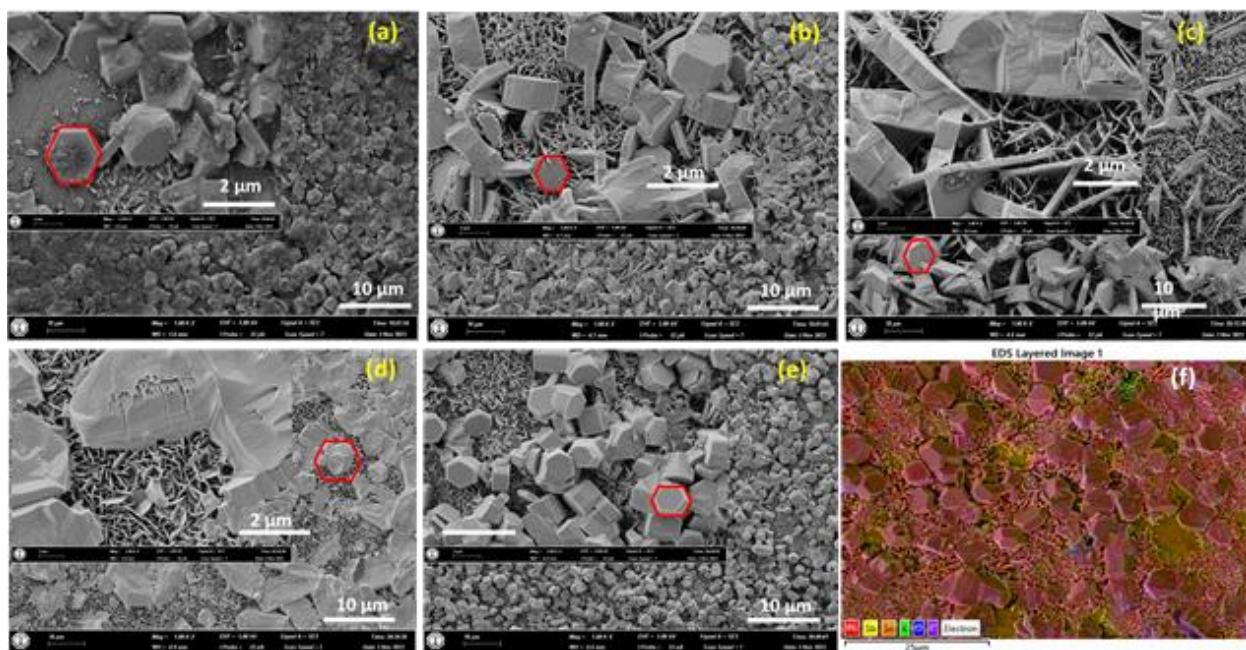


Figure 41. Ex-situ FESEM micrograms of (a) pristine and ORC-treated Pb electrodes at (b) 5 cycles, (c) 10 cycles, (d) 20 cycles, (e) 50 cycles and the elemental distribution on the surface of the electrode is shown in (f). After 1h electrolysis in CO₂-saturated 0

This observation gains further support from the corresponding ex-situ XRD analysis depicted in **Figure 42**. As anticipated, the XRD patterns of both the pristine Pb and all ORC-treated electrodes exhibit characteristic diffraction features primarily associated with PbO, with an additional minor contribution originating from crystalline Pb. Traced characteristic diffraction patterns of Sn and Sb become evident after 1 hour of electrolysis. Furthermore, distinctive diffraction peaks corresponding to lead formate ($\text{Pb}(\text{HCO}_2)_2$) at 18, 20, 34 and 38 degree and formate hydroxide ($\text{Pb}(\text{HCO}_2)_2(\text{OH})_2$) at 13 and 25 degrees are also observed. It has been reported that when leads are exposed to acetic and formic acids, they undergo reactions with the oxide layer, resulting in the formation of powdery deposits of lead acetates and formates. In aqueous medium and presence of atmospheric carbon dioxide, these organic salts react further, leading to the formation of lead carbonates [46].

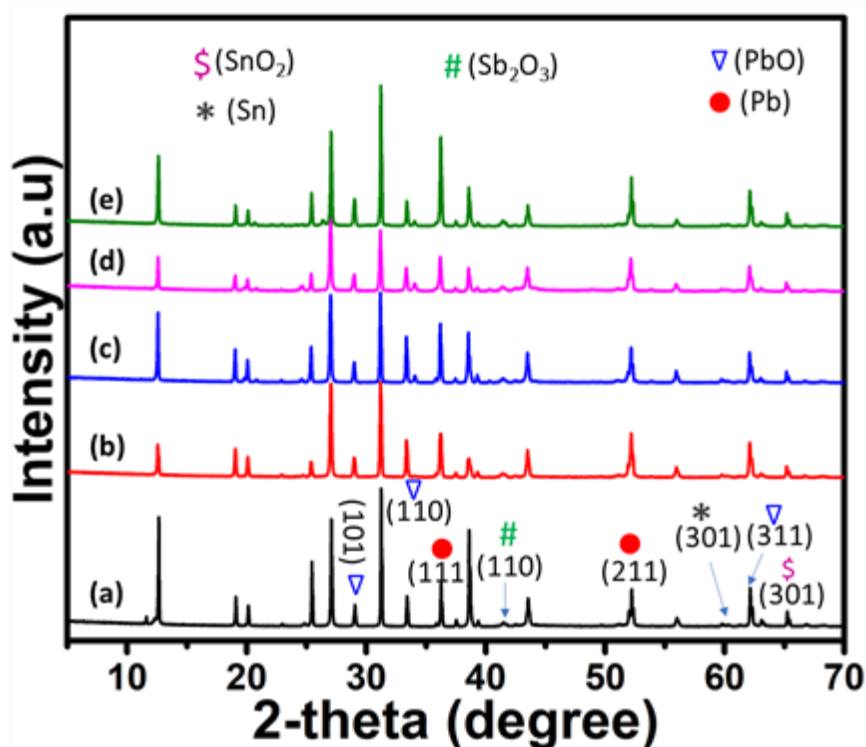


Figure 42. Ex-situ XRD patterns of (a) pristine Pb electrode, and the (b) 5 cycles ORC-treated, (c) 10 cycles treated, (d) 20 cycles treated and (e) 50 cycles treated electrodes. After 1h electrolysis in CO₂-saturated 0.5M KHCO₃.

To further investigate the electrochemical CO₂RR tuning ability of ORC-treated electrodes, first principle DFT simulations were performed to evaluate the free energy changes (ΔG (eV)) for ethanol, methanol, formate, and CO production on ORC-treated electrodes sites (**Figure 43**). For CO₂RR to CO, it is revealed that the first step for the formation of *COOH and HCOO* intermediate ($\text{CO}_2 (\text{g}) + \text{H}^+ + \text{e}^- \rightarrow \text{*COOH}$) exhibits the largest reaction free energy difference of 0.373 eV for PbO (**Figure 43**), indicating that the formation of *COOH intermediate serves as the rate-determining step for CO₂RR. This suggests that the PbO can vastly stabilize the reaction intermediates and change the CO₂RR pathway to CO. In comparison, HCOO*, *CH₂OH and *CH₂CHO intermediates ($\text{CO}_2 (\text{g}) + \text{H}^+ + \text{e}^- \rightarrow \text{*COOH}$ or HCOO*) demonstrate the highest ΔG values of 0.467, 0.854 and 0.884 eV respectively, suggesting the intermediates to be the rate-determining step for CO₂RR to HCOOH, CH₃OH and CH₃CH₂OH products. Evaluation of the CO₂RR energy diagrams shows that the CO product is thermodynamically preferred on PbO with ΔG of -0.040 eV. Thus, in excellent agreement with the experimental results, the DFT calculations

further corroborate with the experimental findings of CO to probably be the major product of CO₂RR on ORC-treated electrodes.

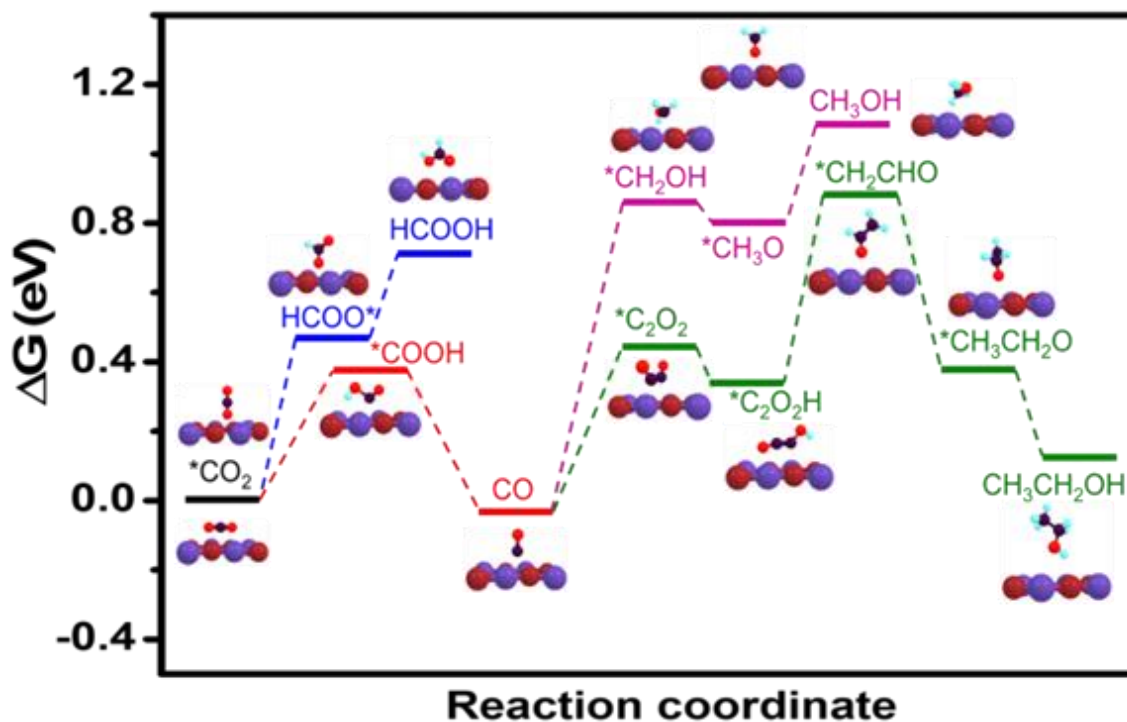


Figure 43. DFT calculated reaction pathways and free energy diagram.

5.7 Conclusions

We have investigated the use of electrochemical surface roughening to enhance the efficiency of electrocatalytic CO₂-to-CO conversion. These findings highlight the significant role of Pb electrode morphology in determining CO selectivity. The experimental results revealed that electrodes treated with ORC exhibited higher electrocatalytic activity and Faraday efficiency compared to the pristine Pb electrodes. Notably, the electrodes treated with 50 cycles demonstrated the highest FE_{CO}, reaching up to 89% at -0.8 V vs RHE, accompanied by a production rate of $30.5 \mu\text{mol h}^{-1} \text{cm}^{-2}$. The improved electrocatalytic activity of ORC-treated electrodes can be attributed to the surface roughening generated during the electrochemical surface roughening process, as confirmed by SEM and 3D optical profiler analysis. Additionally, DFT simulation indicates that

the *COOH intermediate is more likely to be generated and adsorbed on ORC-treated electrodes, while the production of CO products is thermodynamically more feasible in this case.

Acknowledgement

The authors would like to express their gratitude to the Center for Refining and Advanced Chemicals, King Fahd University of Petroleum & Minerals (KFUPM), located in Dhahran, Saudi Arabia, for the support provided, under project INRC2216.

CHAPTER 6

Conclusion and recommendations

6.1 Conclusions

In summary, this study extensively explored nanostructure-based catalysts for CO₂ reduction reactions, focusing on the morphology-performance correlation. Despite various influencing factors such as crystal facets and composition affecting activity and selectivity, the research highlighted the pivotal role of morphology in determining the electrocatalytic activity and product selectivity of transition-based electrocatalysts. The study demonstrated the successful synthesis of ZnO catalysts in distinct morphologies, namely ZnO-NN (nanoneedles) and ZnO-NR (nanorods), which exhibited exceptional activity, selectivity, and stability in CO₂ conversion. Through in-depth analyses, it was revealed that both ZnO-NN and ZnO-NR electrodes underwent transformation into hexagonal metallic Zn crystals during the electrochemical CO₂ reduction, emphasizing the importance of understanding structure-performance relationships based on final electrode states. Additionally, a novel approach for synthesizing Ce_{0.23}-ZIF-zni-CVD catalysts was proposed, showing promising results with a high Faradaic efficiency of up to 87.9%. The study also explored the use of electrochemical surface roughening to enhance the efficiency of CO₂-to-CO conversion, revealing the significant role of Pb electrode morphology in determining CO selectivity. Overall, these findings provide valuable insights into enhancing the electrocatalytic conversion of CO₂ into valuable chemical products and contribute to the advancement of sustainable energy technologies.

6.2 Recommendations

The collective insights from these studies offer promising directions for advancing the field of electrochemical CO₂ reduction. To harness these findings effectively, it is recommended to focus on the following areas:

Morphology-Performance Relationships: Further research into the relationship between catalyst morphology and electrocatalytic performance is essential. Investigating a wider range of catalyst morphologies and understanding their impact on product selectivity and stability will provide valuable insights for designing efficient electrocatalytic systems.

Synergistic Catalyst Design: Exploring synergistic interactions between different catalyst components, as demonstrated with Ce_xO_y and ZIF-zni, opens avenues for the development of novel catalysts. Researchers could delve deeper into understanding these interactions and explore additional combinations of materials to enhance catalytic activity and selectivity further.

Surface Engineering Techniques: The electrochemical surface roughening approach demonstrated significant improvements in selectivity and stability. Future studies could explore various surface engineering techniques and their impact on electrode performance. Tailoring the surface properties of electrodes could lead to the development of highly efficient and selective electrocatalysts for CO_2 reduction.

Integration with Renewable Energy: Integrating electrochemical CO_2 reduction with renewable energy sources, such as solar and wind power, is crucial for sustainable large-scale applications. Future research should focus on developing efficient energy storage solutions and optimizing the coupling of renewable energy systems with electrochemical CO_2 reduction technologies.

Commercialization and Scalability: To transition these innovations from the laboratory to practical applications, it is essential to address scalability challenges. Researchers and industry partners should collaborate to optimize the synthesis processes, ensuring scalability without compromising the performance and selectivity of catalysts.

Multidisciplinary Collaboration: Collaborative efforts between materials scientists, electrochemists, physicists, and engineers are vital. Interdisciplinary research can lead to

innovative approaches, addressing complex challenges from multiple perspectives and accelerating the development of efficient CO₂ reduction technologies.

Policy and Industry Engagement: Engaging policymakers, industries, and stakeholders is crucial to create an enabling environment for the adoption of electrochemical CO₂ reduction technologies. Incentives, regulations, and policies supporting sustainable practices and green technologies can drive investment and accelerate the deployment of these solutions.

By prioritizing these areas of research and collaboration, the scientific community can pave the way for practical, scalable, and sustainable electrochemical CO₂ reduction technologies. These advancements hold the potential to significantly contribute to mitigating climate change, reducing CO₂ emissions, and fostering a greener, more sustainable future.

References

- [1] S. Xu and E. A. Carter, “Theoretical insights into heterogeneous (photo) electrochemical CO₂ reduction,” *Chem. Rev.*, vol. 119, no. 11, pp. 6631–6669, 2018.
- [2] Y. Yang, S. Ajmal, X. Zheng, and L. Zhang, “Efficient nanomaterials for harvesting clean fuels from electrochemical and photoelectrochemical CO₂ reduction,” *Sustain. Energy Fuels*, vol. 2, no. 3, pp. 510–537, 2018.
- [3] A. D. N. Kamkeng, M. Wang, J. Hu, W. Du, and F. Qian, “Transformation technologies for CO₂ utilisation: Current status, challenges and future prospects,” *Chem. Eng. J.*, vol. 409, p. 128138, Apr. 2021, doi: 10.1016/J.CEJ.2020.128138.
- [4] E. C. Commission E, “Paris Agreement | Climate Action, European Commission Climate Action.” [Online]. Available: https://ec.europa.eu/clima/policies/international/negotiations/paris_en
- [5] R. Luo, X. Liu, M. Chen, B. Liu, and Y. Fang, “Recent Advances on Imidazolium-Functionalized Organic Cationic Polymers for CO₂ Adsorption and Simultaneous Conversion into Cyclic Carbonates ChemSusChem,” *ChemSusChem*, vol. 13, pp. 3945–3966, 2020, doi: 10.1002/cssc.202001079.
- [6] A. A. Adelodun, K.-H. Kim, J. C. Ngila, and J. Szulejko, “A review on the effect of amination pretreatment for the selective separation of CO₂,” *Appl. Energy*, vol. 158, pp. 631–642, 2015, doi: <https://doi.org/10.1016/j.apenergy.2015.08.107>.

- [7] M. Sevilla and A. B. Fuertes, "Sustainable porous carbons with a superior performance for CO₂ capture", doi: 10.1039/c0ee00784f.
- [8] Y. Chiang and R. Juang, "Journal of the Taiwan Institute of Chemical Engineers Surface modifications of carbonaceous materials for carbon dioxide adsorption: a review," *J Taiwan Inst Chem Eng*, vol. 71, pp. 214–234, 2017.
- [9] M. Sevilla, C. Falco, M.-M. Titirici, and A. B. Fuertes, "High-performance CO₂ sorbents from algae", doi: 10.1039/c2ra22552b.
- [10] C. W. Lee *et al.*, "New challenges of electrokinetic studies in investigating the reaction mechanism of electrochemical CO₂ reduction," *J. Mater. Chem. A*, vol. 6, no. 29, pp. 14043–14057, 2018.
- [11] M. Dunwell, W. Luc, Y. Yan, F. Jiao, and B. Xu, "Understanding surface-mediated electrochemical reactions: CO₂ reduction and beyond," *Acs Catal.*, vol. 8, no. 9, pp. 8121–8129, 2018.
- [12] K. Elouarzaki, V. Kannan, V. Jose, H. S. Sabharwal, and J. Lee, "Recent Trends, Benchmarking, and Challenges of Electrochemical Reduction of CO₂ by Molecular Catalysts," *Adv. Energy Mater.*, vol. 9, no. 24, p. 1900090, 2019.
- [13] M. de Salles Pupo and R. Kortlever, "Electrolyte Effects on the Electrochemical Reduction of CO₂," *ChemPhysChem*, vol. 20, no. 22, pp. 2926–2935, 2019, doi: 10.1002/cphc.201900680.
- [14] G. F. Manbeck and E. Fujita, "A review of iron and cobalt porphyrins, phthalocyanines and related complexes for electrochemical and photochemical reduction of carbon dioxide," *J. Porphyr. Phthalocyanines*, vol. 19, no. 01n03, pp. 45–64, 2015.
- [15] W. Zhu *et al.*, "Low-coordinated edge sites on ultrathin palladium nanosheets boost carbon dioxide electroreduction performance," *Angew. Chemie*, vol. 130, no. 36, pp. 11718–11722, 2018.
- [16] J. Zhang, R. Yin, Q. Shao, T. Zhu, and X. Huang, "Oxygen Vacancies in Amorphous InO_x Nanoribbons Enhance CO₂ Adsorption and Activation for CO₂ Electroreduction," *Angew. Chemie - Int. Ed.*, vol. 58, no. 17, pp. 5609–5613, Apr. 2019, doi: 10.1002/anie.201900167.
- [17] A. Zhang *et al.*, "Nickel Doping in Atomically Thin TinDisulfide Nanosheets Enables Highly Efficient CO₂ Reduction", doi: 10.1002/anie.201806043.
- [18] Z. Zhang *et al.*, "CO₂ Reduction Reaction Mechanisms of Well-Defined Metal-N₄ Sites in Electrocatalytic CO₂ Reduction", doi: 10.1002/ange.201808593.
- [19] D. Kim, J. Resasco, Y. Yu, A. M. Asiri, and P. Yang, "ARTICLE Synergistic geometric and electronic effects for electrochemical reduction of carbon dioxide using gold-copper bimetallic nanoparticles," 2014, doi: 10.1038/ncomms5948.
- [20] S. Zhao, R. Jin, and R. Jin, "Opportunities and Challenges in CO₂ Reduction by Gold- and Silver-Based Electrocatalysts: From Bulk Metals to Nanoparticles and Atomically Precise Nanoclusters," 2017, doi: 10.1021/acsenergylett.7b01104.
- [21] C. Kim *et al.*, "Achieving Selective and Efficient Electrocatalytic Activity for CO₂ Reduction Using Immobilized Silver Nanoparticles," 2015, doi: 10.1021/jacs.5b06568.

- [22] K. Jiang *et al.*, “Silver Nanoparticles with Surface-Bonded Oxygen for Highly Selective CO₂ Reduction,” 2017, doi: 10.1021/acssuschemeng.7b02380.
- [23] A. Goyal, G. Marcandalli, V. A. Mints, and M. T. M. Koper, “Competition between CO₂ Reduction and Hydrogen Evolution on a Gold Electrode under Well-Defined Mass Transport Conditions,” *Cite This J. Am. Chem. Soc.*, vol. 142, p. 4161, 2020, doi: 10.1021/jacs.9b10061.
- [24] M. Ahaman, A. Bhijit Dutta and P. Broekmann, “Size-Dependent Activity of Palladium Nanoparticles: Efficient Conversion of CO₂ into Formate at Low Overpotentials”, doi: 10.1002/cssc.201601778.
- [25] J. Huang and R. Buonsanti, “Colloidal nanocrystals as heterogeneous catalysts for electrochemical CO₂ conversion,” *Chem. Mater.*, vol. 31, no. 1, pp. 13–25, 2018.
- [26] W. Zhu *et al.*, “Monodisperse Au Nanoparticles for Selective Electrocatalytic Reduction of CO₂ to CO,” *J. Am. Chem. Soc.*, vol. 135, no. 45, pp. 16833–16836, Nov. 2013, doi: 10.1021/ja409445p.
- [27] W. Zhu *et al.*, “Active and Selective Conversion of CO₂ to CO on Ultrathin Au Nanowires,” *J. Am. Chem. Soc.*, vol. 136, no. 46, pp. 16132–16135, Nov. 2014, doi: 10.1021/ja5095099.
- [28] F. S. Roberts, K. P. Kuhl, and A. Nilsson, “High Selectivity for Ethylene from Carbon Dioxide Reduction over Copper Nanocube Electrocatalysts,” *Angew. Chemie Int. Ed.*, vol. 54, no. 17, pp. 5179–5182, 2015, doi: 10.1002/anie.201412214.
- [29] S. Verma, X. Lu, S. Ma, R. I. Masel, and P. J. A. Kenis, “The effect of electrolyte composition on the electroreduction of CO₂ to CO on Ag based gas diffusion electrodes,” *Phys. Chem. Chem. Phys.*, vol. 18, no. 10, pp. 7075–7084, 2016, doi: 10.1039/C5CP05665A.
- [30] Q. Lu *et al.*, “A selective and efficient electrocatalyst for carbon dioxide reduction,” *Nat. Commun.*, vol. 5, no. 1, p. 3242, 2014, doi: 10.1038/ncomms4242.
- [31] R. Daiyan, X. Lu, Y. H. Ng, and R. Amal, “Highly Selective Conversion of CO₂ to CO Achieved by a Three-Dimensional Porous Silver Electrocatalyst,” *ChemistrySelect*, vol. 2, no. 3, pp. 879–884, 2017, doi: 10.1002/slct.201601980.
- [32] C. S. Chen, A. D. Handoko, J. H. Wan, L. Ma, D. Ren, and B. S. Yeo, “Stable and selective electrochemical reduction of carbon dioxide to ethylene on copper mesocrystals,” *Catal. Sci. Technol.*, vol. 5, no. 1, pp. 161–168, 2015, doi: 10.1039/C4CY00906A.
- [33] X. Zhao, B. Luo, R. Long, C. Wang, and Y. Xiong, “Composition-dependent activity of Cu–Pt alloy nanocubes for electrocatalytic CO₂ reduction,” *J. Mater. Chem. A*, vol. 3, no. 8, pp. 4134–4138, 2015, doi: 10.1039/C4TA06608A.
- [34] A. Loiudice *et al.*, “Tailoring Copper Nanocrystals towards C₂ Products in Electrochemical CO₂ Reduction,” *Angew. Chemie Int. Ed.*, vol. 55, no. 19, pp. 5789–5792, 2016, doi: 10.1002/anie.201601582.
- [35] R. Reske, H. Mistry, F. Behafarid, B. Roldan Cuenya, and P. Strasser, “Particle Size Effects in the Catalytic Electroreduction of CO₂ on Cu Nanoparticles,” *J. Am. Chem. Soc.*, vol. 136, no. 19, pp. 6978–6986, May 2014, doi: 10.1021/ja500328k.

- [36] X. Guo *et al.*, “Composition dependent activity of Cu–Pt nanocrystals for electrochemical reduction of CO₂,” *Chem. Commun.*, vol. 51, no. 7, pp. 1345–1348, 2015, doi: 10.1039/C4CC08175G.
- [37] S. Zhang, P. Kang, and T. J. Meyer, “Nanostructured tin catalysts for selective electrochemical reduction of carbon dioxide to formate,” *J. Am. Chem. Soc.*, vol. 136, no. 5, pp. 1734–1737, 2014.
- [38] T.-T. Zhuang *et al.*, “Steering post-C–C coupling selectivity enables high efficiency electroreduction of carbon dioxide to multi-carbon alcohols,” *Nat. Catal.*, vol. 1, no. 6, pp. 421–428, 2018, doi: 10.1038/s41929-018-0084-7.
- [39] U. Mustapha *et al.*, “The role of morphology on the electrochemical CO₂ reduction performance of transition metal-based catalysts,” *J. Energy Chem.*, 2023.
- [40] C. C. Nnadike, I. Abdulazeez, M. Haroon, Q. Peng, A. Jalilov, and A. Al-Saadi, “Impact of Polypyrrole Functionalization on the Anodic Performance of Boron Nitride Nanosheets: Insights From First-Principles Calculations,” *Front. Chem.*, vol. 9, p. 670833, Apr. 2021, doi: 10.3389/fchem.2021.670833.
- [41] M. Umar *et al.*, “A First-Principles Study on the Multilayer Graphene Nanosheets Anode Performance for Boron-Ion Battery,” *Nanomaterials*, vol. 12, no. 8. 2022. doi: 10.3390/nano12081280.
- [42] S. Mohammadzadeh, H. R. Zare, H. Khoshro, K. Ghobadi, and A. Benvidi, “The electrochemical behavior of 4-nitrobenzyl bromide and its catalytic activity for reduction of CO₂ in the acetonitrile solvent at the Cu/Pd/rGO/GCE surface,” *Electrochim. Acta*, vol. 352, p. 136483, 2020.
- [43] E. S. Sanz-Pérez, C. R. Murdock, S. A. Didas, and C. W. Jones, “Direct Capture of CO₂ from Ambient Air,” *Chem. Rev.*, vol. 116, no. 19, pp. 11840–11876, Aug. 2016, doi: 10.1021/acs.chemrev.6b00173.
- [44] Q. Wang, J. Luo, Z. Zhong, and A. Borgna, “CO₂ capture by solid adsorbents and their applications: current status and new trends,” *Energy Environ. Sci.*, vol. 4, no. 1, pp. 42–55, 2011, doi: 10.1039/C0EE00064G.
- [45] L. Zhou and R. Lv, “Rational catalyst design and interface engineering for electrochemical CO₂ reduction to high-valued alcohols,” *J. Energy Chem.*, vol. 70, pp. 310–331, Jul. 2022, doi: 10.1016/J.JEACHEM.2022.02.033.
- [46] J. Canales, J. Ramirez, G. Estiu, and J. Costamagna, “Bis-bipyridine hexa-aza-macrocyclic complexes of zinc(II) and nickel(II) and the catalytic reduction of carbon dioxide,” *Polyhedron*, vol. 19, no. 22–23, pp. 2373–2381, Nov. 2000, doi: 10.1016/S0277-5387(00)00574-X.
- [47] S. Zhang *et al.*, “Assembling well-arranged covalent organic frameworks on MOF-derived graphitic carbon for remarkable formaldehyde sensing,” *Nanoscale*, vol. 12, no. 29, pp. 15611–15619, 2020, doi: 10.1039/D0NR03041D.
- [48] X. Xu *et al.*, “Unprecedented capacitive deionization performance of interconnected iron–nitrogen-doped carbon tubes in oxygenated saline water,” *Mater. Horizons*, vol. 7, no. 5, pp. 1404–1412, 2020, doi: 10.1039/C9MH01829H.

- [49] W. F. Lamb *et al.*, “A review of trends and drivers of greenhouse gas emissions by sector from 1990 to 2018,” *Environ. Res. Lett.*, vol. 16, no. 7, p. 073005, Jul. 2021, doi: 10.1088/1748-9326/abee4e.
- [50] B. K. Sovacool, S. Griffiths, J. Kim, and M. Bazilian, “Climate change and industrial F-gases: A critical and systematic review of developments, sociotechnical systems and policy options for reducing synthetic greenhouse gas emissions,” *Renew. Sustain. Energy Rev.*, vol. 141, p. 110759, 2021, doi: <https://doi.org/10.1016/j.rser.2021.110759>.
- [51] F. Bienen *et al.*, “Degradation study on tin- and bismuth-based gas-diffusion electrodes during electrochemical CO₂ reduction in highly alkaline media,” *J. Energy Chem.*, vol. 62, pp. 367–376, Nov. 2021, doi: 10.1016/J.JECHEM.2021.03.050.
- [52] K. Bilen *et al.*, “Energy production, consumption, and environmental pollution for sustainable development: A case study in Turkey,” *Renew. Sustain. Energy Rev.*, vol. 12, no. 6, pp. 1529–1561, 2008, doi: <https://doi.org/10.1016/j.rser.2007.03.003>.
- [53] W. Gao *et al.*, “Industrial carbon dioxide capture and utilization: state of the art and future challenges,” *Chem. Soc. Rev.*, vol. 49, no. 23, pp. 8584–8686, 2020, doi: 10.1039/D0CS00025F.
- [54] “Carbon Dioxide: Projected emissions and concentrations,” p. http://ipcc-data.org/observ/ddc_co2.html, 2014.
- [55] L. Zhang, Z.-J. Zhao, and J. Gong, “Nanostructured Materials for Heterogeneous Electrocatalytic CO₂ Reduction and their Related Reaction Mechanisms,” *Angew. Chemie Int. Ed.*, vol. 56, no. 38, pp. 11326–11353, Sep. 2017, doi: 10.1002/anie.201612214.
- [56] M. Mikkelsen, M. Jørgensen, and F. C. Krebs, “The teraton challenge. A review of fixation and transformation of carbon dioxide,” *Energy Environ. Sci.*, vol. 3, no. 1, pp. 43–81, 2010, doi: 10.1039/B912904A.
- [57] J. Wang *et al.*, “Recent advances in solid sorbents for CO₂ capture and new development trends,” *Energy Environ. Sci.*, vol. 7, no. 11, pp. 3478–3518, 2014, doi: 10.1039/C4EE01647E.
- [58] A. Mustafa, B. G. Lougou, Y. Shuai, Z. Wang, and H. Tan, “Current technology development for CO₂ utilization into solar fuels and chemicals: A review,” *J. Energy Chem.*, vol. 49, pp. 96–123, 2020, doi: <https://doi.org/10.1016/j.jechem.2020.01.023>.
- [59] F. D. Meylan, V. Moreau, and S. Erkman, “CO₂ utilization in the perspective of industrial ecology, an overview,” *J. CO₂ Util.*, vol. 12, pp. 101–108, 2015, doi: <https://doi.org/10.1016/j.jcou.2015.05.003>.
- [60] M. Ding, R. W. Flaig, H.-L. Jiang, and O. M. Yaghi, “Carbon capture and conversion using metal–organic frameworks and MOF-based materials,” *Chem. Soc. Rev.*, vol. 48, no. 10, pp. 2783–2828, 2019, doi: 10.1039/C8CS00829A.
- [61] R. M.S, S. Shanmuga Priya, N. C. Freudenberg, K. Sudhakar, and M. Tahir, “Metal-organic framework-based photocatalysts for carbon dioxide reduction to methanol: A review on progress and application,” *J. CO₂ Util.*, vol. 43, p. 101374, 2021, doi: <https://doi.org/10.1016/j.jcou.2020.101374>.
- [62] G. Sneddon, A. Greenaway, and H. H. P. Yiu, “The Potential Applications of Nanoporous

- Materials for the Adsorption, Separation, and Catalytic Conversion of Carbon Dioxide,” *Adv. Energy Mater.*, vol. 4, no. 10, p. 1301873, Jul. 2014, doi: 10.1002/aenm.201301873.
- [63] S. Wang and X. Wang, “Imidazolium Ionic Liquids, Imidazolylidene Heterocyclic Carbenes, and Zeolitic Imidazolate Frameworks for CO₂ Capture and Photochemical Reduction,” *Angew. Chemie Int. Ed.*, vol. 55, no. 7, pp. 2308–2320, Feb. 2016, doi: 10.1002/anie.201507145.
- [64] A. Schoedel, Z. Ji, and O. M. Yaghi, “The role of metal–organic frameworks in a carbon-neutral energy cycle,” *Nat. Energy*, vol. 1, no. 4, p. 16034, 2016, doi: 10.1038/nenergy.2016.34.
- [65] C. A. Trickett, A. Helal, B. A. Al-Maythaly, Z. H. Yamani, K. E. Cordova, and O. M. Yaghi, “The chemistry of metal–organic frameworks for CO₂ capture, regeneration and conversion,” *Nat. Rev. Mater.*, vol. 2, no. 8, p. 17045, 2017, doi: 10.1038/natrevmats.2017.45.
- [66] Y. Xie, T.-T. Wang, X.-H. Liu, K. Zou, and W.-Q. Deng, “Capture and conversion of CO₂ at ambient conditions by a conjugated microporous polymer,” *Nat. Commun.*, vol. 4, no. 1, p. 1960, 2013, doi: 10.1038/ncomms2960.
- [67] G. Cui, J. Wang, and S. Zhang, “Active chemisorption sites in functionalized ionic liquids for carbon capture,” *Chem. Soc. Rev.*, vol. 45, no. 15, pp. 4307–4339, 2016, doi: 10.1039/C5CS00462D.
- [68] Y. Li, L. Li, and J. Yu, “Applications of Zeolites in Sustainable Chemistry,” *Chem*, vol. 3, no. 6. Elsevier Inc, pp. 928–949, Dec. 2017. doi: 10.1016/j.chempr.2017.10.009.
- [69] J.-M. Lavoie, “Review on dry reforming of methane, a potentially more environmentally-friendly approach to the increasing natural gas exploitation,” *Front. Chem.*, vol. 2, p. 81, 2014, doi: 10.3389/fchem.2014.00081.
- [70] D. Pakhare and J. Spivey, “A review of dry (CO₂) reforming of methane over noble metal catalysts,” *Chem. Soc. Rev.*, vol. 43, no. 22, pp. 7813–7837, 2014, doi: 10.1039/C3CS60395D.
- [71] K. M. K. Yu, I. Curcic, J. Gabriel, and S. C. E. Tsang, “Recent Advances in CO₂ Capture and Utilization,” *ChemSusChem*, vol. 1, no. 11, pp. 893–899, Nov. 2008, doi: 10.1002/cssc.200800169.
- [72] M. A. A. Aziz, A. A. Jalil, S. Triwahyono, and A. Ahmad, “CO₂ methanation over heterogeneous catalysts: recent progress and future prospects,” *Green Chem.*, vol. 17, no. 5, pp. 2647–2663, 2015, doi: 10.1039/C5GC00119F.
- [73] W. Wang, S. Wang, X. Ma, and J. Gong, “Recent advances in catalytic hydrogenation of carbon dioxide,” *Chem. Soc. Rev.*, vol. 40, no. 7, pp. 3703–3727, 2011, doi: 10.1039/C1CS15008A.
- [74] P. M. Schenk *et al.*, “Second Generation Biofuels: High-Efficiency Microalgae for Biodiesel Production,” *BioEnergy Res.*, vol. 1, no. 1, pp. 20–43, 2008, doi: 10.1007/s12155-008-9008-8.
- [75] Y. Shen, “Carbon dioxide bio-fixation and wastewater treatment via algae photochemical synthesis for biofuels production,” *RSC Adv.*, vol. 4, no. 91, pp. 49672–49722, 2014, doi:

10.1039/C4RA06441K.

- [76] Y. Guo, X. Hong, Z. Chen, and Y. Lv, “Electro-enzyme coupling systems for selective reduction of CO₂,” *J. Energy Chem.*, vol. 80, pp. 140–162, May 2023, doi: 10.1016/J.JECHEM.2023.01.041.
- [77] S. Das and W. M. A. Wan Daud, “A review on advances in photocatalysts towards CO₂ conversion,” *RSC Adv.*, vol. 4, no. 40, pp. 20856–20893, 2014, doi: 10.1039/C4RA01769B.
- [78] Y. Izumi, “Recent advances in the photocatalytic conversion of carbon dioxide to fuels with water and/or hydrogen using solar energy and beyond,” *Coordination Chemistry Reviews*, vol. 257, no. 1, pp. 171–186, Jan. 2013. doi: 10.1016/j.ccr.2012.04.018.
- [79] R. Aerts, W. Somers, and A. Bogaerts, “Carbon Dioxide Splitting in a Dielectric Barrier Discharge Plasma: A Combined Experimental and Computational Study,” *ChemSusChem*, vol. 8, no. 4, pp. 702–716, Feb. 2015, doi: 10.1002/cssc.201402818.
- [80] J. F. de la Fuente, S. H. Moreno, A. I. Stankiewicz, and G. D. Stefanidis, “Reduction of CO₂ with hydrogen in a non-equilibrium microwave plasma reactor,” *Int. J. Hydrogen Energy*, vol. 41, no. 46, pp. 21067–21077, Dec. 2016, doi: 10.1016/j.ijhydene.2016.08.032.
- [81] Albo, Alvarez-Guerra, Castaño, and Irabien, “Towards the electrochemical conversion of carbon dioxide into methanol,” *Green Chem.*, vol. 17, no. 4, pp. 2304–2324, 2015, doi: 10.1039/C4GC02453B.
- [82] S. Verma, B. Kim, H.-R. “Molly” Jhong, S. Ma, and P. J. A. Kenis, “A Gross-Margin Model for Defining Technoeconomic Benchmarks in the Electroreduction of CO₂,” *ChemSusChem*, vol. 9, no. 15, pp. 1972–1979, Aug. 2016, doi: 10.1002/cssc.201600394.
- [83] H. Xie *et al.*, “Achieving highly selective electrochemical CO₂ reduction to C₂H₄ on Cu nanosheets,” *J. Energy Chem.*, vol. 79, pp. 312–320, Apr. 2023, doi: 10.1016/J.JECHEM.2022.11.058.
- [84] Z. Zhu *et al.*, “Improving NiNX and pyridinic N active sites with space-confined pyrolysis for effective CO₂ electroreduction,” *eScience*, vol. 2, no. 4, pp. 445–452, 2022.
- [85] I. Sullivan *et al.*, “Coupling electrochemical CO₂ conversion with CO₂ capture,” *Nat. Catal.*, vol. 4, no. 11, pp. 952–958, 2021, doi: 10.1038/s41929-021-00699-7.
- [86] S. Li *et al.*, “Low-valence Zn^{δ+} (0 < δ < 2) single-atom material as highly efficient electrocatalyst for CO₂ reduction,” *Angew. Chemie Int. Ed.*, vol. 60, no. 42, pp. 22826–22832, 2021.
- [87] I. Hussain, H. Alasiri, W. Ullah Khan, and K. Alhooshani, “Advanced electrocatalytic technologies for conversion of carbon dioxide into methanol by electrochemical reduction: Recent progress and future perspectives,” *Coord. Chem. Rev.*, vol. 482, p. 215081, May 2023, doi: 10.1016/J.CCR.2023.215081.
- [88] M. Jouny, W. Luc, and F. Jiao, “General Techno-Economic Analysis of CO₂ Electrolysis Systems,” *Ind. & Eng. Chem. Res.*, vol. 57, no. 6, pp. 2165–2177, Feb. 2018, doi: 10.1021/acs.iecr.7b03514.
- [89] H. Xu *et al.*, “Highly selective electrocatalytic CO₂ reduction to ethanol by metallic

- clusters dynamically formed from atomically dispersed copper,” *Nat. Energy*, vol. 5, no. 8, pp. 623–632, 2020, doi: 10.1038/s41560-020-0666-x.
- [90] G. A. Olah, A. Goepfert, and G. K. Surya Prakash, “Chemical Recycling of Carbon Dioxide to Methanol and Dimethyl Ether: From Greenhouse Gas to Renewable, Environmentally Carbon Neutral Fuels and Synthetic Hydrocarbons,” *J. Org. Chem.*, vol. 74, no. 2, pp. 487–498, Dec. 2008, doi: 10.1021/jo801260f.
- [91] Y. Huang, A. D. Handoko, P. Hirunsit, and B. Siang Yeo, “Electrochemical Reduction of CO₂ Using Copper Single-Crystal Surfaces: Effects of CO* Coverage on the Selective Formation of Ethylene,” *ACS Catal.*, vol. 7, no. 3, pp. 1749–1756, Feb. 2017, doi: 10.1021/acscatal.6b03147.
- [92] H. Xie, T. Wang, J. Liang, Q. Li, and S. Sun, “Cu-based nanocatalysts for electrochemical reduction of CO₂,” *Nano Today*, vol. 21, pp. 41–54, 2018, doi: <https://doi.org/10.1016/j.nantod.2018.05.001>.
- [93] Z. Weng *et al.*, “Active sites of copper-complex catalytic materials for electrochemical carbon dioxide reduction,” *Nat. Commun.*, vol. 9, no. 1, p. 415, 2018, doi: 10.1038/s41467-018-02819-7.
- [94] B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum, and C. P. Kubiak, “Photochemical and Photoelectrochemical Reduction of CO₂,” *Annu. Rev. Phys. Chem.*, vol. 63, no. 1, pp. 541–569, Apr. 2012, doi: 10.1146/annurev-physchem-032511-143759.
- [95] E. V Kondratenko, G. Mul, J. Baltrusaitis, G. O. Larrazábal, and J. Pérez-Ramírez, “Status and perspectives of CO₂ conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes,” *Energy Environ. Sci.*, vol. 6, no. 11, pp. 3112–3135, 2013, doi: 10.1039/C3EE41272E.
- [96] Q. Xie, G. O. Larrazábal, M. Ma, I. Chorkendorff, B. Seger, and J. Luo, “Copper-indium hydroxides derived electrocatalysts with tunable compositions for electrochemical CO₂ reduction,” *J. Energy Chem.*, vol. 63, pp. 278–284, Dec. 2021, doi: 10.1016/J.JECHM.2021.09.008.
- [97] K. Ghobadi, H. R. Zare, A. Gorji, and A. Benvidi, “Electrochemical activation of CO₂ by a di-Schiff base of N, N'-bis (2-hydroxy-1-naphthaldehyde)-m-phenylenediimine,” *Polyhedron*, vol. 155, pp. 13–19, 2018.
- [98] B. Hu, C. Guild, and S. L. Suib, “Thermal, electrochemical, and photochemical conversion of CO₂ to fuels and value-added products,” *Journal of CO₂ Utilization*, vol. 1. Elsevier Ltd, pp. 18–27, 2013. doi: 10.1016/j.jcou.2013.03.004.
- [99] D. Zhu *et al.*, “A 2D metal–organic framework/Ni(OH)₂ heterostructure for an enhanced oxygen evolution reaction,” *Nanoscale*, vol. 11, no. 8, pp. 3599–3605, 2019, doi: 10.1039/C8NR09680E.
- [100] D. D. Zhu, J. L. Liu, and S. Z. Qiao, “Recent Advances in Inorganic Heterogeneous Electrocatalysts for Reduction of Carbon Dioxide,” *Adv. Mater.*, vol. 28, no. 18, pp. 3423–3452, May 2016, doi: <https://doi.org/10.1002/adma.201504766>.
- [101] H. T. D. Bui *et al.*, “Activity–Selectivity Enhancement and Catalytic Trend of CO₂ Electroreduction on Metallic Dimers Supported by N-Doped Graphene: A Computational Study,” *J. Phys. Chem. C*, vol. 125, no. 24, pp. 13176–13184, Jun. 2021, doi:

10.1021/acs.jpcc.1c02908.

- [102] W. Ni *et al.*, “Electroreduction of Carbon Dioxide Driven by the Intrinsic Defects in the Carbon Plane of a Single Fe–N₄ Site,” *Adv. Mater.*, vol. 33, no. 1, p. 2003238, Jan. 2021, doi: <https://doi.org/10.1002/adma.202003238>.
- [103] Z. Li *et al.*, “Metal-support interactions in designing noble metal-based catalysts for electrochemical CO₂ reduction: Recent advances and future perspectives,” *Nano Res.*, vol. 14, no. 11, pp. 3795–3809, 2021, doi: 10.1007/s12274-021-3363-6.
- [104] F. Marques Mota *et al.*, “Toward an Effective Control of the H₂ to CO Ratio of Syngas through CO₂ Electroreduction over Immobilized Gold Nanoparticles on Layered Titanate Nanosheets,” *ACS Catal.*, vol. 8, no. 5, pp. 4364–4374, May 2018, doi: 10.1021/acscatal.8b00647.
- [105] S. Chatterjee *et al.*, “Free Standing Nanoporous Palladium Alloys as CO Poisoning Tolerant Electrocatalysts for the Electrochemical Reduction of CO₂ to Formate,” *ACS Catal.*, vol. 9, no. 6, pp. 5290–5301, Jun. 2019, doi: 10.1021/acscatal.9b00330.
- [106] T. Osaki, T. Horiuchi, K. Suzuki, and T. Mori, “Catalyst performance of MoS₂ and WS₂ for the CO₂-reforming of CH₄ Suppression of carbon deposition,” *Appl. Catal. A Gen.*, vol. 155, no. 2, pp. 229–238, 1997, doi: [https://doi.org/10.1016/S0926-860X\(96\)00391-2](https://doi.org/10.1016/S0926-860X(96)00391-2).
- [107] P. Abbasi *et al.*, “Tailoring the Edge Structure of Molybdenum Disulfide toward Electrocatalytic Reduction of Carbon Dioxide,” *ACS Nano*, vol. 11, no. 1, pp. 453–460, Jan. 2017, doi: 10.1021/acsnano.6b06392.
- [108] Z. Weng *et al.*, “Electrochemical CO₂ Reduction to Hydrocarbons on a Heterogeneous Molecular Cu Catalyst in Aqueous Solution,” *J. Am. Chem. Soc.*, vol. 138, no. 26, pp. 8076–8079, Jul. 2016, doi: 10.1021/jacs.6b04746.
- [109] X. Zhang *et al.*, “Highly selective and active CO₂ reduction electrocatalysts based on cobalt phthalocyanine/carbon nanotube hybrid structures,” *Nat. Commun.*, vol. 8, no. 1, p. 14675, 2017, doi: 10.1038/ncomms14675.
- [110] G. Zhu, Y. Li, H. Zhu, H. Su, S. H. Chan, and Q. Sun, “Curvature-Dependent Selectivity of CO₂ Electrocatalytic Reduction on Cobalt Porphyrin Nanotubes,” *ACS Catal.*, vol. 6, no. 9, pp. 6294–6301, Sep. 2016, doi: 10.1021/acscatal.6b02020.
- [111] G.-L. Chai and Z.-X. Guo, “Highly effective sites and selectivity of nitrogen-doped graphene/CNT catalysts for CO₂ electrochemical reduction,” *Chem. Sci.*, vol. 7, no. 2, pp. 1268–1275, 2016, doi: 10.1039/C5SC03695J.
- [112] M. Suominen and T. Kallio, “What We Currently Know about Carbon-Supported Metal and Metal Oxide Nanomaterials in Electrochemical CO₂ Reduction,” *ChemElectroChem*, vol. 8, no. 13, pp. 2397–2406, Jul. 2021, doi: <https://doi.org/10.1002/celec.202100345>.
- [113] H. Shi, Y. Cheng, and P. Kang, “Metal Oxide/Nitrogen-Doped Carbon Catalysts Enables Highly Efficient CO₂ Electroreduction,” *Trans. Tianjin Univ.*, vol. 27, no. 3, pp. 269–277, 2021, doi: 10.1007/s12209-021-00287-7.
- [114] Y. Zhao *et al.*, “Spontaneously Sn-Doped Bi/BiOx Core–Shell Nanowires Toward High-Performance CO₂ Electroreduction to Liquid Fuel,” *Nano Lett.*, vol. 21, no. 16, pp. 6907–6913, Aug. 2021, doi: 10.1021/acs.nanolett.1c02053.

- [115] Y. Hori, I. Takahashi, O. Koga, and N. Hoshi, "Selective Formation of C₂ Compounds from Electrochemical Reduction of CO₂ at a Series of Copper Single Crystal Electrodes," *J. Phys. Chem. B*, vol. 106, no. 1, pp. 15–17, Jan. 2002, doi: 10.1021/jp013478d.
- [116] Y. Hori, R. Takahashi, Y. Yoshinami, and A. Murata, "Electrochemical Reduction of CO at a Copper Electrode," *J. Phys. Chem. B*, vol. 101, no. 36, pp. 7075–7081, 1997, doi: 10.1021/jp970284i.
- [117] J. Qiao, Y. Liu, F. Hong, and J. Zhang, "A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels," *Chem. Soc. Rev.*, vol. 43, pp. 631–675, 2014, doi: 10.1039/c3cs60323g.
- [118] R. J. Lim *et al.*, "A review on the electrochemical reduction of CO₂ in fuel cells, metal electrodes and molecular catalysts," *Catal. Today*, vol. 233, pp. 169–180, Sep. 2014, doi: 10.1016/J.CATTOD.2013.11.037.
- [119] H. Gu *et al.*, "Graphdiyne/Graphene Heterostructure: A Universal 2D Scaffold Anchoring Monodispersed Transition-Metal Phthalocyanines for Selective and Durable CO₂ Electroreduction," *J. Am. Chem. Soc.*, vol. 143, no. 23, pp. 8679–8688, Jun. 2021, doi: 10.1021/jacs.1c02326.
- [120] Y. Wu, Y. Liang, and H. Wang, "Heterogeneous Molecular Catalysts of Metal Phthalocyanines for Electrochemical CO₂ Reduction Reactions," *Acc. Chem. Res.*, vol. 54, no. 16, pp. 3149–3159, Aug. 2021, doi: 10.1021/acs.accounts.1c00200.
- [121] S. Jiang, L. D'Amario, and H. Dau, "Copper Carbonate Hydroxide as Precursor of Interfacial CO in CO₂ Electroreduction," *ChemSusChem*, vol. 15, no. 8, p. e202102506, Apr. 2022, doi: <https://doi.org/10.1002/cssc.202102506>.
- [122] B. Yang *et al.*, "Accelerating CO₂ Electroreduction to Multicarbon Products via Synergistic Electric–Thermal Field on Copper Nanoneedles," *J. Am. Chem. Soc.*, vol. 144, no. 7, pp. 3039–3049, Feb. 2022, doi: 10.1021/jacs.1c11253.
- [123] Z.-Z. Niu *et al.*, "Hierarchical Copper with Inherent Hydrophobicity Mitigates Electrode Flooding for High-Rate CO₂ Electroreduction to Multicarbon Products," *J. Am. Chem. Soc.*, vol. 143, no. 21, pp. 8011–8021, Jun. 2021, doi: 10.1021/jacs.1c01190.
- [124] M. C. O. Monteiro, F. Dattila, B. Hagedoorn, R. García-Muelas, N. López, and M. T. M. Koper, "Absence of CO₂ electroreduction on copper, gold and silver electrodes without metal cations in solution," *Nat. Catal.*, vol. 4, no. 8, pp. 654–662, 2021, doi: 10.1038/s41929-021-00655-5.
- [125] C. Ma *et al.*, "Rapid flame synthesis of carbon doped defective ZnO for electrocatalytic CO₂ reduction to syngas," *Electrochim. Acta*, vol. 411, p. 140098, 2022, doi: <https://doi.org/10.1016/j.electacta.2022.140098>.
- [126] X. Jiang *et al.*, "A hierarchically structured tin-cobalt composite with an enhanced electronic effect for high-performance CO₂ electroreduction in a wide potential range," *J. Energy Chem.*, vol. 76, pp. 462–469, 2023, doi: <https://doi.org/10.1016/j.jechem.2022.10.008>.
- [127] B. Qin, Q. Zhang, Y.-H. Li, G. Yang, and F. Peng, "Formation of Lattice-Dislocated Zinc Oxide via Anodic Corrosion for Electrocatalytic CO₂ Reduction to Syngas with a Potential-Dependent CO:H₂ Ratio," *ACS Appl. Mater. Interfaces*, vol. 12, no. 27, pp.

30466–30473, Jul. 2020, doi: 10.1021/acsami.0c08066.

- [128] M. Karamad, H. A. Hansen, J. Rossmeisl, and J. K. Nørskov, “Mechanistic Pathway in the Electrochemical Reduction of CO₂ on RuO₂,” *ACS Catal.*, vol. 5, no. 7, pp. 4075–4081, Jul. 2015, doi: 10.1021/cs501542n.
- [129] J. Qu, X. Zhang, Y. Wang, and C. Xie, “Electrochemical reduction of CO₂ on RuO₂/TiO₂ nanotubes composite modified Pt electrode,” *Electrochim. Acta*, vol. 50, no. 16, pp. 3576–3580, 2005, doi: <https://doi.org/10.1016/j.electacta.2004.11.061>.
- [130] S. Gao *et al.*, “Ultrathin Co₃O₄ Layers Realizing Optimized CO₂ Electroreduction to Formate,” *Angew. Chemie Int. Ed.*, vol. 55, no. 2, pp. 698–702, Jan. 2016, doi: <https://doi.org/10.1002/anie.201509800>.
- [131] L. Chen, F. Li, C. L. Bentley, M. Horne, A. M. Bond, and J. Zhang, “Electrochemical Reduction of CO₂ with an Oxide-Derived Lead Nano-Coralline Electrode in Dimcarb,” *ChemElectroChem*, vol. 4, no. 6, pp. 1402–1410, Jun. 2017, doi: <https://doi.org/10.1002/celc.201700217>.
- [132] K. Ye *et al.*, “In Situ Reconstruction of a Hierarchical Sn-Cu/SnO_x Core/Shell Catalyst for High-Performance CO₂ Electroreduction,” *Angew. Chemie Int. Ed.*, vol. 59, no. 12, pp. 4814–4821, Mar. 2020, doi: <https://doi.org/10.1002/anie.201916538>.
- [133] Y.-W. Choi, F. Scholten, I. Sinev, and B. Roldan Cuenya, “Enhanced Stability and CO/Formate Selectivity of Plasma-Treated SnO_x/AgO_x Catalysts during CO₂ Electroreduction,” *J. Am. Chem. Soc.*, vol. 141, no. 13, pp. 5261–5266, Apr. 2019, doi: 10.1021/jacs.8b12766.
- [134] H. Pan, J. Gong, and Y. Zhang, “Enabling durable selectivity of CO₂ electroreduction to formate achieved by a multi-layer SnO_x structure,” *Appl. Surf. Sci.*, vol. 579, p. 151971, 2022, doi: <https://doi.org/10.1016/j.apsusc.2021.151971>.
- [135] M. Ma, K. Djanashvili, and W. A. Smith, “Selective electrochemical reduction of CO₂ to CO on CuO-derived Cu nanowires,” *Phys. Chem. Chem. Phys.*, vol. 17, no. 32, pp. 20861–20867, 2015, doi: 10.1039/C5CP03559G.
- [136] S. Huo *et al.*, “Coupled Metal/Oxide Catalysts with Tunable Product Selectivity for Electrocatalytic CO₂ Reduction,” *ACS Appl. Mater. Interfaces*, vol. 9, no. 34, pp. 28519–28526, Aug. 2017, doi: 10.1021/acsami.7b07707.
- [137] M. Cao *et al.*, “The Synergy between Metal Facet and Oxide Support Facet for Enhanced Catalytic Performance: The Case of Pd–TiO₂,” *Nano Lett.*, vol. 16, no. 8, pp. 5298–5302, Aug. 2016, doi: 10.1021/acs.nanolett.6b02662.
- [138] H. Yin *et al.*, “Ultrathin platinum nanowires grown on single-layered nickel hydroxide with high hydrogen evolution activity,” *Nat. Commun.*, vol. 6, no. 1, p. 6430, 2015, doi: 10.1038/ncomms7430.
- [139] S. Gao *et al.*, “Partially oxidized atomic cobalt layers for carbon dioxide electroreduction to liquid fuel,” *Nature*, vol. 529, no. 7584, pp. 68–71, 2016, doi: 10.1038/nature16455.
- [140] G. O. Larrazábal, A. J. Martín, S. Mitchell, R. Hauert, and J. Pérez-Ramírez, “Synergistic effects in silver–indium electrocatalysts for carbon dioxide reduction,” *J. Catal.*, vol. 343, pp. 266–277, 2016, doi: <https://doi.org/10.1016/j.jcat.2015.12.014>.

- [141] G. O. Larrazábal, A. J. Martín, S. Mitchell, R. Hauert, and J. Pérez-Ramírez, “Enhanced Reduction of CO₂ to CO over Cu–In Electrocatalysts: Catalyst Evolution Is the Key,” *ACS Catal.*, vol. 6, no. 9, pp. 6265–6274, Sep. 2016, doi: 10.1021/acscatal.6b02067.
- [142] D. Shu, M. Wang, F. Tian, H. Zhang, and C. Peng, “A dual-cathode study on Ag–Cu sequential CO₂ electroreduction towards hydrocarbons,” *J. CO₂ Util.*, vol. 45, p. 101444, 2021, doi: <https://doi.org/10.1016/j.jcou.2021.101444>.
- [143] G. W. Woyessa, J. B. dela Cruz, M. Rameez, and C.-H. Hung, “Nanocomposite catalyst of graphitic carbon nitride and Cu/Fe mixed metal oxide for electrochemical CO₂ reduction to CO,” *Appl. Catal. B Environ.*, vol. 291, p. 120052, 2021, doi: <https://doi.org/10.1016/j.apcatb.2021.120052>.
- [144] K. Allado, M. Liu, A. Jayapalan, D. Arvapalli, K. Nowlin, and J. Wei, “Binary MnO₂/Co₃O₄ Metal Oxides Wrapped on Superaligned Electrospun Carbon Nanofibers as Binder Free Supercapacitor Electrodes,” *Energy & Fuels*, vol. 35, no. 9, pp. 8396–8405, May 2021, doi: 10.1021/acs.energyfuels.1c00556.
- [145] A. S. Agnihotri, A. Varghese, and N. M., “Transition metal oxides in electrochemical and bio sensing: A state-of-art review,” *Appl. Surf. Sci. Adv.*, vol. 4, p. 100072, 2021, doi: <https://doi.org/10.1016/j.apsadv.2021.100072>.
- [146] J. Wang *et al.*, “In–Sn alloy core-shell nanoparticles: In-doped SnO_x shell enables high stability and activity towards selective formate production from electrochemical reduction of CO₂,” *Appl. Catal. B Environ.*, vol. 288, p. 119979, 2021, doi: <https://doi.org/10.1016/j.apcatb.2021.119979>.
- [147] Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov, and T. F. Jaramillo, “Combining theory and experiment in electrocatalysis: Insights into materials design,” *Science (80-.)*, vol. 355, no. 6321, p. eaad4998, Jan. 2017, doi: 10.1126/science.aad4998.
- [148] H. Takeda, C. Cometto, O. Ishitani, and M. Robert, “Electrons, Photons, Protons and Earth-Abundant Metal Complexes for Molecular Catalysis of CO₂ Reduction,” *ACS Catal.*, vol. 7, no. 1, pp. 70–88, Jan. 2017, doi: 10.1021/acscatal.6b02181.
- [149] F. Franco, S. Fernández, and J. Lloret-Fillol, “Advances in the electrochemical catalytic reduction of CO₂ with metal complexes,” *Curr. Opin. Electrochem.*, vol. 15, pp. 109–117, 2019, doi: <https://doi.org/10.1016/j.coelec.2019.04.002>.
- [150] X. Duan *et al.*, “Metal-Free Carbon Materials for CO₂ Electrochemical Reduction,” *Adv. Mater.*, vol. 29, no. 41, p. 1701784, Nov. 2017, doi: <https://doi.org/10.1002/adma.201701784>.
- [151] B. Kumar *et al.*, “New trends in the development of heterogeneous catalysts for electrochemical CO₂ reduction,” *Catal. Today*, vol. 270, pp. 19–30, 2016, doi: <https://doi.org/10.1016/j.cattod.2016.02.006>.
- [152] Y. Cheng, S. Yang, S. P. Jiang, and S. Wang, “Supported Single Atoms as New Class of Catalysts for Electrochemical Reduction of Carbon Dioxide,” *Small Methods*, vol. 3, no. 9, p. 1800440, Sep. 2019, doi: <https://doi.org/10.1002/smtd.201800440>.
- [153] C. Yan, L. Lin, G. Wang, and X. Bao, “Transition metal-nitrogen sites for electrochemical carbon dioxide reduction reaction,” *Chinese J. Catal.*, vol. 40, no. 1, pp. 23–37, 2019, doi:

[https://doi.org/10.1016/S1872-2067\(18\)63161-4](https://doi.org/10.1016/S1872-2067(18)63161-4).

- [154] A. S. Varela, W. Ju, and P. Strasser, “Molecular Nitrogen–Carbon Catalysts, Solid Metal Organic Framework Catalysts, and Solid Metal/Nitrogen-Doped Carbon (MNC) Catalysts for the Electrochemical CO₂ Reduction,” *Adv. Energy Mater.*, vol. 8, no. 30, p. 1703614, Oct. 2018, doi: <https://doi.org/10.1002/aenm.201703614>.
- [155] M. Li, H. Wang, W. Luo, P. C. Sherrell, J. Chen, and J. Yang, “Heterogeneous Single-Atom Catalysts for Electrochemical CO₂ Reduction Reaction,” *Adv. Mater.*, vol. 32, no. 34, p. 2001848, Aug. 2020, doi: <https://doi.org/10.1002/adma.202001848>.
- [156] F. Pan, W. Deng, C. Justiniano, and Y. Li, “Identification of champion transition metals centers in metal and nitrogen-codoped carbon catalysts for CO₂ reduction,” *Appl. Catal. B Environ.*, vol. 226, pp. 463–472, 2018, doi: <https://doi.org/10.1016/j.apcatb.2018.01.001>.
- [157] J. Gu, C.-S. Hsu, L. Bai, H. M. Chen, and X. Hu, “Atomically dispersed Fe³⁺ sites catalyze efficient CO₂ electroreduction to CO,” *Science (80-.)*, vol. 364, no. 6445, pp. 1091–1094, Jun. 2019, doi: [10.1126/science.aaw7515](https://doi.org/10.1126/science.aaw7515).
- [158] S. Zhu, T. Li, W.-B. Cai, and M. Shao, “CO₂ Electrochemical Reduction As Probed through Infrared Spectroscopy,” *ACS Energy Lett.*, vol. 4, no. 3, pp. 682–689, Mar. 2019, doi: [10.1021/acsenenergylett.8b02525](https://doi.org/10.1021/acsenenergylett.8b02525).
- [159] N. Heidary, K. H. Ly, and N. Kornienko, “Probing CO₂ Conversion Chemistry on Nanostructured Surfaces with Operando Vibrational Spectroscopy,” *Nano Lett.*, vol. 19, no. 8, pp. 4817–4826, Aug. 2019, doi: [10.1021/acs.nanolett.9b01582](https://doi.org/10.1021/acs.nanolett.9b01582).
- [160] A. Wuttig *et al.*, “Tracking a Common Surface-Bound Intermediate during CO₂-to-Fuels Catalysis,” *ACS Cent. Sci.*, vol. 2, no. 8, pp. 522–528, Aug. 2016, doi: [10.1021/acscentsci.6b00155](https://doi.org/10.1021/acscentsci.6b00155).
- [161] S. Zhu, B. Jiang, W.-B. Cai, and M. Shao, “Direct Observation on Reaction Intermediates and the Role of Bicarbonate Anions in CO₂ Electrochemical Reduction Reaction on Cu Surfaces,” *J. Am. Chem. Soc.*, vol. 139, no. 44, pp. 15664–15667, Nov. 2017, doi: [10.1021/jacs.7b10462](https://doi.org/10.1021/jacs.7b10462).
- [162] H. Bin Yang *et al.*, “Atomically dispersed Ni(i) as the active site for electrochemical CO₂ reduction,” *Nat. Energy*, vol. 3, no. 2, pp. 140–147, 2018, doi: [10.1038/s41560-017-0078-8](https://doi.org/10.1038/s41560-017-0078-8).
- [163] L. Han *et al.*, “Stable and Efficient Single-Atom Zn Catalyst for CO₂ Reduction to CH₄,” *J. Am. Chem. Soc.*, vol. 142, no. 29, pp. 12563–12567, Jul. 2020, doi: [10.1021/jacs.9b12111](https://doi.org/10.1021/jacs.9b12111).
- [164] D. Ren, J. Fong, and B. S. Yeo, “The effects of currents and potentials on the selectivities of copper toward carbon dioxide electroreduction,” *Nat. Commun.*, vol. 9, no. 1, p. 925, 2018, doi: [10.1038/s41467-018-03286-w](https://doi.org/10.1038/s41467-018-03286-w).
- [165] J. Wang *et al.*, “Tailoring the interactions of heterostructured Ni₄N/Ni₃ZnCo. 7 for efficient CO₂ electroreduction,” *J. Energy Chem.*, vol. 75, pp. 1–7, 2022.
- [166] Z. Wang, X. She, Q. Yu, X. Zhu, H. Li, and H. Xu, “Minireview on the Commonly Applied Copper-Based Electrocatalysts for Electrochemical CO₂Reduction,” *Energy and Fuels*, vol. 35, no. 10, pp. 8585–8601, May 2021, doi: [10.1021/acs.energyfuels.1c01111](https://doi.org/10.1021/acs.energyfuels.1c01111).

- [167] P. Scardi *et al.*, “Anisotropic atom displacement in Pd nanocubes resolved by molecular dynamics simulations supported by x-ray diffraction imaging,” *Phys. Rev. B*, vol. 91, no. 15, p. 155414, 2015.
- [168] M. Liu *et al.*, “Enhanced electrocatalytic CO₂ reduction via field-induced reagent concentration,” *Nature*, vol. 537, no. 7620, pp. 382–386, 2016, doi: 10.1038/nature19060.
- [169] F. Pan and Y. Yang, “Designing CO₂ reduction electrode materials by morphology and interface engineering,” *Energy Environ. Sci.*, vol. 13, no. 8, pp. 2275–2309, 2020, doi: 10.1039/D0EE00900H.
- [170] X. Zhang *et al.*, “Tuning the electron structure enables the NiZn alloy for CO₂ electroreduction to formate,” *J. Energy Chem.*, vol. 63, pp. 625–632, Dec. 2021, doi: 10.1016/J.JECHEM.2021.08.060.
- [171] A. Dutta, M. Rahaman, N. C. Luedi, M. Mohos, and P. Broekmann, “Morphology Matters: Tuning the Product Distribution of CO₂ Electroreduction on Oxide-Derived Cu Foam Catalysts,” *ACS Catal.*, vol. 6, no. 6, pp. 3804–3814, Jun. 2016, doi: 10.1021/acscatal.6b00770.
- [172] T. Burdyny *et al.*, “Nanomorphology-Enhanced Gas-Evolution Intensifies CO₂ Reduction Electrochemistry,” *ACS Sustain. Chem. Eng.*, vol. 5, no. 5, pp. 4031–4040, May 2017, doi: 10.1021/acssuschemeng.7b00023.
- [173] W. Zhu *et al.*, “Monodisperse Au Nanoparticles for Selective Electrocatalytic Reduction of CO₂ to CO,” *J. Am. Chem. Soc.*, vol. 135, no. 45, p. 16833, 2013.
- [174] K. Manthiram, B. J. Beberwyck, and A. Paul Alivisatos, “Enhanced Electrochemical Methanation of Carbon Dioxide with a Dispersible Nanoscale Copper Catalyst,” *J. Am. Chem. Soc.*, vol. 136, no. 38, pp. 13319–13325, Sep. 2014, doi: 10.1021/ja5065284.
- [175] Y. Li, F. Cui, M. B. Ross, D. Kim, Y. Sun, and P. Yang, “Structure-sensitive CO₂ electroreduction to hydrocarbons on ultrathin 5-fold twinned copper nanowires,” *Nano Lett.*, vol. 17, no. 2, pp. 1312–1317, 2017.
- [176] Z. Wang, G. Yang, Z. Zhang, M. Jin, and Y. Yin, “Selectivity on etching: creation of high-energy facets on copper nanocrystals for CO₂ electrochemical reduction,” *ACS Nano*, vol. 10, no. 4, pp. 4559–4564, 2016.
- [177] D. Wang, Q. Li, C. Han, Q. Lu, Z. Xing, and X. Yang, “Atomic and electronic modulation of self-supported nickel-vanadium layered double hydroxide to accelerate water splitting kinetics,” doi: 10.1038/s41467-019-11765-x.
- [178] Q. Yang *et al.*, “Vanadium oxide integrated on hierarchically nanoporous copper for efficient electroreduction of CO₂ to ethanol †,” 2021, doi: 10.1039/d0ta09522b.
- [179] J. Feng *et al.*, “A Mn-N₃ single-atom catalyst embedded in graphitic carbon nitride for efficient CO₂ electroreduction,” doi: 10.1038/s41467-020-18143-y.
- [180] K. Wang *et al.*, “Tuning the local electronic structure of oxygen vacancies over copper-doped zinc oxide for efficient CO₂ electroreduction,” *EScience*, vol. 2, no. 5, pp. 518–528, 2022.

- [181] H. Han *et al.*, “Plasma-induced oxygen vacancies in amorphous MnO_x boost catalytic performance for electrochemical CO₂ reduction,” *Nano Energy*, vol. 79, p. 105492, Jan. 2021, doi: 10.1016/J.NANOEN.2020.105492.
- [182] X. Peng *et al.*, “Efficient Electroreduction CO₂ to CO over MnO₂ Nanosheets,” *Cite This Inorg. Chem*, vol. 58, p. 8914, 2019, doi: 10.1021/acs.inorgchem.9b01018.
- [183] M. Usman *et al.*, “Electrochemical Reduction of CO₂ : A Review of Cobalt Based Catalysts for Carbon Dioxide Conversion to Fuels,” 2021, doi: 10.3390/nano11082029.
- [184] M. Wang *et al.*, “Three-Dimensional Nitrogen-Doped Graphene Aerogel-Supported MnO Nanoparticles as Efficient Electrocatalysts for CO₂ Reduction to CO,” 2020, doi: 10.1021/acssuschemeng.0c01194.
- [185] J. Kossmann, M. L. O. Sánchez-Manjavacas, J. Brandt, T. Heil, N. López-Salas, and J. Albero, “Mn (ii) sub-nanometric site stabilization in noble, N-doped carbonaceous materials for electrochemical CO₂ reduction,” *Chem. Commun.*, vol. 58, no. 31, pp. 4841–4844, 2022.
- [186] B. Zhang *et al.*, “Manganese acting as a high-performance heterogeneous electrocatalyst in carbon dioxide reduction,” *Nat. Commun.*, vol. 10, no. 1, pp. 1–8, 2019.
- [187] X. Ou, K. Chen, L. Wei, Y. Deng, J. Li, and L. Dong, “Effect of Co Doping on Magnetic and CO-SCR Properties of γ -Fe₂O₃,” *Cite This Ind. Eng. Chem. Res*, vol. 60, pp. 5744–5757, 2021, doi: 10.1021/acs.iecr.1c00305.
- [188] Q. Fan, G. Bao, X. Chen, Y. Meng, S. Zhang, and X. Ma, “Iron Nanoparticles Tuned to Catalyze CO₂ Electroreduction in Acidic Solutions through Chemical Microenvironment Engineering,” *ACS Catal.*, vol. 12, no. 13, pp. 7517–7523, Jun. 2022, doi: 10.1021/acscatal.2c01890.
- [189] Q. Liu, Y. Wang, Z. Hu, and Z. Zhang, “Iron-based single-atom electrocatalysts: synthetic strategies and applications,” *Rsc Adv.*, vol. 11, no. 5, pp. 3079–3095, 2021.
- [190] H. Zhang *et al.*, “Electrocatalysis A Graphene-Supported Single-Atom FeN₅ Catalytic Site for Efficient Electrochemical CO₂ Reduction,” vol. 131, pp. 5013–15018, 2019, doi: 10.1002/anie.201906079.
- [191] N. Leonard *et al.*, “Supporting Information The chemical identity, state and structure of catalytically active centers during the electrochemical CO₂ reduction on porous Fe-nitrogen-carbon (Fe-N-C) materials,” 2018.
- [192] Y. Gang, F. Pan, Y. Fei, Z. Du, Y. H. Hu, and Y. Li, “Highly Efficient Nickel, Iron, and Nitrogen Codoped Carbon Catalysts Derived from Industrial Waste Petroleum Coke for Electrochemical CO₂ Reduction,” 2020, doi: 10.1021/acssuschemeng.0c03054.
- [193] F. Pan *et al.*, “Unveiling Active Sites of CO₂ Reduction on Nitrogen-Coordinated and Atomically Dispersed Iron and Cobalt Catalysts,” *ACS Catal*, vol. 8, p. 43, 2018, doi: 10.1021/acscatal.8b00398.
- [194] C. Genovese *et al.*, “Operando spectroscopy study of the carbon dioxide electro-reduction by iron species on nitrogen-doped carbon”, doi: 10.1038/s41467-018-03138-7.
- [195] X. Sun *et al.*, “Structure-activity relationships in metal organic framework derived mesoporous nitrogen-doped carbon containing atomically dispersed iron sites for CO₂

- electrochemical reduction,” *J. Catal.*, vol. 378, pp. 320–330, Oct. 2019, doi: 10.1016/J.JCAT.2019.09.013.
- [196] Y. Wang *et al.*, “Phthalocyanine Precursors To Construct Atomically Dispersed Iron Electrocatalysts,” 2019, doi: 10.1021/acscatal.9b01617.
- [197] M. Duarte, N. Daems, J. Hereijgers, D. Arenas-Esteban, S. Bals, and T. Breugelmans, “Enhanced CO₂ electroreduction with metal-nitrogen-doped carbons in a continuous flow reactor,” *J. CO₂ Util.*, vol. 50, p. 101583, Aug. 2021, doi: 10.1016/J.JCOU.2021.101583.
- [198] L. Zhang *et al.*, “Facile Synthesis of Fe@C Loaded on g-C₃N₄ for CO₂ Electrochemical Reduction to CO with Low Overpotential,” 2022, doi: 10.1021/acsomega.1c07298.
- [199] Z. Chen *et al.*, “Fe 1 N 4-O 1 site with axial Fe-O coordination for highly selective CO₂ reduction over a wide potential range †,” *This J. is Cite this Energy Environ. Sci*, vol. 14, p. 3430, 2021, doi: 10.1039/d1ee00569c.
- [200] A. S. Varela *et al.*, “pH Effects on the Selectivity of the Electrocatalytic CO₂ Reduction on Graphene-Embedded Fe–N–C Motifs: Bridging Concepts between Molecular Homogeneous and Solid-State Heterogeneous Catalysis,” *ACS Energy Lett*, vol. 3, p. 43, 2018, doi: 10.1021/acsenerylett.8b00273.
- [201] J. Huang, X. Guo, G. Yue, Q. Hu, and L. Wang, “Boosting CH₃OH Production in Electrocatalytic CO₂ Reduction over Partially Oxidized 5 nm Cobalt Nanoparticles Dispersed on Single-Layer Nitrogen-Doped Graphene,” 2018, doi: 10.1021/acsaami.8b14822.
- [202] A. Aljabour *et al.*, “Nanofibrous cobalt oxide for electrocatalysis of CO₂ reduction to carbon monoxide and formate in an acetonitrile-water electrolyte solution,” *Appl. Catal. B Environ.*, vol. 229, pp. 163–170, Aug. 2018, doi: 10.1016/J.APCATB.2018.02.017.
- [203] R. Nazir *et al.*, “Nanosheet Synthesis of Mixed Co₃O₄/CuO via Combustion Method for Methanol Oxidation and Carbon Dioxide Reduction,” 2020, doi: 10.1021/acs.langmuir.0c02554.
- [204] H. Yang *et al.*, “Highly efficient utilization of single atoms via constructing 3D and free-standing electrodes for CO₂ reduction with ultrahigh current density,” *Nano Energy*, vol. 70, p. 104454, Apr. 2020, doi: 10.1016/J.NANOEN.2020.104454.
- [205] X. Wang *et al.*, “Electrocatalysis Regulation of Coordination Number over Single Co Sites: Triggering the Efficient Electroreduction of CO₂”, doi: 10.1002/anie.201712451.
- [206] X. Song *et al.*, “Bifunctional Nitrogen and Cobalt Codoped Hollow Carbon for Electrochemical Syngas Production,” *Adv. Sci.*, vol. 5, no. 7, 2018, doi: 10.1002/advs.201800177.
- [207] Y. Cheng *et al.*, “Communication Atomically Dispersed Transition Metals on Carbon Nanotubes with Ultrahigh Loading for Selective Electrochemical Carbon Dioxide Reduction,” *Adv. Mater.*, vol. 30, p. 1706287, 2018, doi: 10.1002/adma.201706287.
- [208] L. Lin *et al.*, “Communication 1903470 (1 of 7) Synergistic Catalysis over Iron-Nitrogen Sites Anchored with Cobalt Phthalocyanine for Efficient CO₂ Electroreduction,” 2019, doi: 10.1002/adma.201903470.

- [209] M. Jia *et al.*, “Carbon-supported Ni nanoparticles for efficient CO₂ electroreduction,” *Chem. Sci.*, vol. 9, no. 47, pp. 8775–8780, 2018.
- [210] D. Tan *et al.*, “Nitrogen-carbon layer coated nickel nanoparticles for efficient electrocatalytic reduction of carbon dioxide”, doi: 10.1007/s12274-019-2372-1.
- [211] Z. Li *et al.*, “Size-Dependent Nickel-Based Electrocatalysts for Selective CO₂ Reduction”, doi: 10.1002/anie.202000318.
- [212] W. Liu *et al.*, “Promoting the activity and selectivity of Ni sites via chemical coordination with pyridinic nitrogen for CO₂-to-CO electrochemical catalysis,” *Int. J. Hydrogen Energy*, vol. 46, no. 50, pp. 25448–25456, Jul. 2021, doi: 10.1016/J.IJHYDENE.2021.05.080.
- [213] R. Daiyan *et al.*, “Antipoisoning Nickel–Carbon Electrocatalyst for Practical Electrochemical CO₂ Reduction to CO,” 2019, doi: 10.1021/acsaem.9b01470.
- [214] Q. He *et al.*, “Syngas Production Very Important Paper Electrochemical Conversion of CO₂ to Syngas with Controllable CO/H₂ Ratios over Co and Ni Single-Atom Catalysts,” vol. 59, pp. 33–3037, doi: 10.1002/ange.201912719.
- [215] Q. Huang, H. Liu, W. An, Y. Wang, Y. Feng, and Y. Men, “Synergy of a Metallic NiCo Dimer Anchored on a C₂N–Graphene Matrix Promotes the Electrochemical CO₂ Reduction Reaction,” 2019, doi: 10.1021/acssuschemeng.9b05042.
- [216] B. Mohanty, S. Basu, and B. K. Jena, “Transition metal-based single-atom catalysts (TM-SACs); rising materials for electrochemical CO₂ reduction,” *J. Energy Chem.*, vol. 70, pp. 444–471, Jul. 2022, doi: 10.1016/J.JECHEM.2022.02.045.
- [217] S. Ma *et al.*, “Atomic Ni Species Anchored N-Doped Carbon Hollow Spheres as Nanoreactors for Efficient Electrochemical CO₂ Reduction,” 2019, doi: 10.1002/cctc.201901643.
- [218] P. Lu *et al.*, “Facile synthesis of single-nickel-atomic dispersed N-doped carbon framework for efficient electrochemical CO₂ reduction,” *Appl. Catal. B Environ.*, vol. 241, pp. 113–119, Feb. 2019, doi: 10.1016/J.APCATB.2018.09.025.
- [219] T. Zhang *et al.*, “Atomically Dispersed Nickel(I) on a Alloy-Encapsulated Nitrogen-Doped Carbon Nanotube Array for High-Performance Electrochemical CO₂ Reduction Reaction”, doi: 10.1002/anie.202002984.
- [220] H.-Y. Jeong *et al.*, “Tris(2-benzimidazolylmethyl)amine-Directed Synthesis of Single-Atom Nickel Catalysts for Electrochemical CO Production from CO₂,” vol. 24, pp. 18444–18454, 2018, doi: 10.1002/chem.201803615.
- [221] S. Asad Abbas, J. Tae Song, Y. Chuan Tan, K. Min Nam, J. Oh, and K.-D. Jung, “Synthesis of a Nickel Single-Atom Catalyst Based on Ni–N_{4-x}C_x Active Sites for Highly Efficient CO₂ Reduction Utilizing a Gas Diffusion Electrode,” *Cite This ACS Appl. Energy Mater.*, vol. 2020, p. 8745, 2020, doi: 10.1021/acsaem.0c01283.
- [222] S. Liu *et al.*, “CO₂ Reduction Hot Paper Elucidating the Electrocatalytic CO₂ Reduction Reaction over a Model Single-Atom Nickel Catalyst”, doi: 10.1002/ange.201911995.
- [223] H. Bin Yang *et al.*, “Atomically dispersed Ni(i) as the active site for electrochemical CO₂ reduction,” *Nat. eNergy* |, vol. 3, pp. 140–147, 2018, doi: 10.1038/s41560-017-0078-8.

- [224] F. Pan *et al.*, “Atomic-level active sites of efficient imidazolate framework-derived nickel catalysts for CO₂ reduction,” *J. Mater. Chem. A*, vol. 7, no. 46, pp. 26231–26237, 2019.
- [225] F. Ismail, A. Abdellah, H.-J. Lee, V. Sudheeshkumar, W. Alnoush, and D. C. Higgins, “Impact of Nickel Content on the Structure and Electrochemical CO₂ Reduction Performance of Nickel–Nitrogen–Carbon Catalysts Derived from Zeolitic Imidazolate Frameworks,” *Cite This ACS Appl. Energy Mater.*, vol. 2022, pp. 430–439, 2022, doi: 10.1021/acsaem.1c02522.
- [226] P. Yao *et al.*, “Atomic-Dispersed Coordinated Unsaturated Nickel–Nitrogen Sites in Hollow Carbon Spheres for the Efficient Electrochemical CO₂ Reduction,” vol. 19, p. 14, 2022, doi: 10.1021/acssuschemeng.1c00743.
- [227] S. Ye, G. Fan, J. Xu, L. Yang, and F. Li, “Nickel-nitrogen-modified porous carbon/carbon nanotube hybrid with necklace-like geometry: An efficient and durable electrocatalyst for selective reduction of CO₂ to CO in a wide negative potential region,” *Electrochim. Acta*, vol. 334, p. 135583, Feb. 2020, doi: 10.1016/J.ELECTACTA.2019.135583.
- [228] Z. Wang, P. Hou, Y. Wang, X. Xiang, and P. Kang, “Acidic Electrochemical Reduction of CO₂ Using Nickel Nitride on Multiwalled Carbon Nanotube as Selective Catalyst,” vol. 19, p. 32, 2022, doi: 10.1021/acssuschemeng.8b06278.
- [229] Y. Gang *et al.*, “One-Step Chemical Vapor Deposition Synthesis of Hierarchical Ni and N Co-Doped Carbon Nanosheet/Nanotube Hybrids for Efficient Electrochemical CO₂ Reduction at Commercially Viable Current Densities,” *ACS Catal.*, vol. 11, no. 16, pp. 10333–10344, 2021.
- [230] H. Wang, X. Wu, G. Liu, S. Wu, and R. Xu, “Bimetallic MOF derived nickel nanoclusters supported by nitrogen-doped carbon for efficient electrocatalytic CO₂ reduction,” 2022, doi: 10.1007/s12274-022-4199-4.
- [231] Z. Chen *et al.*, “In Situ Carbon Encapsulation Confined Nickel-Doped Indium Oxide Nanocrystals for Boosting CO₂ Electroreduction to the Industrial Level,” *ACS Catal.*, vol. 11, no. 23, pp. 14596–14604, 2021.
- [232] L. T. Menisa *et al.*, “Insight into atomically dispersed porous M-N-C single-site catalysts for electrochemical CO₂ reduction †,” vol. 12, p. 16617, 2020, doi: 10.1039/d0nr03044a.
- [233] F. Wang, Y. Liu, Z. Song, Z. Miao, J. Zhao, and T. Mikołajczyk, “Ni-N-Doped Carbon-Modified Reduced Graphene Oxide Catalysts for Electrochemical CO₂ Reduction Reaction,” 2021, doi: 10.3390/catal11050561.
- [234] W. Wang *et al.*, “Joint tuning the morphology and oxygen vacancy of Cu₂O by ionic liquid enables high-efficient CO₂ reduction to C₂ products,” *Chem. Eng. J.*, vol. 436, p. 135029, May 2022, doi: 10.1016/J.CEJ.2022.135029.
- [235] A. Vijayakumar *et al.*, “The length dependent selectivity on aligned Cu nanowires for C₁ products from CO₂ Electroreduction,” *Electrochim. Acta*, vol. 394, p. 139099, Oct. 2021, doi: 10.1016/J.ELECTACTA.2021.139099.
- [236] A. Ahmad *et al.*, “Cu-doped zeolite imidazole framework (ZIF-8) for effective electrocatalytic CO₂ reduction,” *J. CO₂ Util.*, vol. 48, p. 101523, Jun. 2021, doi: 10.1016/J.JCOU.2021.101523.

- [237] C.-J. Chang *et al.*, “Dynamic Reoxidation/Reduction-Driven Atomic Interdiffusion for Highly Selective CO₂ Reduction toward Methane,” *J. Am. Chem. Soc.*, vol. 142, p. 28, 2020, doi: 10.1021/jacs.0c01859.
- [238] D. Tan *et al.*, “Multi-shelled CuO microboxes for carbon dioxide reduction to ethylene”, doi: 10.1007/s12274-020-2692-1.
- [239] H. Jung *et al.*, “Electrochemical Fragmentation of Cu₂O Nanoparticles Enhancing Selective C–C Coupling from CO₂ Reduction Reaction,” 2019, doi: 10.1021/jacs.8b11237.
- [240] B. Liu *et al.*, “Synthesis of Cu₂O Nanostructures with Tunable Crystal Facets for Electrochemical CO₂ Reduction to Alcohols,” *Cite This ACS Appl. Mater. Interfaces*, vol. 13, p. 39177, 2021, doi: 10.1021/acsaami.1c03850.
- [241] Y. Wang, C. Niu, Y. Zhu, D. He, and W. Huang, “Tunable Syngas Formation from Electrochemical CO₂ Reduction on Copper Nanowire Arrays,” 2020, doi: 10.1021/acsaem.0c01504.
- [242] C. Choi *et al.*, “Highly active and stable stepped Cu surface for enhanced electrochemical CO₂ reduction to C₂H₄,” *Nat. Catal.*, vol. 3, no. 10, pp. 804–812, 2020.
- [243] J. Wen, Z. Wan, X. Hu, J. Huang, and X. Kang, “Restructuring of copper catalysts by potential cycling and enhanced two-carbon production for electroreduction of carbon dioxide,” *J. CO₂ Util.*, vol. 56, p. 101846, Feb. 2022, doi: 10.1016/J.JCOU.2021.101846.
- [244] M. Ebaid, K. Jiang, Z. Zhang, W. S. Drisdell, A. T. Bell, and J. K. Cooper, “Production of C₂/C₃ Oxygenates from Planar Copper Nitride-Derived Mesoporous Copper via Electrochemical Reduction of CO₂,” *Cite This Chem. Mater*, vol. 32, p. 3311, 2020, doi: 10.1021/acs.chemmater.0c00761.
- [245] M. Pei *et al.*, “The Role of Undercoordinated Sites on Zinc Electrodes for CO₂ Reduction to CO,” 2022, doi: 10.1002/adfm.202111597.
- [246] N. E. Mendieta-Reyes, A. K. Díaz-García, and R. Gómez, “Simultaneous electrocatalytic CO₂ reduction and enhanced electrochromic effect at WO₃ nanostructured electrodes in acetonitrile,” *ACS Catal.*, vol. 8, no. 3, pp. 1903–1912, 2018.
- [247] H. Wang *et al.*, “Synergistic enhancement of electrocatalytic CO₂ reduction to C₂ oxygenates at nitrogen-doped nanodiamonds/Cu interface,” *Nat. Nanotechnol.*, vol. 15, doi: 10.1038/s41565-019-0603-y.
- [248] D. Le Tri Nguyen *et al.*, “Mass Transport Control by Surface Graphene Oxide for Selective CO Production from Electrochemical CO₂ Reduction,” 2020, doi: 10.1021/acscatal.9b05096.
- [249] H. Lv *et al.*, “Single-Crystalline Mesoporous Palladium and Palladium-Copper Nanocubes for Highly Efficient Electrochemical CO₂ Reduction,” *CCS Chem.*, vol. 4, no. 4, pp. 1376–1385, 2022.
- [250] A. Klinkova *et al.*, “Rational Design of Efficient Palladium Catalysts for Electroreduction of Carbon Dioxide to Formate,” 2016, doi: 10.1021/acscatal.6b01719.
- [251] B. M. Tackett, J. H. Lee, and J. G. Chen, “Electrochemical Conversion of CO₂ to Syngas with Palladium-Based Electrocatalysts,” *Acc. Chem. Res.*, vol. 2020, p. 50, 2022, doi:

- 10.1021/acs.accounts.0c00277.
- [252] Y. Zhao *et al.*, “Surface Reconstruction of Ultrathin Palladium Nanosheets during Electrocatalytic CO₂ Reduction,” vol. 132, pp. 21677–21682, 2020, doi: 10.1002/anie.202009616.
- [253] Q. Yu *et al.*, “Morphology controlling of silver by plasma engineering for electrocatalytic carbon dioxide reduction,” *J. Power Sources*, vol. 453, p. 227846, Mar. 2020, doi: 10.1016/J.JPOWSOUR.2020.227846.
- [254] H. Mistry *et al.*, “CO₂ Electroreduction Hot Paper Enhanced Carbon Dioxide Electroreduction to Carbon Monoxide over Defect-Rich Plasma-Activated Silver Catalysts”, doi: 10.1002/anie.201704613.
- [255] T. an *et al.*, “Electrochemically Driven Formation of Sponge-Like Porous Silver Nanocubes Toward Efficient CO₂ Electroreduction to CO”, doi: 10.1002/cssc.201903558.
- [256] M. Yang *et al.*, “Facet Sensitivity of Capping Ligand-Free Ag Crystals in CO₂ Electrochemical Reduction to CO,” *ChemCatChem*, vol. 10, pp. 5128–5134, 2018, doi: 10.1002/cctc.201801423.
- [257] C.-Y. Lee, Y. Zhao, C. Wang, D. R. G. Mitchell, and G. G. Wallace, “Rapid formation of self-organised Ag nanosheets with high efficiency and selectivity in CO₂ electroreduction to CO † Sustainable Energy & Fuels COMMUNICATION,” vol. 1, pp. 1023–1027, 2017, doi: 10.1039/c7se00069c.
- [258] J. Y. Park, W. J. Dong, and J.-L. Lee, “Monolithic Cl-Modified Nanoporous Ag Nanowires for Electrochemical CO₂ Reduction to CO,” *Cite This ACS Appl. Energy Mater*, vol. 2022, pp. 1627–1634, 2022, doi: 10.1021/acsaem.1c03043.
- [259] S.-Q. Liu, S.-W. Wu, M.-R. Gao, M.-S. Li, X.-Z. Fu, and J.-L. Luo, “Hollow Porous Ag Spherical Catalysts for Highly Efficient and Selective Electrocatalytic Reduction of CO₂ to CO,” vol. 7, 2019, doi: 10.1021/acssuschemeng.9b01635.
- [260] Y. Xiong *et al.*, “Rapid synthesis of amorphous bimetallic copper-bismuth electrocatalysts for efficient electrochemical CO₂ reduction to formate in a wide potential window,” *J. CO₂ Util.*, vol. 51, p. 101621, Sep. 2021, doi: 10.1016/J.JCOU.2021.101621.
- [261] W. Ju *et al.*, “Sn-Decorated Cu for Selective Electrochemical CO₂ to CO Conversion: Precision Architecture beyond Composition Design,” 2018, doi: 10.1021/acsaem.8b01944.
- [262] C. Jong Yoo *et al.*, “Compositional and Geometrical Effects of Bimetallic Cu–Sn Catalysts on Selective Electrochemical CO₂ Reduction to CO,” 2020, doi: 10.1021/acsaem.0c00157.
- [263] Z. Zhang *et al.*, “‘Two Ships in a Bottle’ Design for Zn–Ag–O Catalyst Enabling Selective and Long-Lasting CO₂ Electroreduction,” *Cite This J. Am. Chem. Soc*, vol. 143, pp. 6855–6864, 2021, doi: 10.1021/jacs.0c12418.
- [264] N. Gao *et al.*, “Intercalated Gold Nanoparticle in 2D Palladium Nanosheet Avoiding CO Poisoning for Formate Production under a Wide Potential Window,” *Cite This ACS Appl. Mater. Interfaces*, vol. 14, pp. 10344–10352, 2022, doi: 10.1021/acsami.1c23430.
- [265] T. J. Wang, W. S. Fang, Y. M. Liu, F. M. Li, P. Chen, and Y. Chen, “Heterostructured

- Pd/PdO nanowires for selective and efficient CO₂ electroreduction to CO,” *J. Energy Chem.*, vol. 70, pp. 407–413, Jul. 2022, doi: 10.1016/J.JECHEM.2022.03.001.
- [266] S. Ma, P. Su, W. Huang, S. P. Jiang, S. Bai, and J. Liu, “Atomic Ni species anchored N-doped carbon hollow spheres as nanoreactors for efficient electrochemical CO₂ reduction,” *ChemCatChem*, vol. 11, no. 24, pp. 6092–6098, 2019.
- [267] S. Nitopi *et al.*, “Progress and Perspectives of Electrochemical CO₂ Reduction on Copper in Aqueous Electrolyte,” 2019, doi: 10.1021/acs.chemrev.8b00705.
- [268] D. Karapinar, C. E. Creissen, G. Rivera De La Cruz, M. W. Schreiber, and M. Fontecave, “Electrochemical CO₂ Reduction to Ethanol with Copper-Based Catalysts,” 2021, doi: 10.1021/acsenerylett.0c02610.
- [269] X. Jiang *et al.*, “Oxidation State Modulation of Bimetallic Tin-Copper Oxide Nanotubes for Selective CO₂ Electroreduction to Formate,” *Small*, vol. 18, no. 47, p. 2204148, 2022.
- [270] L. Mandal *et al.*, “Investigating the Role of Copper Oxide in Electrochemical CO₂ Reduction in Real Time,” 2018, doi: 10.1021/acsami.7b15418.
- [271] K. Klingan *et al.*, “Reactivity Determinants in Electrodeposited Cu Foams for Electrochemical CO₂ Reduction,” doi: 10.1002/cssc.201801582.
- [272] G. O. Larrazábal, V. Okatenko, I. Chorkendorff, R. Buonsanti, and B. Seger, “Investigation of Ethylene and Propylene Production from CO₂ Reduction over Copper Nanocubes in an MEA-Type Electrolyzer,” *Cite This ACS Appl. Mater. Interfaces*, vol. 14, pp. 7779–7787, 2022, doi: 10.1021/acsami.1c18856.
- [273] K. R. Phillips, Y. Katayama, J. Hwang, and Y. Shao-Horn, “Sulfide-Derived Copper for Electrochemical Conversion of CO₂ to Formic Acid,” 2018, doi: 10.1021/acs.jpcllett.8b01601.
- [274] T.-C. Chou *et al.*, “Controlling the Oxidation State of the Cu Electrode and Reaction Intermediates for Electrochemical CO₂ Reduction to Ethylene,” *J. Am. Chem. Soc.*, vol. 142, pp. 2857–2867, 2020, doi: 10.1021/jacs.9b11126.
- [275] T. Inomata, H. Yamaguchi, M. Ito, and H. Masuda, “Role of a Hydroxide Layer on Cu Electrodes in Electrochemical CO₂ Reduction,” 2019, doi: 10.1021/acscatal.9b00896.
- [276] J. Huang, T. Yang, K. Zhao, S. Chen, Q. Huang, and Y. Han, “Copper-comprising nanocrystals as well-defined electrocatalysts to advance electrochemical CO₂ reduction,” *J. Energy Chem.*, vol. 62, pp. 71–102, Nov. 2021, doi: 10.1016/J.JECHEM.2021.03.009.
- [277] J. W. Lim, W. J. Dong, J. Y. Park, M. Hong, and J.-L. Lee, “Spontaneously Formed CuS x Catalysts for Selective and Stable Electrochemical Reduction of Industrial CO₂ Gas to Formate,” *Cite This ACS Appl. Mater. Interfaces*, vol. 12, 2020, doi: 10.1021/acsami.0c03606.
- [278] Y. J. Hwang *et al.*, “Materials Chemistry A Materials for energy and sustainability rsc.li/materials-a Controlling the C₂⁺ product selectivity of electrochemical CO₂ reduction on an electrosprayed Cu catalyst Controlling the C₂⁺ product selectivity of electrochemical CO₂ reduction on an electrosprayed Cu catalyst †,” 2020, doi: 10.1039/c9ta13173f.
- [279] C. Zhu *et al.*, “Enhanced electrochemical CO₂-to-C₂⁺ conversion from synergistic

- interaction between terrace and step sites on monocrystalline high-index Cu facets,” *J. Energy Chem.*, vol. 70, pp. 382–387, Jul. 2022, doi: 10.1016/J.JECHEM.2022.02.027.
- [280] Z. Chen *et al.*, “Mechanically induced Cu active sites for selective C-C coupling in CO₂ electroreduction,” *J. Energy Chem.*, vol. 74, pp. 198–202, Nov. 2022, doi: 10.1016/J.JECHEM.2022.07.011.
- [281] F. Ying *et al.*, “Highly active and stable stepped Cu surface for enhanced electrochemical CO₂ reduction to C₂H₄,” *Nat. Catal.*, 1929, doi: 10.1038/s41929-020-00504-x.
- [282] I. Hjorth *et al.*, “Electrochemical syngas production from CO₂ and water with CNT supported ZnO catalysts,” *Catal. Today*, vol. 364, pp. 172–181, Mar. 2021, doi: 10.1016/J.CATTOD.2020.03.055.
- [283] J. Wang *et al.*, “Hydrogen-Mediated Synthesis of 3D Hierarchical Porous Zinc Catalyst for CO₂ Electroreduction with High Current Density,” *J. Phys. Chem. C*, vol. 125, 2021, doi: 10.1021/acs.jpcc.1c07498.
- [284] Y. Lu, B. Han, C. Tian, J. Wu, D. Geng, and D. Wang, “Efficient electrocatalytic reduction of CO₂ to CO on an electrodeposited Zn porous network,” *Electrochem. commun.*, vol. 97, pp. 87–90, Dec. 2018, doi: 10.1016/J.ELECOM.2018.11.002.
- [285] H. S. Jeon *et al.*, “Operando Evolution of the Structure and Oxidation State of Size-Controlled Zn Nanoparticles during CO₂ Electroreduction,” *J. Am. Chem. Soc.*, vol. 140, p. 10, 2018, doi: 10.1021/jacs.8b05258.
- [286] M. A. O. Lourenç *et al.*, “Biochar/Zinc Oxide Composites as Effective Catalysts for Electrochemical CO₂ Reduction,” 2021, doi: 10.1021/acssuschemeng.1c00837.
- [287] H. S. Jeon *et al.*, “Operando Insight into the Correlation between the Structure and Composition of CuZn Nanoparticles and Their Selectivity for the Electrochemical CO₂ Reduction,” 2019, doi: 10.1021/jacs.9b10709.
- [288] C. Zhang *et al.*, “Emerging interstitial/substitutional modification of Pd-based nanomaterials with nonmetallic elements for electrocatalytic applications,” *Nanoscale*, vol. 14, no. 8, pp. 2915–2942, 2022.
- [289] D. Gao, H. Zhou, F. Cai, J. Wang, G. Wang, and X. Bao, “Pd-Containing Nanostructures for Electrochemical CO₂ Reduction Reaction,” 2018, doi: 10.1021/acscatal.7b03612.
- [290] B. Xu, Y. Zhang, L. Li, Q. Shao, and X. Huang, “Recent progress in low-dimensional palladium-based nanostructures for electrocatalysis and beyond,” *Coord. Chem. Rev.*, vol. 459, p. 214388, May 2022, doi: 10.1016/J.CCR.2021.214388.
- [291] Y. Wang *et al.*, “Ligand and temperature effects of porous palladium nanoparticle ensembles with grain boundaries for highly efficient electrocatalytic CO₂ reduction Energy materials”, doi: 10.1007/s10853-022-07107-w.
- [292] H. Tao *et al.*, “Doping palladium with tellurium for the highly selective electrocatalytic reduction of aqueous CO₂ to CO †,” 2018, doi: 10.1039/c7sc03018e.
- [293] Q. He *et al.*, “Accelerating CO₂ Electroreduction to CO Over Pd Single-Atom Catalyst,” 2020, doi: 10.1002/adfm.202000407.
- [294] D. Gao *et al.*, “Enhancing CO₂ Electroreduction with the Metal–Oxide Interface,” 2017,

doi: 10.1021/jacs.7b00102.

- [295] Y. Yoon, A. Shoji Hall, Y. Surendranath, Y. Yoon, A. S. Hall, and Y. Surendranath, "Tuning of Silver Catalyst Mesostructure Promotes Selective Carbon Dioxide Conversion into Fuels", doi: 10.1002/ange.201607942.
- [296] H.-K. Lim *et al.*, "Embedding Covalency into Metal Catalysts for Efficient Electrochemical Conversion of CO₂," *J. Am. Chem. Soc.*, vol. 136, pp. 11355–11361, 2014, doi: 10.1021/ja503782w.
- [297] M. Ma, K. Liu, J. Shen, R. Kas, and W. A. Smith, "In Situ Fabrication and Reactivation of Highly Selective and Stable Ag Catalysts for Electrochemical CO₂ Conversion," *ACS Energy Lett.*, vol. 3, p. 59, 2018, doi: 10.1021/acsenerylett.8b00472.
- [298] Y. Chen *et al.*, "In situ construction of thiol-silver interface for selectively electrocatalytic CO₂ reduction", doi: 10.1007/s12274-021-3978-7.
- [299] X. Peng, S. G. Karakalos, and W. E. Mustain, "Preferentially Oriented Ag Nanocrystals with Extremely High Activity and Faradaic Efficiency for CO₂ Electrochemical Reduction to CO," 2017, doi: 10.1021/acsami.7b16164.
- [300] S. Liu *et al.*, "Shape-Dependent Electrocatalytic Reduction of CO₂ to CO on Triangular Silver Nanoplates," *J. Am. Chem. Soc.*, vol. 139, p. 47, 2017, doi: 10.1021/jacs.6b12103.
- [301] L. Wei *et al.*, "Thiocyanate-Modified Silver Nanofoam for Efficient CO₂ Reduction to CO," 2019, doi: 10.1021/acscatal.9b04633.
- [302] K. Chen, X. Zhang, T. Williams, L. Bourgeois, and D. R. MacFarlane, "Electrochemical reduction of CO₂ on core-shell Cu/Au nanostructure arrays for syngas production," *Electrochim. Acta*, vol. 239, pp. 84–89, Jun. 2017, doi: 10.1016/J.ELECTACTA.2017.04.019.
- [303] J. Ge *et al.*, "Vertical Silver@Silver Chloride Core–Shell Nanowire Array for Carbon Dioxide Electroreduction," *Cite This ACS Appl. Energy Mater.*, vol. 2, pp. 6163–6169, 2019, doi: 10.1021/acsaem.9b01286.
- [304] C. Han *et al.*, "Site-selected synthesis of novel Ag@AgCl nanoframes with efficient visible light induced photocatalytic activity," 2014, doi: 10.1039/c4ta01941e.
- [305] R. G. Mariano, K. McKelvey, H. S. White, and M. W. Kanan, "Selective increase in CO₂ electroreduction activity at grain-boundary surface terminations," *Science (80-.)*, vol. 358, no. 6367, pp. 1187–1192, 2017.
- [306] Z. Wang *et al.*, "Hydrophobically made Ag nanoclusters with enhanced performance for CO₂ aqueous electroreduction," *J. Power Sources*, vol. 476, p. 228705, Nov. 2020, doi: 10.1016/J.JPOWSOUR.2020.228705.
- [307] M. Ma, K. Liu, J. Shen, R. Kas, and W. A. Smith, "In Situ Fabrication and Reactivation of Highly Selective and Stable Ag Catalysts for Electrochemical CO₂ Conversion," *ACS Energy Lett.*, vol. 3, no. 6, pp. 1301–1306, Jun. 2018, doi: 10.1021/ACSENERGYLETT.8B00472/SUPPL_FILE/NZ8B00472_SI_001.PDF.
- [308] P. L. Cheung, S. C. Kapper, T. Zeng, M. E. Thompson, and C. P. Kubiak, "Improving photocatalysis for the reduction of CO₂ through non-covalent supramolecular assembly," *J. Am. Chem. Soc.*, vol. 141, no. 38, pp. 14961–14965, 2019.

- [309] N. M. Orchanian, L. E. Hong, J. A. Skrainka, J. A. Esterhuizen, D. A. Popov, and S. C. Marinescu, "Surface-immobilized conjugated polymers incorporating rhenium bipyridine motifs for electrocatalytic and photocatalytic CO₂ reduction," *ACS Appl. Energy Mater.*, vol. 2, no. 1, pp. 110–123, 2018.
- [310] S. Tan, B. M. Tackett, Q. He, J. H. Lee, J. G. Chen, and S. S. Wong, "Synthesis and electrocatalytic applications of flower-like motifs and associated composites of nitrogen-enriched tungsten nitride (W₂N₃)," *Nano Res.*, vol. 13, no. 5, pp. 1434–1443, 2020.
- [311] X. Q. Han, N. Lin, M. Chen, Z. Y. Wang, Y. Tang, and C. Ma, "In situ synthesis of dicobalt phosphide on tungsten carbide-cobalt cemented carbide substrates as a hydrogen evolution reaction electrocatalyst," *Scr. Mater.*, vol. 204, p. 114159, 2021.
- [312] B. Zhang *et al.*, "Cobalt tungsten phosphide with tunable W-doping as highly efficient electrocatalysts for hydrogen evolution reaction," *Nano Res.*, vol. 14, no. 11, pp. 4073–4078, 2021.
- [313] M. Esmailirad *et al.*, "Gold-like activity copper-like selectivity of heteroatomic transition metal carbides for electrocatalytic carbon dioxide reduction reaction," *Nat. Commun.*, vol. 12, no. 1, pp. 1–10, 2021.
- [314] X. Li and J. A. Panetier, "Mechanistic Study of Tungsten Bipyridyl Tetracarbonyl Electrocatalysts for CO₂ Fixation: Exploring the Roles of Explicit Proton Sources and Substituent Effects," *Top. Catal.*, vol. 65, no. 1, pp. 325–340, 2022.
- [315] S. Wannakao, N. Artrith, J. Limtrakul, and A. M. Kolpak, "Catalytic activity and product selectivity trends for carbon dioxide electroreduction on transition metal-coated tungsten carbides," *J. Phys. Chem. C*, vol. 121, no. 37, pp. 20306–20314, 2017.
- [316] S. Ananthaneni, Z. Smith, and R. B. Rankin, "Graphene supported tungsten carbide as catalyst for electrochemical reduction of CO₂," *Catalysts*, vol. 9, no. 7, p. 604, 2019.
- [317] Y. Yang *et al.*, "The electrochemical performance and CO₂ reduction mechanism on strontium doped lanthanum ferrite fuel electrode in solid oxide electrolysis cell," *Electrochim. Acta*, vol. 284, pp. 159–167, 2018.
- [318] V. Singh, H. Muroyama, T. Matsui, S. Hashigami, T. Inagaki, and K. Eguchi, "Feasibility of alternative electrode materials for high temperature CO₂ reduction on solid oxide electrolysis cell," *J. Power Sources*, vol. 293, pp. 642–648, 2015.
- [319] G. Valderrama, A. Kiennemann, and M. R. Goldwasser, "La-Sr-Ni-Co-O based perovskite-type solid solutions as catalyst precursors in the CO₂ reforming of methane," *J. Power Sources*, vol. 195, no. 7, pp. 1765–1771, 2010.
- [320] D. J. Deka *et al.*, "Investigation of hetero-phases grown via in-situ exsolution on a Ni-doped (La, Sr) FeO₃ cathode and the resultant activity enhancement in CO₂ reduction," *Appl. Catal. B Environ.*, vol. 286, p. 119917, 2021.
- [321] Z. Liang, L. Song, M. Sun, B. Huang, and Y. Du, "Tunable CO/H₂ ratios of electrochemical reduction of CO₂ through the Zn-Ln dual atomic catalysts," *Sci. Adv.*, vol. 7, no. 47, p. eabl4915, 2021.
- [322] J. Wyndorps, H. Ostovari, and N. Von der Assen, "Is electrochemical CO₂ reduction the future technology for power-to-chemicals? An environmental comparison with H₂-based

- pathways,” *Sustain. Energy Fuels*, vol. 5, no. 22, pp. 5748–5761, 2021.
- [323] W. Luo, Q. Zhang, J. Zhang, E. Moiola, K. Zhao, and A. Züttel, “Electrochemical reconstruction of ZnO for selective reduction of CO₂ to CO,” *Appl. Catal. B Environ.*, vol. 273, p. 119060, 2020.
- [324] Y. Wang, N. Ma, Y. Zhang, B. Liang, and J. Fan, “Cu₄@C₂N for effective electrochemical CO₂ reduction and intermediates dependent adsorption behaviours: A computational study,” *Appl. Surf. Sci.*, vol. 626, p. 157126, Jul. 2023, doi: 10.1016/J.APSUSC.2023.157126.
- [325] S. S. A. Shah *et al.*, “Metal oxides for the electrocatalytic reduction of carbon dioxide: Mechanism of active sites, composites, interface and defect engineering strategies,” *Coord. Chem. Rev.*, vol. 471, p. 214716, Nov. 2022, doi: 10.1016/j.ccr.2022.214716.
- [326] W. Luo, J. Zhang, M. Li, and A. Züttel, “Boosting CO production in electrocatalytic CO₂ reduction on highly porous Zn catalysts,” *ACS Catal.*, vol. 9, no. 5, pp. 3783–3791, 2019.
- [327] D. H. Won *et al.*, “Highly efficient, selective, and stable CO₂ electroreduction on a hexagonal Zn catalyst,” *Angew. Chemie*, vol. 128, no. 32, pp. 9443–9446, 2016.
- [328] J. Rosen, G. S. Hutchings, Q. Lu, R. V Forest, A. Moore, and F. Jiao, “Electrodeposited Zn dendrites with enhanced CO selectivity for electrocatalytic CO₂ reduction,” *Acs Catal.*, vol. 5, no. 8, pp. 4586–4591, 2015.
- [329] X. Jiang *et al.*, “Electrocatalytic reduction of carbon dioxide over reduced nanoporous zinc oxide,” *Electrochem. commun.*, vol. 68, pp. 67–70, 2016.
- [330] D. L. T. Nguyen, M. S. Jee, H.-S. Oh, B. K. Min, and Y. J. Hwang, “Effect of halides on nanoporous Zn-based catalysts for highly efficient electroreduction of CO₂ to CO,” *Catal. Commun.*, vol. 114, pp. 109–113, 2018.
- [331] T. Zhang *et al.*, “Multilayered Zn nanosheets as an electrocatalyst for efficient electrochemical reduction of CO₂,” *J. Catal.*, vol. 357, pp. 154–162, 2018.
- [332] H. F. McMurdie *et al.*, “Standard X-ray diffraction powder patterns from the JCPDS research associateship,” *Powder Diff.*, vol. 1, no. 2, pp. 64–77, 1986.
- [333] E. Velayi and R. Norouzbeigi, “Robust superhydrophobic needle-like nanostructured ZnO surfaces prepared without post chemical-treatment,” *Appl. Surf. Sci.*, vol. 426, pp. 674–687, Dec. 2017, doi: 10.1016/J.APSUSC.2017.07.216.
- [334] S. F. Wei, J. S. Lian, and Q. Jiang, “Controlling growth of ZnO rods by polyvinylpyrrolidone (PVP) and their optical properties,” *Appl. Surf. Sci.*, vol. 255, no. 15, pp. 6978–6984, May 2009, doi: 10.1016/J.APSUSC.2009.03.023.
- [335] T. Chankhanittha, J. Watcharakitti, and S. Nanan, “PVP-assisted synthesis of rod-like ZnO photocatalyst for photodegradation of reactive red (RR141) and Congo red (CR) azo dyes,” *J. Mater. Sci. Mater. Electron.*, vol. 30, pp. 17804–17819, 2019.
- [336] S. J. Chen *et al.*, “Structural and optical properties of uniform ZnO nanosheets,” *Adv. Mater.*, vol. 17, no. 5, pp. 586–590, 2005.
- [337] R. Cuscó *et al.*, “Temperature dependence of Raman scattering in ZnO ,” *Phys. Rev. B*, vol. 75, no. 16, p. 165202, Apr. 2007, doi: 10.1103/PhysRevB.75.165202.

- [338] D. Ren, B. S.-H. Ang, and B. S. Yeo, "Tuning the selectivity of carbon dioxide electroreduction toward ethanol on oxide-derived Cu x Zn catalysts," *Acs Catal.*, vol. 6, no. 12, pp. 8239–8247, 2016.
- [339] M. J. Isaacson, F. R. McLarnon, and E. J. Cairns, "Current Density and ZnO Precipitation-Dissolution Distributions in Zn-ZnO Porous Electrodes and Their Effect on Material Redistribution: A Two-Dimensional Mathematical Model," *J. Electrochem. Soc.*, vol. 137, no. 7, p. 2014, 1990.
- [340] M. Michaelis, C. Fischer, L. Colombi Ciacchi, and A. Luttge, "Variability of zinc oxide dissolution rates," *Environ. Sci. Technol.*, vol. 51, no. 8, pp. 4297–4305, 2017.
- [341] C. M. López and K.-S. Choi, "Electrochemical synthesis of dendritic zinc films composed of systematically varying motif crystals," *Langmuir*, vol. 22, no. 25, pp. 10625–10629, 2006.
- [342] D. Esrafilzadeh *et al.*, "Room temperature CO₂ reduction to solid carbon species on liquid metals featuring atomically thin ceria interfaces," *Nat. Commun.*, vol. 10, no. 1, Dec. 2019, doi: 10.1038/S41467-019-08824-8.
- [343] X.-L. Chen, L.-S. Ma, W.-Y. Su, L.-F. Ding, H.-B. Zhu, and H. Yang, "ZIF-derived bifunctional Cu@Cu–N–C composite electrocatalysts towards efficient electroreduction of oxygen and carbon dioxide," *Electrochim. Acta*, vol. 331, p. 135273, 2020, doi: <https://doi.org/10.1016/j.electacta.2019.135273>.
- [344] Z. Lian, L. Huimin, and Y. Lisha, "Microwave ionothermal synthesis of ZIF-61 and its application on the curing process of cyanate ester (CE)," *Mater. Lett.*, vol. 125, pp. 59–62, 2014, doi: <https://doi.org/10.1016/j.matlet.2014.03.148>.
- [345] B. Chen, Z. Yang, Y. Zhu, and Y. Xia, "Zeolitic imidazolate framework materials: recent progress in synthesis and applications," *J. Mater. Chem. A*, vol. 2, no. 40, pp. 16811–16831, 2014, doi: 10.1039/C4TA02984D.
- [346] C. Duan, Y. Yu, F. Li, Y. Wu, and H. Xi, "Ultrafast room-temperature synthesis of hierarchically porous metal–organic frameworks with high space–time yields," *CrystEngComm*, vol. 22, no. 15, pp. 2675–2680, 2020, doi: 10.1039/C9CE01676G.
- [347] S. Ackermann, L. Sauvin, R. Castiglioni, J. L. M. Rupp, J. R. Scheffe, and A. Steinfeld, "Kinetics of CO₂ Reduction over Nonstoichiometric Ceria," 2015, doi: 10.1021/acs.jpcc.5b03464.
- [348] S. Omar, E. D. Wachsman, J. L. Jones, and J. C. Nino, "Crystal Structure-Ionic Conductivity Relationships in Doped Ceria Systems", doi: 10.1111/j.1551-2916.2009.03273.x.
- [349] C. B. Gopal and S. M. Haile, "An electrical conductivity relaxation study of oxygen transport in samarium doped ceria," 2014, doi: 10.1039/c3ta13404k.
- [350] W. C. Chueh and S. M. Haile, "A thermochemical study of ceria: exploiting an old material for new modes of energy conversion and CO₂ mitigation," *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.*, vol. 368, no. 1923, pp. 3269–3294, 2010.
- [351] J. R. Scheffe and A. Steinfeld, "Thermodynamic Analysis of Cerium-Based Oxides for Solar Thermochemical Fuel Production," 2012, doi: 10.1021/ef201875v.

- [352] R. Yu *et al.*, “CeO_x Promoted Electrocatalytic CO₂ Reduction to Formate by Assisting in the Critical Hydrogenation Step,” *ACS Mater. Lett.*, vol. 2022, pp. 1749–1755, 2022, doi: 10.1021/acsmaterialslett.2c00512.
- [353] S. Lee, M. Kim, K. Taek Lee, J. T. S Irvine, and T. Ho Shin, “Enhancing Electrochemical CO₂ Reduction using Ce(Mn,Fe)O₂ with La(Sr)Cr(Mn)O₃ Cathode for High-Temperature Solid Oxide Electrolysis Cells,” 2021, doi: 10.1002/aenm.202100339.
- [354] J. Wang *et al.*, “Catalytic CeO₂ washcoat over microchanneled supporting cathodes of solid oxide electrolysis cells for efficient and stable CO₂ reduction,” *J. Power Sources*, vol. 412, pp. 344–349, Feb. 2019, doi: 10.1016/J.JPOWSOUR.2018.11.050.
- [355] W. eng *et al.*, “Platinum-Decorated Ceria Enhances CO₂ Electroreduction in Solid Oxide Electrolysis Cells,” doi: 10.1002/cssc.202001002.
- [356] Z. Zhao, X. Li, J. Wang, X. Lv, and H. Bin Wu, “CeO₂-modified Cu electrode for efficient CO₂ electroreduction to multi-carbon products,” *J. CO₂ Util.*, vol. 54, p. 101741, Dec. 2021, doi: 10.1016/J.JCOU.2021.101741.
- [357] T. Wu, T. Vegge, and H. A. Hansen, “Enhanced activity for electrocatalytic H₂ production through cooperative Pr and Bi co-doping of CeO₂ in solid oxide electrolysis cells,” *J. Catal.*, vol. 402, pp. 310–314, Oct. 2021, doi: 10.1016/J.JCAT.2021.08.045.
- [358] S. M. Cheng and M. Cheng, “As featured in: Showcasing research from the Solid Oxide Fuel Cell Group of Prof,” *Chem. Commun.*, p. 777, 2013, doi: 10.1039/c2cc37007g.
- [359] Z. Huang, Z. Zhao, H. Qi, X. Wang, B. Tu, and M. Cheng, “Enhancing cathode performance for CO₂ electrolysis with Ce_{0.9}Mn_{0.1}O_{2-δ} (M=Fe, Co, Ni) catalysts in solid oxide electrolysis cell,” *J. Energy Chem.*, vol. 40, pp. 46–51, Jan. 2020, doi: 10.1016/J.JECHEM.2019.02.007.
- [360] X. Zhang *et al.*, “Enhancing electrocatalytic CO₂ reduction in solid oxide electrolysis cell with Ce_{0.9}Mn_{0.1}O_{2-δ} nanoparticles-modified LSCM-GDC cathode,” *J. Catal.*, vol. 359, pp. 8–16, Mar. 2018, doi: 10.1016/J.JCAT.2017.12.027.
- [361] Y. Zhou, F. Wei, and H. Wu, “Fe-decorated on Sm-doped CeO₂ as cathodes for high-temperature CO₂ electrolysis in solid oxide electrolysis cells,” *Electrochim. Acta*, vol. 419, p. 140434, Jul. 2022, doi: 10.1016/J.ELECTACTA.2022.140434.
- [362] A. M. Bumstead, M. F. Thorne, A. F. Sapnik, C. Castillo-Blas, G. I. Lampronti, and T. D. Bennett, “Investigating the chemical sensitivity of melting in zeolitic imidazolate frameworks,” *Dalt. Trans.*, vol. 51, no. 36, pp. 13636–13645, 2022, doi: 10.1039/D2DT02142K.
- [363] D. Tocco *et al.*, “Conformational changes and location of BSA upon immobilization on zeolitic imidazolate frameworks,” *J. Colloid Interface Sci.*, vol. 641, pp. 685–694, 2023.
- [364] R. Banerjee *et al.*, “High-throughput synthesis of zeolitic imidazolate frameworks and application to CO₂ capture,” *Science (80-.)*, vol. 319, no. 5865, pp. 939–943, 2008.
- [365] D. Huang *et al.*, “Synergistic effects of zeolite imidazole framework@ graphene oxide composites in humidified mixed matrix membranes on CO₂ separation,” *RSC Adv.*, vol. 8, no. 11, pp. 6099–6109, 2018.
- [366] D. Tocco *et al.*, “Enzyme immobilization on metal organic frameworks: Laccase from

- Aspergillus sp. is better adapted to ZIF-zni rather than Fe-BTC,” *Colloids Surfaces B Biointerfaces*, vol. 208, p. 112147, 2021, doi: <https://doi.org/10.1016/j.colsurfb.2021.112147>.
- [367] M. Mukhtar Sirati *et al.*, “Single-step hydrothermal synthesis of amine functionalized Ce-MOF for electrochemical water splitting,” vol. 16, no. 1, pp. 525–534, 2022, doi: 10.1080/16583655.2022.2079310.
- [368] R. Jain, A. S. Poyraz, D. P. Gamliel, J. Valla, S. L. Suib, and R. Maric, “Comparative study for low temperature water-gas shift reaction on Pt/ceria catalysts: Role of different ceria supports,” *Appl. Catal. A Gen.*, vol. 507, pp. 1–13, 2015.
- [369] L. Wang, F. Meng, K. Li, and F. Lu, “Characterization and optical properties of pole-like nano-CeO₂ synthesized by a facile hydrothermal method,” *Appl. Surf. Sci.*, vol. 286, pp. 269–274, 2013.
- [370] H. Li, F. Meng, J. Gong, Z. Fan, and R. Qin, “Structural, morphological and optical properties of shuttle-like CeO₂ synthesized by a facile hydrothermal method,” *J. Alloys Compd.*, vol. 722, pp. 489–498, 2017.
- [371] J. Gong, F. Meng, X. Yang, Z. Fan, and H. Li, “Controlled hydrothermal synthesis of triangular CeO₂ nanosheets and their formation mechanism and optical properties,” *J. Alloys Compd.*, vol. 689, pp. 606–616, 2016.
- [372] X. Ren *et al.*, “Oxygen vacancy enhancing CO₂ electrochemical reduction to CO on Ce-doped ZnO catalysts,” *Surfaces and Interfaces*, vol. 23, p. 100923, Apr. 2021, doi: 10.1016/J.SURFIN.2020.100923.
- [373] Y. Zhang, C. Chen, Q.-H. Zheng, Z.-K. Guo, B.-X. Dong, and Y.-L. Teng, “S-Doped NiII-Triazolate Derived Ni–S–C Catalyst for Electrochemical CO₂ Reduction to CO,” *ACS Appl. Energy Mater.*, 2022.
- [374] Z. Yang, F. E. Oropeza, and K. H. L. Zhang, “P-block metal-based (Sn, In, Bi, Pb) electrocatalysts for selective reduction of CO₂ to formate,” *APL Mater.*, vol. 8, no. 6, p. 60901, 2020.
- [375] M. C. Figueiredo, I. Ledezma-Yanez, and M. T. M. Koper, “In Situ Spectroscopic Study of CO₂ Electroreduction at Copper Electrodes in Acetonitrile,” *ACS Catal.*, vol. 6, no. 4, pp. 2382–2392, Mar. 2016, doi: 10.1021/acscatal.5b02543.
- [376] Q. H. Low, N. W. X. Loo, F. Calle-Vallejo, and B. S. Yeo, “Enhanced electroreduction of carbon dioxide to methanol using zinc dendrites pulse-deposited on silver foam,” *Angew. Chemie Int. Ed.*, vol. 58, no. 8, pp. 2256–2260, 2019.
- [377] S. Chu and A. Majumdar, “Opportunities and challenges for a sustainable energy future,” *Nature*, vol. 488, no. 7411, pp. 294–303, 2012.
- [378] R. He *et al.*, “Achieving the widest range of syngas proportions at high current density over cadmium sulfoselenide nanorods in CO₂ electroreduction,” *Adv. Mater.*, vol. 30, no. 7, p. 1705872, 2018.
- [379] E. Ruiz-López, J. Gandara-Loe, F. Baena-Moreno, T. R. Reina, and J. A. Odriozola, “Electrocatalytic CO₂ conversion to C₂ products: Catalysts design, market perspectives and techno-economic aspects,” *Renew. Sustain. Energy Rev.*, vol. 161, p. 112329, Jun.

2022, doi: 10.1016/J.RSER.2022.112329.

- [380] Y. Wang, C. Niu, Y. Zhu, D. He, and W. Huang, "Tunable Syngas Formation from Electrochemical CO₂ Reduction on Copper Nanowire Arrays," *ACS Appl. Energy Mater.*, vol. 3, no. 10, pp. 9841–9847, Sep. 2020, doi: 10.1021/acsaem.0c01504.
- [381] S. Hernández, M. Amin Farkhondeh, F. Sastre, M. Makkee, G. Saracco, and N. Russo, "Syngas production from electrochemical reduction of CO₂: current status and prospective implementation," vol. 19, p. 2326, 2017, doi: 10.1039/c7gc00398f.
- [382] D. Kim, J. Resasco, Y. Yu, A. M. Asiri, and P. Yang, "Synergistic geometric and electronic effects for electrochemical reduction of carbon dioxide using gold–copper bimetallic nanoparticles," *Nat. Commun.*, vol. 5, no. 1, p. 4948, 2014.
- [383] P. Saha, S. Amanullah, and A. Dey, "Selectivity in Electrochemical CO₂ Reduction," *Acc. Chem. Res.*, vol. 55, no. 2, pp. 134–144, Jan. 2022, doi: 10.1021/acs.accounts.1c00678.
- [384] Q. Li *et al.*, "Tuning Sn-Catalysis for Electrochemical Reduction of CO₂ to CO via the Core/Shell Cu/SnO₂ Structure," *J. Am. Chem. Soc.*, vol. 139, no. 12, pp. 4290–4293, Mar. 2017, doi: 10.1021/jacs.7b00261.
- [385] X. Bai *et al.*, "Exclusive formation of formic acid from CO₂ electroreduction by a tunable Pd-Sn alloy," *Angew. Chemie*, vol. 129, no. 40, pp. 12387–12391, 2017.
- [386] H. Yang *et al.*, "Selective CO₂ reduction on 2D mesoporous Bi nanosheets," *Adv. Energy Mater.*, vol. 8, no. 35, p. 1801536, 2018.
- [387] D. Johnson, Z. Qiao, and A. Djire, "Progress and Challenges of Carbon Dioxide Reduction Reaction on Transition Metal Based Electrocatalysts," *ACS Appl. Energy Mater.*, vol. 4, no. 9, pp. 8661–8684, Aug. 2021, doi: 10.1021/acsaem.1c01624.
- [388] R. L. MacHunda, H. Ju, and J. Lee, "Electrocatalytic reduction of CO₂ gas at Sn based gas diffusion electrode," *Curr. Appl. Phys.*, vol. 11, no. 4, pp. 986–988, Jul. 2011, doi: 10.1016/J.CAP.2011.01.003.
- [389] Y. Kwon and J. Lee, "Formic acid from carbon dioxide on nanolayered electrocatalyst," *Electrocatalysis*, vol. 1, pp. 108–115, 2010.
- [390] Z. He *et al.*, "Electrochemically created roughened lead plate for electrochemical reduction of aqueous CO₂," *Catal. Commun.*, vol. 72, pp. 38–42, Dec. 2015, doi: 10.1016/J.CATCOM.2015.08.024.
- [391] Z. Xia *et al.*, "Highly selective electrochemical conversion of CO₂ to HCOOH on dendritic indium foams," *ChemElectroChem*, vol. 5, no. 2, pp. 253–259, 2018.
- [392] S. Wang, B. Yuan Guan, and X. Wen David Lou, "Construction of ZnIn₂S₄–In₂O₃ Hierarchical Tubular Heterostructures for Efficient CO₂ Photoreduction," *J. Am. Chem. Soc.*, vol. 140, no. 15, pp. 5037–5040, Mar. 2018, doi: 10.1021/jacs.8b02200.
- [393] X. Zhang, T. Lei, Y. Liu, and J. Qiao, "Enhancing CO₂ electrolysis to formate on facilely synthesized Bi catalysts at low overpotential," *Appl. Catal. B Environ.*, vol. 218, pp. 46–50, Dec. 2017, doi: 10.1016/J.APCATB.2017.06.032.
- [394] M. Tahir and N. A. S. Amin, "Indium-doped TiO₂ nanoparticles for photocatalytic CO₂ reduction with H₂O vapors to CH₄," *Appl. Catal. B Environ.*, vol. 162, pp. 98–109, Jan.

- 2015, doi: 10.1016/J.APCATB.2014.06.037.
- [395] Z. Zhang *et al.*, “Rational Design of Bi Nanoparticles for Efficient Electrochemical CO₂ Reduction: The Elucidation of Size and Surface Condition Effects,” *ACS Catal.*, vol. 6, no. 9, pp. 6255–6264, Aug. 2016, doi: 10.1021/acscatal.6b01297.
 - [396] Y. i Hori, “Electrochemical CO₂ reduction on metal electrodes,” *Mod. Asp. Electrochem.*, pp. 89–189, 2008.
 - [397] C. Ampelli *et al.*, “CO₂ capture and reduction to liquid fuels in a novel electrochemical setup by using metal-doped conjugated microporous polymers,” *J. Appl. Electrochem.*, vol. 45, pp. 701–713, 2015.
 - [398] J. García, C. Jiménez, F. Martínez, R. Camarillo, and J. Rincón, “Electrochemical reduction of CO₂ using Pb catalysts synthesized in supercritical medium,” *J. Catal.*, vol. 367, pp. 72–80, Nov. 2018, doi: 10.1016/J.JCAT.2018.08.017.
 - [399] D. Yang *et al.*, “Selective electroreduction of carbon dioxide to methanol on copper selenide nanocatalysts,” *Nat. Commun.*, vol. 10, no. 1, p. 677, 2019.
 - [400] A. R. Woldu, Z. Huang, P. Zhao, L. Hu, and D. Astruc, “Electrochemical CO₂ reduction (CO₂RR) to multi-carbon products over copper-based catalysts,” *Coord. Chem. Rev.*, vol. 454, p. 214340, Mar. 2022, doi: 10.1016/J.CCR.2021.214340.
 - [401] A. N. Ivanovskaya *et al.*, “Electrochemical roughening of thin-film platinum for neural probe arrays and biosensing applications,” *J. Electrochem. Soc.*, vol. 165, no. 12, p. G3125, 2018.
 - [402] C. Hoon Lee and M. W. Kanan, “Controlling H⁺ vs CO₂ Reduction Selectivity on Pb Electrodes,” *ACS Catal.*, vol. 5, no. 1, pp. 465–469, Dec. 2014, doi: 10.1021/cs5017672.
 - [403] P. Wang *et al.*, “Synergized Cu/Pb Core/Shell Electrocatalyst for High-Efficiency CO₂ Reduction to C₂⁺ Liquids,” *ACS Nano*, vol. 15, no. 1, pp. 1039–1047, Dec. 2021, doi: 10.1021/acsnano.0c07869.
 - [404] C. Xu Zhao, Y. Fan Bu, W. Gao, and Q. Jiang, “CO₂ Reduction Mechanism on the Pb(111) Surface: Effect of Solvent and Cations,” *J. Phys. Chem. C*, vol. 121, no. 36, pp. 19767–19773, Aug. 2017, doi: 10.1021/acs.jpcc.7b04375.
 - [405] B. Jiang, X.-G. Zhang, K. Jiang, D.-Y. Wu, and W.-B. Cai, “Boosting Formate Production in Electrocatalytic CO₂ Reduction over Wide Potential Window on Pd Surfaces,” *J. Am. Chem. Soc.*, vol. 140, no. 8, pp. 2880–2889, Feb. 2018, doi: 10.1021/jacs.7b12506.
 - [406] M. J. Frisch *et al.*, “Gaussian 09, Revision D. 01, 2009, Gaussian,” *Inc., Wallingford CT*, 2009.
 - [407] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, “A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu,” *J. Chem. Phys.*, vol. 132, no. 15, p. 154104, 2010.
 - [408] S. Grimme, S. Ehrlich, and L. Goerigk, “Effect of the damping function in dispersion corrected density functional theory,” *J. Comput. Chem.*, vol. 32, no. 7, pp. 1456–1465, 2011.
 - [409] P. Kumar *et al.*, “Alpha lead oxide (α -PbO): a new 2D material with visible light

sensitivity,” *Small*, vol. 14, no. 12, p. 1703346, 2018.

- [410] Y. K. Zeng, T. S. Zhao, X. L. Zhou, L. Wei, and Y. X. Ren, “A novel iron-lead redox flow battery for large-scale energy storage,” *J. Power Sources*, vol. 346, pp. 97–102, 2017.
- [411] D. T. Hofsommer, M. Gautam, S. S. Uttarwar, C. A. Grapperhaus, and J. M. Spurgeon, “Prolonged Stability of Pb-Catalyzed CO₂ Electroreduction to Methyl Formate in Acidic Methanol,” *ACS Appl. Energy Mater.*, vol. 6, no. 4, pp. 2624–2632, Feb. 2023, doi: 10.1021/acsaem.3c00166.
- [412] N. M. Thanh, N. D. Luyen, T. Thanh Tam Toan, N. Hai Phong, and N. Van Hop, “Voltammetry determination of Pb (II), Cd (II), and Zn (II) at bismuth film electrode combined with 8-hydroxyquinoline as a complexing agent,” *J. Anal. Methods Chem.*, vol. 2019, 2019.
- [413] X. Zhao *et al.*, “Highly Efficient Electrochemical CO₂ Reduction on a Precise Homonuclear Diatomic Fe–Fe Catalyst,” *ACS Catal.*, vol. 12, no. 18, pp. 11412–11420, 2022.
- [414] Y. Hori, H. Wakebe, T. Tsukamoto, and O. Koga, “Electrocatalytic process of CO selectivity in electrochemical reduction of CO₂ at metal electrodes in aqueous media,” *Electrochim. Acta*, vol. 39, no. 11–12, pp. 1833–1839, 1994, doi: 10.1016/0013-4686(94)85172-7.
- [415] J.-P. Jones, G. K. S. Prakash, and G. A. Olah, “Electrochemical CO₂ Reduction: Recent Advances and Current Trends,” *Isr. J. Chem.*, vol. 54, no. 10, pp. 1451–1466, Oct. 2014, doi: 10.1002/ijch.201400081.
- [416] G. M. Tomboc, S. Choi, T. Kwon, Y. J. Hwang, and K. Lee, “Potential link between Cu surface and selective CO₂ electroreduction: perspective on future electrocatalyst designs,” *Adv. Mater.*, vol. 32, no. 17, p. 1908398, 2020.
- [417] Z. Sun, T. Ma, H. Tao, Q. Fan, and B. Han, “Fundamentals and Challenges of Electrochemical CO₂ Reduction Using Two-Dimensional Materials,” *Chem*, vol. 3, no. 4, pp. 560–587, Oct. 2017, doi: 10.1016/j.chempr.2017.09.009.
- [418] B. Qin *et al.*, “Electrochemical Reduction of CO₂ into Tunable Syngas Production by Regulating the Crystal Facets of Earth-Abundant Zn Catalyst,” *ACS Appl. Mater. Interfaces*, vol. 10, no. 24, pp. 20530–20539, Jun. 2018, doi: 10.1021/acsaami.8b04809.
- [419] K. Jiang, H. Wang, W. Bin Cai, and H. Wang, “Li Electrochemical Tuning of Metal Oxide for Highly Selective CO₂ Reduction,” *ACS Nano*, vol. 11, no. 6, pp. 6451–6458, 2017, doi: 10.1021/acsnano.7b03029.
- [420] K. Liu, J. Wang, M. Shi, J. Yan, and Q. Jiang, “Simultaneous Achieving of High Faradaic Efficiency and CO Partial Current Density for CO₂ Reduction via Robust, Noble-Metal-Free Zn Nanosheets with Favorable Adsorption Energy,” *Adv. Energy Mater.*, vol. 9, no. 21, p. 1900276, Apr. 2019, doi: 10.1002/aenm.201900276.
- [421] M. Morimoto *et al.*, “Visualization of catalytic edge reactivity in electrochemical CO₂ reduction on porous Zn electrode,” *Electrochim. Acta*, vol. 290, pp. 255–261, Nov. 2018, doi: 10.1016/j.electacta.2018.09.080.
- [422] Z. Geng *et al.*, “Oxygen Vacancies in ZnO Nanosheets Enhance CO₂ Electrochemical

- Reduction to CO,” *Angew. Chemie - Int. Ed.*, vol. 57, no. 21, pp. 6054–6059, May 2018, doi: 10.1002/anie.201711255.
- [423] Z. Han *et al.*, “Tuning the Pd-catalyzed electroreduction of CO₂ to CO with reduced overpotential †,” *Cite this Catal. Sci. Technol*, vol. 8, p. 3894, 2018, doi: 10.1039/c8cy01037d.
- [424] L. Fu *et al.*, “Construction of Cr-embedded graphyne electrocatalyst for highly selective reduction of CO₂ to CH₄: A DFT study,” *Chem. Eng. J.*, vol. 414, p. 128857, 2021.
- [425] J. E. Pander, J. W. J. Lum, and B. S. Yeo, “The importance of morphology on the activity of lead cathodes for the reduction of carbon dioxide to formate,” *J. Mater. Chem. A*, vol. 7, no. 8, pp. 4093–4101, 2019.
- [426] W. Yu *et al.*, “Facile treatment tuning the morphology of Pb with state-of-the-art selectivity in CO₂ electroreduction to formate,” *Chem. Commun.*, vol. 57, no. 60, pp. 7418–7421, 2021.
- [427] N. Zhang *et al.*, “Charge-acquired Pb²⁺ boosts actively and selectively electrochemical carbon dioxide reduction reaction to formate,” *Appl. Catal. B Environ.*, vol. 326, p. 122404, Jun. 2023, doi: 10.1016/J.APCATB.2023.122404.
- [428] F. Köleli, T. Atilan, N. Palamut, A. M. Gizir, R. Aydin, and C. H. Hamann, “Electrochemical reduction of CO₂ at Pb-and Sn-electrodes in a fixed-bed reactor in aqueous K₂CO₃ and KHCO₃ media,” *J. Appl. Electrochem.*, vol. 33, pp. 447–450, 2003.
- [429] B. Innocent, D. Liaigre, D. Pasquier, F. Ropital, J.-M. Léger, and K. B. Kokoh, “Electroreduction of carbon dioxide to formate on lead electrode in aqueous medium,” *J. Appl. Electrochem.*, vol. 39, pp. 227–232, 2009.
- [430] C. H. Lee and M. W. Kanan, “Controlling H⁺ vs CO₂ reduction selectivity on Pb electrodes,” *Acs Catal.*, vol. 5, no. 1, pp. 465–469, 2015.

APPENDIX A

ADDITIONAL DATA

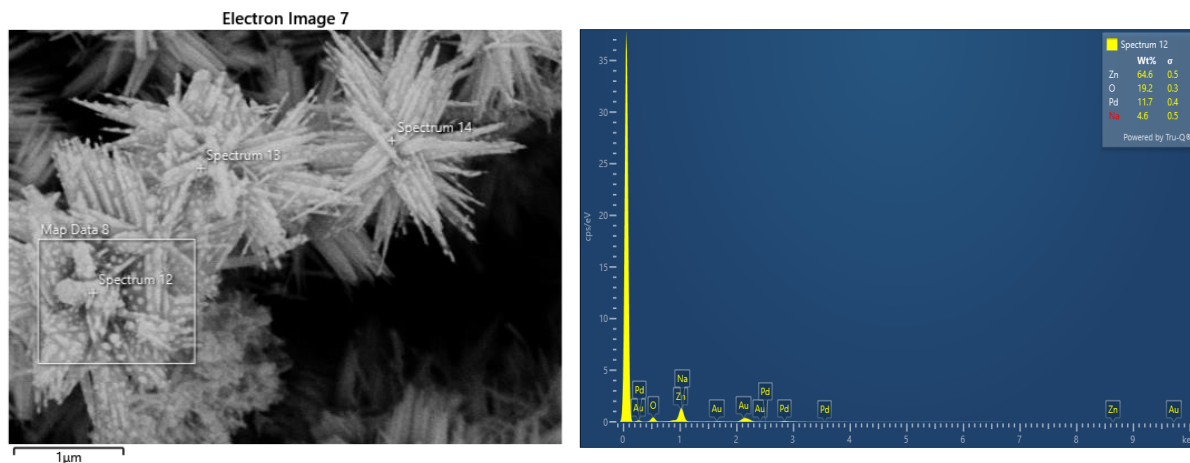


Figure SI1. SEM and EDX for ZnO-NN

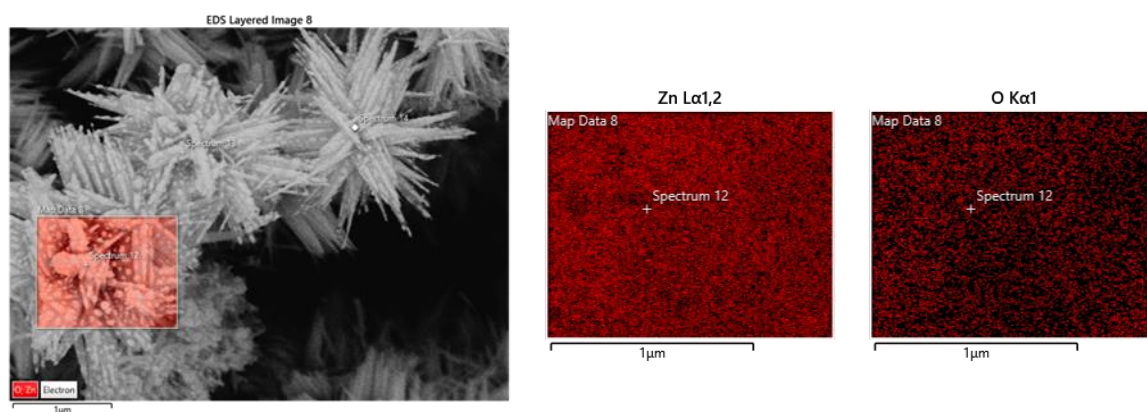


Figure SI2. SEM and EDX mapping for ZnO-NN

Table SI1. Percent Elemental composition (%) of ZnO-NN

Spectrum 12								
Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Standard Label	Factory Standard	Standard Calibration Date
O	K series	6.52	0.02193	19.20	0.27	SiO2	Yes	
Na	K series	1.10	0.00464	4.56	0.48	Albite	Yes	

Zn	L series	10.51	0.10510	64.57	0.51	Zn	Yes	
Pd	L series	1.98	0.01981	11.66	0.42	Pd	Yes	
Total:				100.00				

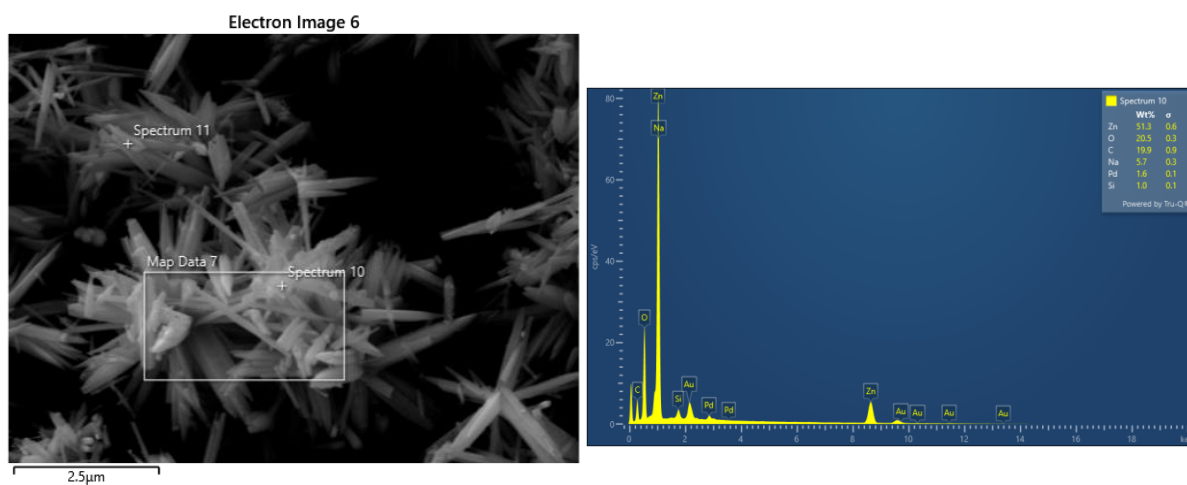


Figure SI3. SEM and EDX for ZnO-NR

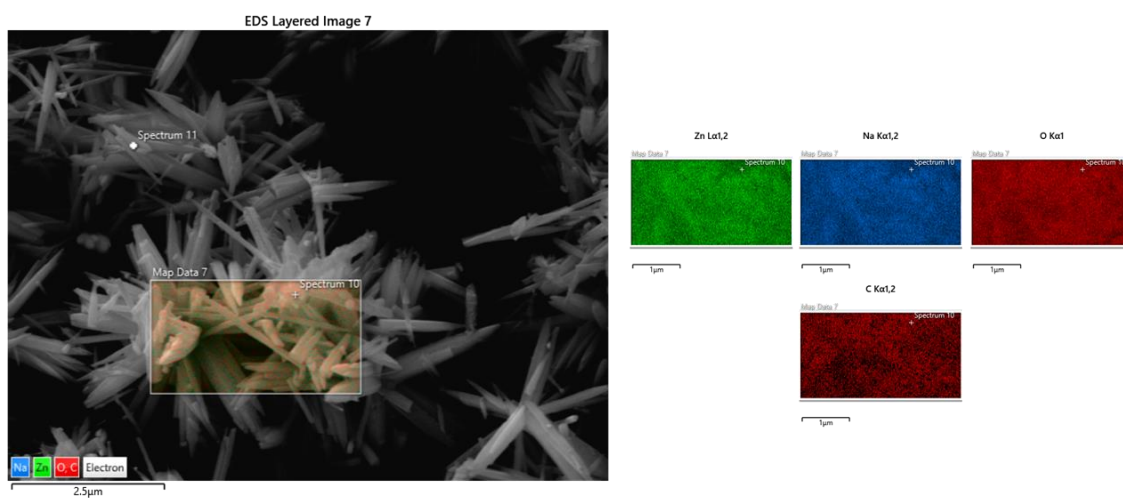


Figure SI4. SEM and EDX mapping for ZnO-NR

Table SI2. Percent Elemental composition (%) of ZnO-NR

Spectrum 10								
Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Standard Label	Factory Standard	Standard Calibration Date
C	K series	7.77	0.07773	19.91	0.91	C Vit	Yes	
O	K series	46.10	0.15513	20.53	0.31	SiO ₂	Yes	
Na	K series	9.84	0.04153	5.73	0.33	Albite	Yes	
Si	K series	1.77	0.01406	1.00	0.05	SiO ₂	Yes	
Zn	L series	79.14	0.79139	51.25	0.64	Zn	Yes	
Pd	L series	2.72	0.02717	1.57	0.12	Pd	Yes	
Total:				100.00				

Table SI3. Comparison of CO₂ reduction performance of the reported Zn catalysts

Electrode	Electrolyte	Applied potential (V vs. RHE)	Overpotential (mV)	FE _{CO} (%)	Reference
ZnO-NN	0.5 M KHCO₃	-0.88	347.6	91.3%	This work
ZnO-NR		-0.98		62.5%	
Zn-1	0.1 M KHCO ₃	-0.85	~750	93.6%	[323]
Zn-2				90.6%	
Zn-3				90.1%	
Porous Zn	0.1 M KHCO ₃	-0.95	—	94.4%	[326]
Zn-nanoflakes	0.1 M KHCO ₃	-0.9	—	70%	[418]
Li-tuned-Zn	0.1 M KHCO ₃	-1.17	948	91.1%	[419]
Hexagonal-Zn	0.5 M KHCO ₃	-0.9	—	84.8%	[327]
Multilayer-Zn	0.5 M KHCO ₃	-1.13	—	88%	[331]
Zn nanosheets	0.1 M KHCO ₃	-1.0	—	90%	[420]
Zn crystals	0.1 M KHCO ₃	-0.79	—	81%	[421]

Oxide-derived Zn on carbon fiber	0.1 M KHCO ₃	-0.9	—	~15%	[419]
ZnO with oxygen vacancy	0.1 M KHCO ₃	-1.1	~ —	83%	[422]

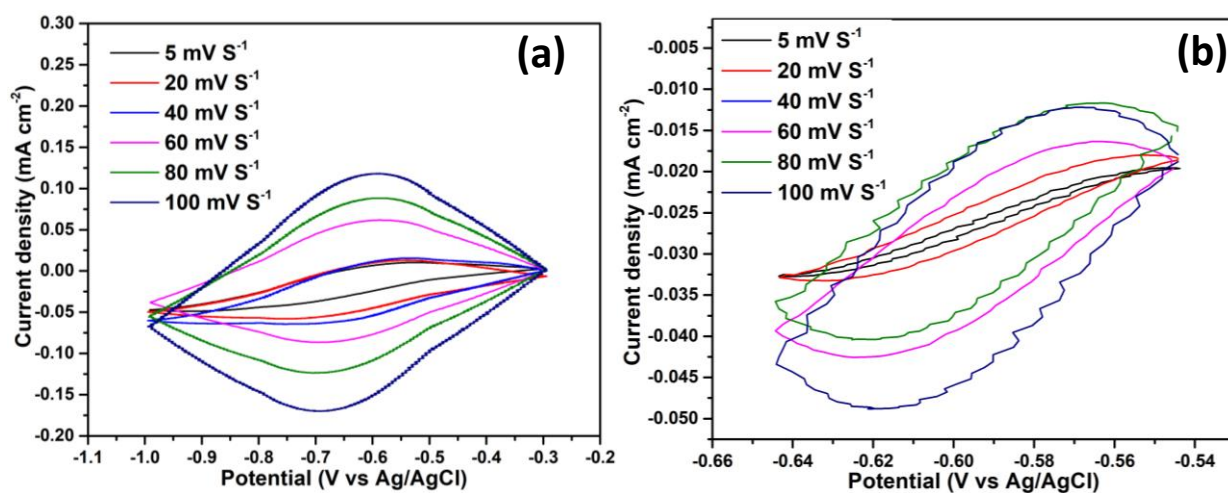


Figure S15. CVs for (a) ZnO-NR and (b) ZnO-NN at various scan rate.

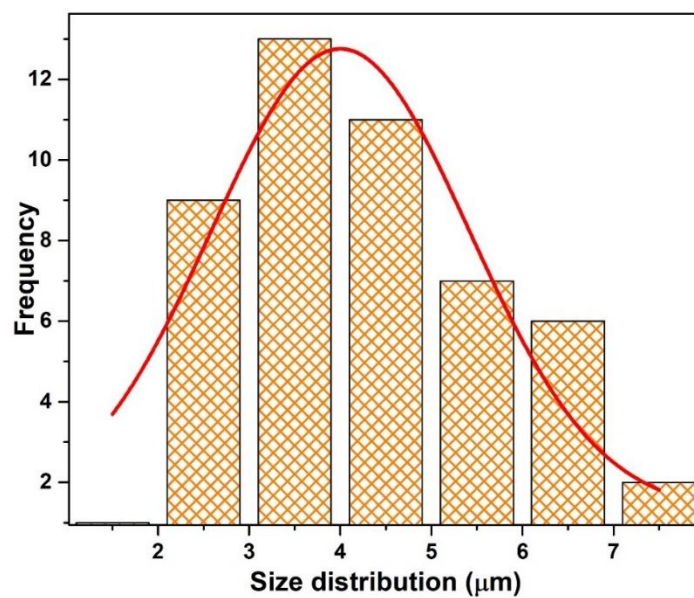


Figure S16. Particle size distribution histogram of ZIF-zni

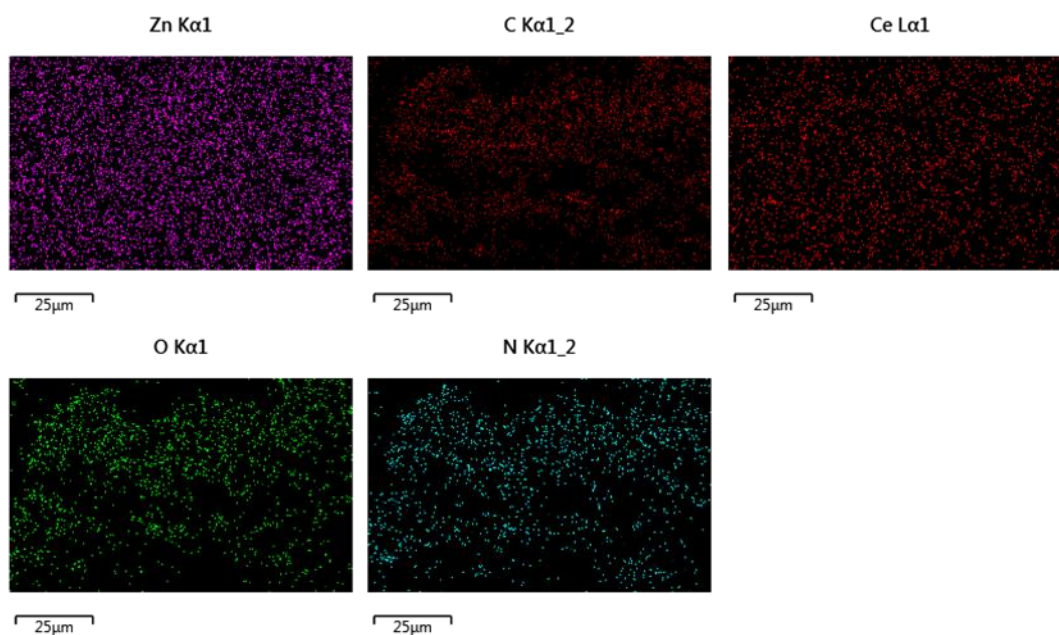


Figure SI7. EDS mapping and elemental analysis of the catalyst

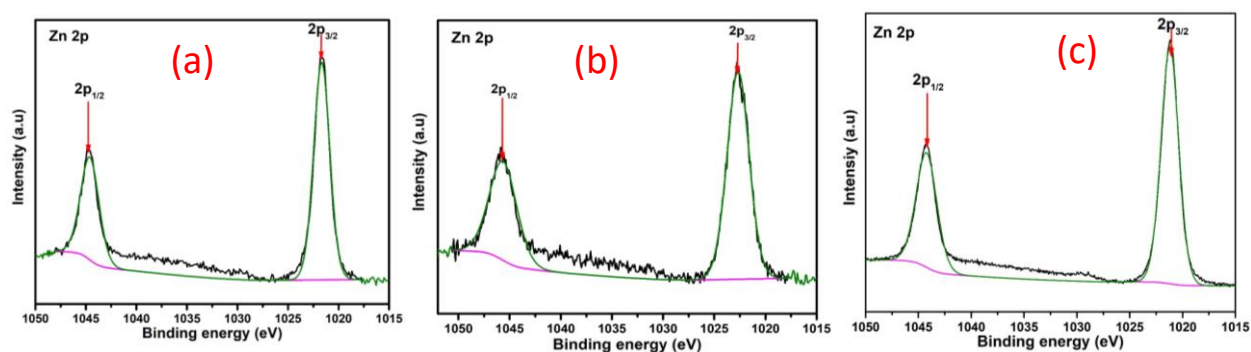


Figure SI8. High-resolution XPS spectra of Zn 2p of (a) ZIF-zni, (b) $Ce_{0.23}$ -ZIF-zni (d) and (c) $Ce_{0.23}$ -ZIF-zni-CVD

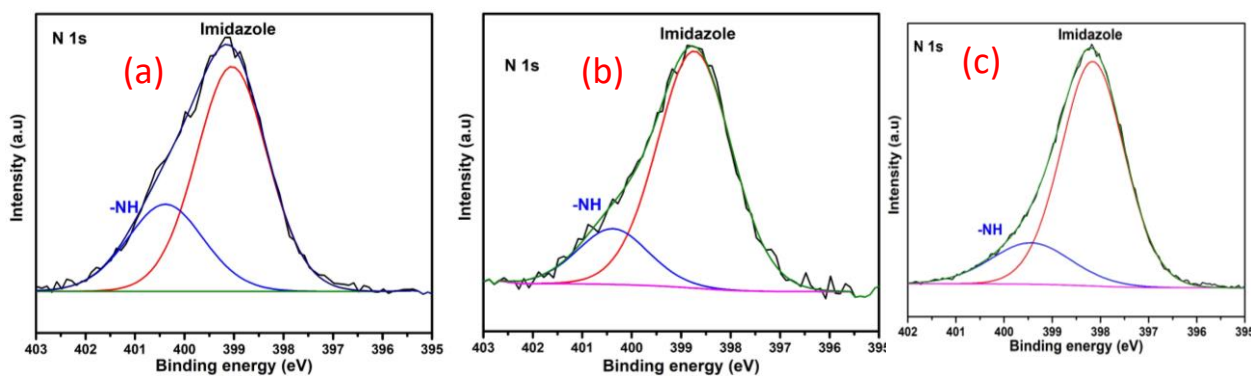


Figure SI9. High-resolution XPS spectra of N 1s of (a) ZIF-zni, (b) $Ce_{0.23}$ -ZIF-zni (d) and (c) $Ce_{0.23}$ -ZIF-zni-CVD

Table SI4. XPS elemental composition (%) of Ce_{0.23}-ZIF-zni

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %	Q
C1s Scan B	287.8	1.63	765.26	3.86	1
C1s Scan A	285.62	2.03	3821.64	19.24	1
C1s	284.36	1.71	15288.32	76.91	1

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %	Q
O1s	528.82	1.5	536.43	5.34	1
O1s Scan B	531.22	2.42	4108.62	40.95	1
O1s Scan C	532.21	2.49	5384.51	53.71	1

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %	Q
Ce3d	886.41	3.37	2385.85	20.59	1
Ce3d Scan A	899.47	3.37	1810.89	15.83	1
Ce3d Scan B	903.13	3.37	1770.68	15.54	1
Ce3d Scan C	922.19	3.37	358.86	3.21	1
Ce3d Scan D	883	3.37	2270.68	19.53	1
Ce3d Scan E	906.73	3.37	1297.89	11.43	1
Ce3d Scan F	917.14	3.37	861.75	7.67	1
Ce3d Scan G	889.77	3.37	715.19	6.19	1

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %	Q
Zn2p	1022.67	2.52	11257.26	61.92	1
Zn2p Scan A	1045.64	3.17	6716.78	38.08	1

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %	Q
N1s	398.73	1.77	6787.51	81.63	1
N1s Scan A	400.38	1.69	1525.64	18.37	1

Table SI5. XPS elemental composition (%) of Ce_{0.23}-ZIF-zni-CVD

Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic %	Q
C1s A	284.79	1.75	108161.1	40.26	1
C1s B	286.6	3.25	31470.55	11.72	1
O1s A	531.4	2.52	102230.15	13.89	1
O1s B	529.14	1.27	10519.43	1.43	1
Ce3d A	924.68	3.36	5295	0.05	1
Ce3d5 B	889.74	3.36	9159.22	0.21	1
Ce3d3 B	907.34	3.36	6342.39	0	0

Ce3d3 C	893.65	3.36	3132.28	0	0
Ce3d5 D	897.36	3.36	8440.45	0.13	1
Ce3d3 D	914.96	3.36	5844.67	0	0
Ce3d E	904.91	3.48	4125.91	0.04	1
Ce3d F	911.12	4	5654.72	0.05	1
Zn2p A	1021.19	1.97	304262.76	5.46	1
Zn2p B	1044.23	2.3	172437.35	3.16	1
N1s A	398.16	1.55	89996.06	19.14	1
N1s B	399.44	1.97	21059.24	4.48	1

Table SI6. Comparison of electrochemical CO₂ reduction activity and selectivity for different Ce based electro-catalysts

Catalyst	Electrolysis medium	Over-potential (mV)	FE _{CO} (%)	FE _{H2} (%)	Ref
xPdTe _x Ce _x /C	0.1 M KHCO ₃	270	84	~15	1
Ce _x Zn _{1-x} O	0.5 M KHCO ₃	470	88	~12	2
Au–CeO _x /C	0.1 M KHCO ₃	360	89.1	-	3
Zn-1	0.1 M KHCO ₃	~750	93.6	~3	4
Zn-2			90.6	~5	
Zn-3			90.1	~5	
Li-tuned-Zn	0.1 M KHCO ₃	948	91.1	~8	5
Hexagonal-Zn	0.5 M KHCO ₃	370	84.8	15.9	6
Cu _{0.5} Zn _{0.5} /ZIF-8	0.5 M KHCO ₃	470	88.5	~11	7
Fe _{0.3} Zn _{0.7} /ZIF-8		670	48	~50	
ZIF-8-5%	0.5 M NaHCO ₃	670	79	~20	8
Porous network Zn	0.5 M KHCO ₃	570	80	~10	9
Zn dendrite	0.5 M KHCO ₃	570	80	-	10
Cu ₂₅ Zn-A	0.5 M KHCO ₃	450	94.5	~5.6	11
Ce_{0.23}-ZIF-zni-CVD	0.5 M KHCO₃	170	87.9	12	Present work

Electrochemical Measurement

For the electrocatalytic reduction experiments, controlled potential coulometry was performed in a sealed two-compartment H-type cell configuration, with a Nafion-117 proton exchange membrane separating the compartments. This setup utilized a three-electrode system, including a platinum wire as the counter electrode, an Ag/AgCl as the reference electrode, and the synthesized electrocatalyst as the working electrode. To prepare the working electrode, a catalyst amounting to 5 mg was mixed with 4 mL of methanol, followed by the addition of 2 μL of Nafion solution (5 wt%). The resulting mixture or ink was subjected to sonication for 15 minutes. Subsequently, 50 μL of this catalyst ink was deposited onto a 1 cm $\times$ 1 cm carbon paper and allowed to air dry overnight at room temperature. The assembled electrode configuration consisted of the aforementioned working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. In this setup, both the anode and cathode electrolytes were 0.5 M KHCO_3 . Prior to the electrolysis, highly pure CO_2 (99.999%) was introduced into the electrolyte for 30 minutes at a flow rate of 50 standard cubic centimeters per minute (sccm), which was then maintained at 5 sccm throughout the electrolysis. This procedure ensured the removal of residual air and continuous CO_2 supply. Gas products generated during the electrolysis were continuously monitored and analyzed using a Clarus 580 gas chromatograph (Perkin Elmer). The GC is equipped with Hayesep and Molecular sieve columns, as well as thermal conductivity (TCD) and flame ionization (FID) detectors, respectively. Additionally, the headspace products were intermittently injected into the gas chromatograph at 20-minute intervals. At the conclusion of a 1-hour electrolysis period,

the electrolyte solution was collected and subjected to analysis to identify and quantify liquid products by ^1H NMR.

The faradaic efficiency (FE) of the products were estimated using the eq:

$$FE = \left(\frac{Z * C * F}{Q} \right) * 100$$

Where, Z represents the number of transferred electrons during the electrolysis, C is the molar concentration of the products (mol/L) as detected on GC, F is the Faraday constant (96485 C mol⁻¹ of electrons), and Q is the overall charge over the period of 1 h electrolysis.

Unless where stated, all of the potentials reported in this study were converted to the reversible hydrogen electrode, RHE using the eq:

$$E_{RHE} = E_{(Ag/AgCl)} + E_{\left(\frac{Ag}{AgCl}\right)}^0 + 0.059 * pH$$

Where, $E_{(Ag/AgCl)}^0$ was taken as 0.1976 V, and the pH of CO₂-saturated 0.5 M KHCO₃ was measured as 7.2.

The electrodes were characterized through Linear Sweep Voltammetry (LSV) measurements spanning a potential range of 0 to -1.6 V versus Ag/AgCl, employing a scan rate of 50 mV s⁻¹. The LSV plots were presented without employing iR correction. The Electrochemical surface area (ECSA) was determined by calculating the electrical double layer capacitance (Cdl). Additionally, Cyclic Voltammetry (CV) measurements were conducted by assessing Cdl across a variety of scan rates within a non-Faradaic potential range versus RHE. Furthermore, potentiostatic Electrochemical Impedance Spectroscopy (EIS) measurements were performed in an electrolyte containing 0.5 M KHCO₃ saturated

with CO₂. The impedance spectra were recorded across a frequency span from 100 kHz to 100 mHz, while applying an amplitude of 10 mV root mean square (r.m.s.).

Theoretical calculation

DFT calculations were performed using the Dmol3 module within the Materials Studio software for ZIF-zni, Ce_xO_x/ZIF-zni, and Ce_xO_xH₂/ZIF-zni systems. The electron exchange-correlation interactions were described using the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerh (PBE) functions, and the Double Numerical plus Polarization (DNP) served as the basis set. A convergence tolerance for energy of 10⁻⁶ Hartree was applied, while the maximum allowed force and displacement values were set at 0.002 Hartree/Å and 0.005 Å, respectively [373], [424].

To determine the interaction energy of CO₂ and its intermediates on the ZIF-zni, Ce_xO_x/ZIF-zni, and Ce_xO_xH₂/ZIF-zni models, the following equation was used:

$$E_{\text{ads}} = E_{\text{(complex)}} - E_{\text{(intermediate)}} - E_{\text{(catalyst model)}}.$$

where, E_{ads} represents the adsorption energy, $E_{\text{(complex)}}$ represents the total energy of the analyte molecule adsorbed on the catalyst model, and $E_{\text{(intermediate)}}$ and $E_{\text{(catalyst model)}}$ represent the total energies of the analyte molecule and the catalyst model, respectively.

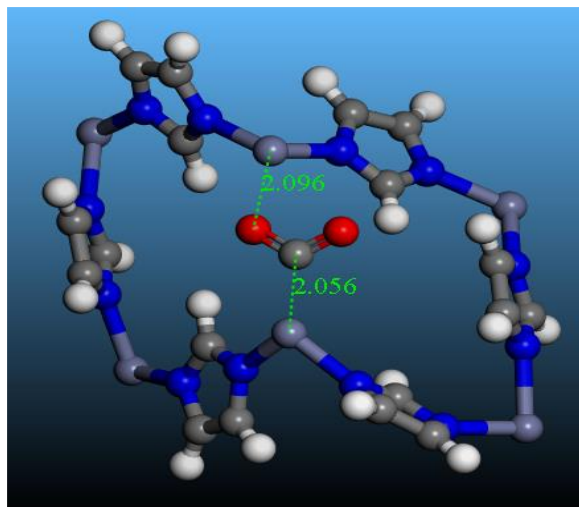


Figure SI10. DFT calculations of the optimized structures for CO₂ on ZIF-zni surface

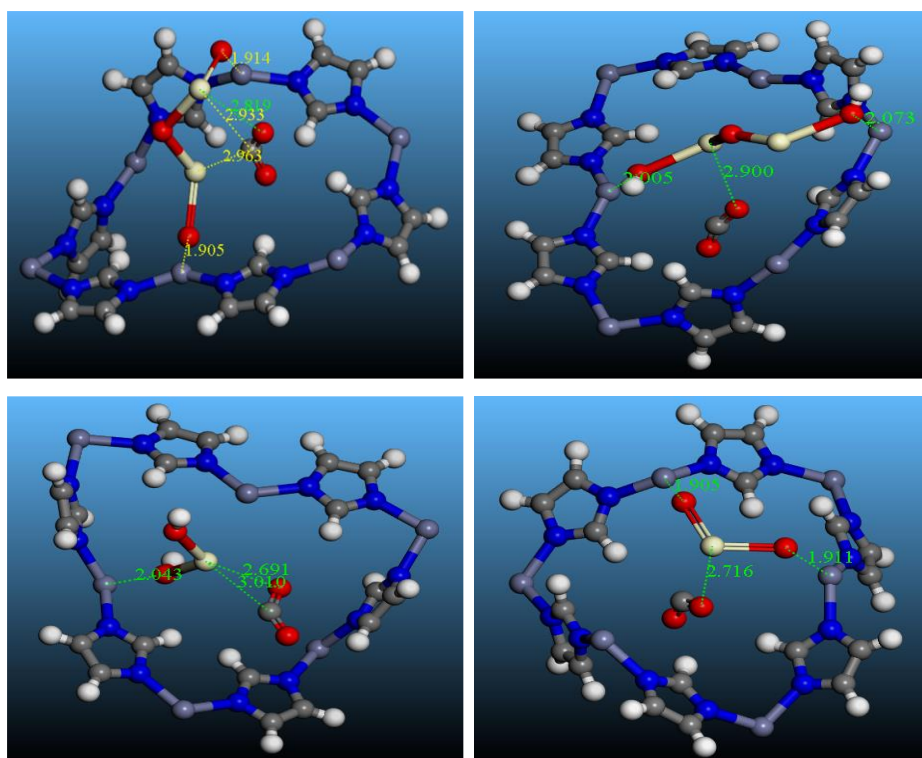


Figure SI11. DFT calculations of the optimized structures for CO₂ on Ce_xO_x-ZIF-zni and Ce_xO_xH₂-ZIF-zni surface

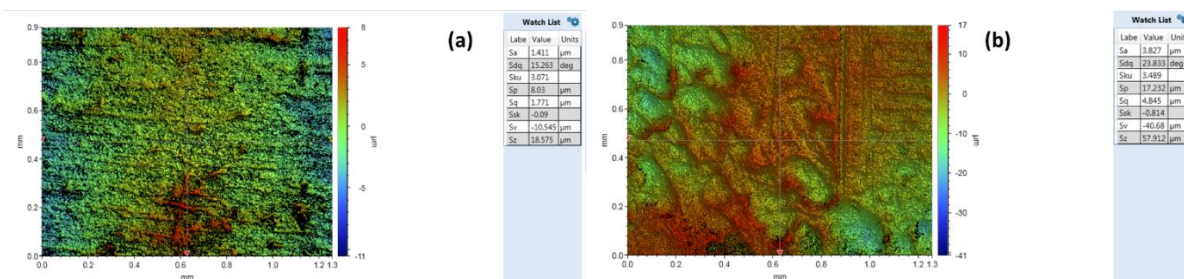


Fig. SI12. Optical profiler surface scan of (a) pristine Pb electrode, and the (b) 50 cycles ORC-treated, in 0.3 M KCl electrolyte solution.

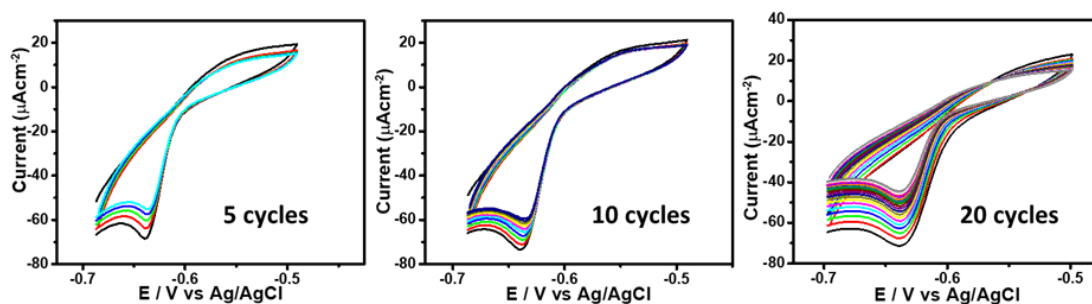


Fig. SI13. CV curves corresponding to ORC treated electrodes.

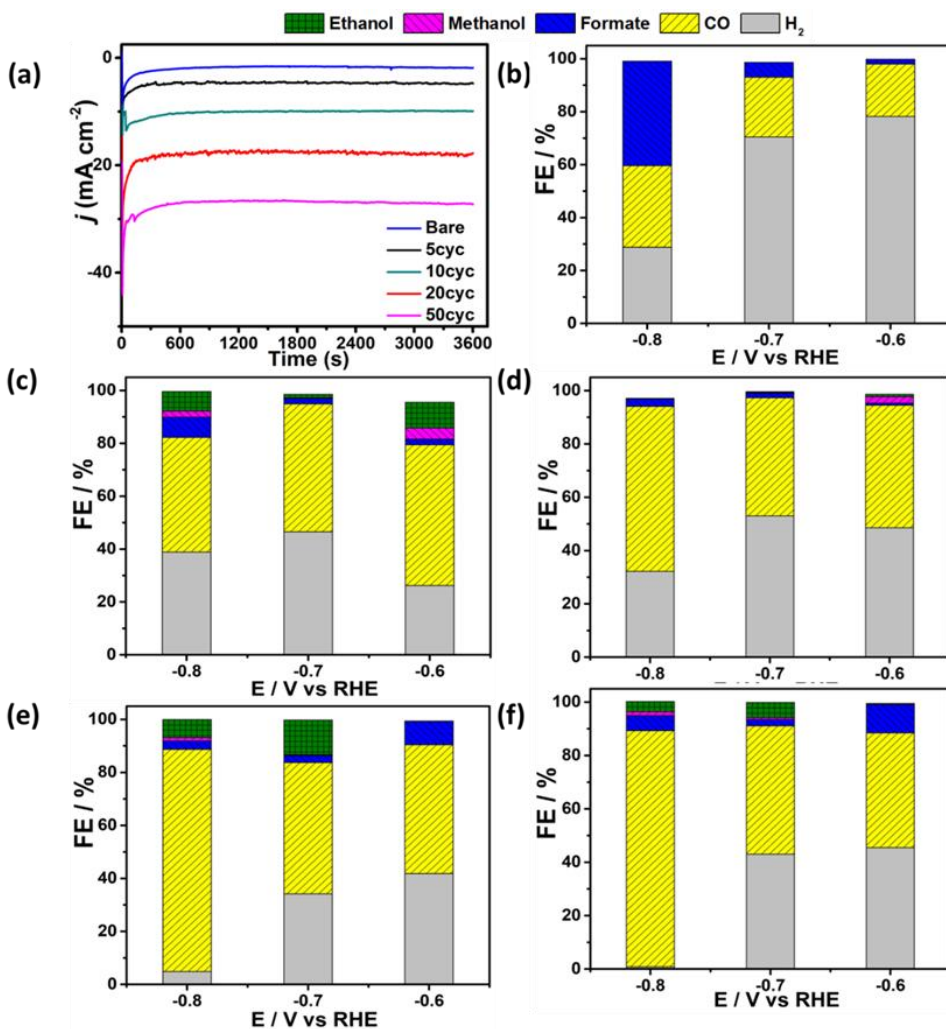


Fig. SI14. (a) Current density–time dependent curves (applied potentials) of the pristine Pb and ORC-treated electrodes and electrochemical CO₂RR performances of (b) Pristine Pb (c) 5 cycles (d) 10 cycles (e) 20 cycles and (f) 50 cycles treated electrodes in CO₂-saturated 0.5 M KHCO₃,

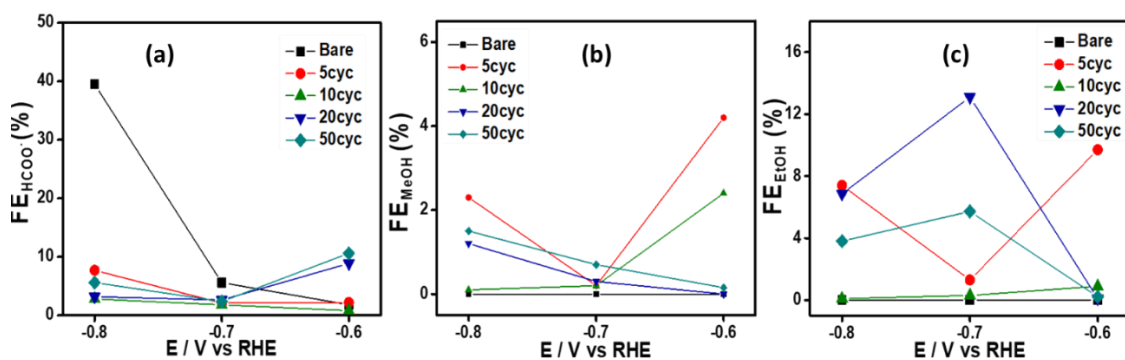


Fig. SI15. Faradaic efficiencies (%) plots of (a) HCOO⁻ (b) CH₃OH and (c) CH₃CH₂OH

Table SI7. Comparison of the electrocatalytic CO₂RR performance of recently reported Pb and Sn based electrocatalysts.

Catalysts	Electrolyte	V vs. RHE	FE _{HCOO⁻} %	FE _{CO} %	j _{CO} / mA cm ⁻²	Ref.
Oxidative derived Pb in water	0.1 M KHCO ₃	-1.08	64	0.7	12	[425]
Sulfide derived.			88	0.17	3.1	
Pb (111) facets	0.1 M KHCO ₃	-0.83	98.03	N.R	0.53 2.6	[426]
Co-PbCO ₃ @CNS	0.1 M KHCO ₃	-0.7	98.15	<1	9.65	[427]
Pb	0.1 M K ₂ CO ₃	-1.1	40	N.R	0.5	[428]
Pb	0.5 M NaOH	-0.95	70	N.R	2.5	[429]
OD-Pb	0.5 M KHCO ₃	-1.0	100	N.R	4	[430]
Pb NP	0.5 M KHCO ₃	-0.2	97	NR	22	[250]
Oxidation-reduction cycling (ORC) derived Pb in 0.3M KCl	0.5 M KHCO ₃	-0.8	5.6	89	7.1	This work

Vitae.

Name : Mustapha Umar

Nationality : Nigerian

Date of Birth : 26/04/1989

Email : mustee2009@yahoo.com

Address : DD No. 53 Dawaki Quarters, 760212, Gombe Nigeria

Academic Background :

1. PhD Chemistry (Material Chemistry), 2023
King Fahd University Petroleum and Minerals Dhahran KSA.
2. Msc Chemistry (Material Chemistry), 2019
King Fahd University Petroleum and Minerals Dhahran KSA.
3. B.Sc. Degree in Chemistry, 2015
Federal University Kashere (FUK), Gombe State, Nigeria
Graduated with second class upper honors.
4. Secondary School Certificate,
Government Secondary School Bwari, Abuja (WAEC), 2010
5. National Business and Technical Examinations Board (NABTEB), 2010
6. Computer Certificate, Netcom Institute Gombe (a Division of Chisco Mechanic Nigeria Ltd), 2007.

PUBLICATIONS

S/N	Journal	IF	Q-Rank
1	Abdulkadir Tanimu, Saheed A. Ganiyu, Shehzada Muhammad Sajid Jillani, Mustapha Umar , Sagir Adamu, and Khalid Alhooshani. "Sono-assisted synthesis of silicalite-1 as NiMo support for hydrodesulphurization of dibenzothiophene: Role of sonication time on support mesoporosity and catalytic activity" industrial and engineering chemistry research . https://pubs.acs.org/doi/abs/10.1021/acs.iecr.9b03358 .	4.2	Q1
2	Mustapha Umar , Tanimu Abdulkadir, Saheed A. Ganiyu, Dafalla Hatim, Kozhevnikov Ivan, Alhooshani Khalid. "Role of 3D alumina foam support on the formation and dispersion of active NiMoS phase for hydrodesulfurization application". https://pubs.acs.org/doi/abs/10.1021/acs.energyfuels.0c01236 .	5.3	Q1
3	Mustapha Umar , Chidera C. Nnadike, Ismail Abdulazeez, Khalid Alhooshani, Abdulaziz A. Al-Saadi. "Nitrogen-Enhanced Charge Transfer Efficacy on the Carbon Sheet: A Theoretical Insight into the Adsorption of Anionic Dyes" Arabian Journal for Science and Engineering . https://link.springer.com/article/10.1007/s13369-021-05648-x .	2.8	Q1
4	Mustapha Umar , Ismail Abdulazeez, Tanimu Abdulkadir, Saheed A. Ganiyu Khalid Alhooshani. "Modification of ZSM-5 mesoporosity and application as catalyst support in hydrodesulfurization of dibenzothiophene: Experimental and DFT studies" Journal of Environmental Chemical Engineering . https://www.sciencedirect.com/science/article/abs/pii/S2213343721017152 .	7.7	Q1
5	Mustapha Umar , Chidera C. Nnadike, Muhammad Haroon, Ismail Abdulazeez, Khalid Alhooshani, Abdulaziz A. Al-Saadi, Qing Peng "A First-Principles Study on the Multilayer Graphene Nanosheets Anode Performance for Boron-Ion Battery". Journal of Nanomaterials . https://www.mdpi.com/2079-4991/12/8/1280 .	5.3	Q2
6	Chidera C. Nnadike ¹ , Mustapha Umar , I. Abdulazeez ¹ , K. R. Al-hooshani ¹ , A. A. Al-Saadi ¹ "Alkali metal ion-doped heptazine-based g-C ₃ N ₄ quantum dots for efficient adsorption of methyl blue: A DFT perspective": Journal surface and interface . https://www.sciencedirect.com/science/article/pii/S2468023023002225 .	6.2	Q1
7	Mustapha Umar , Chidera C. Nnadike, Maria A. Alhaboudal, Umar Yunusa, AbdulHakam S. Abdullahi, Ismail Abdulazeez, Ijaz Hussain, Saheed A. Ganiyu, Khalid Alhooshani "The role of morphology on the electrochemical CO ₂ reduction performance of transition metal-based catalysts". Journal of energy chemistry . https://www.sciencedirect.com/science/article/pii/S2095495623003558 .	13.1	Q1
8	Ijaz Hussain, Mustapha Umar , Zuhair Malaibari, Ahmed T. Al-Qathmi, Saheed A. Ganiyu, Khalid Alhooshani "A critical role intrinsic Physicochemical properties of catalysts for CO ₂ hydrogenation into methanol: A state of the art review". Journal of Industrial and Engineering Chemistry . https://www.sciencedirect.com/science/article/abs/pii/S1226086X23005099 .	6.1	Q1
9	Basiru O. Yusuf, Mustapha Umar , Esraa Kotob, Abdullahi Abdulhakam, Omer A. Taialla, Mohammed Mosaad Awad, Ijaz Hussain, Saheed A. Ganiyu, Khalid Alhooshani "An overview of recent advances in bimetallic catalysts for	4.1	Q1

	methane steam reforming in hydrogen production: Current trends, challenges, and future prospects". Accepted Chemistry- An Asian Journal		
10	Mohammed Mosaad Awad, Ijaz Hussain, Mustapha Umar , Omar Ahmed Taialla, Aliyu Musa Alhassan, AbdulHakam Shafiu Abdullahi, Saheed A. Ganiyu and Khalid Alhooshani "A critique of synergistic effects between catalytic and physiochemical properties for dry reforming of methane: emerging trends, current challenges, and machine learning". Under review in the Coordination Chemistry Reviews	20.6	Q1
11	Omar Ahmed Taialla, Mustapha Umar , AbdulHakam Shafiu Abdullahi, Esraa Kotob, Mohammed Mosaad Awad, Aliyu Musa Alhassan, Ijaz Hussain, Saheed A. Ganiyu and Khalid Alhooshani "Unlocking the potential of ZIF-based electrocatalysts for electrochemical reduction of CO ₂ : Recent advances, current trends, and Machine Learnings". Under review in the Coordination Chemistry Reviews	20.6	Q1
12	Mustapha Umar , Ismail Abdulazeez, Abdulkadir Tanimu, Saheed A. Ganiyu, Khalid Alhooshani, "Synergistic Effect of Ce _x O _y and Zn ion within the ZIF-zni Framework for Enhanced Electrocatalytic Reduction of CO ₂ ". Under review in the Journal of chemical engineering	15.1	Q1
13	Mustapha Umar , Ismail Abdulazeez, Ijaz Hussain, Abduljamiu O. Amao, Saheed A. Ganiyu, Khalid Alhooshani "New insight into selectivity modulation of lead-based electrode in electrochemical CO ₂ reduction to CO: Effect electrochemical roughening. Under review in the Journal of energy chemistry	13.1	Q1
14	Mansur Aliyu, Basiru O. Yusuf, Abdulhakam Abdullahi, Idris A. Bakare, Mustapha Umar , Saheed Ganiyu "Ti ₂ C-Mxene/Activated Carbon Nanocomposite for Efficient CO ₂ Capture: Insights into Thermodynamics Properties". Under review in the Journal of chemical engineering	15.1	Q1
15	Mustapha Umar , Ismail Abdulazeez, Abduljamiu O. Amao, Saheed A. Ganiyu, Khalid Alhooshani "Modulating the electrocatalytic reduction of CO ₂ to CO via surface reconstruction of ZnO nanoshapes". Under review in the Journal of CO₂ utilization	6	Q1
16	Abdulwahab Muhammad Bello, Anas Muhammad Salisu, Abduljamiu O. Amao, Mustapha Umar , and Khalid Al-Ramadan "Experimental Nucleation of Chlorite: Insights from Kaolinite Precursor". Under review in Front. Earth Sci.	3.7	Q1
17	Abdullahi Abdulhakam, Mustapha Umar , Ijaz Hussain, Omer A. Taialla, Esraa Abas, Mohammed Ali, Basiru O. Yusuf, Ismail Abdulazeez, Saheed A. Ganiyu, Khalid R. Alhooshani "Review of recent advancements in the electrocatalytic reduction of CO ₂ to Formate/Formic acid: the role of conducting polymers". Submitted to Coordination Chemistry Reviews	20.6	Q1

Conferences paper/poster presentation

1	Mustapha Umar , Ismail Abdulazeez, Saheed A. Ganiyu, Khalid Alhooshani, "Reflux assisted synthesis of ZIF-61 and CO ₂ reduction at very low overpotential on Oxide-Derived Ce _x O _x Nanoparticles". ACS spring 2023 meetings, Indianapolis USA. Accepted
2	Khalid Alhooshani, Ijaz Hussain, Mustapha Umar , Saheed A. Ganiyu, "Highly efficient strategy for CO ₂ methanation using Ni/SiO ₂ -MgO nanocomposite catalyst for synthetic natural gas production:

Thermodynamics and catalytic insights". ACS FALL 2023 ". **ACS FALL 2023 meetings (Harnessing the Power of Data), San Francisco USA. Accepted**

- 3** Poster presentation on modified ZSM-5 supported on NiMo-S for hydrodesulfurization application at **29th annual Saudi-Japan symposium Nov. 3-4, 2019.**
-