

**MODULATING Cu BASED CATALYST FOR CO₂
ELECTROCHEMICAL CONVERSION TO
C₂+ PRODUCTS INTEGRATED WITH INSITU
CHARACTERIZATIONS AND DFT SIMULATION**

BY

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

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

Chemistry

March, 2025

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN- 31261, SAUDI ARABIA
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This work is dedicated to those whose unwavering support and inspiration have fueled my academic journey. Their belief in my abilities and their encouragement in times of challenge have been the driving force behind the completion of this master's thesis.

*To my **family**, who have been a constant source of love and encouragement, thank you for your patience, understanding, and belief in my potential. Your unwavering support has been my anchor throughout this academic endeavor. To my thesis advisor and CCU leader, **Dr. Saheed Ganiyu and Prof. Khalid Alhooshani**, whose guidance and expertise have been invaluable. Your dedication to the pursuit of knowledge and commitment to excellence have left an indelible mark on my academic and personal growth. To my friends and colleagues, thank you for the camaraderie, shared experiences, and the collaborative environment that made this academic journey more enriching and enjoyable. In honor of Dr. Mustapha Umar, whose wisdom and support shaped my path. Your guidance and inspiration remain with me, and this work is a testament to your enduring impact. To all those who have played a role, big or small, in my academic pursuit, I extend my deepest gratitude. This achievement is as much yours as it is mine.*

ACKNOWLEDGMENTS

I would like to express my deepest gratitude to all those who have contributed to the completion of this master's thesis. This journey has been a challenging yet rewarding experience, and I am fortunate to have received support and guidance from a myriad of individuals. First and foremost, I am profoundly thankful to my thesis advisor **Dr. Saheed Ganiyu**, for his unwavering support, invaluable insights, and endless patience throughout this research endeavor. His expertise, encouragement, and constructive feedback have been instrumental in shaping the trajectory of this work. I extend my sincere appreciation to the members of my thesis committee, **Dr. Tarek Kandial** and **Dr. Ismail Abdulazeez**, for their valuable feedback and insightful suggestions that significantly enriched the quality of this thesis. Their expertise and commitment to academic excellence have been a constant source of inspiration.

In honor of Dr. Mustapha Umar, whose wisdom and support shaped my path. Your guidance and inspiration remain with me, and this work is a testament to your enduring impact.. I am deeply grateful to my family for their unconditional love, encouragement, and understanding during the demanding phases of this thesis. Their unwavering belief in my abilities has been a constant source of motivation. Lastly, I want to acknowledge the countless individuals who may not be named here but who, in various ways, contributed to the realization of this thesis. Your collective impact has not gone unnoticed and is sincerely appreciated.

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LIST OF ABBREVIATIONS

CO ₂	:	Carbon dioxide
GHGs	:	Greenhouse gases
IPCC	:	International Panel on Climate Change
CCU	:	CO ₂ -capture and utilization
CO ₂ -ECR	:	Electrochemical CO ₂ reduction
HER	:	Hydrogen evolution reaction
Non-MHA	:	Nonmetal heteroatoms
EDL	:	Electrical double layer
IHL	:	Inner Helmholtz layer
OHL	:	Outer Helmholtz layer
GDE	:	Gas diffusion electrode
MD	:	Molecular dynamics
PDEs	:	Partial differential equations
SHE	:	Standard hydrogen electrode
CHE	:	Computational hydrogen electrode
CV	:	Cyclic voltammetry
LDHs	:	Layered double hydroxide materials
BF	:	Blood flow
LbL	:	Layer-by-Layer
UTFs	:	Ultrathin films
FLU	:	Fluorescein
RHE	:	Reverse hydrogen electrode
RR	:	Reaction Rate
TCD	:	Thermal conductivity detector

FID	:	Flame ionization detector
^1H NMR	:	^1H nuclear magnetic resonance spectroscopy
D_2O	:	Deuterium oxide
n	:	Number of electrons transferred during electrolysis
Z	:	The number of moles of products formed
F	:	Faraday's constant
Q	:	Amount of charge passed during the electrolysis in coulombs
FEG-SEM	:	Field Emission Gun Scanning Electron Microscopy
HRTEM	:	High-resolution Transmission Electron Microscopy
SAED	:	Selected area diffraction
XRD	:	X-ray diffraction
FTIR	:	Fourier-Transform Infrared Spectroscopy
XPS	:	X-ray Photoelectron Spectroscopy
EDS	:	Energy dispersive spectroscopy
SEM	:	Scanning Electron Microscopy
TEM	:	Transmission Electron Microscopy
ECSA	:	Electrochemical active surface area
Cdl	:	Double-layer capacitance

]

ABSTRACT

Full Name : Esraa Ragab Abas Kotob
Thesis Title : Modulating Cu based catalyst for CO₂ electrochemical conversion to C₂+ products integrated with insitu characterizations and DFT simulation
Major Field : [Chemistry]
Date of Degree : [March/2025]

This work demonstrates the tunable synthesis of copper nanocrystals for the facet-selective electroreduction of CO₂ (CO₂RR) in an H-cell. Cu nanocrystals with distinct morphologies, termed respectively as blood-flow (BF) ({100} facets) first time reported, spherical (SP) ({111} facets), and trigonal (TR) ({100} & {111} facets) were synthesized and evaluated. BF nanocrystals achieved ~60% Faradaic efficiency for ethylene at -90 mA cm⁻², while TR and SP nanocrystals exhibited 85% Faradaic efficiency for formate at -39 mA cm⁻² and 78% for CO at -35 mA cm⁻², respectively. Operando Raman spectroscopy revealed the potential intermediate for different pathway of C₁ and C₂ products. Density functional theory (DFT) simulations illustrated energy barriers, highlighting the critical role of nanocrystal morphology in CO₂RR performance. This study demonstrates how precise control over Cu nanocrystal morphology and crystal phases can be harnessed to achieve high selectivity for specific CO₂RR products, offering a pathway to rational catalyst design without the need for complex modifications or additives.

ملخص الرسالة

الاسم الكامل: اسراء رجب عباس قطب

عنوان الرسالة:

تعديل الحفازات القائمة على النحاس لتحويل ثاني أكسيد الكربون إلكترونياً إلى منتجات C_2 مدمج مع التوصيفات في الموقع ومحاكاة DFT

التخصص: كيمياء

تاريخ الدرجة العلمية: مارس-2025

يوضح هذا العمل التخليق القابل للتعديل للبلورات النانوية النحاسية من أجل الاختزال الكهروكيميائي الانتقائي لثاني أكسيد الكربون (CO_2RR) في خلية H. تم تصنيع وتقييم بلورات نانوية نحاسية ذات أشكال مميزة، حيث تم الإبلاغ لأول مرة عن البلورات النانوية ذات الشكل "تدفق الدم" (BF) ذات الواجهات $\{100\}$ ، بالإضافة إلى الأشكال الكروية (SP) ذات الواجهات $\{111\}$ ، والثلاثية (TR) ذات الواجهات $\{100\}$ و $\{111\}$ و $\{111\}$. حققت البلورات النانوية BF كفاءة فارادية بلغت حوالي 60% لإنتاج الإيثيلين عند تيار 90 mA cm^{-2} ، بينما أظهرت البلورات النانوية TR و SP كفاءة فارادية بلغت 85% لإنتاج الفورمات عند 39 mA cm^{-2} و 78% لإنتاج أول أكسيد الكربون عند 35 mA cm^{-2} ، على التوالي.

كشفت قياسات رامان أثناء التشغيل عن الوسطاء المحتملين لمسارات تكوين المنتجات C_1 و C_2 كما أوضحت محاكاة نظرية دالة الكثافة (DFT) الحواجز الطاقية، مما يبرز الدور الحاسم لشكل البلورات النانوية في أداء CO_2RR . توضح هذه الدراسة كيف يمكن الاستفادة من التحكم الدقيق في شكل البلوري للبلورات النانوية النحاسية لتحقيق انتقائية عالية لمنتجات CO_2RR محددة، مما يتيح مساراً لتصميم الحفازات بشكل عقلاني دون الحاجة إلى تعديلات معقدة أو إضافات.

CHAPTER 1

INTRODUCTION

1.1 Background information

Over the past century, the Earth's temperatures have been increasing because of the growing emissions of carbon dioxide (CO₂) [1,2]. By 2040, global energy consumption is projected to rise by over 48%. Fossil fuels, which remain the primary source of energy, are major contributors to the emission of CO₂ into the atmosphere [3,4]. Renewable energies like wind solar energy offer viable alternatives to fossil fuels, helping to mitigate this issue [5,6]. However, these sources are subject to seasonal variations, nocturnal, and geographical. Furthermore, various industries such as textiles, paper and pulp, aluminum refineries, iron, cement, steel, and landfills generate additional CO₂ emissions during their processes [7,8]. In fact, CO₂ alone accounts for approximately 77% of total greenhouse gas (GHG) emissions [9][10]. While natural processes like ocean absorption and forest growth do remove some CO₂ from the atmosphere, they are insufficient to counterbalance the excess CO₂ present in the air [11].

The Paris Agreement commits to cutting CO₂ emissions, aiming to limit global warming below 2 °C. The agreement prioritizes reducing human activities that generate CO₂ and developing technologies that can reduce and transform CO₂ emissions into value-added products within a circular economy framework [12]. To meet these goals, a sustainable method for removing 800 Gt (giga tone) of CO₂ from the atmosphere between 2010 and 2150 must be established [13–15]. Currently, the world can utilize just 10% of global CO₂ emissions, or 3.7 Gt/year. Nonetheless, the possibility of CO₂ sequestration may be greatly

expanded by combining companies with suitable carbon capture and storage (CCS) mechanism [16]. This integration might also allow for continuous generation of fuels and other valuable products. This worldwide effort has the potential to generate a \$0.8–1.1 trillion yearly market for carbon-based products, even if it just uses 10% of the CO₂ supply [9]. As a result, carbon capture, utilization, storage (CCUS), and another energy application like the CO₂ and methane reforming provides a medium-term strategy for lowering global CO₂ emissions [17] [18]. Advancements in technology that focus on decreasing energy consumption and adapting current facilities for CO₂ utilization are expected to be promising in the coming years [3]. Implementing CCS technology in fossil fuel-dependent power production systems is the only way to meet the 40% reduction in GHG emissions objective set by Europe's energy road plan towards a low-carbon energy system by 2030 [19].

Recent research has focused on catalytic processes that transform CO₂ into valuable chemicals and fuels for energy applications [20]. Essentially, there are multiple strategies for reducing CO₂ emissions: physical, biochemical, electrochemical, photochemical, radiochemical, thermochemical, carbon sequestration and storage, and chemical. Physical methods, such as deep-sea sequestration and geological storage, are limited by high costs and complexity [21,22]. Chemical approaches for CO₂ conversion include the use of homogeneous [23] and heterogeneous catalysts [24], as well as biochemical [25], electrochemical [26], photochemical [27], radiochemical [28], and thermochemical processes [29] [30]. While these methods show promise for producing valuable chemicals, several challenges hinder their advancement. These include the exceptional stability of CO₂, high energy and temperature requirements [31] scalability issues in industrial applications, the need for multifunctional active phases, the complex nature of tandem

cascade reactions, and the difficulties in understanding and controlling reaction mechanisms. These obstacles lead to inefficiencies and economic disadvantages. Nonetheless, the exploration and extensive development of innovative alternatives provide promising opportunities for improvement [32].

SACs and Metal-Single Atom Catalysts (M-SACs) have recently developed as potential catalysts for CO₂ utilization processes (CO₂UPs) due to their outstanding performance [33,34]. SACs, which contain separated metal atoms disperse on a conductive support, introduce a novel approach to catalysis by merging the benefits of both heterogeneous and homogeneous catalysts [35], [36]. SACs are catalysts in which individual metal atoms are dispersed and stabilized on a supporting material, often exhibiting unique catalytic properties due to their atomic-level dispersion. Unlike zeolites and metal-organic frameworks (MOFs), which are porous materials that primarily function as hosts for catalytic sites or reactants, SACs rely on isolated metal atoms as the active sites. These isolated atoms often achieve higher atomic utilization and exhibit distinct electronic structures compared to the clusters or nanoparticles found in zeolites and MOFs, leading to unique catalytic behavior [37].

The downsizing of metal sites to the atomic scale offers several benefits, including unique low-coordination of metal atoms, strong metal-support interactions, electronic structures, and maximum utilization of metal atoms [38][39,40]. Solid-state heterogeneous SACs with analogous M-N_x moieties have recently attracted significant attention for various CO₂ utilization methods. This is due to their ease of preparation, unique electronic and geometric structures, excellent conductivity (particularly when supported on carbon materials), structural stability, and outstanding CO₂UPs performance and durability [41–

43]. In a short period, the field of SACs for CO₂UPs has grown fast, resulting in the research of diverse single metal sites and reduction products [44]. Nonetheless, as the specific surface area of SACs rises, their surface free energy experiences a pronounced increase, which in turn facilitates the tendency for agglomeration coupling and the creation of sizable clusters during both their preparation and reaction processes [45]. Maiden research on catalysts with isolated metal atomic sites can be traced back to 1979, when Yates and coworkers confirmed the presence of isolated rhodium (Rh) single atoms on the surface of Al₂O₃ using nuclear magnetic resonance and ¹³C relaxation time distribution [46]. In addition to oxide systems, Thomas et al., [47] they designed a Ti single site catalyst in 1995 by directly attaching a metal-organic combination onto the inner surface of mesoporous silica. This catalyst demonstrated exceptional selectivity and efficiency in the process of epoxidizing cyclohexene and pinene with tert-butyl hydroperoxide. In 1999, Asakura et al., [47] demonstrated that atomically dispersed Pt ions stabilized on magnesium oxide exhibited comparable activity to Pt nanoparticles in the combustion of propane at low temperatures. They used X-ray absorption fine structure (XAFS) data to verify the absence of platinum particles. Subsequently, Abbet et al., [48] prepared Pd_n (1–30) clusters and single Pd sites on magnesium oxide films using a selective soft-landing method. The single Pd atoms catalyzed the formation of benzene at a low temperature of 300 K. During this period, numerous studies were conducted on supported catalysts, particularly single metal species on oxide substrates. The soft-landing method for precise nanoclusters was widely developed, and significant progress was made in catalytic research for various important conversions. Atomically dispersed metal sites are the principal active centers in these catalysts, whereas coordinated atoms (mostly carbon and nitrogen) surrounding the metal sites contribute to CO₂ activation or intermediate dissociation via electronic

polarization [49–51]. The synergetic effects of heterogeneous SACs considerably improve the catalytic performance of CO₂UPs.

1.2 CO₂ different utilization approaches

1.2.1 CO₂ dry reforming

In the dry reforming of methane (DRM), methane and CO₂ are converted into a mixture of CO and H₂ called syngas [52]. However, in this reaction, heterogeneous catalysts employ a broad size distribution of active metals, with only a small portion effectively serving as active sites [53]. To enhance metal utilization efficiency, SACs have been developed [54]. Tang et al. [55] introduced a SAC featuring Ru and Ni atoms on CeO₂ nanorods, showcasing exceptional low-temperature dry DRM activity. These single-atom sites worked synergistically to enhance H₂ production, as confirmed by Density functional theory (DFT) calculations. Similarly, noble metal SACs like the Pt/CeO₂ catalyst developed by Shen et al. [56] exhibited improved metal utilization and demonstrated effective DRM reactivity at 350 °C, with the Pt–CeO₂ interface playing a crucial role in CH₄ activation and CO₂ dissociation. Other notable SACs include a Rh–La₂Ti₂O₇ catalyst, which achieved over 25% conversion of CH₄ and CO₂ at 550 °C. This remarkable catalytic performance is attributed to the coexistence of Rh⁰ and Rh^{δ+} species in Rh–La₂Ti₂O₇, which enhances electron transport and increases the mobility of active oxygen species [57]. Also, a Ni/HAP SAC by Akri et al. [58], which displayed significant DRM performance at 750 °C with excellent resistance to coke formation. Despite these advantages, SACs face challenges in synthesis and stabilization and have not consistently outperformed traditional heterogeneous catalysts. Additionally, SACs often struggle with stability in fixed-bed reactors for DRM reactions [59].

A synergistic effect of single-atom Ni₁ and Ru₁ sites on CeO₂ nanorods (Ce_{0.95}Ni_{0.025}Ru_{0.025}O₂) has been reported for DRM (CH₄ + CO₂) [55]. This catalyst, featuring highly active SACs, achieves a turnover rate of 73.6 H₂ molecules per site per second at 560 °C, with 98.5% selectivity to H₂. The Ni₁ and Ru₁ sites remain atomically dispersed and cationic even at temperatures up to 600 °C, working together to reduce the activation barrier and enhance H₂ and CO production rates. This performance surpasses that of catalysts containing only Ni₁ or Ru₁ sites. Computational studies reveal that Ni₁ sites activate CH₄ to form CO, while Ru₁ sites dissociate CO₂ to CO, with H₂ forming through H atom coupling on Ru₁ sites. Small active sites at the atomic level often face synthesis challenges and show minimal improvement in catalytic reactivity. For the DRM reaction, nanocluster and nanoparticle level metal sites (larger than 1 nm) are more effective. Recent studies have shown that Ni sites sized 10–20 nm exhibit significant DRM activity and reduced coke formation above 700 °C. Below 700 °C, Ni sintering effects are less significant, but coke formation increases and catalyst activity decreases, especially for CH₄ activation [60][61]. Therefore, proper sizing of active sites is crucial for achieving high activity and coke resistance in low-temperature DRM reactions. Further research is needed to understand the size effects of active metals and guide the synthesis of cost-effective, highly active catalysts. Kim et al. [62] reported a Pt-NiCe@SiO₂ single-atom alloy (SAA) prepared by the reverse microemulsion method for DRM. [Figure 1a](#) shows the TEM image of the reduced Pt_{0.25}-NiCe@SiO₂ SAA catalyst. The yolks are well distributed within the SiO₂ shell, with an average cavity diameter of 106.5 nm and a wall thickness of 6.6 nm. Isolated Pt atoms, highlighted in yellow circles, confirm the SAA structure. HRTEM images shown in [Figure 1\(c-d\)](#) reveal lattice fringes of 0.20 nm (Ni (111)), 0.18 nm (Ni (200)), 0.31 nm (CeO₂ (111)), and 0.27 nm (CeO₂ (200)), indicating a Ni–CeO₂

interaction. Pt–Ni alloys are mostly at the yolk edges, suggesting Pt-terminated Pt–Ni catalysts form a stable core–shell structure under reducing conditions. The yolk-shell morphology and Pt–Ni SAA structures prevent carbon formation and enhance catalyst stability. This design facilitates CO desorption and reduces carbon deposition. Adding 0.25 wt % Pt ensures 120 h stability at 500°C during DRM by forming Pt–Ni SAA structures within the SiO₂ shell, enhancing interactions and suppressing carbon formation.

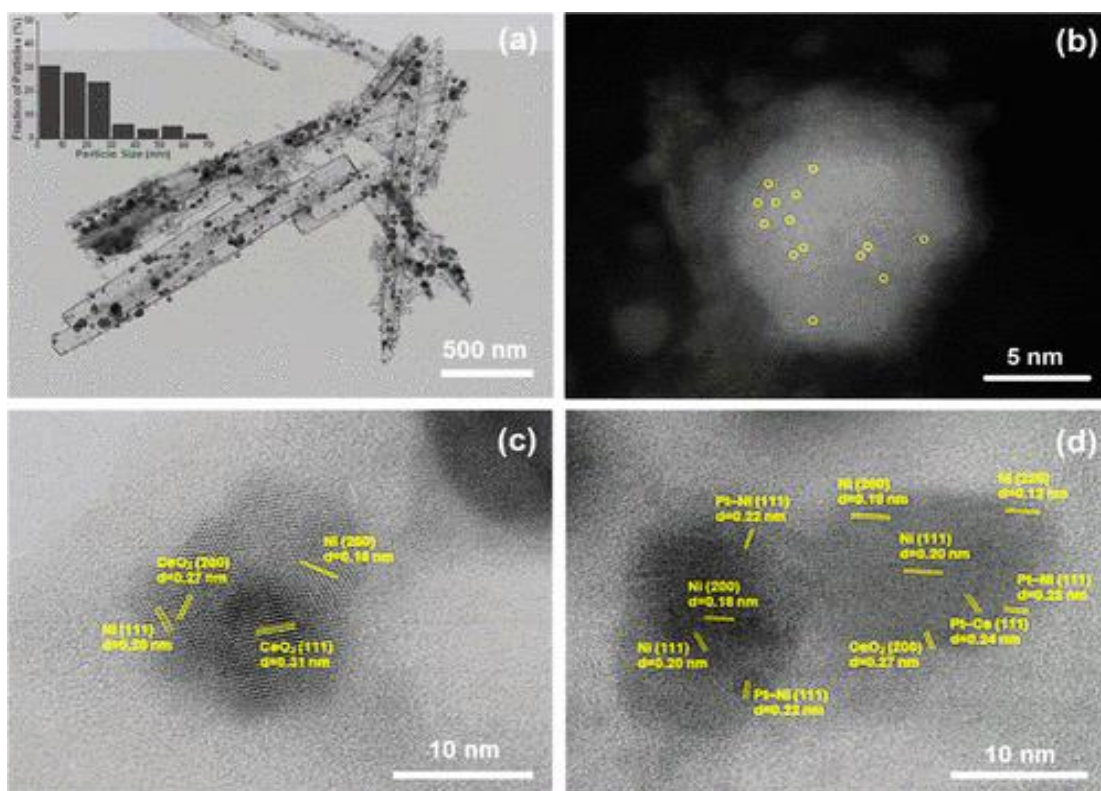


Figure 1: (a) TEM, (b) AC-HAADF-STEM, and (c, d) HRTEM images of the reduced nanotubular yolk-shell Pt_{0.25}-NiCe@SiO₂ SAA catalyst. Reprinted with permission from [63].

Rao et al. [64] introduced a concept for achieving highly durable DRM at low temperatures by integrating active sites with light irradiation. They successfully developed two types of

active sites on CeO₂: Ni–O coordination (Ni_{SA}/CeO₂) and Ni–Ni coordination (Ni_{NP}/CeO₂). These sites enabled two distinct reaction paths to produce the key intermediate CH₃O*, which helps prevent coke formation. However, under light irradiation, formate (HCO₂*) increased, linearly adsorbed CO decreased, and gaseous CO bands became more prominent depicted in [Figure 2a](#). A minimal change occurred in the dark, as shown in [Figure 2b](#). Light enhances Ni_{SA}/CeO₂ activity by accelerating carbonate-to-CO conversion and CO desorption. Switching to ¹³CO₂/¹²CH₄/Ar showed a distinct isotope effect, indicating light speeds up CH₃O* to CO conversion. In situ Raman with C¹⁸O₂ revealed that light significantly accelerates Ce–O ionization and CH₃O* formation, with a shift of 27 cm⁻¹ under light compared to 18 cm⁻¹ in the dark as shown in [Figure 2c](#) and [d](#). This study revealed that the CH₃* to CH₃O* path over Ni_{SA}/CeO₂ is crucial for anticoking. Additionally, light irradiation further enhanced this reaction path during DRM, as demonstrated by operando DRIFTS-SSITKA.

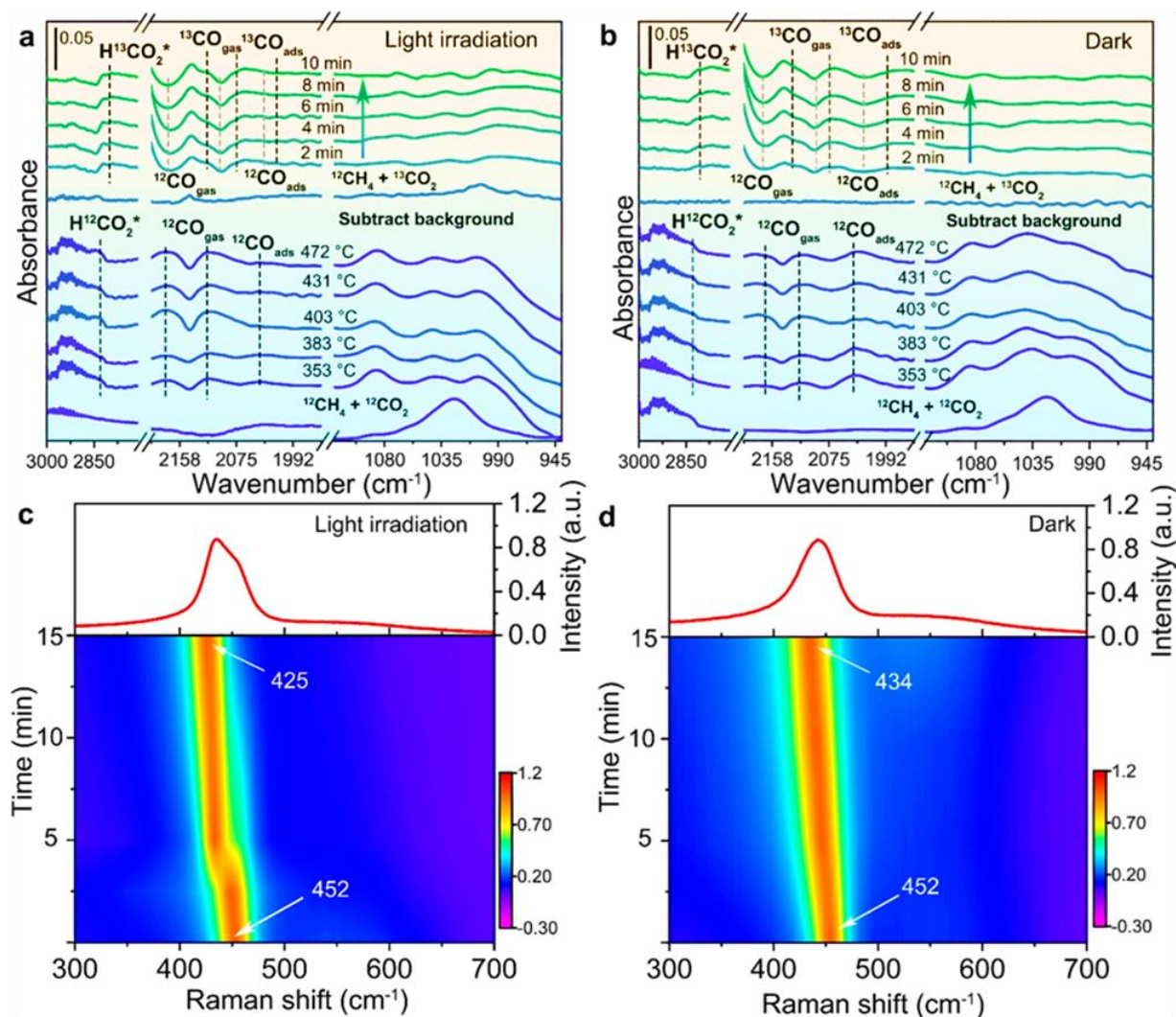


Figure 2: Operando DRIFT-SSITKA and in situ Raman spectra of DRM reaction over NiSA/CeO₂. Reprinted with permission from [64].

Li et al. [65] developed ordered mesoporous ceria (mp-CeO₂) to stabilize Ni single atoms in DRM. As shown in Figure 3, the Ni1@mp-CeO₂ catalyst exhibited superior DRM performance with a lower CO₂ deactivation rate (k_d) of $0.1 \times 10^{-3} \text{ h}^{-1}$, compared to $9.6 \times 10^{-3} \text{ h}^{-1}$ for Ni₁/CeO₂. Figure 3d illustrates that catalyst deactivation in DRM is caused by coke deposition and Ni sintering. Remarkably, the Ni₁@mp-CeO₂ catalyst-maintained stability for 120 h without significant deactivation (see Figure 3e), due to its strong metal-support interaction and confinement effect. This demonstrates that Ni single atoms supported on mesoporous

CeO₂ offer better stability than those on bulk CeO₂. The Ni1@mp-CeO₂ catalyst, featuring many oxygen vacancies and basic sites, activates CO₂ and removes carbon deposits more effectively than the Ni₁/CeO₂ catalyst. The mesoporous structure also prevents Ni cluster sintering, improving stability. This study shows that Ni single atoms can grow into nanoclusters during DRM and using them as precursors helps suppress carbon deposition.

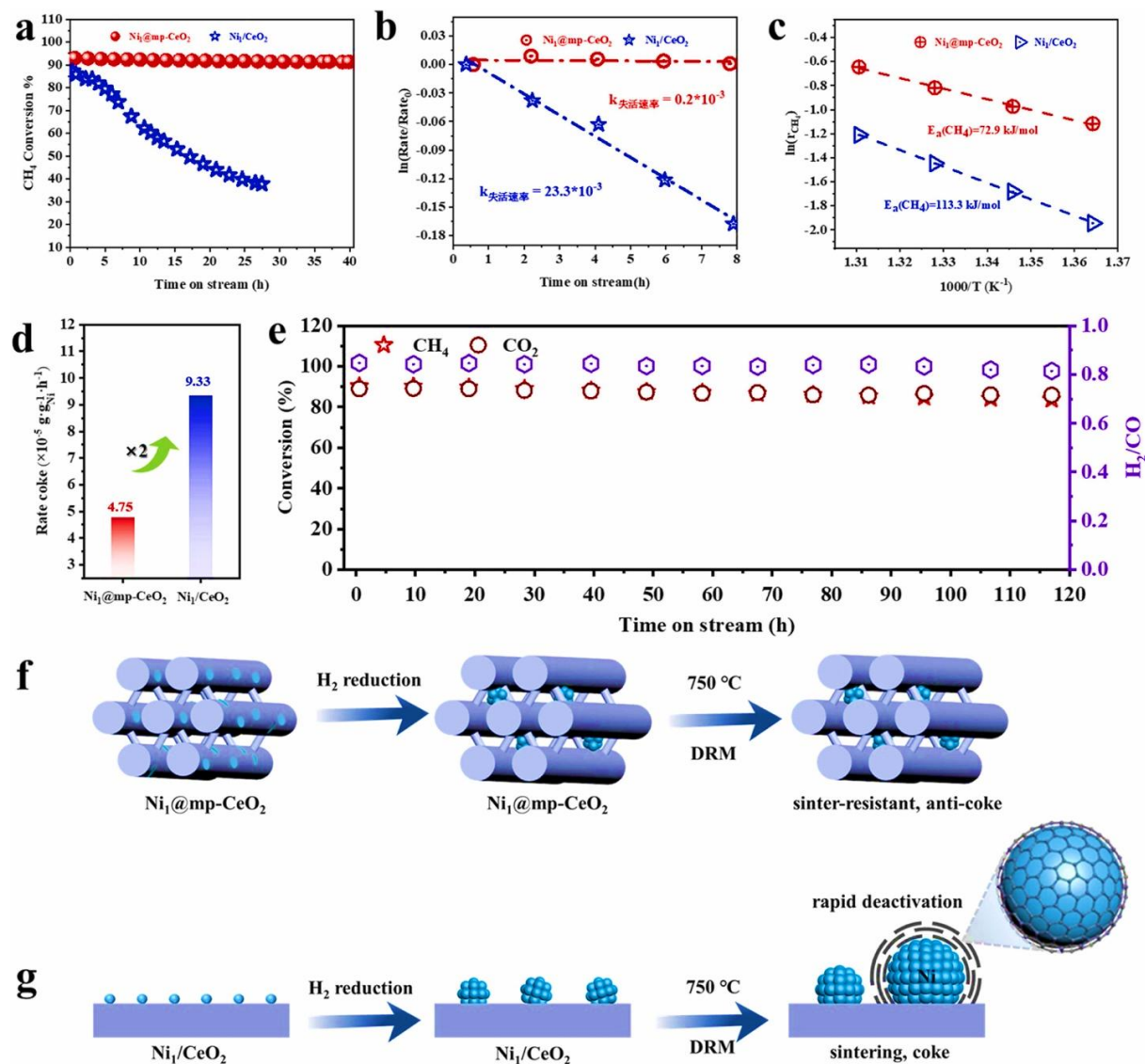


Figure 3: The catalytic performance of the reduced Ni₁@mp-CeO₂ and Ni₁/CeO₂ at 750 °C: (a) CH₄ conversion. (b) Corresponding changes of CH₄ rates with respect to the initial rates (r/r₀); (c) Arrhenius plot; (d) TGA data of the spent catalysts after reaction. (e) Stability test of Ni₁@mp-CeO₂ catalyst in continuous DRM for 120 h. (f-g) Schematic illustration of the structure evolution of the two Ni single atom catalysts supported on bulk CeO₂ and mesoporous CeO₂ during the DRM. Reprinted with permission from [65].

Zhang et al. [66] developed a Ru₁/Mg-CeO₂-NR SAC that exceeded the thermodynamic equilibrium limit for syngas production under photo-thermal catalysis (PTC) conditions, even at high flow rates. The catalyst achieved syngas production rates of 0.56 mol g⁻¹ h⁻¹ for H₂ and 0.85 mol g⁻¹ h⁻¹ for CO at 500 °C. Operando experiments demonstrated the Ru-O-Ce electron transfer path and its impact on the rate-determining step (RDS) of the DRM. During these experiments, no significant correlation was observed between b-CO₃^{*} or COOH^{*} concentrations and catalyst performance (see Figure 4). However, CH_x concentration was strongly linked to performance in Ru₁/CeO₂-NR and Ru₁/Mg-CeO₂-NR, with the Ru-O-Mg structure in Ru₁/Mg-CeO₂-NR enhancing CH_x levels and performance, indicating CH₄ dissociation as the rate-determining step in DRM. UV light boosts CH₄ dissociation, leading to higher H^{*} generation and H₂ production (see Figures 4(d-e)), which improves the H₂/CO ratio and overall performance under photo-thermal conditions. Mg doping and the nanorod structure increase CO₂ adsorption and COOH^{*} conversion (see Figure 4(a-c)), further enhancing CO production. Light irradiation also improves CO₂ adsorption (see Figure 4(d-e)), contributing to the superior photo-thermal catalytic performance of Ru₁/Mg-CeO₂-NR.

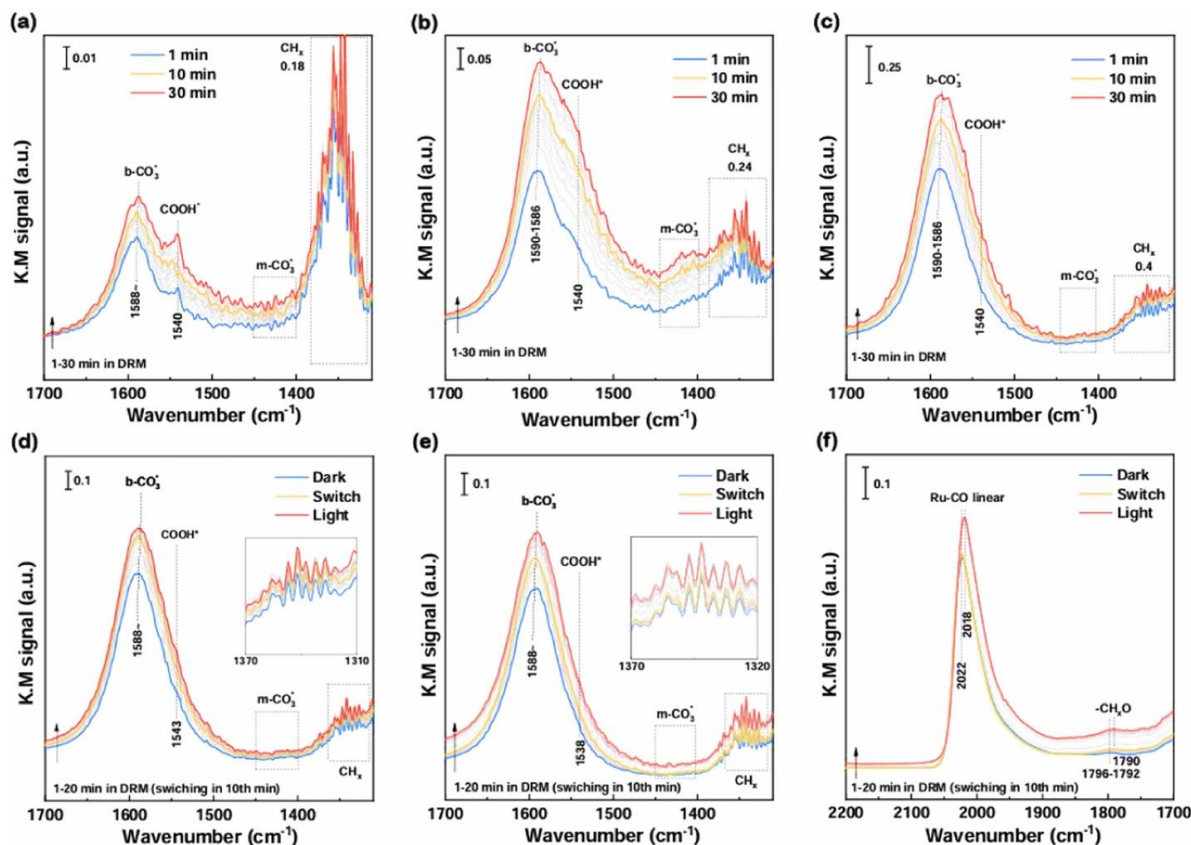


Figure 4: In situ DRIFTS spectra and mechanism of DRM reaction. (a-c) 1310–1700 cm^{-1} spectra over $\text{Ru}_1/\text{CeO}_2\text{-NP}$, $\text{Ru}_1/\text{CeO}_2\text{-NR}$ and $\text{Ru}_1/\text{Mg-CeO}_2\text{-NR}$ under dark conditions at 450 °C; (d) 1310–1700 cm^{-1} spectra over $\text{Ru}_1/\text{Mg-CeO}_2\text{-NR}$ under dark and > 650 nm illumination at 450 °C; (e) 1310–1700 cm^{-1} spectra over $\text{Ru}_1/\text{Mg-CeO}_2\text{-NR}$ under dark and full spectrum illumination at 450 °C and (f) 1700–2200 cm^{-1} spectra over $\text{Ru}_1/\text{Mg-CeO}_2\text{-NR}$ under dark and full spectrum illumination at 450 °C; micro-steps of DRM reaction. Reprinted with permission from [66]

DRM typically requires high temperatures, leading to the exsolution and redistribution of active sites. However, characterizing these catalysts after cooling and sample preparation often results in the active atoms diffusing back into the bulk. Mekker et al. [67] investigated the factors influencing the migration dynamics of atoms on the surface and subsurface of supported SACs during the DRM at 700–900 °C. The catalysts' performance improved with reaction as rhodium atoms migrated from the subsurface to the surface. While

the oxidation state of rhodium changed from Rh(III) to Rh(II) or Rh(0) during catalysis, atom migration was the primary factor affecting performance. Multiple processes have been hypothesized for SACs stimulating impact, including stronger interactions with support, the formation of low-coordinated active sites, and active site-support [68,69][70]. However, these contributions frequently interact, confusing the understanding of their catalytic nature and impeding rational SAC evolution [71]. Zuo et al. [72] studied single-atom Ni₁/Mg(100) and single-site Ni₄/Mg(100) catalysts in DRM, combining DFT, kinetic Monte Carlo (KMC) simulations, and experiments studies. This approach clarified the reaction mechanisms on SACs, including pathway interplay, conversion, selectivity, carbon deposition/elimination sources, and the roles of Ni sites and MgO support.

1.2.2 CO₂ methanation

CO₂ methanation is an exothermic, thermodynamically favorable reaction. Supported nickel catalysts are effective but face kinetic limitations at lower temperatures. The catalyst's structure greatly influences its activity and selectivity, and understanding the mechanism remains challenging due to structural complexity [73]. Converting CO₂ to CH₄ offers a sustainable alternative to fossil fuels and is useful for syngas production. CH₄ is a crucial raw material for syngas and other chemical products, compatible with existing equipment, and a potential fossil fuel substitute. However, the conversion of CO₂ at lower temperatures is challenging but desirable [74]. Effective catalysts must be stable and active at high pressures and temperatures, often requiring precise tuning [75]. The support material prevents metal agglomeration and maintains activity, while its properties (size, surface area, porosity, acidity, and basicity) impact catalytic performance and selectivity. Supported metal catalysts offer a cost-effective alternative to expensive Ru, Pt, and Pd-based catalysts. By doping 4–6

wt% of precious metal onto a cheaper support, SACs enhance catalytic performance and reduce costs [76]. Atomically dispersed metals provide active sites and maximize efficiency [77]. Similarly, Shi et al. [78] developed an atomic-scale photocatalyst, Pt@Def-CN, for CO₂ methanation with H₂O by embedding single Pt atoms into defect sites of carbon nitride (CN) and adding -OH groups. This catalyst achieved high CO₂ reduction activity (6.3 μmol g⁻¹ h⁻¹ CH₄) and 99% CH₄ selectivity in pure water. The -OH groups enhanced CO₂ adsorption, while Pt atoms activated CO₂ to form CH₄ and produced H and O₂ from H₂O. Pt sites reduced the rate-limiting step's energy barrier and improved CH₄ selectivity. Pt@Def-CN was made by first creating primitive CN (P-CN) from melamine, then hydrothermally treating it to form Def-CN with -OH groups. Pt was introduced at Def-CN edges and bound through low-temperature calcination. XRD and FTIR confirmed no structural changes to CN, while AC-HAADF-STEM and EDS mapping showed uniform dispersion of atomically isolated Pt.

Vogt et al. [79] employed operando XAS and FT-IR to explore the size effect of SiO₂-supported Ni catalysts for CO₂ methanation. They found that sub-2 nm Ni particles had lower d-band energy, affecting catalytic activity. Smaller Ni particles favored CO production, while larger particles were more methane selective. Single-atom Ni catalysts produced only CO. The size effect in Ni/SiO₂ catalysts was attributed to changes in the electronic structure for particles 1–7 nm, whereas for larger particles (8–21 nm), the effect was due to increased active site abundance. Additionally, Ru/Mg-CeO₂ catalyst was developed based on single-atom and photo-thermal catalysis concepts [80]. It achieved a CH₄ formation rate of 469 mmol g⁻¹ h⁻¹ at 400 °C under photo-thermal conditions, demonstrating good stability. Characterization revealed the advantages of single Ru atoms, the Ru-O-Ce structure, and alkaline metal doping. ISI-XPS experiments confirmed electron migration from Ce and Mg to Ru via Ru-O-Ce and Ru-

O-Mg paths under photo-thermal catalysis. As shown in [Figure 5\(a-b\)](#), the Ru/Mg-CeO₂ catalyst achieved higher CH₄ formation rates and CO₂ conversion compared to Ru/CeO₂, demonstrating that Mg doping enhances reaction performance. The Mg-doped catalyst also lowered the initial CO₂ methanation temperature and showed noticeable CO₂ conversion at 573 K. Additionally, Mg doping improved methane selectivity as shown in [Figure 5\(c-e\)](#), likely due to increased H₂ dissociation capacity from enhanced activation of H₂ at Ru sites, facilitated by electron migration from low-valence metals. Furthermore, Li et al. [81] developed a photothermal system using a selective light absorber to achieve temperatures up to 288 °C under ineffective solar irradiation (1 kW m⁻²), three times higher than traditional systems. They synthesized ultrathin amorphous Y₂O₃ nanosheets with single Ni atoms (SA Ni/Y₂O₃), which showed excellent CO₂ methanation performance. The system achieved 80% CO₂ conversion and a CH₄ production rate of 7.5 L m⁻² h⁻¹ under solar irradiation (0.52 to 0.7 kW m⁻²), demonstrating its effectiveness for converting CO₂ to valuable chemicals using dispersed solar energy. The UV-Vis-IR spectrum [Figure 6 \(a\)](#) shows full solar absorption (300 nm to 2 μm) and high IR absorption (2–10 μm), leading to heat dissipation and limiting temperatures to 78 °C under 1 kW m⁻² (see [Figure 6\(c\)](#)). The selective light absorber absorbs 300–1300 nm (~100% of the solar spectrum) with minimal IR absorption (see [Figure 6 \(b\)](#)). The radiative heat loss from the absorber is 0.21 kW m⁻² at 200 °C, much lower than that of Ni/Y₂O₃. The photothermal system with the selective light absorber on a quartz tube enhances temperatures. Ni/Y₂O₃ nanosheets reach 288°C under 1 kW m⁻², which is 3.7 times higher than direct irradiation (see [Figure 6 \(c\)](#)). The system achieves 80% CO₂ methanation efficiency, outperforming Ni/Al₂O₃ systems that only reach 81 °C, as illustrated in [Figure 6 \(d\)](#) [82].

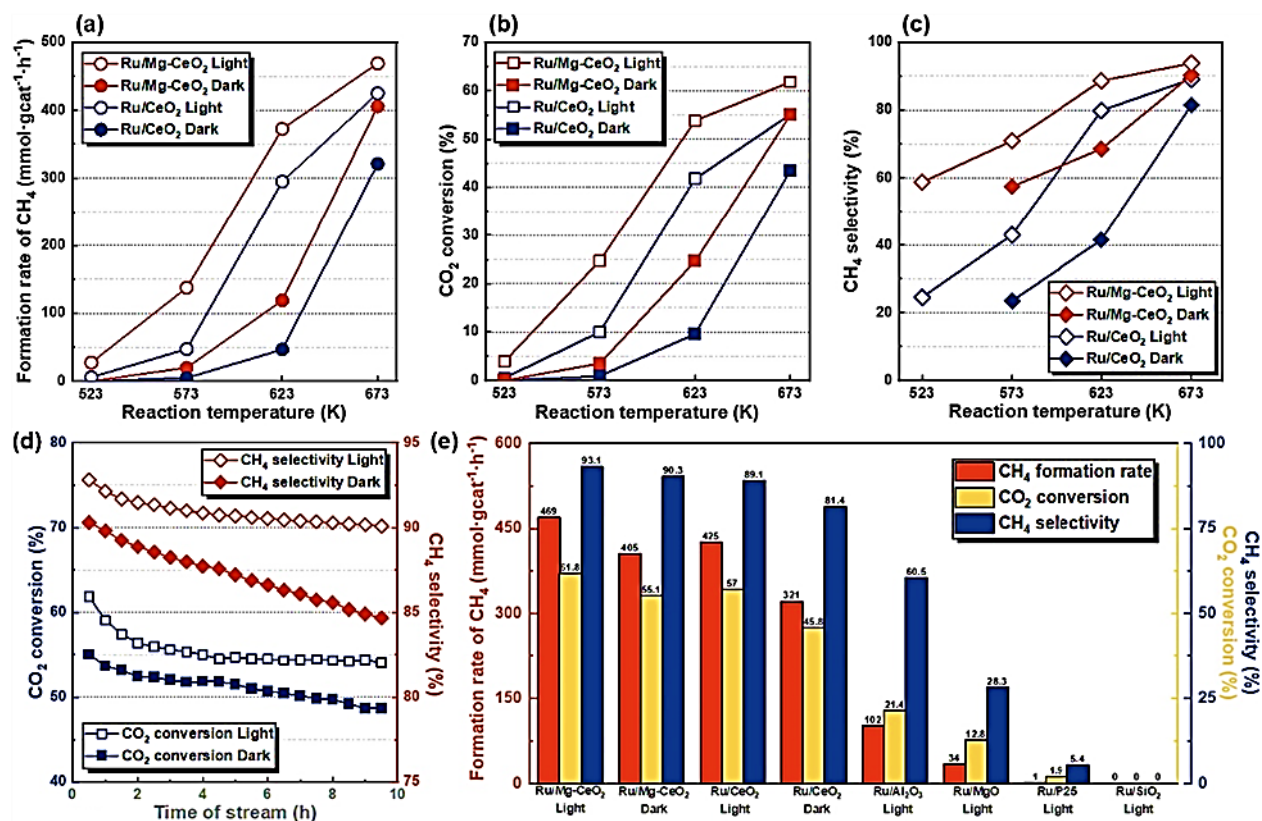


Figure 5: Initial (a) CH₄ formation rate, (b) CO₂ conversion and (c) CH₄ selectivity over Ru/CeO₂ and Ru/Mg-CeO₂ under thermal and photo-thermal conditions; (d) CO₂ conversion and CH₄ selectivity during 10 h evaluation test; (e) CH₄ formation rate, CO₂ conversion and CH₄ selectivity over different catalysts; (f) performance comparison of CH₄ formation rate. Reprinted with permission from [80]

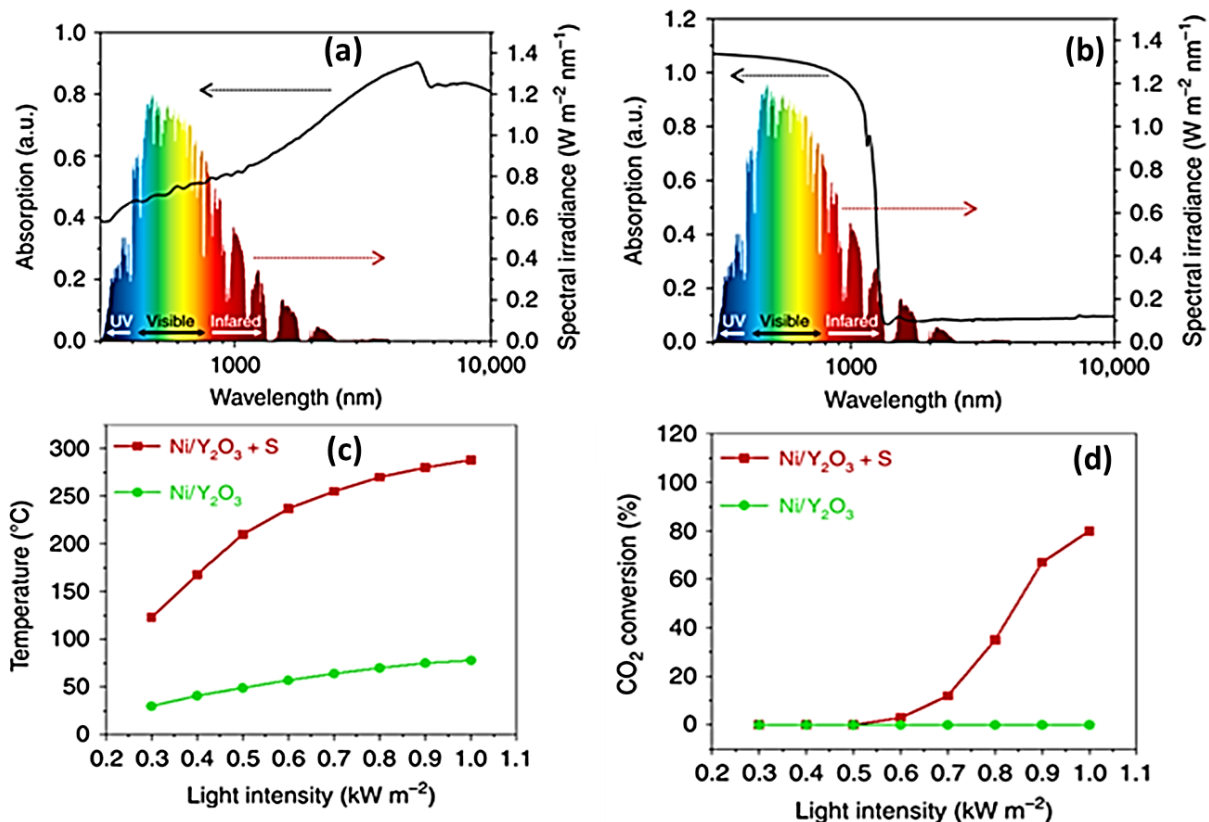


Figure 6: (a) Ni/Y₂O₃ nanosheets powder. (b) UV-Vis-IR spectrum of Ni/Y₂O₃ nanosheets. (d) SEM image of the selective light absorber (AlN_x/Al foil). (e) UV-Vis-IR spectrum of the selective light absorber. (f) Solar energy absorption and thermal radiation at 200°C for the selective light absorber; thermal radiation is much lower than absorbed energy. (g) Schematic of the photothermal system for CO₂ methanation. (h, i) Temperature and CO₂ conversion rates for Ni/Y₂O₃ nanosheets with (Ni/Y₂O₃ + S red) and without (Ni/Y₂O₃ green) the selective light absorber under various sunlight intensities. Scale bar in d: 2000 nm. Reprinted with permission from [82].

1.2.3 CO₂ Formylation with Aniline

Converting CO₂ into valuable products using efficient and reusable catalysts is crucial for mitigating carbon emissions [83,84]. Developing a catalyst that effectively promotes the N-formylation reaction under mild conditions is highly desirable. N-Formamides serve as crucial intermediates in the production of numerous pharmaceuticals and function as protective agents for amines. Additionally, they catalyze various chemical reactions [85]. SAC

offer exceptional potential due to their optimal atom utilization and remarkable catalytic activity [86] [87]. Various fabrication methods for utilizing SACs in N-formylation have been documented, including atomic layer deposition [88], wet chemistry [89] and MOF derivative [90]. However, these methods often demand harsh conditions, such as high temperature, high pressure, acids, or complex reaction procedures. Facilitating large-scale industrial applications, developing straightforward and efficient methods for producing SACs is crucial. Qiang Cao et al. developed a highly efficient zinc-based SAC for converting CO₂ into valuable N-formanilide under mild conditions. Their catalyst exhibits exceptional activity and recyclability, offering a promising approach to carbon dioxide utilization and environmental sustainability [91]. The effective synthesis of a single-atom zinc catalyst based on a porous organic polymer was achieved by Yingjun Li et al. Under moderate reaction conditions, this catalyst demonstrated outstanding efficiency in transforming carbon dioxide into valuable N-formanilide. Their finding highlighted that the exceptional catalyst activity and selectivity can be ascribed to the uniform distribution of zinc single atoms and the permeable structure of the support material. Crucially, this catalyst can be reused several times without a substantial decrease in activity, showcasing its promise for practical usage in carbon dioxide valorization systems [92]

1.2.4 CO₂ Hydrogenation

The production of higher alcohols has gained significant attention due to their versatile applications as solvents and fuel additives in various industries [93–96]. Given the natural process of photosynthesis, where fossil fuels originated from carbon and hydrogen, artificially combining CO₂ and H₂ to recreate hydrocarbon fuels presents a promising

approach to sustainability [97,98]. Converting CO₂ into valuable products through direct hydrogenation presents challenges due to CO₂'s stability. However, significant advancements have been made in producing single-carbon compounds like formic acid, carbon monoxide, methane, and methanol using this method [98,99]. Both direct hydrogen reduction and chemical reduction in water have been explored to achieve these products [100–105]. The conversion of CO₂ into methane through thermocatalysis is a relatively straightforward process that can be achieved under mild conditions. This method has demonstrated high efficiency in converting CO₂ to methane. Additionally, producing carbon monoxide from CO₂ can be accomplished through the reverse water-gas shift reaction. Furthermore, the industrial-scale production of methanol from CO₂ has already been realized in Iceland, utilizing geothermal energy and catalytic processes [106–108].

Jotheeswari et al. [107] developed a highly efficient homogeneous catalytic system for converting CO₂ into CH₃OH. This system utilizes pentaethylenhexamine and Ru-Macho-BH (1) as catalysts, operating at temperatures between 125–165 °C in an ethereal solvent. It achieves an initial turnover frequency of 70 h⁻¹ at 145 °C and maintains robustness over five cycles with a turnover number exceeding 2000. The system can process CO₂ from various sources, including air with its low concentration of 400 ppm CO₂. Remarkably, this represents the first successful demonstration of direct methanol production from air-captured CO₂, achieving a yield of 79%. Also, Hironobu et al. introduced [109,110] a PdMo intermetallic catalyst that enables low-temperature CO₂ hydrogenation. Synthesized via the simple ammonolysis of an oxide precursor, this catalyst shows excellent stability in both air and reaction environments, significantly boosting catalytic activity for converting CO₂ to

methanol and CO compared to a Pd catalyst. A turnover frequency of 0.15 h^{-1} for methanol synthesis was achieved at 0.9 MPa and 25°C , matching or surpassing state-of-the-art heterogeneous catalysts operating under higher pressures (4–5 MPa). **Table 1.** Summarizes key advancements in SACs for CO_2 utilization, emphasizing improvements in catalytic performance, selectivity, and stability. It provides an overview of various SACs, their synthesis methods, active sites, and their effectiveness in electrocatalytic or thermocatalytic CO_2 reduction. Notable trends include the development of SACs with well-defined metal-N-C structures, which enhance CO_2 adsorption and activation. Recent research focuses on tuning electronic structures through coordination engineering to improve selectivity toward C_{2+} products

1.3 Statement of the problem

The increasing concentration of CO_2 in the atmosphere, driven by fossil fuel consumption and industrial activities, poses a severe threat to global climate stability. Despite efforts to mitigate emissions through renewable energy sources, seasonal and geographical limitations hinder their effectiveness. Existing natural carbon sinks, such as forests and oceans, are insufficient to counteract the rising CO_2 levels, necessitating alternative technological interventions. While carbon capture, utilization, and storage (CCUS) strategies offer promising solutions, their scalability, energy requirements, and economic feasibility remain significant challenges.

Among various CO_2 conversion approaches, catalytic transformation into valuable chemicals and fuels is a promising strategy. However, traditional heterogeneous and homogeneous catalysts suffer from low efficiency, high energy demands, and poor selectivity due to the

inherent stability of CO₂ molecules. The emergence of single-atom catalysts (SACs) presents a novel paradigm, combining the advantages of both catalytic systems through atomically dispersed metal sites. SACs exhibit exceptional reactivity, electronic tunability, and metal utilization, making them attractive for CO₂ utilization processes (CO₂UPs). However, challenges such as catalyst stability, metal aggregation, and understanding reaction mechanisms hinder their widespread adoption. Despite rapid advancements in SACs for CO₂ conversion, fundamental knowledge gaps remain regarding their structure-performance relationships, scalability, and practical implementation in industrial applications. Therefore, a comprehensive evaluation of recent developments, limitations, and future perspectives in SAC-based CO₂UPs is essential to bridge the gap between laboratory research and real-world applications, ultimately contributing to sustainable carbon management and circular economy goals.

1.4 Research objectives

This study aims to explore the electrochemical conversion of CO₂ using Cu nanoparticles as catalysts, focusing on their efficiency, selectivity, and mechanistic insights. The specific objectives are:

1. To investigate the role of Cu nanoparticles in CO₂ electroreduction – Examine the catalytic properties of Cu nanoparticles in facilitating the electrochemical conversion of CO₂ into valuable products.
2. To analyze product selectivity and reaction pathways – Identify the major reduction products (e.g., CO, CH₄, C₂H₄, C₂H₅OH) and elucidate the underlying reaction mechanisms influenced by Cu nanoparticle morphology and oxidation states.

3. To evaluate the influence of structural and electronic properties – Assess how factors such as nanoparticle size, surface defects, and electronic structure impact catalytic activity and selectivity in CO₂ electroreduction.
4. To optimize reaction conditions for enhanced efficiency – Explore the effects of electrolyte composition, applied potential, pH, and reaction kinetics on the performance of Cu-based catalysts.
5. To address challenges and propose strategies for improvement – Identify limitations such as catalyst stability, overpotential requirements, and competing side reactions, proposing innovative approaches to enhance efficiency and long-term viability.

CHAPTER 2

LITERATURE REVIEW

2.1 CO₂ utilization

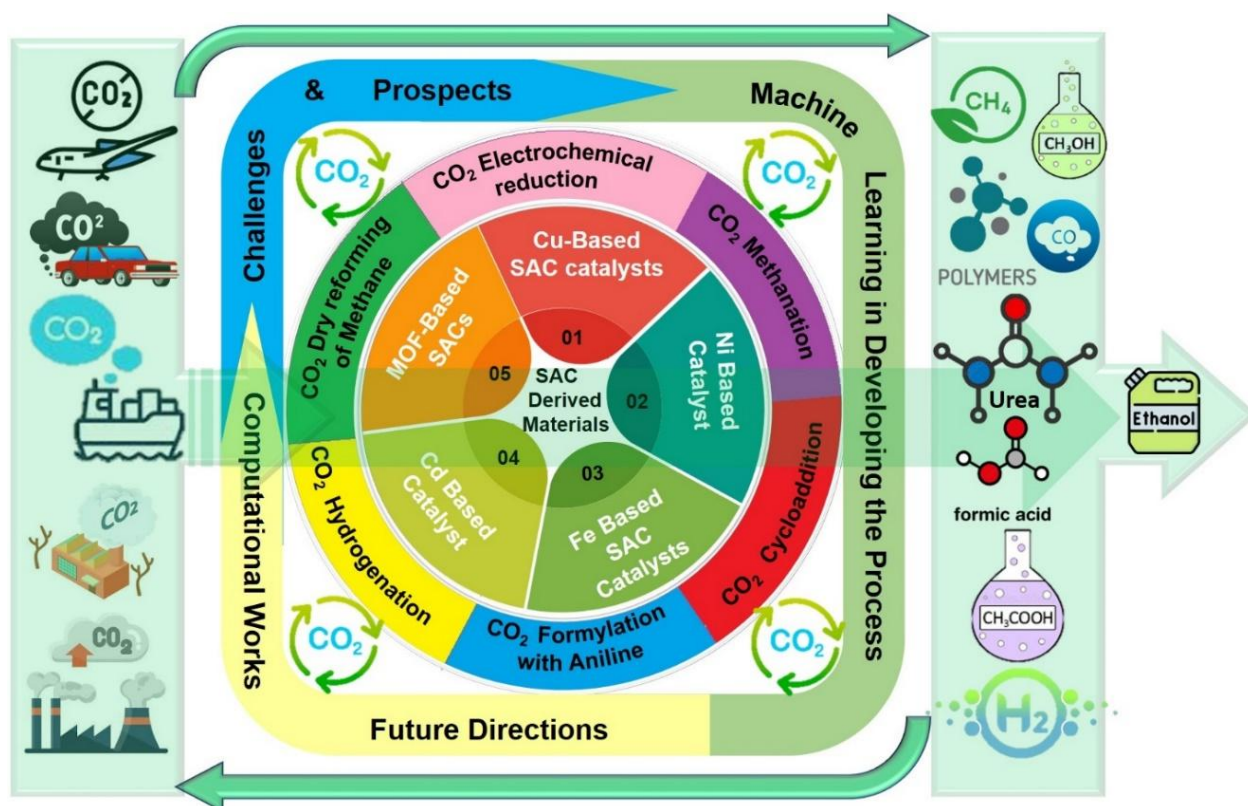


Figure 7: CO₂ utilization pathway (Data obtained from Web of Science).

2.2 From bulk to atomics, a history of single-atom catalyst development

The concept of isolated atoms acting as catalysts isn't new. Even before its application in modern heterogeneous catalysts with supported metals, nature utilized single atoms in various forms to drive crucial chemical reactions. Examples include metalloenzymes, organometallic complexes, and open framework structures [111]. Pioneering work by Flytzani-Stephanopoulos et al., [112]. and Bashyam and Zelenay [113] challenged the traditional view of metal nanoparticles in catalysis. These researchers demonstrated that isolated ionic gold/platinum and oxidized cobalt/iron species were responsible for activity in the water-gas shift and oxygen reduction reactions, respectively. Advancements in experimental techniques later confirmed the presence of these isolated centers, solidifying the concept of SACs as in Figure 8 showing the timeline for SACs concept.

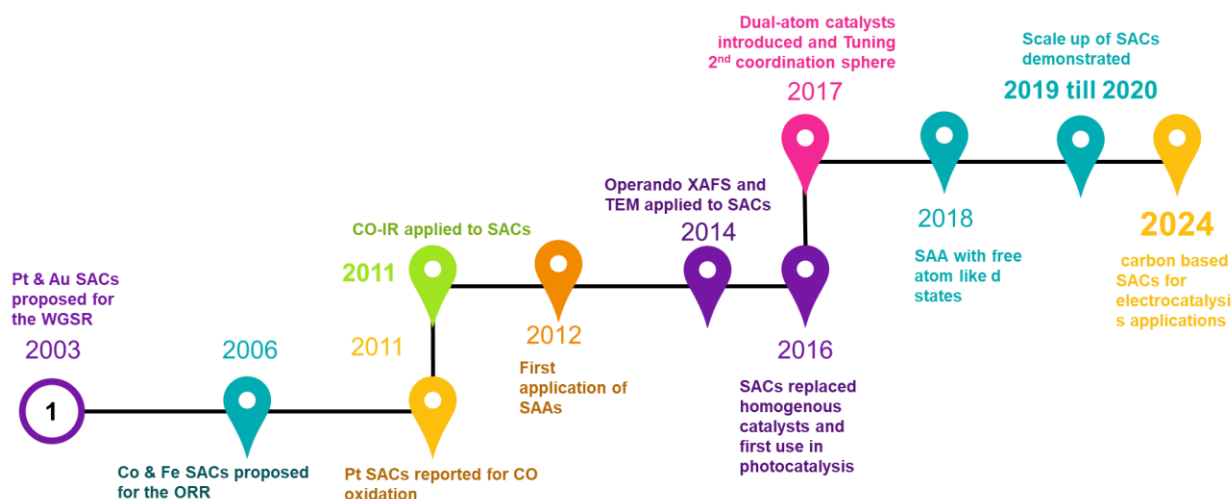


Figure 8: SACs a decade of stunning advancement and the ability for a bright future (Data obtained from Web of Science).

Notably, Zhang et al., landmark work showcased the high productivity of platinum single atoms on iron oxide for CO oxidation, ushering in a new era in heterogeneous catalysis

[114][115]. Single-atom catalysis has exploded in popularity over the past decade, becoming a major focus in modern chemical research. Early researchers soon realized the potential cost advantages of using atomically dispersed species for precious metals, and enhancing their utilization became a key focus in the field [116]. Over the 10-year journey since the topic's consolidation, single-atom catalysis has explored the entire periodic table. The variety of host materials has also grown. Although metal oxides were initially the most extensively studied, customized carbons have become the most dominant in recent years. The range of applications has broadened, with an increasing emphasis on heterogeneous catalysis [117]. Iron, cobalt, and nickel atoms dispersed individually on nitrogen-doped carbon materials have exhibited remarkable catalytic activity in key energy-related processes, such as oxygen reduction [113], hydrogen evolution reaction [118], and carbon dioxide conversion [119]. While research on single atom photocatalysts is still in its infancy compared to electrocatalysts, this field also holds great promise for addressing the energy crisis [120]. The starting point for single atoms was the concept of subnanometer clusters, which paved the way for moving beyond the nanoparticle scale [121].

2.3 Advantages of subnanometer clusters and single atoms over nanoparticles

The significance of particle sizes in determining catalytic properties is well-established, leading to the development of various catalyst forms, including nanoparticles, nanosized clusters, and monatomic catalysts, to enhance their effectiveness [122,123]. Transitioning metal active sites from nanoparticles to sub-nanometer clusters and then to single atoms introduces differences in metal atom aggregation and coordination structures in supported catalysts [124–126]. Homogeneous catalysts, heterogeneous nanoparticles, and SACs of the

same metal often exhibit distinct catalytic behaviors due to differences in atomic utilization and coordination environments [127]. For instance, homogeneous nickel complexes demonstrate high activity for CO₂ activation in hydrogenation reactions but suffer from poor stability and recyclability, limiting their practical applications[128]. In contrast, nickel nanoparticles supported on oxides offer improved durability; however, their catalytic activity and selectivity are largely influenced by particle size, leading to variations in performance[129]. Single-atom Ni catalysts anchored on nitrogen-doped carbon overcome these limitations by achieving nearly 100% atomic utilization, significantly enhancing CO₂ conversion efficiency and selectivity[130]. Similarly, copper-based homogeneous catalysts efficiently catalyze CO₂ reduction but require ligand stabilization to maintain their activity[131] [132]. While Cu nanoparticles supported on zirconia provide better stability, their performance is hindered by low selectivity due to the presence of multiple active sites[133]. In contrast, Cu-SACs anchored on carbon-based supports demonstrate superior catalytic efficiency, attributed to their well-defined single-atom active sites that optimize electronic interactions with the support material[134][135][136]. For instance, Yang et al. reported that Cu-SACs exhibit significantly enhanced CO₂ hydrogenation selectivity compared to Cu nanoparticles, achieving higher conversion efficiency and product specificity [137]. These examples underscore the critical role of SACs in bridging the gap between homogeneous and heterogeneous catalysis, offering a promising avenue for advancing CO₂ utilization technologies by improving activity, stability, and selectivity. However, stabilizing high-surface-energy metal particles on supporting materials is challenging, as it requires significantly reducing the loading and consequently the availability of active sites for the catalytic route [138].

Supported sub-nanometer cluster catalysts (SNCCs, <2 nm) offer nearly fully exposed active atoms, maximizing atom utilization and enhancing specific activity [139]. Notably, studies by Hu et al. and Wang et al. have shown that reducing metal particles to ~1 nm shifts the d-band center closer to the Fermi level, enhancing electron delocalization, reducing activation energy, and improving catalytic activity [140,141]. Positioned between nanoparticles and SACs, sub-nano clusters balance active site availability with oxidation state modulation, making them advantageous for catalytic reactions [141,142]. Their novel geometric structures and metal–support interactions can be flexibly regulated to optimize intermediate adsorption and reaction pathways, offering unique catalytic performances and high selectivity [143–146] [147]

In contrast, SACs represent the ultimate downscaling of catalysts, with isolated metal atoms stabilized on supports [148]. SACs achieve 100% atom utilization efficiency and precise active site control, addressing challenges in adsorption and activation of intermediates [149,150]. Since the groundbreaking work of Qiao et al. in 2011, where SACs with separated Pt atoms were synthesized, SACs have demonstrated high activity and stability [120]. For instance, Pt-based SACs are active for specific reactions but may lack efficiency in others due to the absence of metal–metal bonds [151,152]. The development of robust support materials and advanced techniques, such as aberration-corrected microscopy, has enabled better stabilization and characterization of SACs [153]. Despite their reduced number of active sites compared to SNCCs, SACs exhibit unique electronic properties due to the isolation of metal atoms, making them effective for specific reactions such as CO₂ conversion and oxygen reduction [126,154–157]. Two-dimensional (2D) materials, such as Ti₃C₂T_x MXene, are promising supports for SACs due to their high specific surface area, excellent

conductivity, and active basal planes [158–164]. These supports enhance the exposure and stability of active sites, improving catalytic performance [165,166]. Furthermore, SACs anchored on oxide supports benefit from surface imperfections that act as anchoring sites for metal clusters and individual atoms [167–169]. The practical fabrication of SACs remains challenging due to their inherent mobility and sintering tendencies under realistic reaction conditions [170]. Nevertheless, advancements in synthesis methods and support materials continue to push the boundaries of SAC applications

The concept of SACs has advanced significantly since its inception, with applications in thermocatalysis, electrocatalysis, and photocatalysis [171]. For example, SACs have shown promise in fuel cell reactions and CO₂ conversion due to their precise engineering of active sites [172–175]. However, challenges such as synthesis scalability, stability under reaction conditions, and limitations in adsorption and activation for complex reactions persist. Comparatively, while nanoparticles provide abundant active sites, their interior atoms remain inaccessible, limiting overall efficiency [151,152]. Sub-nanometer clusters, with their high surface atom fraction and tunable electronic properties, offer a middle ground between nanoparticles and SACs [49,125,176,177]. By leveraging their distinct advantages, SACs and SNCCs complement each other in advancing catalytic technologies, paving the way for sustainable and efficient processes.

2.4 Synergetic effect of Single atom and Cascade system

In the pursuit of sustainable and effective solutions to address the global challenge of CO₂ emissions, researchers have delved into innovative approaches within CO₂ conversion technologies. One groundbreaking concept involves the implementation of cascade systems for CO₂ conversion. This approach integrates multiple catalytic stages, each

conducting distinct chemical transformations, to convert CO₂ into valuable products. By harnessing synergistic effects through sequential catalytic reactions, cascade systems promise improved selectivity and overall conversion efficiency. This novel approach opens possibilities to transform CO₂ into a diverse range of valuable multi-carbon products, including hydrogen, hydrocarbons, alcohols, and other high-value chemicals [178]. Previously explored cascade systems have included permutations of electrochemical, thermochemical, and biochemical reactions in CO₂ upgrades to multicarbon products [179–188]. However, these often rely on harsh reaction conditions (high temperature and pressure) and generate by-products, necessitating costly separation [189–193]. Cascade electrochemical and biochemical processes utilize ambient conditions but have, thus far, led to limited productivity of C₄ chemicals. Cascade systems for CO₂ conversion encompass various innovative designs, each optimized to achieve specific product selectivity and overall efficiency. A common type involves the integration of multiple catalysts in a tandem arrangement, where the product of one catalytic [183] stage becomes the feedstock for the subsequent stage. For instance, the first catalyst may convert CO₂ to an intermediate, such as CO, which is then fed to a second catalyst for further transformation into hydrocarbons by yield more than 60% or alcohols. An alternative variant employs a multifunctional catalyst with separate active sites, which enables consecutive reactions to efficiently convert carbon dioxide into desired products in a single reactor. Researchers have also explored photocascade systems, where light-driven catalysis initiates specific reactions followed by subsequent thermal catalytic steps. These multi-stage configurations offer the potential to unlock higher selectivity and synergistic effects, facilitating the conversion of carbon dioxide into a different of valuable fuels and chemicals [185]. The incorporation of SACs into

cascade systems represents a cutting-edge approach in CO₂ conversion research. By combining the exceptional properties of single atoms with the efficiency of cascade systems, researchers aim to accomplish unprecedented selectivity and conversion rates in transforming CO₂ into value added products. In such a setup, SACs can serve as the building blocks of individual catalytic stages within the cascade system. Placing each single-atom catalyst strategically at specific stages enables targeted chemical transformations, creating a highly tailored and efficient reaction pathway. The utilization of SACs ensures atomic precision, allowing for precise control over reaction intermediates and products [194]. Moreover, the high surface area and tunable properties of SACs can be leveraged to enhance the interaction among different catalytic stages, advancing efficient mass and energy transfer within the cascade system. Despite the challenges, the integration of SACs into cascade systems holds immense promise in advancing CO₂ conversion technologies, providing a sustainable and versatile solution to mitigate CO₂ emissions while producing valuable chemicals and fuels [195]. Nevertheless, the process of obtaining controlled production of SACs continues to be difficult because of the rapid migration as well as aggregation of active atoms throughout manufacturing or later application procedures. The most practical and efficient method to achieve SACs is to sustain monodispersed atoms on suitable substrates. Various techniques, including confinement impacts, coordination effects, and chemical bonding, have been documented to provide isolated metal sites on supports. These methods involve restricting the loading quantity of the active component, enhancing interactions among metal atoms and supports, and utilizing defects or voids on the support [149,196–198]. A recent study explored the tandem conversion of CO₂ to 1-butene (1-C₄H₈) through a system combining a CO₂-to-C₂H₄ electrolyzer with a C₂H₄ dimerization step. Using

a bimetallic metal-organic framework (MOF) with tunable pore structures and periodic channels, the study optimized selectivity and activity for the dimerization process. The most effective MOF, containing Ru and Ni catalytic sites, achieved a 1-C₄H₈ production rate of 1.3 mol g_{cat}⁻¹ h⁻¹ with 97% C₂H₄ conversion. The cradle-to-gate carbon intensity was estimated at -2.1 kg CO₂e/kg 1-C₄H₈, assuming CO₂ from direct air capture and wind-powered electricity, demonstrating the potential of cascade systems for sustainable CO₂ utilization[199].

2.5 Characterizations of SACs

The development of SACs has necessitated advanced characterization methods to elucidate their structural and electronic properties [200,201]. These techniques provide critical insights into the atomic dispersion, coordination environment, and catalytic mechanisms of SACs, facilitating their optimization for CO₂ conversion [202]. However, SAC characterization presents several challenges, including the difficulty of detecting isolated atoms, distinguishing them from nanoparticles, and understanding their dynamic behavior under reaction conditions [203] [204]. A combination of microscopic, spectroscopic, and operando techniques is often required to achieve a comprehensive characterization of SACs [200,205–207].

Microscopic techniques provide direct visualization of SAC structures, offering insights into atomic dispersion and morphology. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and transmission electron microscopy (TEM) are commonly used to confirm single-atom dispersion [208]. For example, HAADF-STEM imaging ([Figure 9d](#)) of Cu-SA/Ti₃C₂T_x identifies individual Cu atoms as bright dots uniformly distributed across the Ti₃C₂T_x lattice, indicating the absence of Cu clusters and

confirming atomic dispersion. TEM imaging (Figure 9c) further reveals the nanosheet morphology of the catalyst, which enhances surface area and facilitates electron transfer, improving catalytic performance. Although X-ray diffraction (XRD) is useful for determining structural properties [209], [210–213], it lacks the sensitivity to detect isolated atoms [214]. Bao et al. employed XRD to confirm that the Cu-SA/Ti₃C₂T_x catalyst retains its Ti₃C₂T_x-like crystal structure, with the absence of diffraction peaks for copper species (Figure 9b) suggesting that Cu atoms remain atomically dispersed rather than forming nanoparticles or clusters. Additional microscopic techniques, such as high-resolution transmission electron microscopy (HR-TEM), may be required to further resolve atomic structures [37].

Spectroscopic methods provide elemental, electronic, and coordination information, which is crucial for understanding the behavior of SACs. X-ray photoelectron spectroscopy (XPS) is commonly used to analyze oxidation states and electronic interactions [22,215,216]. In the case of Cu-SA/Ti₃C₂T_x, XPS reveals Cu 2p binding energies at 932.5 and 952.4 eV, indicating a mixed Cu⁰ and Cu¹⁺ oxidation state. This suggests partial electron transfer between Cu and Ti₃C₂T_x, influencing catalytic selectivity [37]. X-ray absorption spectroscopy (XAS), including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), offers additional structural insights [217]. XANES analysis at the Cu K-edge (Figure 9e) confirms that the Cu valence state lies between metallic Cu⁰ and Cu¹⁺, while EXAFS (Figure 9f) reveals a dominant Cu–O coordination peak at ~1.6 Å, with no Cu–Cu scattering at 2.2 Å, reinforcing atomic dispersion. Further EXAFS fitting (Figure 9g) suggests a Cu–O₃ coordination environment, aligning with Bader charge analysis (+0.42), which indicates electronic interactions between Cu and surface oxygen groups. Inductively coupled plasma-optical emission

spectrometry (ICP-OES) quantifies Cu loading at 0.2 wt.%, validating the effectiveness of the synthesis approach in achieving a well-defined SAC structure [37].

Operando and in situ characterization techniques are essential for studying the dynamic behavior of SACs under reaction conditions. Yang et al. investigated the structural evolution of Cu nanocatalysts during CO₂ reduction using operando analysis, including four-dimensional electrochemical liquid-cell scanning transmission electron microscopy. Their findings revealed that metallic Cu nanograins oxidize into single-crystal Cu₂O nanocubes upon exposure to air after electrolysis, highlighting the dynamic nature of SACs [216]. Additionally, Amirbeigi et al. demonstrated the spontaneous formation of low-coordinated Cu surface species at the onset of CO₂ electroreduction using in situ scanning tunneling microscopy (STM), surface XRD (SXRD), and Raman spectroscopy. STM imaging showed a disordered adlayer on Cu terraces, suggesting the presence of immobile molecular species, while SXRD provided atomic-level insights into surface restructuring. Raman spectroscopy further confirmed the formation of bidentate carbonates and carbonate anions, which are crucial for catalytic performance [218].

Despite advancements in characterization techniques, significant challenges remain in fully understanding SACs. The primary difficulties include detecting single atoms, as conventional techniques like XRD lack the sensitivity to identify isolated atomic sites, necessitating advanced imaging methods like HAADF-STEM. Distinguishing single atoms from nanoparticles requires complementary techniques such as XAS and EXAFS to confirm atomic dispersion and avoid misinterpretation of agglomeration. Understanding dynamic changes under reaction conditions remains complex, even with operando techniques, as real-time tracking of atomic-scale transformations is challenging. Additionally, correlating structure with catalytic performance demands a multi-technique approach integrating

spectroscopy, electrochemical analysis, and theoretical modeling to establish structure-activity relationships in SACs. Future research should focus on improving in situ and operando techniques, developing higher-resolution imaging methods, and integrating computational simulations with experimental data to gain deeper insights into SAC behavior. Addressing these challenges will enhance the design and optimization of SACs for CO₂ conversion and other catalytic applications.

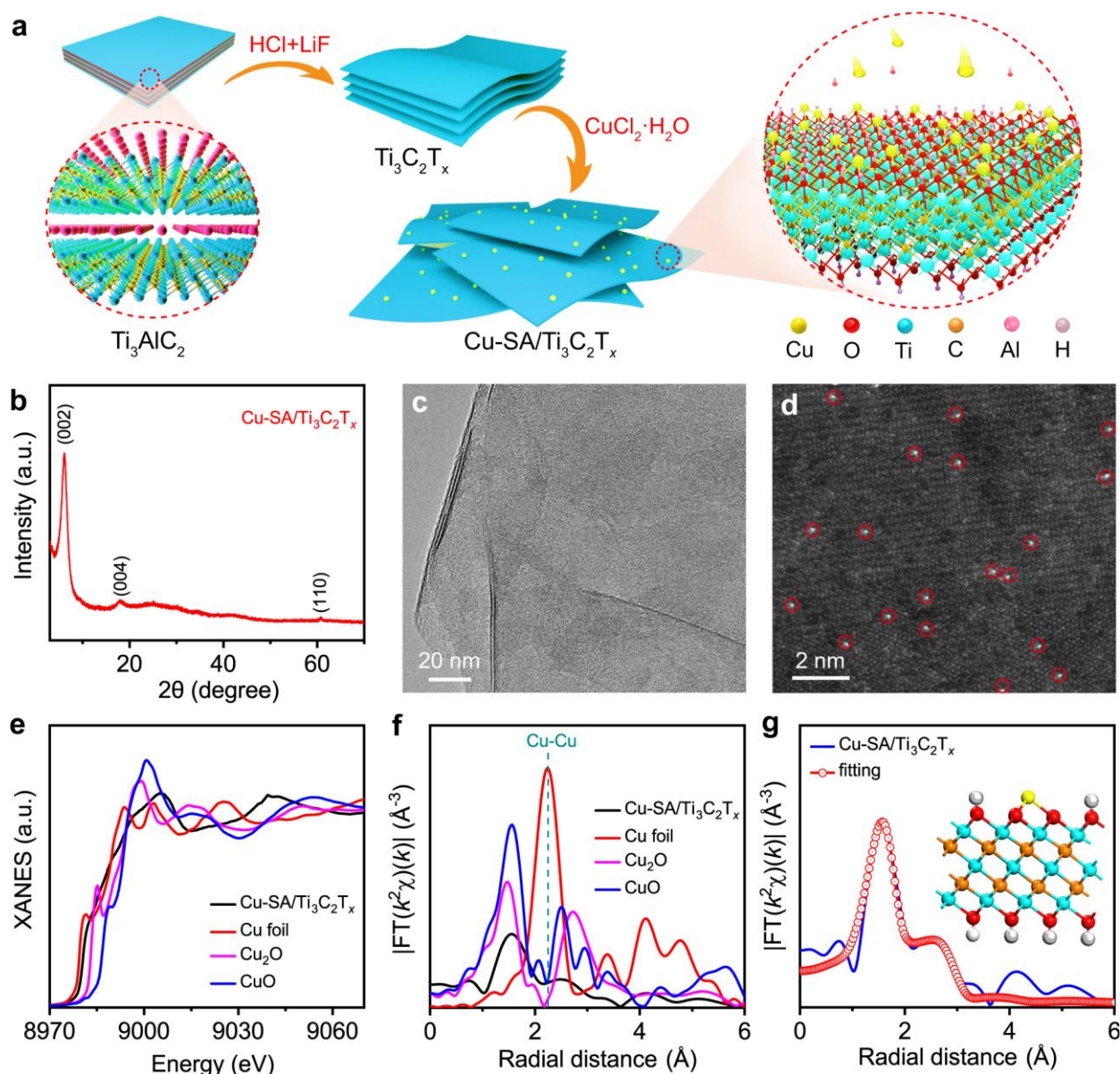


Figure 9: (a) Preparation and structural characterization of Cu-SA/Ti₃C₂T_x. (b) XRD pattern. (c) TEM image. (d) HAADF-STEM image in which some of the Cu SAs are highlighted by red circles. (e) XANES spectra at the Cu K-edge with CuO, Cu₂O and Cu foil as referenc. (f) The k²-weighted Fourier transform (FT) EXAFS curves in which $\chi(k)$ denotes the EXAFS oscillation function. (g) EXAFS fitting curve of Cu-SA/Ti₃C₂T_x, insert is an illustration of Cu-SA/Ti₃C₂T_x structure. The yellow, blue, dark yellow, red and white balls represent Cu, Ti, C, O and H, respectively. Reprinted with permission from [37]

2.6 SACs based Catalysts

SACs have lately gained prominence in catalysis due to their ability to use the advantages of both homogeneous and heterogeneous catalysts, while also incorporating distinctive characteristics that bridge the gap between them [35]. In contrast to heterogeneous catalysts, SACs optimize atom utilization and possess homogenous active sites with adjustable electronic environments, resulting in exceptionally high catalytic activity and selectivity. Additionally, SAC exhibits enhanced stability and exceptional recyclability [34], [195], [219,220]. The utilization of single atoms in CO₂ conversion represents a groundbreaking approach that holds immense potential for addressing environmental challenges and advancing sustainable chemistry [221,222]. Single atoms, precisely isolated on suitable catalyst materials, offer unique electronic and structural properties that can significantly impact CO₂ conversion reactions[223]. This innovation has far-reaching applications and effects across various aspects of CO₂ conversion [2 2 3] . The advantages of SACs for CO₂ conversion include highly active catalytic centers that enhance CO₂ activation and facilitate specific chemical transformations. These catalysts can significantly accelerate reaction rates and improve overall conversion efficiency [224–226].

2.6.1 Cu-Based SAC catalysts

Single site decorated copper catalysts represent a cutting-edge approach in the realm of CO₂ conversion [227]. These catalysts involve the precise placement of individual catalytic centers, often Cu atoms, onto a supporting material [228], [229]. The primary aim of this technology is to efficiently accelerate the conversion of CO₂ molecules into valuable chemical products through catalytic reactions [229,230]. The uniqueness of single site decorated copper catalysts lies in the isolated copper atoms, strategically dispersed on the

supporting material [231]. These single atoms possess distinct electronic and geometric properties that enable precise CO₂ activation and subsequent conversion reactions. The isolated nature of the copper atoms minimizes undesired side reactions, leading to enhanced selectivity and catalytic efficiency in CO₂ conversion processes. The supporting material is crucial in maintaining and improving the catalytic efficiency of copper catalysts that are modified with single-site decoration. This material often possesses a high porosity and surface area, ensuring maximum exposure of the active phase to CO₂ molecules. The interaction between the Cu atoms and the supporting material makes an optimal environment for catalytic reactions, resulting in improved overall efficiency [232]. For instance, Chen et al., Both theoretical and experimental evidence have emphasized the crucial function of Lewis acid in a Cu/Al₂O₃ SAC for the electrochemical conversion of carbon dioxide. Through theoretical calculations, it was shown that Lewis's acid sites in metal oxides, such as aluminium oxide and Cr₂O₃, have the ability to adjust the electronic structure of copper atoms by maximizing intermediate absorption. This, in turn, leads to an improvement in CO₂ methanation [75]

Recently, two-dimensional (2D) materials have garnered significant attention as a robust platform for supporting SA catalysts due to their large specific surface areas, numerous exposed active sites, and exceptional catalytic activities [179,233,234]. In particular, 2D Ti₃C₂T_x MXene (where T_x represents surface functional groups) has been extensively studied for various catalytic reactions because of its excellent electronic conductivity, catalytically active basal planes, and unique graphene-like layered structures [235], [236], [237]. Moreover, its abundant ability to reduce, suitable surface imperfections, and hydrophilic surface properties render it a perfect contender for providing support and

stability to individual atoms [238,239]. Bao et al. demonstrated through experimental and theoretical studies that atomically dispersed Cu-O₃ sites on 2D Ti₃C₂T_x MXene facilitate C-C coupling of CO molecules, leading to the formation of the key *CO-CHO intermediate. Theoretical simulations further reveal that these Cu-O₃ sites lower the free energy barrier of the potential-determining step, thereby enhancing the catalytic activity and selectivity of copper single atoms for CO reduction. This synergistic effect accounts for the remarkable performance of Cu-based SACs in CO₂ conversion [37].

2.6.2 Fe-Based SAC catalysts

Fe-based SACs hold significant promise in addressing the global challenge of CO₂ emissions and advancing sustainable CO₂ utilization technologies [240,241]. These catalyst systems involve the integration of iron (Fe) atoms in unique configurations on supporting materials to assist the efficient transformation of CO₂ molecules into valuable chemical products through catalytic reactions. The support material used in Fe-based single-atom catalysts play a crucial role in stabilizing and enhancing their catalytic performance [242,243]. This material typically possesses a large porosity and surface area, ensuring maximum exposure of the active sites to CO₂ molecules [244]. The coordination between the iron atoms and the supporting material establishes a suitable environment for catalytic processes, leading to improved overall efficiency. In CO₂ conversion, the Fe-based SACs interact with CO₂ molecules to initiate various chemical reactions. These reactions often involve reduction pathways that lead to the formation of valuable compounds like CO, formic acid, or methane. The specific reaction mechanisms depend on the unique properties of the Fe atoms, the supporting material, and the reaction conditions [242]. Furthermore, beyond just maximizing the utilization efficiency of their single sites and

ensuring well-defined active sites with high selectivity, the precise configurations and synergistic effects significantly boost both catalytic efficiency and selectivity [242], [245,246]. This renders them indispensable to advancing effective carbon capture and conversion strategies. Ongoing research seeks to optimize the design of these catalysts, uncover novel reaction pathways, and explore their potential in various CO₂ conversion applications. Fe Single atoms exhibit distinctive electronic and geometric properties that enable precise CO₂ activation and subsequent conversion reactions. The isolation of the iron atoms reduces undesired side reactions, leading to improved selectivity and catalytic efficiency in CO₂ conversion processes [245,247]. For instance, Takele et al., and Li et al., described a catalyst composed of atomically dispersed Fe coordinated with nitrogen-doped carbon, which exhibited heightened activity in CO₂ reduction to produce CO [247], [248]. Lately, scientists have been investigating the synergistic interplay between the active sites and the intricate networks of hierarchical carbon nanotubes (CNTs) and graphene nanoribbons (GNRs). This catalytic setup combines two distinct elements: iron-nitrogen (Fe-N) active sites and a complex network of CNTs and GNRs. By optimizing the design and composition of the catalyst, researchers seek to enhance its performance in CO₂ conversion processes. Ultimately, the development of Fe-N sites on hierarchically mesoporous CNTs and GNRs represents a significant advancement in the field of sustainable energy and chemical production. These catalysts offer a tailored approach to addressing CO₂ emissions by harnessing the unique properties of the active sites and the nanostructured support network [249]. The straightforward conversion of commercial carbon nanotubes (CNT) into isolated Fe-N₄ sites anchored on carbon CNT and GNR networks Fe-N/CNT@GNR was described by Pan et al. Oxidation-induced partial removal of carbon nanotubes leads to the formation of GNR nanolayers connected to the remaining fibrous carbon

nanotube frameworks. This process reticulates a hierarchically mesoporous complex, allowing for a large active surface area and efficient mass translocation. The Fe residues derived from carbon nanotube development seeds operate as sources of iron to create separate Fe-N₄ groups situated at the basal plane and margins of CNTs and graphene nanoribbons (GNRs). These moieties possess a strong inherent ability to activate carbon dioxide and inhibit hydrogen evolution, as depicted in Figure 10 [249].

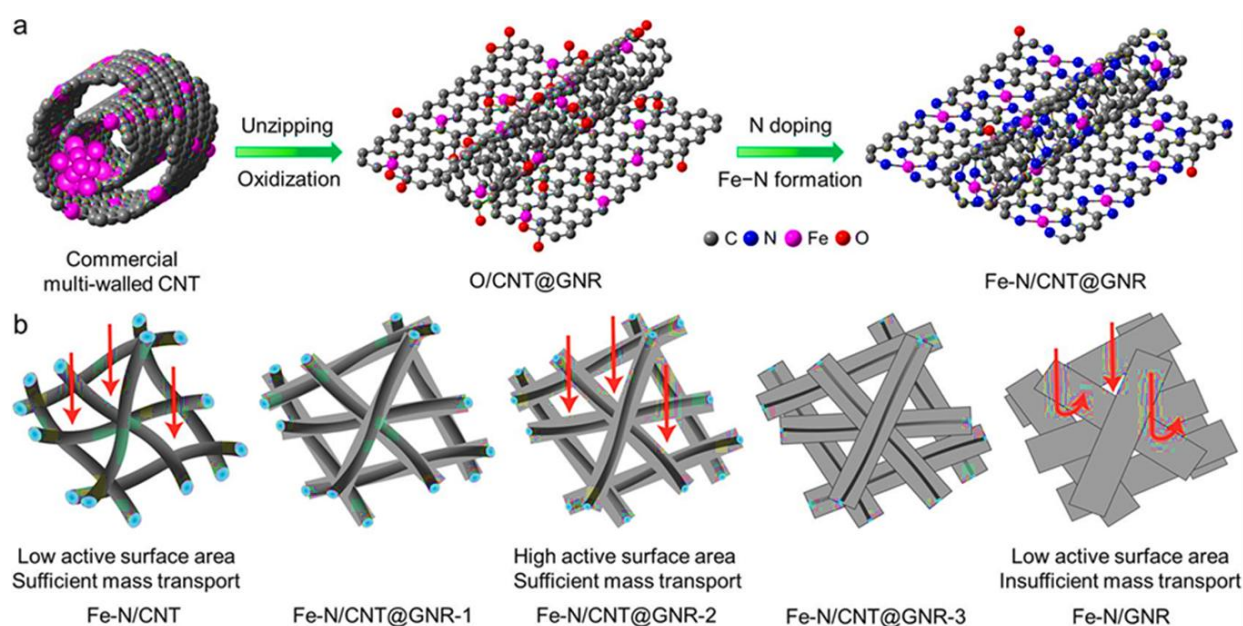


Figure 10: (a) Schematic representation shows the conversion of multiwalled CNTs into Fe-N/CNT@GNR. (b) Modifying the mass ratios of KMnO₄ and CNTs to induce structural changes from CNTs to CNT@GNR to GNR. Reprinted with permission from [249].

2.6.3 Fe³⁺-Based SAC catalysts

Another class of Fe based SAC catalysts are atomically dispersed Fe³⁺ sites which play a crucial role in the catalytic conversion of CO₂ into valuable products [250]. These catalytic sites involve the presence of individual Fe ions, in their trivalent Fe³⁺ state, dispersed on a suitable support material. These sites are designed to facilitate the activation and

transformation of CO₂ molecules, contributing to efforts aimed at reducing CO₂ emissions and harnessing this greenhouse gas for sustainable chemical processes. The significance of atomically dispersed Fe³⁺ sites lie in their ability to mimic the active sites found in natural enzymes. These sites frequently feature metal ions with unique electronic properties that influence the activation of CO₂ molecules by adsorbing and stabilizing them, facilitating favorable chemical transformations to targeted valuable products, such as CO, formic acid, or other organic compounds, depending on the specific catalytic conditions. [250]. Moreover, by preventing the clustering of metals, atomically dispersed Fe³⁺ sites maintain their catalytic effectiveness and ability to selectively promote desired reactions over extended periods of time. For instance, Jun Gu and colleagues developed a catalyst featuring dispersed single-atom Fe sites, capable of producing carbon monoxide. Through operando X-ray absorption spectroscopy, they identified the active sites as isolated Fe³⁺ ions coordinated with pyrrolic nitrogen (N) atoms on an N-doped carbon support. The Fe³⁺ ion remains in its +3-oxidation state during catalysis, likely due to electronic interactions with the conductive carbon matrix as illustrated in [Figure 11](#). The improved catalytic performance of these Fe³⁺ sites is attributed to their enhanced CO₂ adsorption and reduced CO adsorption compared to traditional Fe²⁺ sites. Structural characterization confirmed the atomic dispersion of Fe sites within the carbon matrix. HAADF-STEM imaging ([Figure 11a](#)) revealed a well-defined porous structure, while energy dispersive X-ray spectroscopy (EDS) mappings ([Figure 11b-c](#)) demonstrated a uniform distribution of Fe and N within the carbon framework. Further insights from atomic-resolution aberration-corrected HAADF-STEM imaging ([Figure 11d](#)) revealed bright spots (~0.2 nm) corresponding to atomically dispersed Fe and Zn sites. The Fe K-edge XANES spectrum ([Figure 11f](#)) and Fe 2p_{3/2} XPS spectrum exhibited binding and edge energies consistent with Fe₂O₃ and Fe³⁺-

tetraphenylporphyrin-Cl, verifying the +3-oxidation state of Fe. This indicates that Fe ions underwent oxidation from +2 to +3 during pyrolysis, in agreement with previous reports on Fe-containing organic precursors. The Fe K-edge EXAFS spectrum (Figure 11h) further confirmed the atomic dispersion of Fe sites, with spectral fitting suggesting a planar Fe-X₄ (X = N or C) coordination structure. The average coordination numbers for Fe-N and Fe-C were 3.4 and 0.5, respectively, with no detectable Fe-Fe bonding [250], [251], [252].

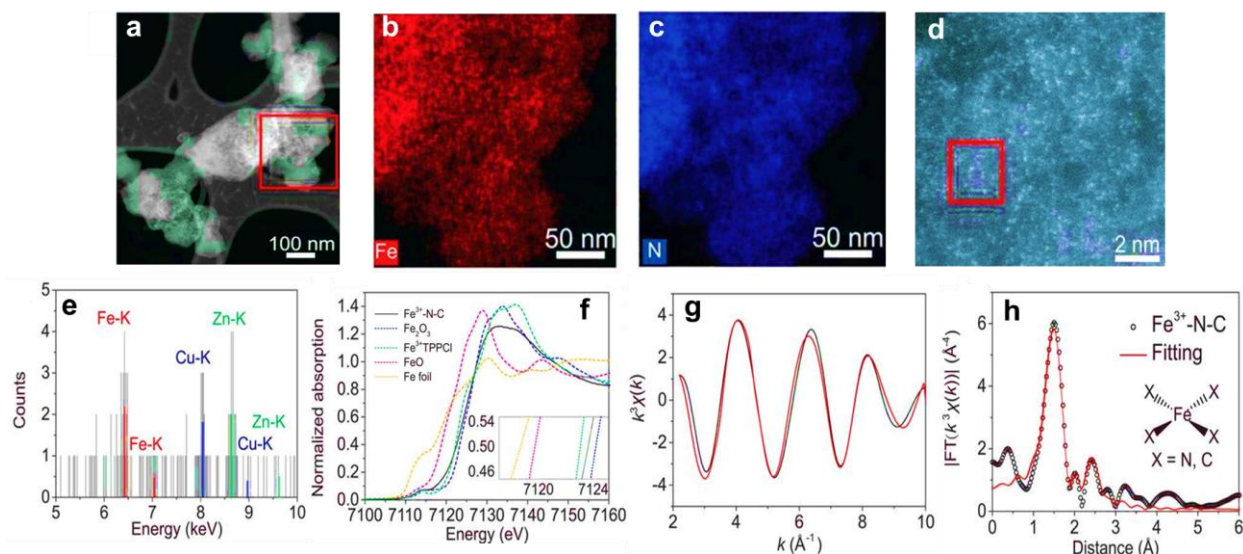


Figure 11: (a) HAADF-STEM image and EDS mappings of (b) Iron and (c) Nitrogen of the region represented by the red square. (d) Aberration-corrected HAADF-STEM image and (e) EDS spectrum of the red square region. (f) Fe K-edge XANES spectra of Fe³⁺-N-C (black), Fe₂O₃ (blue dashed), Fe³⁺TPPCL (green dashed), FeO (pink dashed), and Fe foil (orange dashed). (Inset) The enlargement of the main edges. (g) k-space and (h) R-space Fe K-edge EXAFS spectra. Shown are data (black) and fitting curves (red). Reprinted with permission from [250]

2.6.4 MOF-Based SAC catalysts

MOF-SACs, or metal-organic framework-based single-atom catalysts, are novel types of catalysts that show great promise in converting carbon dioxide into useful chemicals. This catalytic system integrates the accuracy of SAC sites with the special qualities of MOFs. MOFs are porous materials with well-defined nanoporous architectures made of metal nodes joined by organic linkers [253]. The integration of single metal atoms into MOFs

results in MOF-SACs, which offer several advantages for CO₂ conversion: The porous nature of MOFs offers a large surface area, enabling efficient CO₂ adsorption and access to the single-atom catalytic sites [9], [254].

Single metal atoms within the MOF structure act as isolated catalytic centers. Their precise arrangement allows for fine-tuning of reactivity and selectivity, mimicking the reactivity of natural enzymes [255]. The electronic properties of both the MOF framework and the single metal atom enhance CO₂ activation and conversion, even under mild reaction conditions. The MOF structure stabilizes and isolates the single metal atoms, preventing agglomeration and maintaining catalytic activity over time [256]. Depending on the specific reaction conditions and the properties of the catalyst, products like CO, formic acid, or more complex hydrocarbons can be generated [257]. Ongoing research aims to optimize the synthesis and design of MOF-SACs as depicted in [Figure 12 \(a-b\)](#) [254], uncover their catalytic mechanisms, and develop scalable processes for industrial applications [258]. The development of MOF-Based SACs presents an exciting avenue for advancing sustainable CO₂ utilization technologies, bridging the gap between porous materials and precise catalysis [254,259–261].

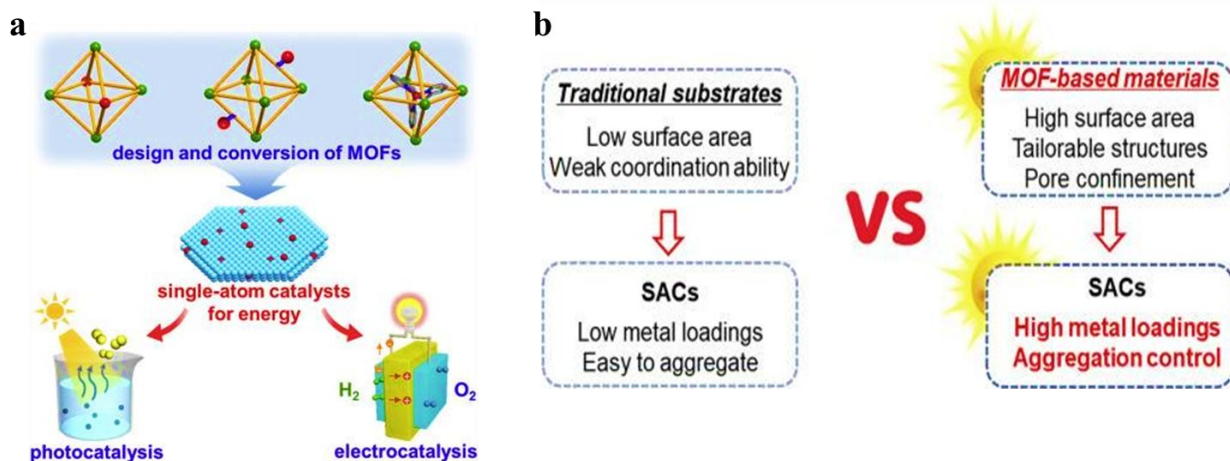


Figure 12: (a) MOFs based single atom catalysis, (b) Potential Advantages of MOFs over Traditional Substrates for the Fabrication of SACs. Copyright with permission from [261] .

2.6.5 Ni-Based SAC catalysts

Single-Atom Nickel (Ni) sites are advanced catalysts for efficient CO₂ conversion [111]. These catalysts feature isolated nickel atoms on a high-surface-area support material, working as active sites. The exceptional properties of these single atoms allow precise CO₂ adsorption and activation, minimizing side reactions and enhancing selectivity and efficiency. The support material stabilizes the nickel atoms and enhances catalytic activity by providing an optimal environment for CO₂ interaction. Single-Atom Ni sites can convert CO₂ into valuable products like syngas, CO, formic acid, or methane, liable on the catalytic material and reaction parameters as in illustrated Figure 13 [262–265].

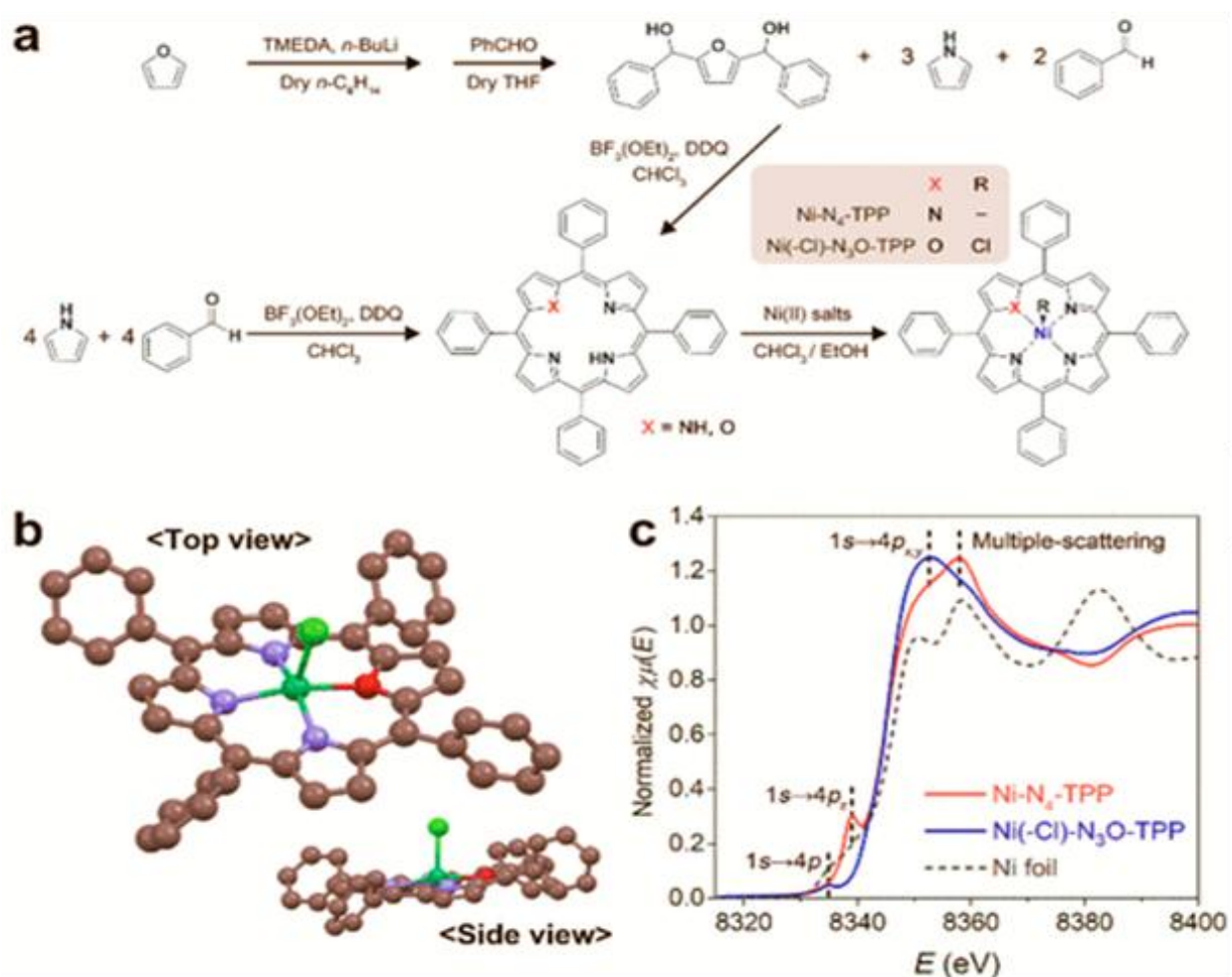


Figure 13: Synthesis and physical properties of prepared porphyrins. (a) Synthetic illustration for Ni-N₄-TPP & Ni(-Cl)-N₃O-TPP by modified Lindsey's methods. (b) 3D molecular structure of Ni(-Cl)-N₃O-TPP established by SC-XRD. (c) Ni K-edge XANES spectra of Ni-N₄-TPP, Ni(-Cl)-N₃O-TPP, and Ni foil. Reprinted with permission from [262].

Another category of Ni-based SACs includes nickel dual-atom sites, which represent a state-of-the-art catalyst system designed for the efficient conversion of CO₂ into valuable chemical products. This advanced catalyst involves the strategic arrangement of two nickel atoms within a specific configuration on a supporting material. The primary goal of this technology is to improve the activation and transformation of CO₂ molecules through catalytic reactions [266]. The distinctive feature of nickel dual-atom sites lies in the precise

arrangement of two nickel atoms in close proximity. This arrangement creates synergistic effects that significantly boost the catalytic selectivity and activity of the catalyst. The close interaction between the dual nickel atoms facilitates efficient CO₂ adsorption, activation, and subsequent transformation into desired products [267]. The supporting material used in this catalyst system provides a stable platform for anchoring and stabilizing the dual nickel atoms [268]. Typically, this material possesses high surface area and porosity, allowing for maximum exposure of the active sites to CO₂ molecules. The combination of the dual nickel atoms and the supporting material creates an optimal environment for catalytic reactions, minimizing unwanted side reactions and enhancing overall efficiency [244,269]. In CO₂ conversion, the nickel dual-atom sites engage with CO₂ molecules to initiate chemical transformations. These reactions often involve reduction pathways that lead to the formation of valuable compounds such as CO, formic acid, or methane [270]. The specific reaction mechanisms depend on the unique properties of the dual nickel atoms, the supporting material, and the reaction conditions. The development of nickel dual-atom sites holds great promise for advancing the field of CO utilization and mitigating CO₂ emissions [271]. The synergistic effects resulting from the close arrangement of two nickel atoms enhance the catalyst's efficiency, making it an essential component of sustainable CO₂ conversion technologies. Ongoing research focuses on optimizing the catalyst's design, uncovering new reaction pathways, and exploring its potential in various CO₂ conversion applications [272]. For example, Hao et al., established a catalyst with nickel dual-atom sites through in situ conversion of nanoparticles into dual atoms. Both experimental and theoretical investigations showed that during the catalytic process, the Ni dual-atom sites facilitate the adsorption of hydroxyl, creating electron-rich active centers. These centres present a modest reaction kinetic barriers for *COOH production and *CO desorption. This

catalytic microenvironment results in faster kinetics compared to either bare dual-atom sites or adsorption of hydroxyl-regulated single-atom sites [273].

A single Ni atom supported on a hybridized boron, carbon, and nitrogen (BCN) nanosheet represents a promising catalyst system in the realm of CO₂ conversion. This innovation involves the integration of a single nickel atom, a two-dimensional nanosheet composed of BCN, and a specific hybridized structure [274]. The primary objective of this catalyst system is to facilitate the transformation of CO₂ into valuable chemical products through catalytic reactions. The single nickel atom serves as a highly active and selective catalytic site due to its unique catalytic properties and reactivity [275]. The atom is intentionally isolated and distributed on the surface of the BCN nanosheet, allowing for precise control over its interactions with reactant molecules [276]. This isolation enhances the atom's catalytic efficiency, enabling specific CO₂ activation and conversion processes. The hybridized BCN nanosheet offers several advantages in this context. Its composition combines boron, carbon, and nitrogen, which collectively create a versatile platform with tailored chemical properties [274] , [277]. This composition enhances the nanosheet's affinity for CO₂ adsorption and activation, providing an ideal environment for catalytic reactions [277,278]. The 2D structure also provides a large surface area, ensuring ample exposure of active sites and promoting the accessibility of reactants [279,280]. In CO₂ conversion, the catalyst's single nickel atom interacts with CO₂ molecules adsorbed onto the hybridized BCN nanosheet. These interactions lead to the activation of CO₂ and subsequent chemical transformations, such as reduction reactions that yield valuable products like CO, formic acid, or methane [281,282]. The specific reaction pathways and mechanisms can vary based on factors such as reaction conditions and the unique properties of the catalyst system. The incorporation of a single Ni atom supported on a

hybridized BCN nanosheet holds significant potential for addressing the global challenge of CO₂ emissions [283]. By harnessing the atom's reactivity and the nanosheet's tailored properties, this catalyst system offers a pathway to convert CO₂ into useful chemicals, thereby contributing to sustainable and environmentally friendly CO₂ utilization strategies [284].

2.6.6 Cd-Based SAC catalysts

Cd-based SACs represent an emerging and innovative approach in the field of catalytic CO₂ conversion. These catalysts involve the incorporation of individual Cd atoms onto a suitable support material, aiming to efficiently facilitate the transformation of CO₂ molecules into valuable chemical products through catalytic reactions. The uniqueness of Cd-based SACs lies in the isolated cadmium atoms, which serve as highly active and selective catalytic centers [285]. These single atoms possess distinct electronic and geometric properties that enable precise CO₂ activation and conversion reactions. The isolation of the cadmium atoms minimizes unwanted side reactions, leading to improved selectivity and catalytic efficiency in CO₂ conversion processes [286]. The choice of support material is crucial in stabilizing and enhancing the catalytic activity of Cd-based SACs. This material typically possesses a high surface area and porosity, ensuring optimal exposure of the active sites to CO₂ molecules. The interaction between the Cd atoms and the support material creates an ideal environment for catalytic reactions, resulting in enhanced overall efficiency [286]. Although SACs show significant promise in heterogeneous catalysis, achieving high loading levels of these catalysts continues to be a major challenge. Ongoing research aims to optimize the design of these catalysts, explore novel reaction pathways, and assess their potential in various CO₂ conversion applications. For example, an extremely high loading of

Cd-based SACs was achieved through a trapping, emitting strategy and gas migration. This approach resulted in a loading of 30.3 wt.%, with the emitting process enabling the adjustment of the loading amount from 30.3 to 1.4 wt.%. In the context of CO₂RR applications, the Cd-NC SACs with an 18.4 wt.% loading demonstrated optimal Faradaic efficiency (FE) performance [287].

2.7 SACs Applications for CO₂ Conversion

The catalytic transformation of carbon dioxide into valuable fuels and chemicals presents a promising and economically viable alternative to fossil feedstocks, while also enabling large-scale CO₂ recycling [288] [289]. Cost-effective and highly efficient catalysts are crucial for reducing the costs associated with CO₂ utilization as in [Figure 14](#) [290][291]. Conventional catalysts based on metal nanoparticles frequently lack efficiency in utilizing active metals, effective catalytic activity, and proper selectivity [292] [293]. Consequently, there has been an increasing fascination with SACs, which provide optimal atom usage, a distinctive electrical configuration, and robust metal-support interactions. These characteristics make SACs a promising approach to enhance catalytic efficiency and long-term durability. Additionally, the well-defined structures of SACs facilitate in-depth studies of the mechanisms and active sites involved in CO₂ conversion [294–296].

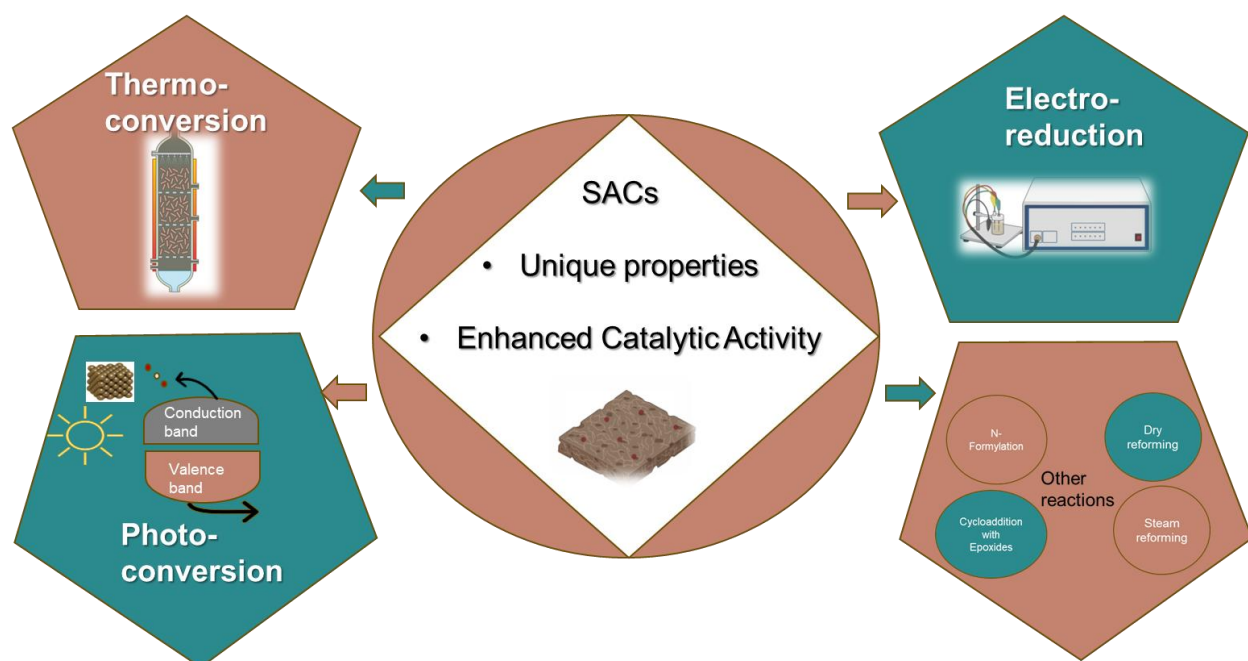


Figure 14: An overview of SACs application in chemical CO₂ conversion displayed in this review.

2.8 CO₂ electrochemical conversion

Advancements in science and technology have led to increased global energy consumption, posing significant environmental challenges in the 21st century [297]. The electrocatalytic conversion of CO₂ into carbon-based fuels has attracted attention due to its ability to operate in ambient conditions, adjust the reduction products via external parameters, store renewable electrons from solar, tidal, and wind energy, and have the potential to reduce global demand for fossil fuels [298]. This method offers a means to close the carbon cycle and utilize off-peak, intermittent renewable electricity [299–302]. However, CO₂ activation presents challenges due to its high thermodynamic stability, requiring substantial overpotentials and reducing energy efficiency. Electrocatalytic CO₂ reduction faces difficulties such as sluggish reaction kinetics, complex reaction pathways, and competing water reduction reactions in aqueous environments [287,303–305]. Despite these obstacles,

CO₂RR can yield a variety of products, including carbon monoxide, formic acid, methane, methanol, ethanol, and ethylene [306]. A major obstacle to making CO₂RR viable for renewable energy storage is the similar thermodynamic potential of its products.

Catalysts play a crucial role in CO₂RR, with different metals exhibiting varying adsorption strengths for intermediate products, which influence product distribution [24]. Categorically, metal catalysts can be classified into four types based on their properties and behavior towards products of CO₂RR: formate-selective metals (e.g., Sn, Pb, In), CO-selective metals (e.g., Ag, Zn, Au), hydrocarbon-selective Cu, and hydrogen-selective metals (e.g., Pt, Ni, Fe, Co, Pd, Ga) [307]–[308–311]. Other extensively investigated catalysts encompass two-dimensional transition metal carbide/nitride [312], [313], transition-metal complexes with organic ligands [314], and copper-based multinary sulfides (CMSs) [315]. Despite progress, existing catalysts are still inefficient for practical applications, with the high cost of noble metal catalysts adding to the challenge

Promising solutions are emerging through catalyst design, aiming to overcome these energy efficiency and selectivity barriers [316]. Catalysts are driving a paradigm shift in CO₂ conversion processes, enabling advancements in areas like electrochemical CO₂RR. Despite significant efforts, the primary obstacle to large-scale CO₂RR implementation remains the lack of highly reactive, selective, and cost-effective electrocatalysts. Therefore, designing and synthesizing high-performance CO₂RR electrocatalysts is crucial. SACs are promising candidates for catalyzing electrochemical CO₂RR due to their maximized atomic utilization. A partial-carbonization approach was proposed by Yanming Cai et al. to alter the electronic structures of single-atom catalysts. This approach led to the development of a carbon-dots-based SAC containing CuN₂O₂ sites as shown in [Figure 15](#). The SAC demonstrates a Faradaic

efficiency of 78% and selectivity of 99% for CH₄, achieving a current density of 40 mA/cm². Their findings also highlighted that the high faradaic efficiency and selectivity is attributed to the introduction of the oxygen ligand into the catalyst structure which lowered the endothermic energy of the intermediate [246]. Single-atom metal catalysts, such as Me-N-C catalysts with metals like Ni, Fe, Co, Zn, Mn, etc., are unique cases that deviate from the basic properties of metallic materials. These catalysts involve the atomic dispersion and bonding of metal ions to nonmetallic functional groups. They have attracted considerable interest for their ability to selectively produce CO from CO₂ reduction reactions [318,319]. Significantly, single-atom nickel catalysts have shown exceptional efficiency in converting CO₂ to CO, exceeding that of conventional metal-organic-carbon catalysts and even competing with catalysts using noble metals [320]. For instance, at -0.81 V RHE, a Ni-N-C catalyst synthesized by topochemical transformation attained about 100% CO selectivity. This high selectivity is attributed to the protective carbon layer, which effectively promotes topochemical transformation while maintaining the Ni-N₄ structure. Additionally, it prevents the aggregation of Ni atoms into particles, thereby providing a large number of active sites for catalytic reactions [321]. An analogous Ni-N-C catalyst in a gas diffusion electrode setup achieved a CO partial current density over 200 mA cm⁻² and maintained a consistent CO Faradaic efficiency of around 85%, underscoring its considerable promise for future industrial uses.

Another intriguing SAC in CO₂ conversion is the Cd-based SACs, which interact with CO₂ molecules to initiate various chemical reactions. These reactions often involve reduction pathways leading to the formation of valuable compounds such as CO, formic acid, or methane. The specific reaction mechanisms depend on the unique properties of the Cd

atoms, the supporting material, and the reaction conditions [270], [285]. Their isolated and active nature enhances catalytic efficiency, making them a significant player in the development of effective carbon capture and conversion strategies [223]

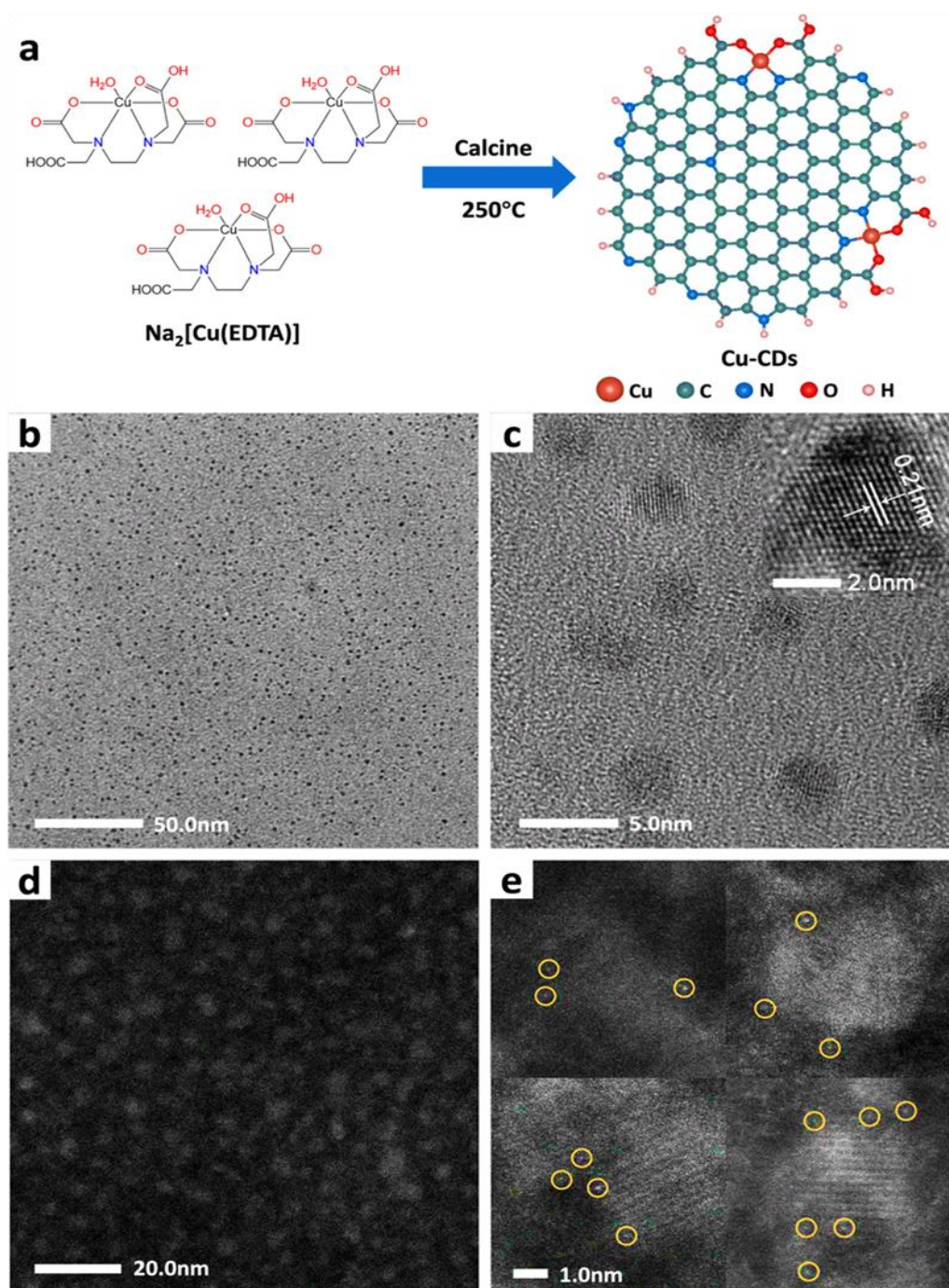


Figure 15: (a) Diagram of the Cu-CD catalyst prepared using low-temperature calcining process. (b) large field of view and (c) magnified view of TEM images (the inset is the crystal lattice). (d) Relatively large-field of view and e typical view of HAADF-STEM images of distributed single Cu atoms in carbon dots. Yellow circles in (e) indicates typical single Cu atoms. Reprinted with permission from [317].

Table 1: Recent advances in catalysts for CO₂ utilization

Catalyst	Synthesis methods	Applications	Catalytic efficiency	Key product	Key findings	Ref.
Pd-Cu Pt-Cu SACs	Galvanic displacement	CO ₂ R	60% C ₂ + products	C ₂ H ₄ and CH ₄	Atomically dispersed platinum group metal (PGM) species on copper surfaces suppress HER and promote CO ₂ reduction by facilitating CO* hydrogenation and CO-CHO* coupling via Pd-Cu dual-site pathways, enabling selective CH ₄ and C ₂ H ₄ production.	[267]
Cu-N/O single sites	Spray the decoration on commercial catalyst	CO ₂ R	71% C ₁	CH ₄	A coordination strategy using EDTA stabilizes Cu ions, forming Cu-N/O single sites and regulating Cu cluster size, achieving 71% CH ₄ selectivity (Faradaic efficiency) under acidic CO ₂ reduction with minimal CO ₂ loss (<3%). The process halves energy intensity compared to conventional methods, enhancing efficiency.	[322]
p-block Al SAC	pyrolysis	CO ₂ R	98.76% C ₁	CO, HCOOH	The Al-NC single-atom catalyst with Al-N ₄ sites overcomes transition metal limitations in CO ₂ RR by balancing *COOH formation and *CO	[323]

					desorption, achieving 98.76% CO Faradaic efficiency and a turnover frequency of 3.60 s^{-1} . It delivers high CO partial currents ($309 \text{ mA}\cdot\text{cm}^{-2}$ in a flow cell, 605 mA in an MEA) with exceptional efficiency.	
Ni single atoms	Pyrolysis	CO ₂ R R	100 % C ₁	CO	A scalable Ni single-atom catalyst on carbon black achieves $>100 \text{ mA cm}^{-2}$ current density with nearly 100% CO selectivity and minimal hydrogen evolution in a gas-phase reactor. Scaled to a $10 \times 10 \text{ cm}^2$ cell, it delivers 8 A current and 3.34 L hr^{-1} CO production, though limited Ni site density affects the 60% CO selectivity.	[324]
BiCu-SAA	insitu electrochemical reconstruction	CO ₂ R R	73.4 % C ₂₊	C ₂ H ₄	The BiCu-SAA electrocatalyst enhances CO ₂ reduction to C ₂₊ products with a 73.4% Faradaic efficiency by promoting C–C coupling, outperforming conventional Cu-based catalysts. It maintains high structural stability and performance at 400 mA cm^{-2} in a flow cell system.	[325]
Cu–Ag	spatially dispersed	CO ₂ R R	69.9 % C ₂₊	C ₂ H ₅ O H	A coordination-controlled Ag–Cu alloy catalyst with spatially dispersed Cu clusters enhances *CO binding through Cu–Cu and Cu–Ag interactions,	[326]

					shifting CO ₂ reduction selectivity from ethylene (69.6% FE) to ethanol (40.4% FE).	
Cu surfaces and Cu(i) species	Electrodeposition	CO ₂ R R	76 % C ₂₊	C ₂ H ₅ O H	Single-atom Cu (Cu ₁) catalysts lack intrinsic activity for C ₂₊ product generation due to insufficient active sites for *CO hydrogenation and CO–CO coupling, but small Cu clusters formed via aggregation enable efficient CO–CO coupling. The C ₂₊ performance of these Cu clusters is substrate-dependent, offering guidance for catalyst optimization.	[327]
F-doped Cu SACs	one-step solid-state pyrolysis	CO ₂ R R	7.03 mmol h ⁻¹ mg _{per Cu} ⁻¹ C ₂₊	C ₂ H ₄	A fluorine doping strategy enables the reconstruction of isolated Cu atoms into Cu nanocrystals with stable Cu ⁺ species, achieving high C ₂₊ product generation with exceptional Cu utilization. In situ Raman spectroscopy and DFT confirm fluorine's role in enhancing structural evolution and catalytic performance.	[328]
Sn single atom	two-step stabilization strategy	CO ₂ R R	92.4 % C ₁	HCOO H	High-density Sn SACs achieve efficient acidic CO ₂ reduction to formic acid (Faradaic efficiency: 90.8%, current density: -178.5 mA cm ⁻²) by creating a favorable alkaline microenvironment	[329]

					and optimizing the pH-dependent $\ast\text{CO}_2^-$ intermediate adsorption strength, suppressing HER competition.	
single-atom Cu/ZrO ₂	impregnation	Hydrogenation	100 % C ₁	CH ₃ O H	A single-atom Cu–Zr catalyst with Cu ₁ –O ₃ units enables selective CO ₂ hydrogenation to methanol at 180°C, while Cu clusters or nanoparticles favor CO by-product formation. The migration of Cu ₁ –O ₃ units to the surface enhances catalytic activity, offering insights for designing efficient copper-based catalysts.	[330]
single-atom Rh embedded on Ti-doped CeO ₂	impregnating	Hydrogenation	99.1 % C ₂₊	C ₂ H ₅ O H	The Rh ₁ /CeTiO _x single-atom catalyst exhibits ultra-high ethanol selectivity ($\approx 99.1\%$) and turnover frequency (493.1 h ⁻¹), with excellent stability. Synergistic Ti-doping and monoatomic Rh enhance CO ₂ activation and C–C coupling, contributing to outstanding catalytic performance.	[331]
Ir ₁ –In ₂ O ₃ single-atom	precipitation method.	Hydrogenation	99 %	C ₂ H ₅ O H	The Ir ₁ –In ₂ O ₃ single-atom catalyst achieves >99% ethanol selectivity and high turnover frequency (481 h ⁻¹) by utilizing a bifunctional design with isolated Ir atoms and adjacent oxygen vacancies. Synergistic activation of CO ₂ and C–C bond	[332]

					formation via a Lewis acid-base pair enhances its catalytic efficiency.	
Rh ₁ /ZrO ₂ SAC	impregnating	Hydrogenation	9.4 molCO gRh ⁻¹ h ⁻¹	CO	The Rh ₁ /ZrO ₂ single-atom catalyst enables efficient switching from CH ₄ to CO with >99% CO selectivity in CO ₂ hydrogenation, achieving high activity (9.4 molCO g _{Rh1} h ⁻¹) and stability by tuning both Rh ₁ atoms and alkali ions. The alkali ions alter the reaction pathway and improve catalyst stability by reinforcing Rh ₁ -support interactions.	[333]
Co Single Atoms in ZrO ₂	isolated Co atoms into ZrO ₂	Hydrogenation	95 %	CO	The Co/ZrO ₂ single-atom catalyst achieves over 95% CO selectivity in CO ₂ hydrogenation by exploiting oxygen vacancies near isolated Co atoms, which facilitate CO ₂ activation and prevent further hydrogenation to methane or methanol.	[333]
Pd-promoted ZnZrO _x	coprecipitation method	Hydrogenation	85 %	CH ₃ OH	The Pd-ZnZrO _x catalyst exhibits enhanced methanol production and stability by atomically dispersing Pd in the ZnZrO _x matrix, which increases oxygen vacancies and facilitates H ₂ dissociation. This promotes CO ₂ hydrogenation on adjacent Zn sites, resulting in high activity and	[334]

					robustness.	
FeK/Co-NC SAC	atomically dispersing	Hydrogenation	42.2 % C ₅₊	C ₅₊	The FeK/Co-NC catalyst shows efficient CO ₂ conversion to long-chain hydrocarbons with up to 42.4% C ₅₊ selectivity, stable performance over 100 hours, and reduced methane formation, thanks to Fe-Co alloy formation on the Co-NC support.	[335]
Na-CoFe ₂ O ₄ /CNT SAC	Pyrolysis	Hydrogenation	39 % C ₁	CH ₄	The Na-CoFe ₂ O ₄ /CNT catalyst exhibits high CO ₂ conversion (~34%) and selectivity toward light olefins (~39%) by forming a stable bimetallic alloy carbide (Fe _{1-x} Co _x) ₅ C ₂ , outperforming single-metal and mixed-metal catalysts.	[336]
Rh ₁ /TiO ₂ SAC	depositing functionalized	Hydrogenation	80 %	CO	The Rh ₁ /TiO ₂ catalyst, modified with amine-functionalized phosphonic acid monolayers, shows an ~8× increase in CO ₂ reduction turnover frequency at 150 °C and improved on-stream stability. The modification enhances CO selectivity and CO ₂ hydrogenation activity by positioning amine groups near Rh ₁ sites.	[337]
Rh ₁ /CeO ₂	dispersing Rh atoms onto CeO ₂	Dry reforming	>80 %	H ₂ /CO	The Rh ₁ /CeO ₂ single-atom catalyst undergoes product-driven restructuring, transitioning from single Rh atoms to nanoparticles and clusters,	[338]

					which affects its catalytic performance in methane reforming by CO ₂ , highlighting the dynamic nature of single-atom catalysts under reaction conditions.	
Yolk-Shell Pt-NiCe@SiO ₂	Core-shell synthesis	Dry reforming	45 %	H ₂ /CO	The Pt-NiCe@SiO ₂ single-atom-alloy (SAA) catalyst exhibits exceptional carbon resistance and stability in dry reforming of methane (DRM) due to its yolk-shell structure and Pt-Ni SAA, which prevent carbon formation and enhance reducibility at 500 °C for 120 hours.	[63]
RuNi SAC	Thermal reduction	Dry reforming	0.44 mmol·g ⁻¹ ·min ⁻¹	H ₂ /CO	The RuNi-SAA catalyst supported on Al ₂ O ₃ enhances CO and H ₂ production in solar-driven dry reforming of methane (DRM), achieving high rates under photothermal conditions.	[339]
Ni-Ce SAC	Pyrolysis	Dry reforming	60,000 mL g _{cat} ⁻¹ h ⁻¹	H ₂ /CO	Ce-doped HAP supports Ni single atoms, preventing coking and sintering during dry reforming of methane (DRM), enhancing catalyst stability and selectivity for methane activation, leading to high activity and stability over 100 hours.	[340]
Ni-Mo SAC	Pyrolysis	Dry reform	60 %	H ₂ /CO	The molybdenum-doped nickel nanocatalyst stabilized at the edges of a single-crystalline MgO	[341]

		ming			support shows no coking or sintering, with stable operation for over 850 hours during dry reforming of methane, achieving continuous synthesis gas production	
Pt-TiO ₂ -SAC	spatial confinement	Dry reforming	34.41 mol gPt ⁻¹ h ⁻¹	H ₂ /CO	he catalyst developed using spatial confinement on TiO ₂ surfaces effectively controls platinum species from single atoms to nanoclusters, optimizing syngas production with high activity and stability. It achieves an outstanding syngas generation rate of 34.41 mol gPt ⁻¹ h ⁻¹ and a high turnover frequency of 1289 h ⁻¹ .	[342]
Ir@CeO _{2-x}	hydrothermal method	Dry reforming	973 $\mu\text{mol}_{\text{CH}_4} \text{g}_{\text{cat}}^{-1} \text{s}^{-1}$	H ₂ /CO	The 0.6% Ir/CeO _{2-x} catalyst achieves high CH ₄ (~72%) and CO ₂ (~82%) conversion with a CH ₄ reaction rate of ~973 $\mu\text{mol}_{\text{CH}_4} \text{g}_{\text{cat}}^{-1} \text{s}^{-1}$, maintaining stability for 100 hours at 700°C. The metal-support interface structure facilitates CH ₄ dissociation and prevents coke formation, ensuring long-term performance.	[343]
Ru1/3L-TiO ₂	DFT-D3 method	CO ₂ methanation	60%	CH ₄	The process of hydrogenation of CO* → HCO* is recognized as the rate-limiting step. The methanation process occurring on the Ru1/3L-	[343]

					TiO ₂ realized a lower activation energy and was accompanied by a significantly reduced endothermic heat, in contrast to the reactions on the Ru1/2L-TiO ₂ .	
1 % Ni SAs- Bi ₃ O ₄ Br	Wet chemical method	Hydro genati on	100 % selectivity for HCOO	HCOO H	The defect self-regulation mechanism enables photo-induced reconstruction, wherein Ni single atoms inhibit the migration of oxygen species to the oxygen vacancy surface, thereby preventing deactivation and guaranteeing prolonged catalytic stability.	[344]
Co doped copper catalyst	electroreduct ion of a Co- Cu precursor	CO ₂ metha nation	exceeding 60%	CH ₄	Mechanistic studies showed that the inclusion of individual Co atoms facilitates the activation and dissociation of H ₂ O molecules, therefore reducing the energy barrier for the hydrogenation of *CO intermediates.	[345]
Ru1Ni/Si O ₂	Hydrotherma l synthesis	CO ₂ metha nation	100%	CH ₄	Both in situ experiments as well as theoretical calculations validate that the interface sites of Ru1Ni-SAA serve as the intrinsic active sites, facilitating the direct dissociation of CO ₂ and reducing the energy barrier for the hydrogenation	[346]

					of the CO* intermediate, thus directing and augmenting the hydrogenation of CO ₂ to CH ₄ .	
Pt-CN catalyst	Hydrothermal synthesis	CO ₂ methanation	99 %	CH ₄	The Pt sites were not significantly involved in H ₂ development due to the distinctive environment established by -OH groups and adsorbed CO ₂ .	[347]
Cu/C-Al ₂ O ₃ SAC	Hydrothermal synthesis	Electrochemical CO ₂ methanation	62%	CH ₄	The results indicate that the hydrogenation of CO ₂ to methane is enhanced on Lewis's acid oxide-supported Cu single atoms.	[348]
Zn-TpPa	Wet chemical method	N-formylation of amines	TOF 17,155 h ⁻¹ amon	N-methylaniline	Out of all the catalysts that were available, Zn-TpPa demonstrated the greatest TOF, promoting the N-formylation of N-methylaniline with CO ₂ and hydrosilanes that were highly recyclable.	[349]
Zn(OAc) ₂ @P(BiPy-DVB)-1	Copolymerization	N-formylation	94%	N-methylformal	Under moderate circumstances, the ideal single-atom Zn catalyst had the greatest TOF among all recorded heterogeneous catalysts.	[350]

		of amine s		nilide		
Ru-POM- ILs/BMI mOAc	Wet chemical method	N- formy lation of amine s	96.0%	forma mides	The current catalyst can be recycled without noticeable loss of activity and has improved long- term storage stability even in the air.	[351]

2.9 Computational works

In the quest for efficient CO₂ conversion using SACs, DFT methods have emerged as indispensable tools for deciphering the underlying molecular mechanisms and catalytic pathways. DFT offers a computational framework to explore the intricate electronic and structural changes during CO₂ conversion, providing insights into reaction energetics, intermediate species, and reaction kinetics. From traditional functionals like local density approximation (LDA) and generalized gradient approximation (GGA) to more advanced hybrid and dispersion-corrected functionals, DFT methods offer a spectrum of accuracy and computational efficiency [261[352]]. Additionally, approaches such as van der Waals-corrected DFT and advanced spin-orbit coupling calculations allow researchers to capture subtle interactions and electronic properties essential in CO₂ conversion. This introduction highlights the spectrum of DFT methods employed in elucidating CO₂ conversion mechanisms by SACs, showcasing their pivotal role in guiding experimental design, optimizing catalysts, and advancing the field towards sustainable and selective carbon transformation technologies [353,354]. For example, Jiao et al., used DFT calculations to illustrate the effect of adsorption configuration on the activation energy, which has impact on the selectivity and stability under the applied potential. Their results indicated that the Cu₁₀-Cu_{1x+} site in an atom-pair catalyst (APC) promotes CO₂ activation via a 'biatomic activating bimolecular' mechanism. This offers an ideal model of interface design at the atomic level, because the afforded APC features two different atomic centers to absorb two different molecules. However, the concept of APC is an effective and competent supplement to SAC and will afford numerous new opportunities for atomic- level dispersed catalysts to

be applied in more complex catalytic reactions [355]. An adsorption design reduces the activation energy, leading to enhanced activity, selectivity, as well as stability at comparatively low potentials. In a different report [356], DFT computations demonstrated that N/O coordinated Cu decoration sites enhance CH₄ selectivity by stabilizing the adsorption of *CHO and *O key intermediates as shown in [Figure 16](#). This strategy achieved a CH₄ FE of 71% at a current density of 100 mA cm⁻² and a CH₄ energy efficiency (EE) of 21%. The produced CH₄ has 50% the energy intensity of that produced in the best prior electrolyzers [356].

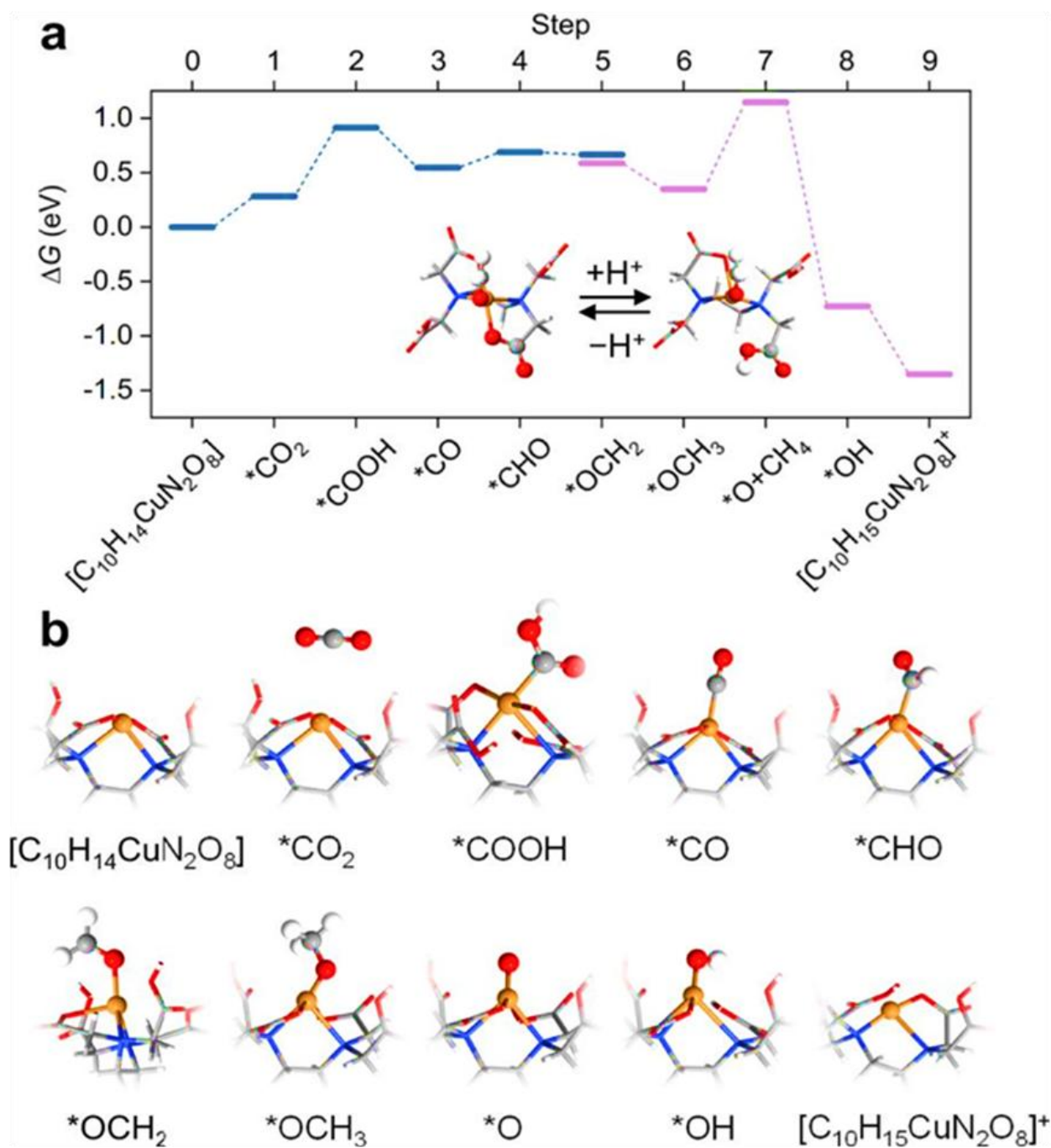
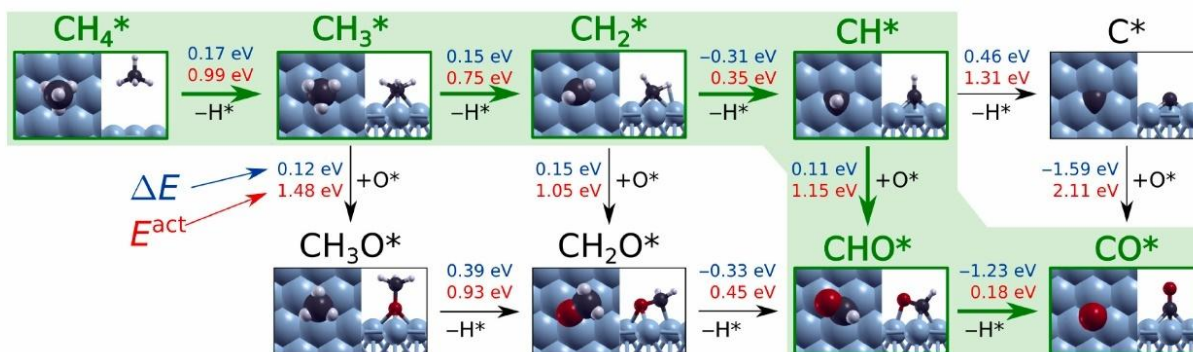


Figure 16: DFT calculations on CO_2 protonation to CH_4 . Reprinted with permission from [356].

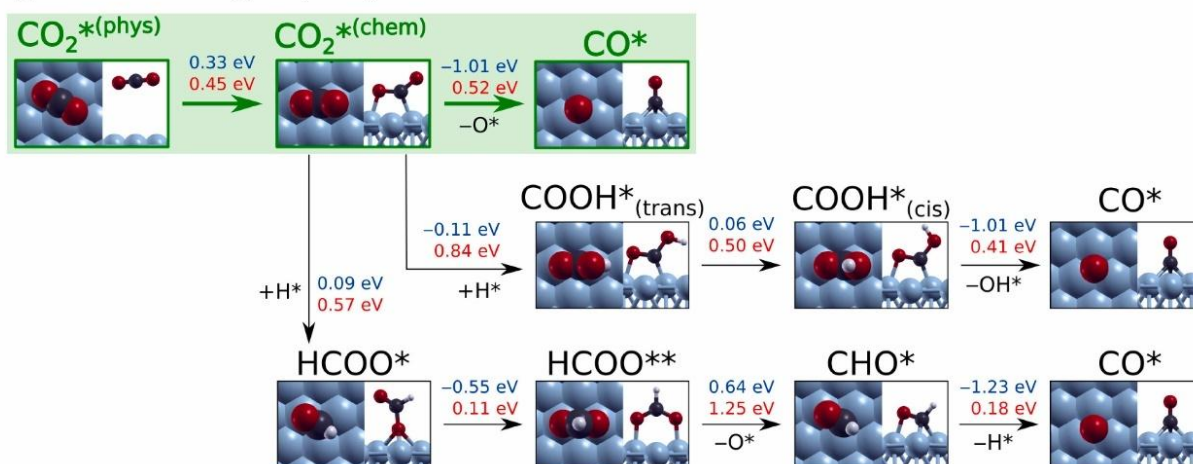
In addition to experimental methods, several computational tools are employed to study the DRM mechanism and evaluate the impact of experimental variables on the response [357–359]. Density functional theory modelling and microkinetic modelling are used to investigate

the fundamental chemical processes in the breakdown of methane and carbon dioxide on different metal surfaces [360–362]. Lea Gašparič et al., [363] utilized the fundamental chemical processes of dry reforming of methane (DRM) on Ni(111) and NiO(100) using Density Functional Theory simulations as models for metallic and oxidized nickel catalysts. The results indicate that although DRM may be achieved on metallic Ni at elevated temperatures, a notable challenge arises from the occurrence of coke production, which coincides with the same activation barriers for C* creation and DRM product synthesis. Although nickel oxide prevents the production of coke, it is not very efficient as a catalyst due to its high activation energy and sluggish surface diffusion of H*. This research also elucidates the observed disparities in DRM efficiency between Ni catalysts based on undoped CeO₃ (Ni/CeO₃) and CeO₃ doped with MnO (Ni/MnCeO₃). The lack of the 2020 cm⁻¹ vibrational peak on the Ni/MnCeO₂ catalyst is due to the absence of carbon monoxide adsorbed on the top surface of metallic Ni, which is commonly found on Ni/CeO₂ catalyst. The existence of this peak on Ni/CeO₂ suggested that nickel particles possess a high degree of metallicity and are susceptible to carbon poisoning. In contrast, the lack of the peak on Ni/MnCeO₂ indicates that Ni particles have undergone sufficient oxidation to reduce carbon poisoning, while still enabling DRM. This explains why Ni/MnCeO₂ is a superior DRM catalyst compared to Ni/CeO₂ as in shown [Figure 17](#).

CH₄ dissociation @ Ni(111)



CO₂ dissociation @ Ni(111)



Reactions of common intermediates @ Ni(111)

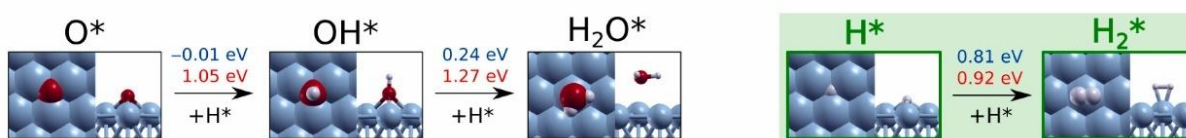


Figure 17: The snapshots and computed reaction (ΔE , blue) plus activation (E_{act} , red) energies of the primary steps in the breakdown of CH₄ and carbon dioxide, as well as the production of water and hydrogen molecules, on Ni(111) are presented. For each reaction, the reaction pathways that include the primary steps with the smallest activation barriers are depicted in green. All computed reaction energy pathways and their matching IS, TS, & FS structures are displayed. Reprinted with permission from [363]

Despite numerous experimental studies aimed at characterizing the reaction mechanism on Single alloy catalysts, the underlying reasons for the observed promoting effects remain unclear. This has shifted the focus towards guiding the experimental design of more effective

single alloy catalysts for methanol synthesis. In the realm of catalyst design, theoretical calculations provide a highly advantageous methodology for the identification of reaction routes, intermediates, and active sites. By combining empirical and theoretical investigations, scholars can acquire a more profound understanding of carbon dioxide hydrogenation, thereby facilitating the advancement of more effective catalysts for methanol production [364][365]. Lingna Liu [366] they used DFT calculations to investigate the adsorption properties and reaction process of CO₂ hydrogenation to CH₃OH on a copper-based catalyst with varying Ir doping ratios. Throughout the reverse water-gas shift (RWGS) pathway, CO₂ initially hydrogenates to trans-COOH, which then isomerizes to cis-COOH and subsequently dissociates into CO + OH. CO further hydrogenates sequentially to form HCO, H₂CO, H₃CO, and the final product, H₃COH. The results reveal that the rate-determining step for the Ir₆Cu₃(111) surface is the formation of CO + OH, while for Ir₆Cu₃(111) and IrMLCu(111), it is the formation of HCO, with energy barriers of 1.21 eV, 1.35 eV, and 1.34 eV, respectively. Additionally, H₂ dissociation is nearly spontaneous on IrCu(111) surfaces, providing ample hydrogen for the reaction. The study highlights the significant influence of Ir doping ratios on the hydrogenation process, particularly on the IrMLCu(111) surface. These findings offer valuable insights for designing and optimizing Ir-doped Cu-based catalysts for carbon dioxide hydrogenation to methanol as in illustrated [Figure 18](#).

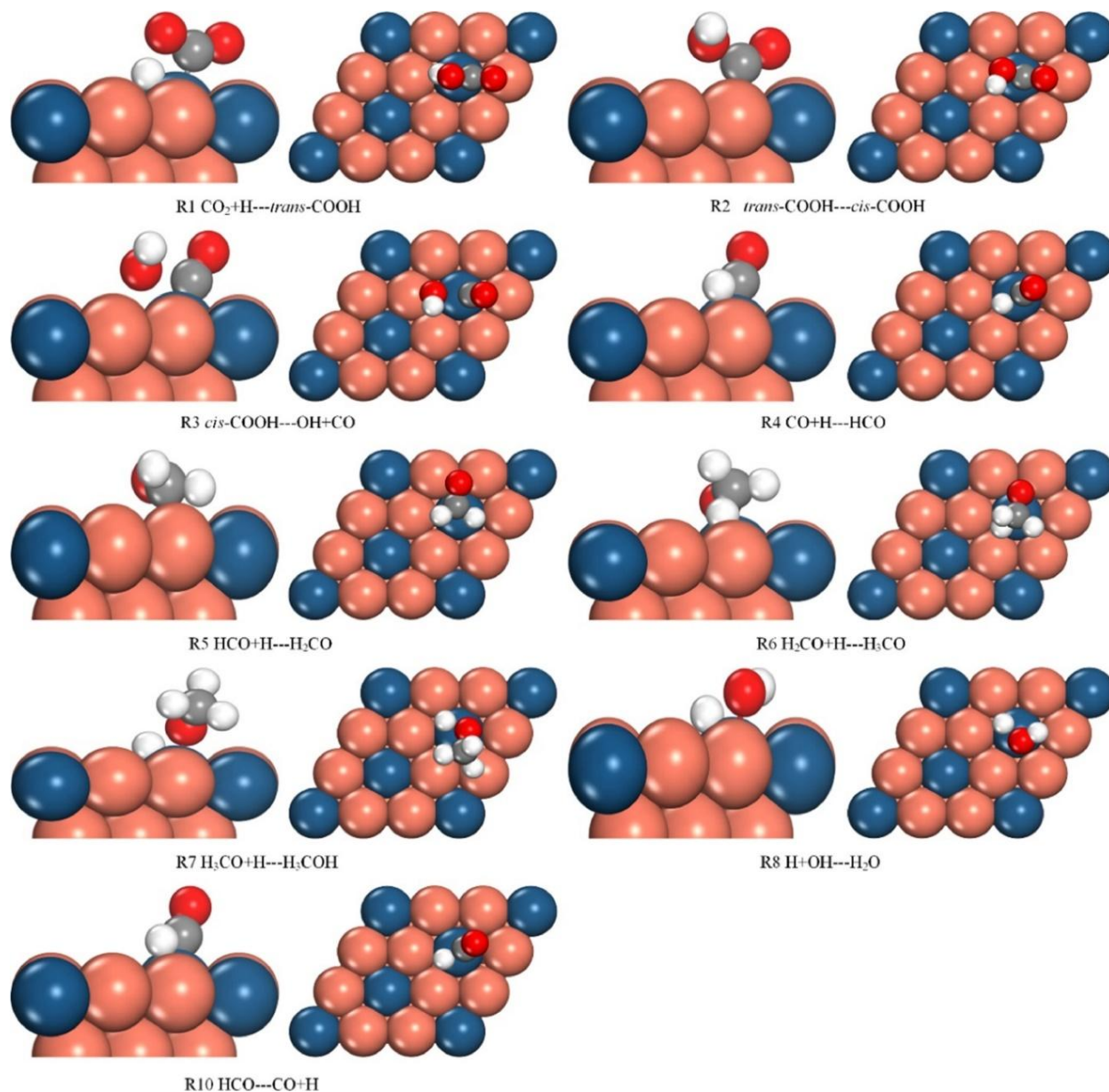


Figure 18: The transition states of the primary steps involved in carbon dioxide hydrogenation on $\text{Ir}_3\text{Cu}_6(111)$ surface. Red, Oxygen atom; White, Hydrogen atom; grey, Carbon atom. Reprinted with permission from [366].

2.9.1 Impact of Machine learning in developing the process

In the advancement of renewable energy transformation technology, catalysts play a pivotal role [367]. These solutions offer a sustainable and environmentally friendly approach to tackle the energy problem as well as global climate change concerns [368].

Conventional heterogeneous catalysts typically comprise multiple metal particles of varying sizes, with only a small fraction of metal atoms acting as catalytic active species [369]. Additionally, the presence of multiple active sites with different selectivities leads to variations in product distributions, reducing metal utilization efficiency and selectivity [370]. SACs, along with double-atom (DACs) and triple-atom catalysts (TACs), bridge the gap between homogeneous and heterogeneous catalysis. However, designing highly efficient SACs is challenging due to the extensive combinatorial design space. The combination of 44 metals with various substrate supports could lead to millions of possible SACs [371]. Traditional experimental and computational methods, including DFT, face significant time and cost constraints, making purely trial-and-error approaches infeasible. ML, a rapidly evolving artificial intelligence technique, has transitioned from theoretical research to practical applications in materials science. ML is widely used to analyze complex datasets, detect structural flow abnormalities in disordered materials [372], and investigate relationships between physical characteristics and catalytic performance [373] [374]. Specifically, ML has been instrumental in understanding the adsorption energy of reaction intermediates and the maximum adsorption capacities of SACs supported on graphene-based solid-state electrolytes [375]. Various ML algorithms, including K-nearest neighbor regression (KNN) [376], random forest regression [377], support vector regression (SVR) [378], gradient boosting regression (GBR) [379], extreme gradient boosting regression (XGBR), deep neural networks (DNN) [380], and Gaussian process regression (GPR) [381] have been employed for SAC design (see [Figure 19](#)), are now being employed for the design of SAC [381]. Among these, RFR, GBR, DNN, and GPR have shown promising results in catalyst optimization [382].

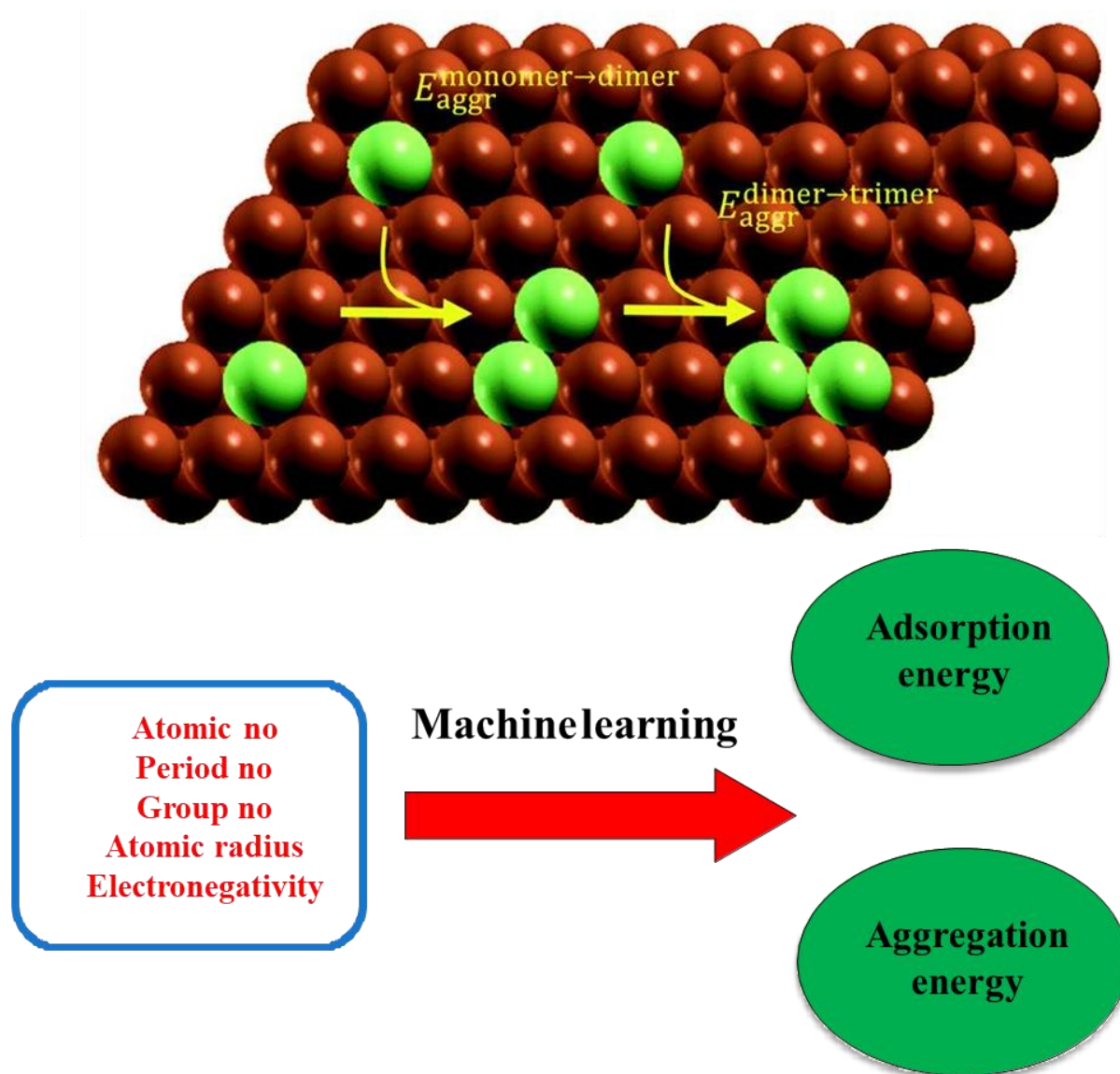


Figure 19: Modeling the aggregation energy of SA-bimetallic catalysts with both clean and O^* adsorbed surfaces using machine learning algorithms. Reprinted with modification from [381].

ML has been instrumental in advancing CO_2 electroreduction [3 8 3] , which relies on CO as a key intermediate for generating multi-carbon hydrocarbons and oxygenates. Traditional catalyst evaluation often depends on a single assessment criterion, which may lead to biased outcomes. To address this, an XGBR-based predictive model was developed, using RFR, GBR, KNR, and SVR as training algorithms for comparison. The final XGBR model

demonstrated the highest prediction accuracy, integrating a DFT database with ML techniques to rapidly screen potential catalysts for CO₂ electroreduction [384]. This framework identified 94 prospective SACs for CO₂ electroreduction by overlaying results from CO₂ reduction and hydrogen evolution reaction (HER) studies. By employing feature engineering and high-throughput screening, ML-based models enable researchers to efficiently identify promising catalysts before conducting detailed experimental investigations [384]. Additionally, ML has been applied in DRM to mitigate catalyst deactivation due to coke formation and sintering at high reaction temperatures [385][386][387]. Traditional DRM catalyst development relies on expensive trial-and-error approaches, but ML models have facilitated the prediction of key performance parameters such as methane and CO₂ conversion rates, syngas ratios, and carbon deposition [388–391]. Jiwon Roh et al. [392] proposed an interpretable ML framework that reduces computational costs while offering valuable insights into catalyst performance. Their framework utilized Shapley additive explanations and partial dependence values for enhanced data preparation and analysis, achieving an R² value of 0.96. Experimental validation confirmed its potential to accelerate catalyst discovery. The effectiveness of this framework was validated through experimental tests focused on the dry reforming of methane, confirming its potential to significantly accelerate the rational design of catalysts as shown in [Figure 20](#).

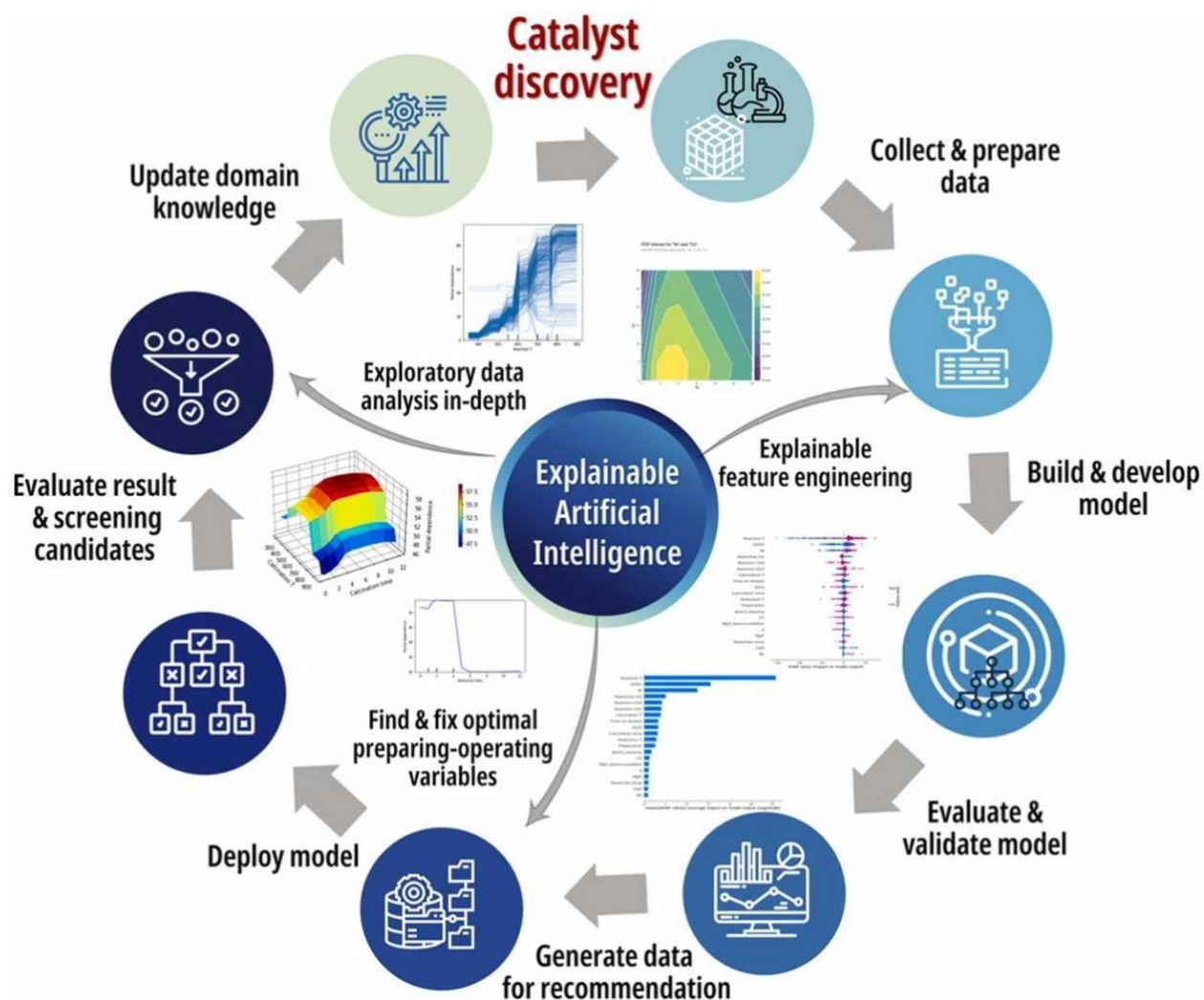


Figure 20: Workflow of Explainable Artificial Intelligence in Catalyst Discovery. Reprinted with modification form [392].

ML has also emerged as a powerful tool in CO₂ hydrogenation, particularly in methanol synthesis. Direct catalytic hydrogenation of CO₂ is a promising strategy to meet growing fuel demands while reducing anthropogenic CO₂ emissions [393]. However, the reaction's thermodynamic constraints necessitate catalysts with high selectivity to minimize unwanted byproducts [394]. Several ML models, including Multi-Linear Regression, LASSO, Ridge Regression, SVR, GPR, RFR, GBR, and artificial neural networks (ANN), have been developed to predict CO₂ conversion efficiency and methanol selectivity. Using 698 experimental data

points from fixed-bed reactors (2010–2020), Pallavi et al. [395] demonstrated that GBRT and ANN exhibited superior predictive accuracy, with R^2 values of ~ 0.95 . Their analysis highlighted catalyst composition and calcination temperature as key factors influencing performance as in illustrated Figure 21.

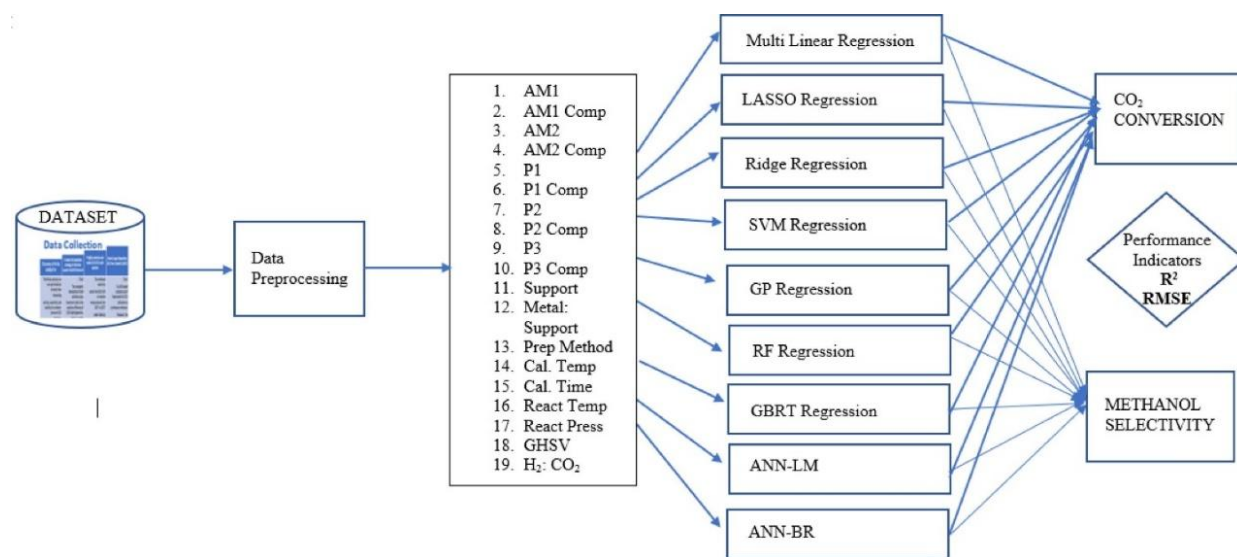


Figure 21: Methodology for development of ML models. Reprinted with modification form [395]

The integration of ML into catalyst research has significantly advanced materials discovery, enabling rapid screening and optimization of catalysts for CO₂ electroreduction, DRM, and hydrogenation processes. By leveraging ML-based predictive models, researchers can efficiently explore large design spaces, reducing reliance on traditional, resource-intensive methods. As ML techniques continue to evolve, they will play an increasingly vital role in accelerating the development of next-generation catalysts for sustainable energy applications.

In conclusion, this review provided an in-depth analysis of the significant advancements and the current state of SACs. The historical evolution of SACs highlights their transition from theoretical concepts to practical applications, driven by advancements in synthesis

methods such as pyrolysis, wet chemistry, and coordination confinement. These methods have enabled the precise control of SAC structures, crucial for their unique catalytic properties. Comprehensive characterizations using techniques like high-resolution transmission electron microscopy (HR-TEM), XAS, and atomic force microscopy (AFM) have provided detailed insights into the atomic distribution and electronic environment of SACs, furthering our understanding and optimization of these catalysts. The review also emphasizes the versatility of SAC-derived materials, including Cu-based, Fe-based, Ni-based, and Cd-based catalysts, as well as more complex structures like yolk shell Pd@Fe and MOF-based SACs. Each of these materials demonstrates specific advantages in various catalytic reactions, underscoring the broad applicability of SACs. Particularly noteworthy is their role in CO₂ conversion applications, where SACs facilitate processes such as electrochemical reduction, hydrogenation, reforming of CH₄, methanation, cycloaddition with epoxides, and polymer production. These applications not only contribute to mitigating CO₂ emissions but also offer pathways for generating valuable chemicals and materials, highlighting the environmental and economic benefits of SACs. The integration of machine learning and computational methods has significantly impacted the field, enabling the optimization of synthesis processes and the prediction of catalyst performance. Computational studies, including DFT calculations, provide atomic-level insights into the mechanisms of SACs, guiding experimental research and accelerating the discovery of new catalysts. Despite these advancements, challenges such as scalability, stability, and cost-effectiveness remain. Addressing these issues is critical for the broader industrial adoption of SACs, and future research must focus on developing more robust supports, optimizing atom-support interactions, and reducing production costs. The future of SACs lies in interdisciplinary approaches that combine advancements in materials

science, chemistry, and computational technologies. Collaborative efforts across academia, industry, and government will be essential to drive innovation and tackle global challenges. Continued exploration of SACs for emerging applications, particularly in renewable energy and environmental remediation, will be crucial. This review underscores the transformative potential of SACs in catalysis, offering unparalleled opportunities for scientific discovery and practical applications. With ongoing research and technological advancements, SACs are poised to play a pivotal role in shaping a sustainable future, revolutionizing catalytic processes, reducing environmental impact, and contributing to the development of green technologies.

CHAPTER 3

RESULTS AND CONCLUSION

Interplay of morphology and facet orientation of Cu nanocrystals directing CO₂ electroreduction to value-added products

In this study, we detail the wet chemistry of copper derived from a CuCl₂ precursor. This technique allows for the concurrent control of the morphology, crystal phases, and size of Cu nanoparticles. We examined the influence of various morphologies, crystal phases, and sizes on the production of specific products and the attainment of high (J) in an H-cell configuration. This study was integrated with DFT calculations and real-time Raman spectroscopy analysis for operando characterization as in **Figure 22. (b)**. NaBH₄ is a strong reducing agent that also influences morphology control [396]. Initially, we explored the impact of varying amounts of NaBH₄ and PVP molecular weight (40,000) on controlling the morphology, crystal phases, and size of Cu nanoparticles as in **Figure 22. (a)**. Adding 0.06 M of NaBH₄ resulted in a blood flow morphology (BF), predominantly exposing {100} crystal faces, which achieved a high ethylene yield (60%) with a (J) at greater than -90 mA cm⁻² at -1.14 V (vs RHE). By utilizing 0.13 M of NaBH₄ produced a triangular morphology (TR) with a balanced presence of {100} and {111} crystal phases, leading to a high formate yield (85%) with a (J) of -39 mA cm⁻² at -1.0 V (vs RHE). In addition, when we use 0.26 M of NaBH₄, the resulting spherical morphology (SP), primarily featuring {111} crystal phases, yielded 78% CO with a (J) of -35 mA cm⁻² at -1.1 V (vs RHE). Our findings present a promising approach

for developing efficient, cost-effective catalysts with good selectivity for multi-carbon compounds. Additionally, it provides an optimal environment for evaluating the significant impact of catalyst shape, crystal phases, and size on the CO₂RR efficiency.

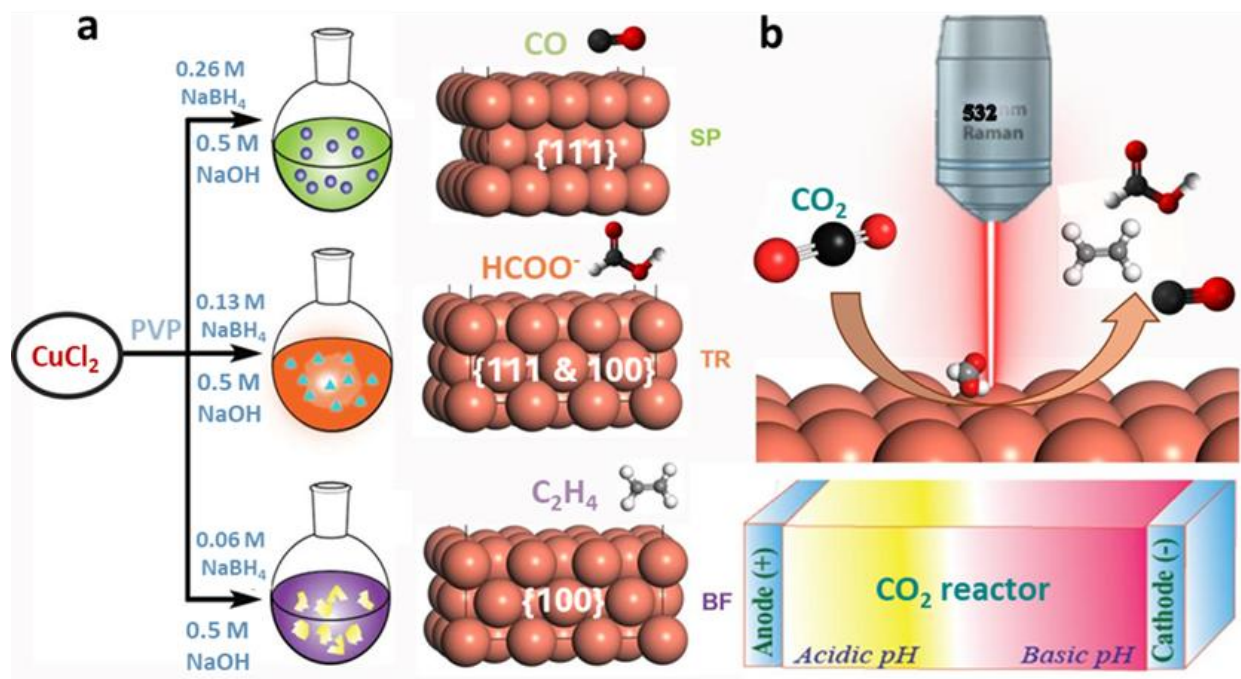


Figure 22: Schematic diagrams for (a) Formation of Cu nanoparticles in different morphologies. (b) CO₂RR reactor in the bottom and the in-situ Raman spectroscopy system in the top.

3.1 Synthesis and characterization of different copper catalysts.

Figure 23 showcases the rapid and scalable production of Cu-NPs with diverse morphologies. Scanning electron microscopy (SEM) was utilized to investigate the surface morphology of the diverse Cu-NPs across three catalysts at different magnifications. Panels (a) in **Figure 23** illustrate the BF catalyst, which exhibits a morphology akin to blood cells in veins, hence termed Blood Flow (BF).

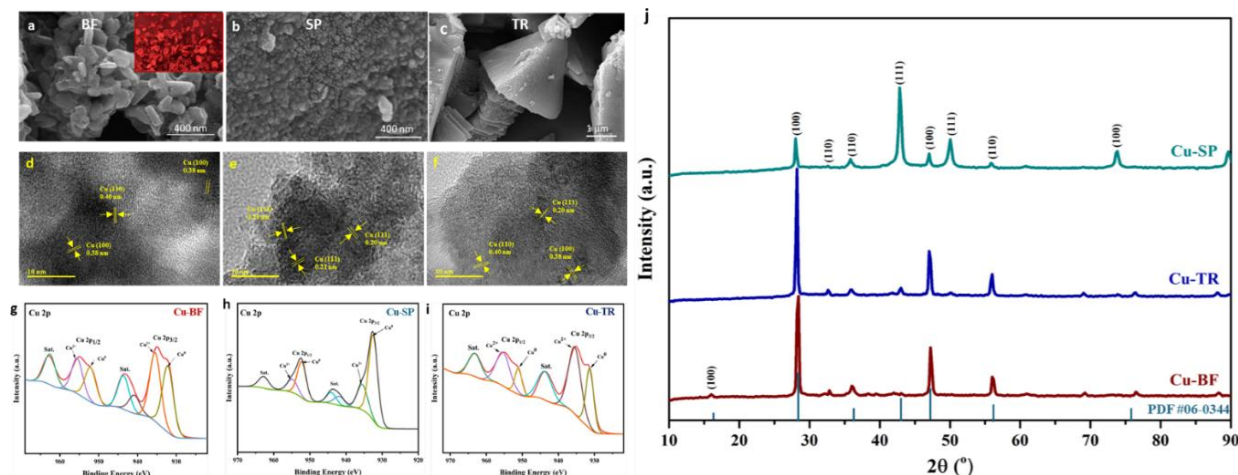


Figure 23: Morphologies and chemical states of Cu catalysts (a-c) SEM images for Cu-BF {blood flow morphology}, Cu-SP {spherical morphology} and Cu-TR {triagonal morphology} catalysts; respectively. (d-f) HRTEM images for Cu-BF, Cu-SP and Cu-TR catalysts; respectively. (j) XRD patterns of Cu-BF at the bottom, Cu-TR in the middle, and Cu-SP at the top.

The particle size ranges from 100-200 nm, as indicated by the Zeta potential characterization in **Figure 24 (a)**. Panel (b) in **Figure 23** depicts the SP catalyst, characterized by a spherical shape with particle sizes ranging from 60-200 nm, as shown in **Figure 24 (b)**. The third catalyst, Trigonal shape (TR), is shown in panel (c) in **Figure 23**, with a particle size range of 250-500 nm, as detailed in **Figure 24 (c)**. From this diverse range of particle sizes and crystal phases, we validated our concept. The micrographs in **Figure 23 (d-f)** feature high-resolution transmission electron microscope (HR-TEM) images of the different copper morphologies: BF, SP, and TR, respectively. These images reveal interlayer spacings of 0.380 nm for the BF catalyst's {100} plane, 0.21 nm for the SP catalyst's {111} plane, and a balance of 0.380 nm and 0.21 nm for the TR catalyst, corresponding to the {100} and {111} planes. Through the use of pixel intensity integration over 10 atomic layers, the extensive HR-TEM images, as shown in **Figure 25**, revealed an interplanar spacing of 0.21–0.38 nanometres. Following the predicted lattice characteristics of metallic copper {100} and Cu⁺ {111}, this

measurement reveals that a significant proportion of the Cu {100} and {111} facets are exposed on the Cu-NPs that are responsible for the formation of the BF, SP, and TR catalysts. The X-ray photoelectron spectroscopy (XPS) shown in **Figure 23 (g)** illustrates the various Cu in Cu⁰, Cu⁺, and Cu²⁺ oxidation states at 930-960 peaks in BF catalyst. To address this, we electrochemically reduced the surface of the catalyst for 5 minutes at -0.8 V (vs RHE) in an H-cell. As depicted in **Figure 27 (b)**, operando Raman spectroscopy was performed from 100 s to 900 s, revealing shifts at 250-300 cm⁻¹ and 600 cm⁻¹ at open circuit refers to Cu²⁺, which disappeared after 900 s. This step confirmed the complete reduction of Cu²⁺ to Cu⁰, which enhances ethylene production [397]. Panels **(h)** and **(i)** in **Figure 23** display the different intensities of Cu⁰ and Cu²⁺ for the SP and TR catalysts, respectively. While complete reduction was applied to these two catalysts, the results were not as significant as with the BF catalyst for ethylene production. The binding energies (of Cl 2p and C 1s) 2p_{3/2} for the Cu BF catalyst were approximately 200 eV, as shown in **Figure 26 (a)**. The oxygen 1s spectra, with peaks at 530 eV, demonstrated the existence of specific oxidized species on the surfaces of the copper BF catalyst. Similarly, **Figure 26 (b-c)** displays the binding energies (of Cl 2p and C 1s) 2p_{3/2} for the SP and TR catalysts, respectively. The oxygen 1s spectra for these catalysts also exhibited peaks at 530 eV, suggesting the existence of oxidized species on the surfaces of copper SP and TR. To further understand the crystallinity besides chemical composition of Cu nanoparticles, X-ray diffraction (XRD) analysis was performed on the synthesized catalysts, as shown in **Figure 23 (j)**. The BF catalyst exhibited a predominant presence of {100} faces, the TR catalyst showed a balance between {100} and {111} faces,

and the SP catalyst had an abundance of {111} crystal faces.

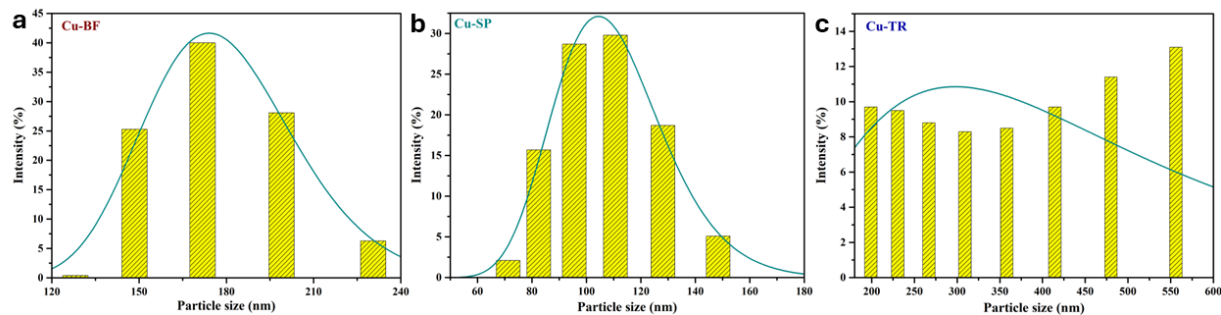


Figure 24: Particle sizes calculated from zeta potential for Cu-BF, Cu-SP and Cu-TR; respectively.

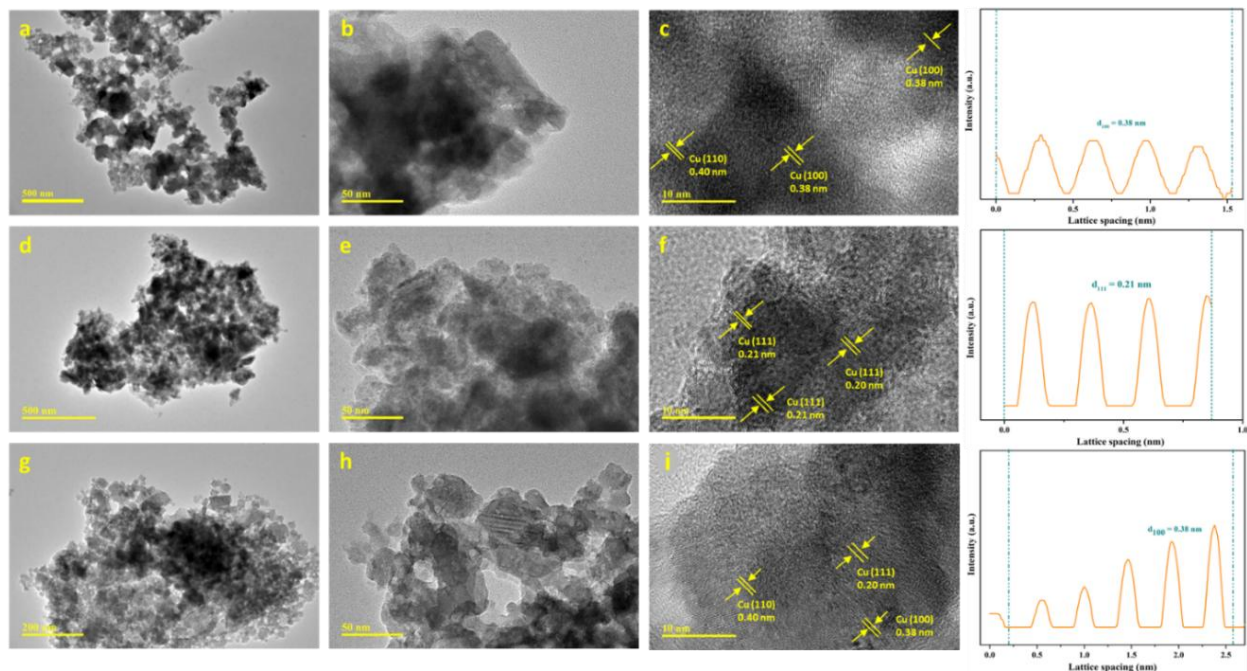


Figure 25: Morphologies and Lattice spacing of Cu catalyst. (a-c) HR- TEM images for Cu-BF, (d-f) Cu-SP catalyst, (g-i) Cu-TR catalysts.

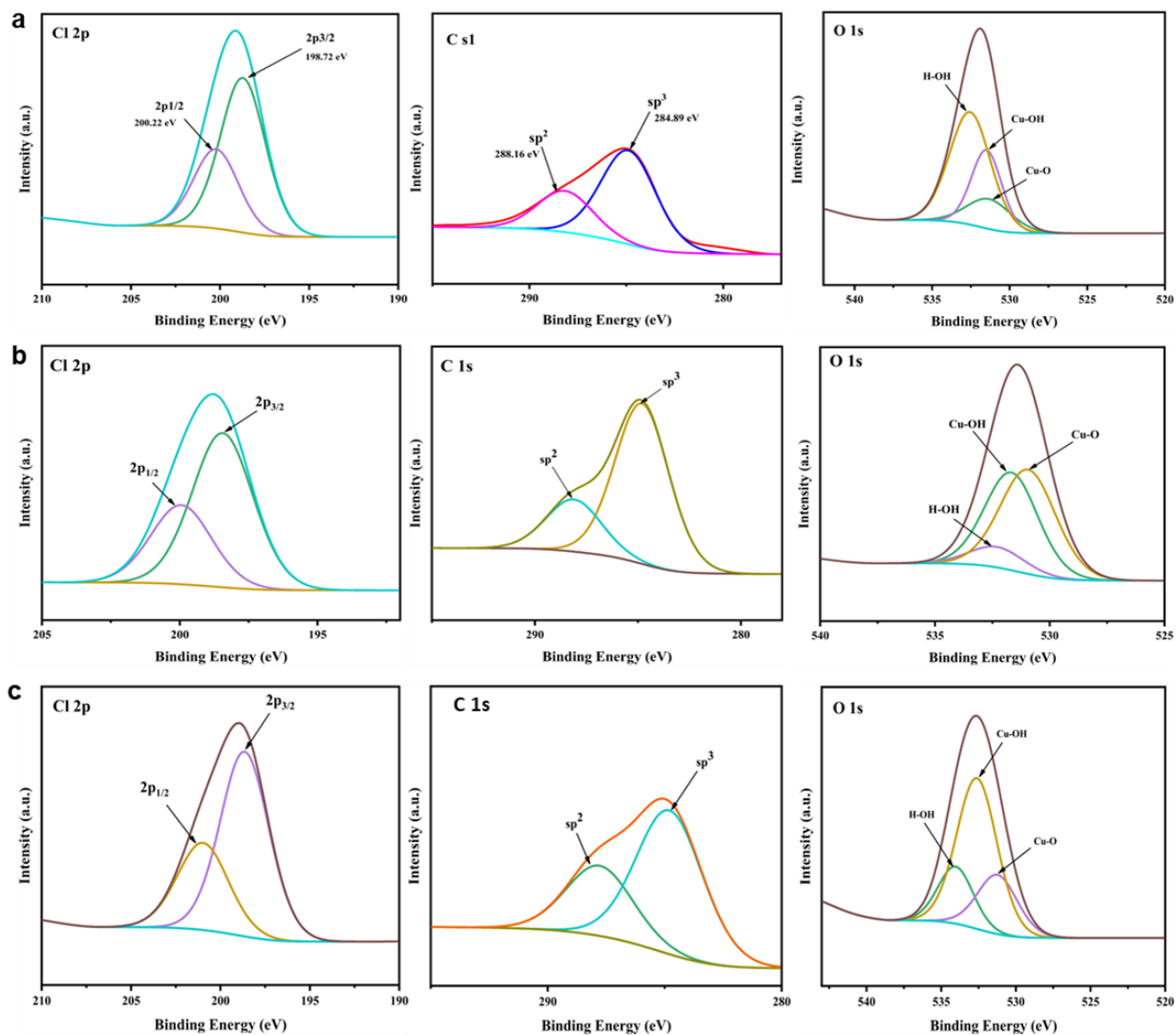


Figure 26: Chemical states of Cu catalyst. (a) XPS spectrum {Cl 2p, C 1s, O 1s, respectively} of Cu-BF catalyst; (b) XPS spectrum {Cl 2p, C 1s, O 1s, respectively} of Cu-SP catalyst; (c) XPS spectrum {Cl 2p, C 1s, O 1s, respectively} of Cu-TR catalyst.

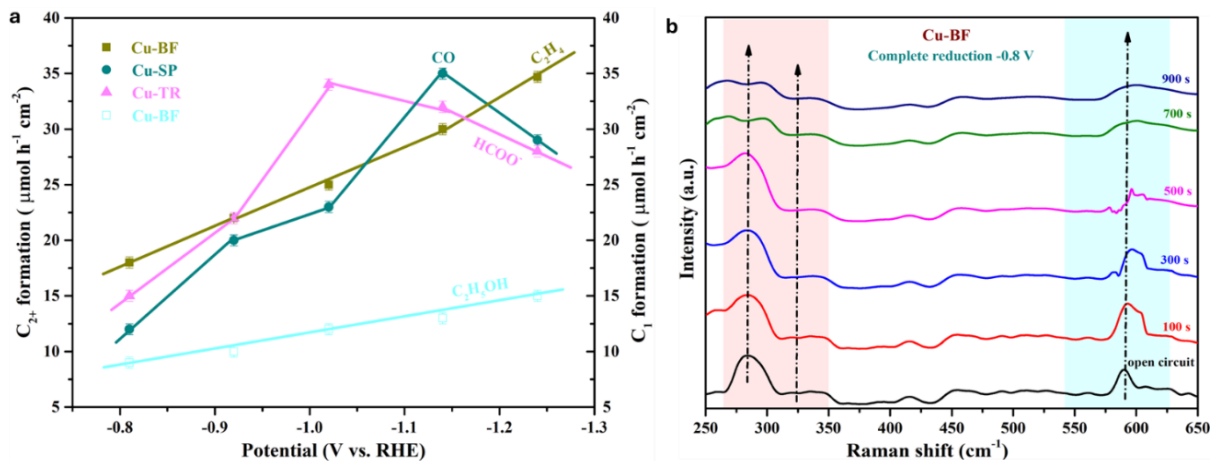


Figure 27: C_{2+} and C_1 formation rates by ECSA of Cu catalysts under different applied potentials in 1.0 M KHCO_3 ; (b) complete reduction for Cu-BF catalyst at -0.8 v (vs. RHE) at different time(s).

3.2 Density functional theory (DFT) calculations:

DFT simulations were conducted on Materials Studio 8.0 suite [398] on the DMol3 module using the parameterized method of Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) [399],[400]. The choice of this model owns to the fact that it yields accurate description of electronic sub-states, and due to the high level of accuracy of the DMol3 module [401]. The crystallographic information file (CIF) of the copper electrocatalysts were downloaded from the Materials Project database [402], and structurally relaxed. A threshold of 1.0×10^{-5} Ha was imposed on the self-consistent field (SCF) converge to yield exact charge densities and to provide variational independence during the search for wavefunctions of the non-occupied states. The maximum energy plus force tolerance were adjusted as 10^{-5} Ha and 2×10^{-3} Ha/ $\text{\AA}$, respectively, while the Monkhorst-Pack grid of $3 \times 3 \times 1$ Gamma k-points was chosen to efficiently sample the Brillouin zone. The three electrocatalysts whose X-ray diffraction patterns matches the experimental correspond to the body-centered cubic copper which represent the Cu-BF; the

tetragonal copper lattice which represent the Cu-TR; and the face-centered cubic Bravais lattice which represent the Cu-SP electrocatalyst. To investigate how the structural variety affects the electrocatalytic selectivity of the constructed system, Cu{100} surface was created due to its unique electronic properties, relative simplicity, and high stability [403], Periodic 3×3 slabs were built, and vacuum of 15 Å thickness were created to prevent the adjacent slabs from interacting. All the surfaces were structurally optimized until a value of less than 0.03 eV/Å was achieved for the overall residual forces on the atoms as presented in Figure **Figure (28-30)**. The linear synchronous transit/quadratic synchronous transit (LST/QST) technique were used to estimate the transition states along the reaction coordinates, while the energy barrier (E_{barrier}) was estimated using the equation:

$$E_{\text{barrier}} = E_{\text{TS}} - E_{\text{intermediate}}$$

Where E_{TS} is the energy of the transition state, and $E_{\text{intermediate}}$ is intermediate energy.

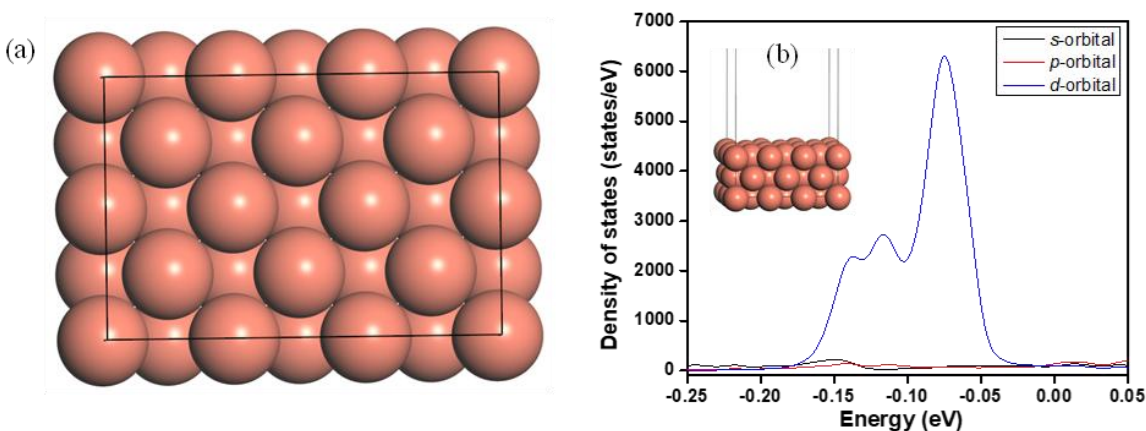


Figure 28: (a) Top view, and (b) PDOS plot of body-centered cubic Cu (100) surface representing the Cu-BF electrocatalyst.

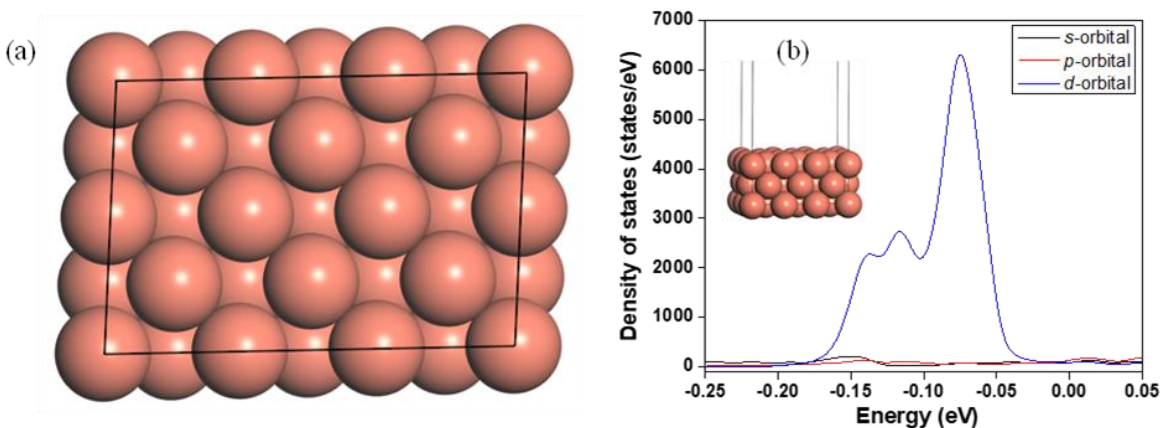


Figure 29: (a) Top view, and (b) PDOS plot of tetragonal Cu (100) surface representing the Cu-TR electrocatalyst.

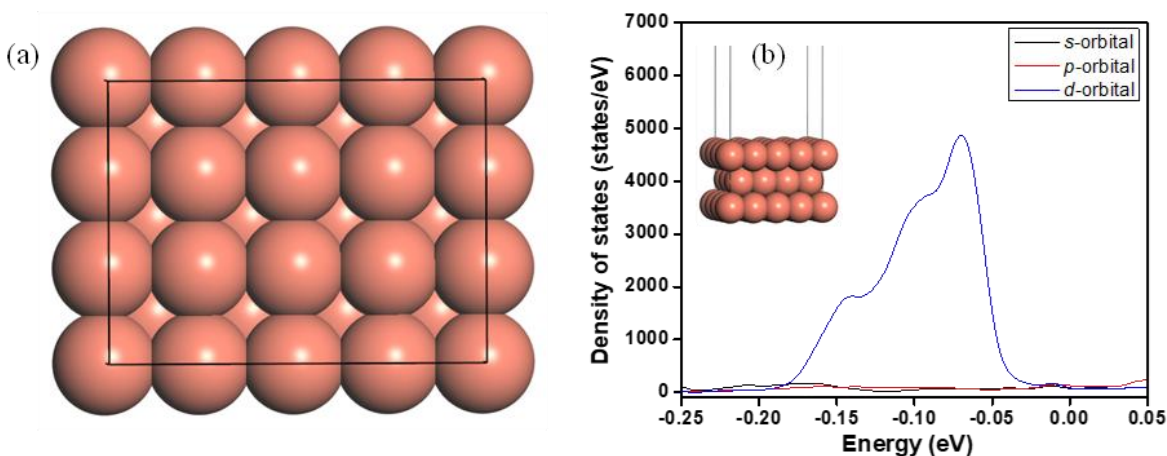


Figure 30: (a) Top view, and (b) PDOS plot of face-centered cubic Cu (100) surface representing the Cu-SP electrocatalyst.

3.3 Computational results

The critical step in CO₂RR is the initial H⁺/e⁻ transfer to absorb CO₂ molecules on the surface of the electrode. This often results in the intermediates binding to the catalyst either via carbon or oxygen. Considering the significance of this stage, which is termed the rate-determining step 1 (RDS 1), an in-depth understanding of the microstructural contribution of the three electrocatalysts in the present study is essential to provide insights on the

molecular level interactions and the mechanistic pathways leading to the CO₂RR products [404],[405]. **Figure 31 (i)** shows the geometrically optimized CO₂RR pathway on the Cu-SP and the Cu-TR electrocatalysts, while the corresponding energy profiles are presented in **Figure 31 (ii)**. Whereas several reports have shown that copper-based catalysts preferentially catalyze CO₂RR to C₂ fuels because of the unique modest binding of copper to the intermediate carbon monoxide molecules [406],[407],[408]. The morphology, facet and the structure of the catalyst is strongly believed to enhance selectivity and products distribution. The activation of the electrode surface which enhanced the adsorption of carbon dioxide molecules on the Cu-SP (**Figure 31 (i) (a)**) and the Cu-TR (**Figure 31 (i) (b)**) surfaces resulted in adsorption energies (E_{ads}) of -35.5 and -48.2 kJ/mol, respectively. The face-centered cubic (fcc) Cu-SP surface preferentially binds via the carbon atoms with a binding distance of 3.01 Å, while the tetragonal Cu-TR surface binds strongly via the oxygen atoms with Cu-O distances of 2.55 and 2.60 Å. Meanwhile, the C-O bonds distorted outwardly on the Cu-SP and form an inward distortion with a V-shape on the Cu-TR, affirming the preferences of the surfaces. Further hydrogenation of the adsorbed *CO₂ resulted in the C-O bond elongation by 1.53 and 0.88 Å on both surfaces relative to the isolated estimated distance in gas phase, signifying the facile formation and desorption of CO molecules. The adsorption of CO₂ via oxygen atoms on both surfaces (**Figure 31 (i) (c-d)**) resulted in E_{ads} of -38.7 and -30.6 kJ/mol on the Cu-SP and Cu-TR, respectively. This is followed by proton transfer and the subsequent desorption of HCOOH. The energetics of these processes however (**Figure 31 (ii)**), revealed that the adsorbed *CO₂ on Cu-SP stabilizes the catalyst by 0.18 eV, while the Cu-TR's energy was raised by 0.59 eV upon CO₂ adsorption. The E_{barrier} to the production of *COOH favors hydrogenation on Cu-SP with a barrier of 0.59 eV, in

comparison to the Cu-TR with the value of 0.59 eV. The successive protonation, loss of water and the desorption of CO thus showed the selectivity of the fcc Cu-SP resulting in higher FE ($\Delta G = 0.09$ eV). The dimerization mechanism of CO to *COCO (leading to formation of C₂ compounds), and the hydrogenation to C₁ compounds (CH₄ plus CH₃OH) on both surfaces were thermodynamically unfavorable due to the high energetics, hence such products were not detected. Similarly, the *OCHO intermediate formed via the Cu-O adsorption pathway resulted in energy barriers of 0.25 and -0.54 eV downhill on the Cu-SP and Cu-TR surfaces, implying the spontaneous formation of HCOOH on the tetragonal Cu-TR surface, consistent with the greater selectivity reported in the experiment.

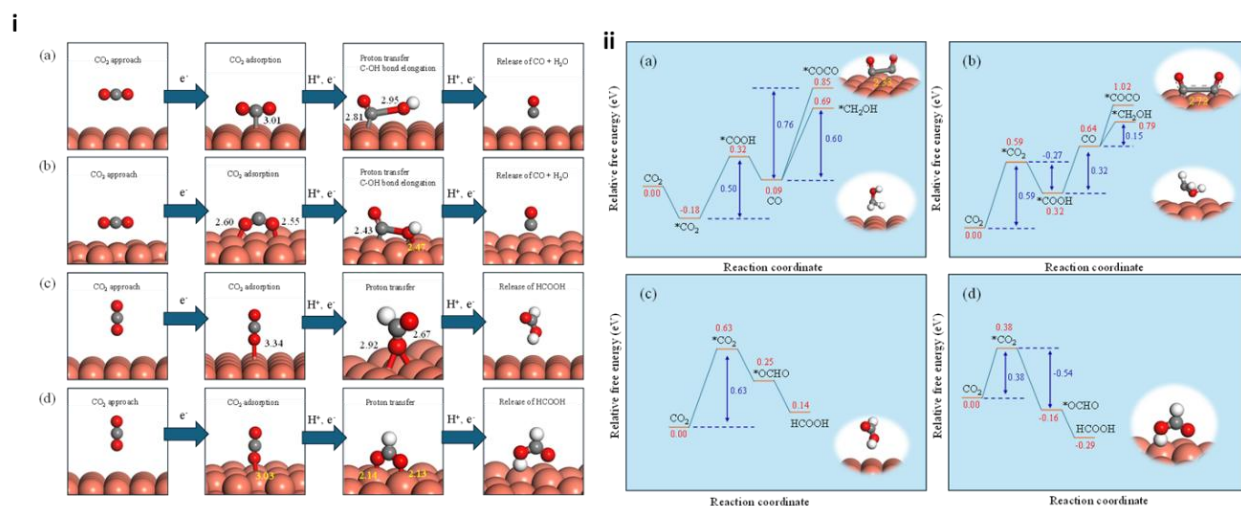


Figure 31: (i) panel The optimized mechanistic pathway of CO₂RR to CO on (a) Cu-SP, (b) Cu-TR; and CO₂RR to formate on (c) Cu-SP, (d) Cu-TR electrocatalysts. (ii) panel The energetics and reaction coordinates of the CO₂RR to CO on (a) Cu-SP, (b) Cu-TR; and CO₂RR to formate on (c) Cu-SP, (d) Cu-TR electrocatalysts.

The strong attraction of the body-centered cubic (bcc) Cu-BF electrocatalyst to carbon atom of the adsorbed *CO₂ favors the dimerization of CO with subsequent hydrogenation to C₂H₄ and CH₃CH₂OH as shown in **Figure 32**. Energetics of the CO₂RR revealed that while the Cu-BF exhibited facile formation of CO with E_{barrier} of - 0.10 eV downhill, the strong adsorption

energy of the $^*\text{CO}$ ($E_{\text{ads}} = -65.5 \text{ kJ/mol}$) resulted in weak desorption of the molecule, further dimerizing via C-C coupling to form the bidentate intermediate $^*\text{COCO}$ with an E_{barrier} of -0.16 eV . This step separates the pathways to C_1 and C_n ($n \geq 2$) products and is termed the second rate-determining step (RDS 2) [409],[410]. Further hydrogenation of the $^*\text{COCO}$ yielded the glyoxal $^*\text{OCCOH}$ intermediate, which upon loss of water afforded the $^*\text{OCCH}$ while passing through energy barriers of 0.36 and 0.03 eV , in turn. Several debates are still on-going on the exact mechanistic pathways to the formation of higher hydrocarbons during CO_2RR [411]. Clark and Bell [412], argued that the glyoxal pathway is critical to the formation of ethanol, while according to Calle-Vallejo and Koper [413], the acetaldehyde intermediate is essential to the formation of either ethanol or ethylene. The energetics of CO_2RR on Cu-BF surface revealed that the formation of ethylene is more favored with little possibilities of ethanol formation. Consequently, the $^*\text{OCCH}$ intermediate is further hydrogenated to $^*\text{OCHCH}$, then to $^*\text{OCHCH}_2$ and lastly the formation and desorption of ethylene with energy barriers of 0.31 , -0.14 and -0.07 eV , respectively. Similarly, as postulated by Luo et al.,[414] the $^*\text{OCH}_2\text{CH}_3$ intermediate was possible with E_{barrier} of 0.36 eV , resulting in the production of ethanol. Hence, the development of ethylene on Cu-BF electrocatalyst is highly favored as revealed by the DFT calculations, with minor products such as CO and ethanol. Overall, the DFT results agree well with the electrolysis results and suggest the significance of the Bravais lattice and the catalyst coordination number in the construct of effective electrocatalysts for CO_2RR .

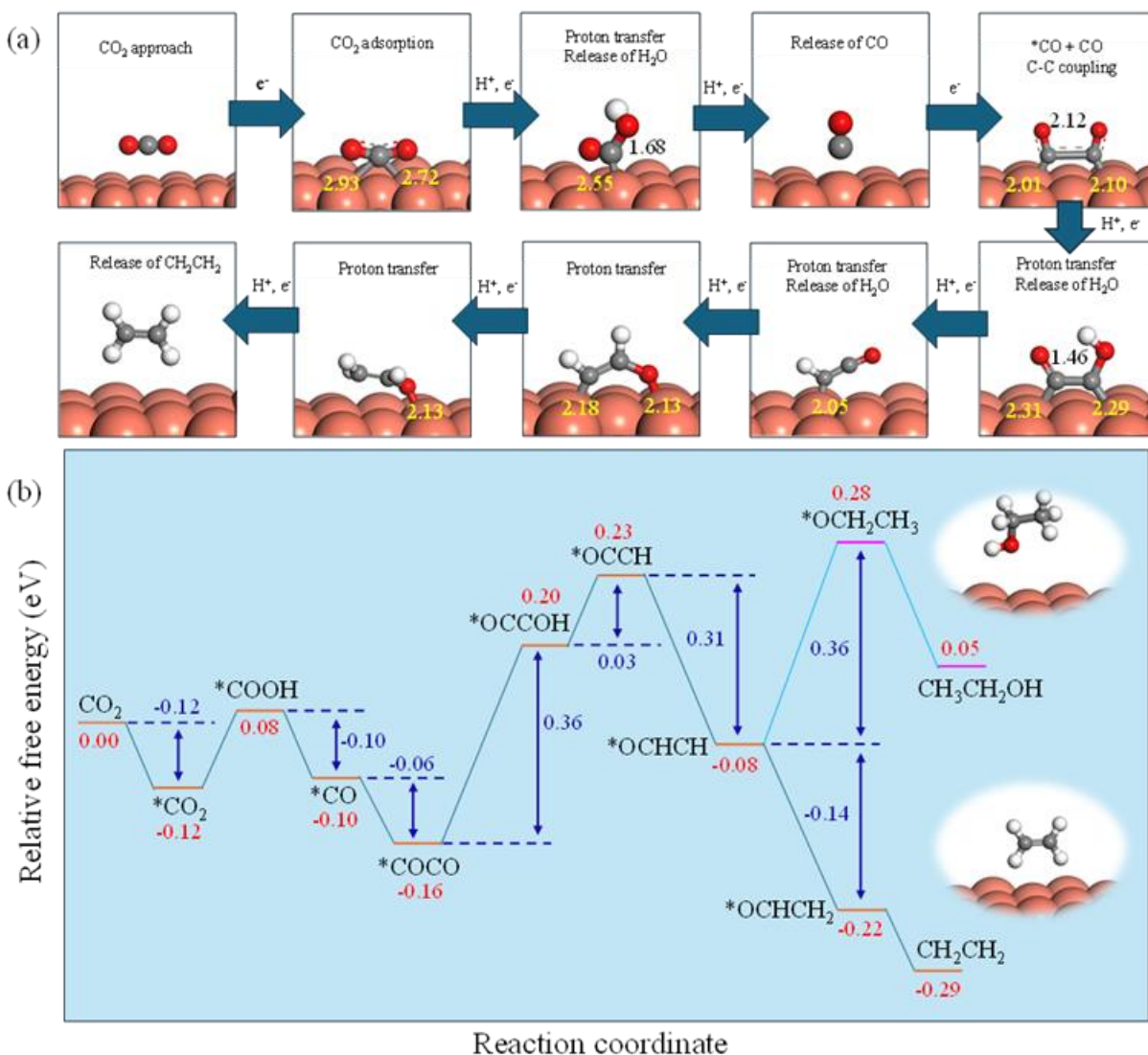


Figure 32: (a) The optimized mechanistic pathway of CO₂RR to CH₂CH₂, and (b) the energetics and reaction coordinates of CO₂RR to CH₂CH₂ and CH₃CH₂OH on the Cu-BF electrocatalyst.

3.4 Electrocatalytic CO₂RR on different copper catalysts.

It is noteworthy that these three Cu nanostructures serve as excellent platforms for examining structural property correlations and discovering the relationship between product selectivity copper morphology, crystal phases plus particle size. The CO₂RR catalytic selectivity and activity of different Cu-NPs with varying morphologies BF, SP, and TR were assessed under the same conditions using a CO₂-saturated 1 M KHCO₃ aqueous electrolyte at

potential range of -0.8 to -1.2 V (vs RHE). Online gas chromatography (GC) 580 GC (Perkin Elmer) with FID and xTCD detector was utilized to quantify the gas products, while nuclear magnetic resonance (NMR) (Delta Jeol) spectroscopy was employed to measure the liquid products. The calculations of FE% are specified in the supplementary data.

Electrocatalytic performance of copper nanoparticle catalysts

As indicated in **Figure 34 (a)** and **Figure 35 (a)** panels representing H_2 , CO, and C_{2+} products were formed on copper BF at different cathodic potentials (-0.8 to -1.2 V vs. RHE) in both electrolytes. A slight difference in performance was detected between the two electrolytes, as detailed in **Figure 36 (a-c)** for BF, TR, and SP, respectively. In **Figure 34 (b)** and **Figure 35 (b)** panels, TR displays the formation of carbon monoxide, HCOO^- , and hydrogen products across a similar potential range (-0.8 to -1.2 V vs. RHE) in both electrolytes, with small differences in two electrolytes as in the BF catalyst. **Figure 34 (c)** and **Figure 35 (c)** panels illustrate the FE of SP catalyst for CO, HCOO^- , and H_2 over the same potential range in both electrolytes (1M KOH and KHCO_3). All investigation were carryout in an H-cell electrolyze with a $5 \text{ mL}\cdot\text{min}^{-1}$ flow rate of pure carbon dioxide. The copper BF catalyst exhibited a broad spectrum of J , ranging from 13 to over $90 \text{ mA}\cdot\text{cm}^{-2}$, when the applied potential was varied between -0.8 and -1.2 V vs. RHE. The J exhibited stability throughout the electrocatalytic process at every applied voltage, as shown in the i-t curves in **Figure 37**. At an applied voltage of -1.2 V (vs. RHE) in a 1 M KHCO_3 electrolyte with a carbon dioxide flow rate of $5 \text{ mL}\cdot\text{min}^{-1}$, the FE reached its maximum value of 60% for ethylene as the primary product.

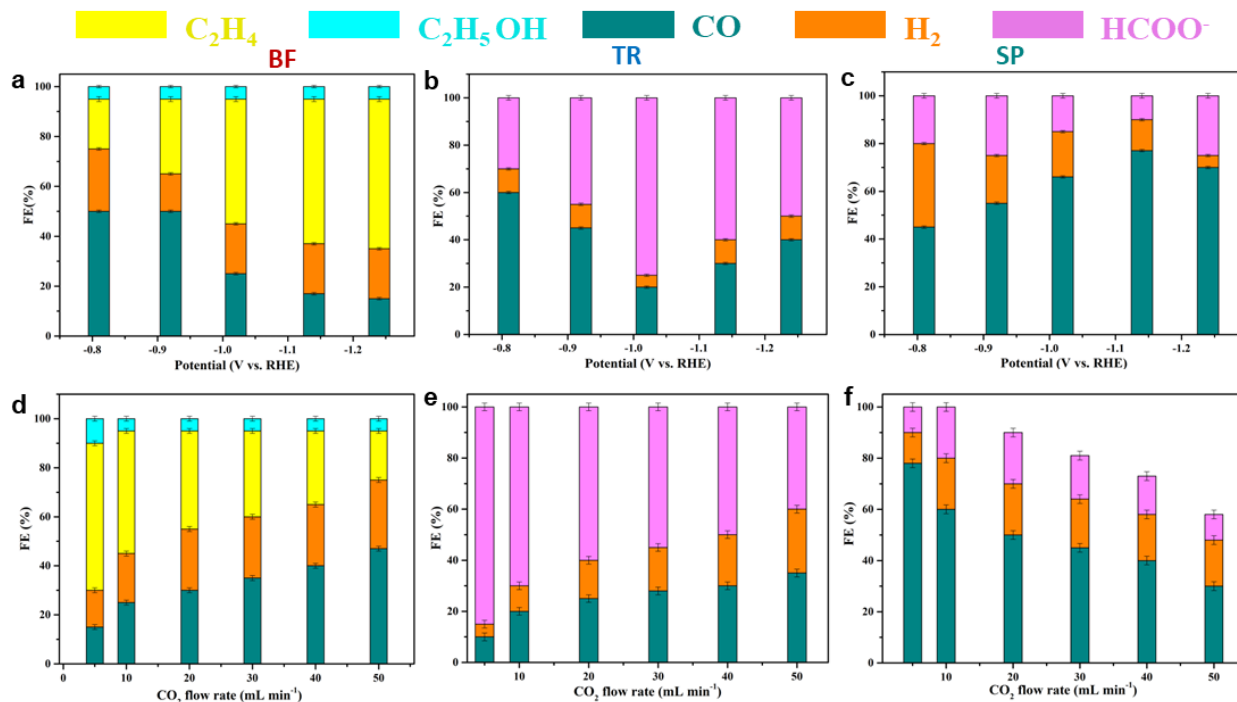


Figure 33: Electrocatalytic CO₂RR performances. (a-c) FE% of Cu-BF, Cu-TR and Cu-SP catalysts in 1 M KHCO₃, respectively; (d) Cu-BF catalyst with different CO₂ flow rate { 5,10,20,30,40,50} mL.min⁻¹ in 1 M KHCO₃ at -0.8 V (vs. RHE); (e) Cu-TR catalyst with different CO₂ flow rate { 5,10,20,30,40,50} mL.min⁻¹ in 1 M KHCO₃ at -0.8 V (vs. RHE); (f) Cu-SP catalyst with different CO₂ flow rate { 5,10,20,30,40,50} mL.min⁻¹ in 1 M KHCO₃ at -0.8 V (vs. RHE).

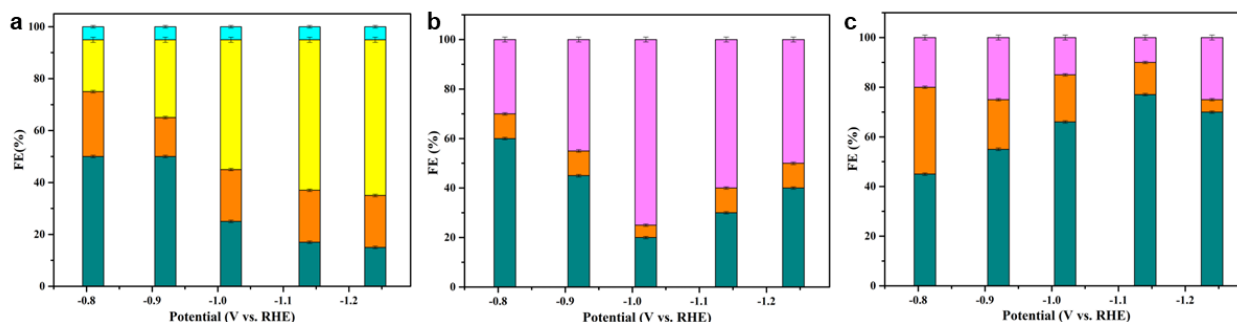


Figure 34: Electrocatalytic CO₂RR performances. (a-c) FE% of Cu-BF, Cu-TR and Cu-SP catalysts in 1 M KOH; respectively.

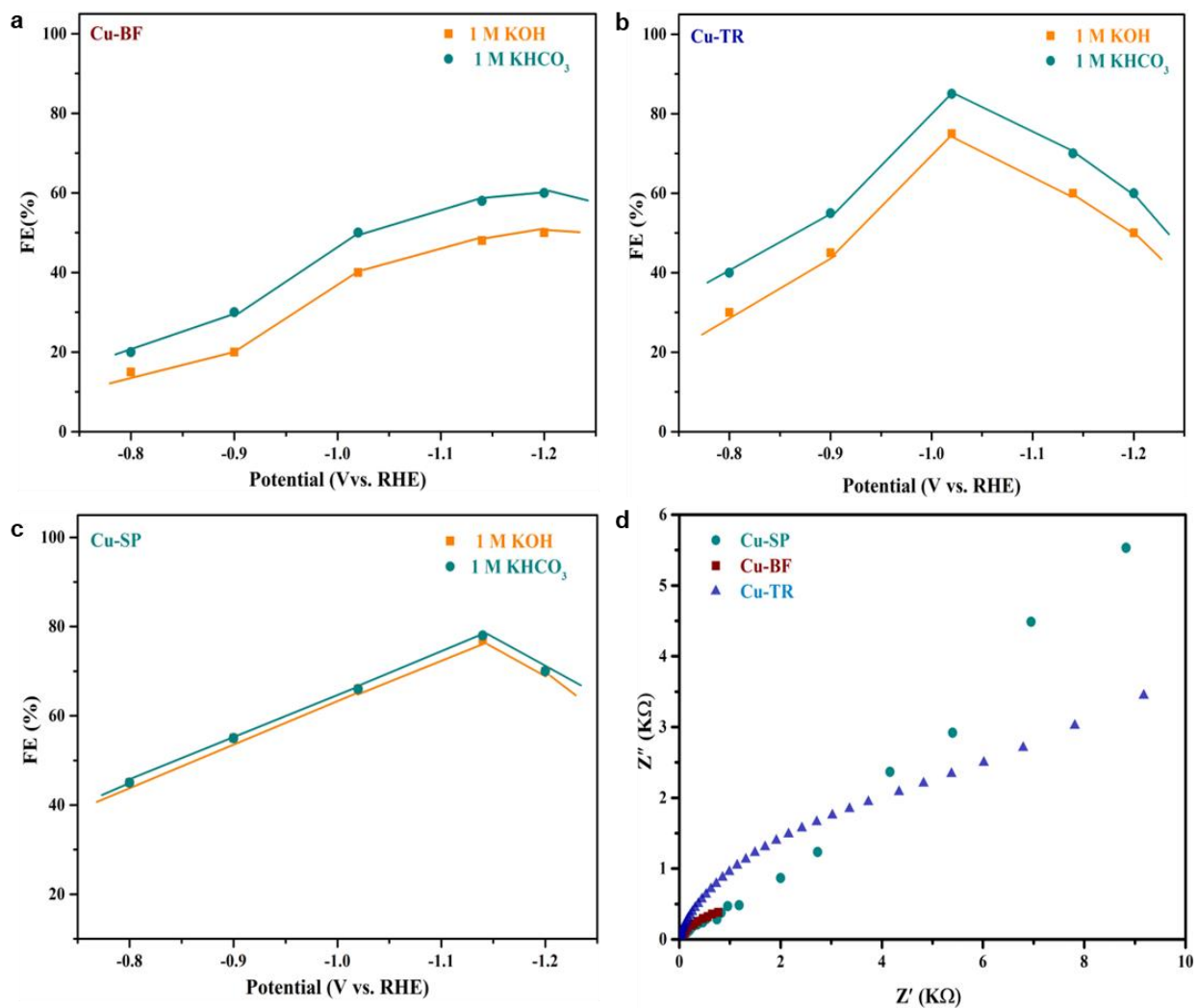


Figure 35: Electrocatalytic CO₂RR performances. (a-c) FE % of Cu-BF, Cu-TR, and Cu-SP catalysts for products {C₂H₄, HCOO⁻, CO}, respectively, in different electrolyte (1 M KHCO₃ and 1 M KOH); (d) EIS (Electrochemical impedance spectroscopy) for Cu catalysts in high range potential.

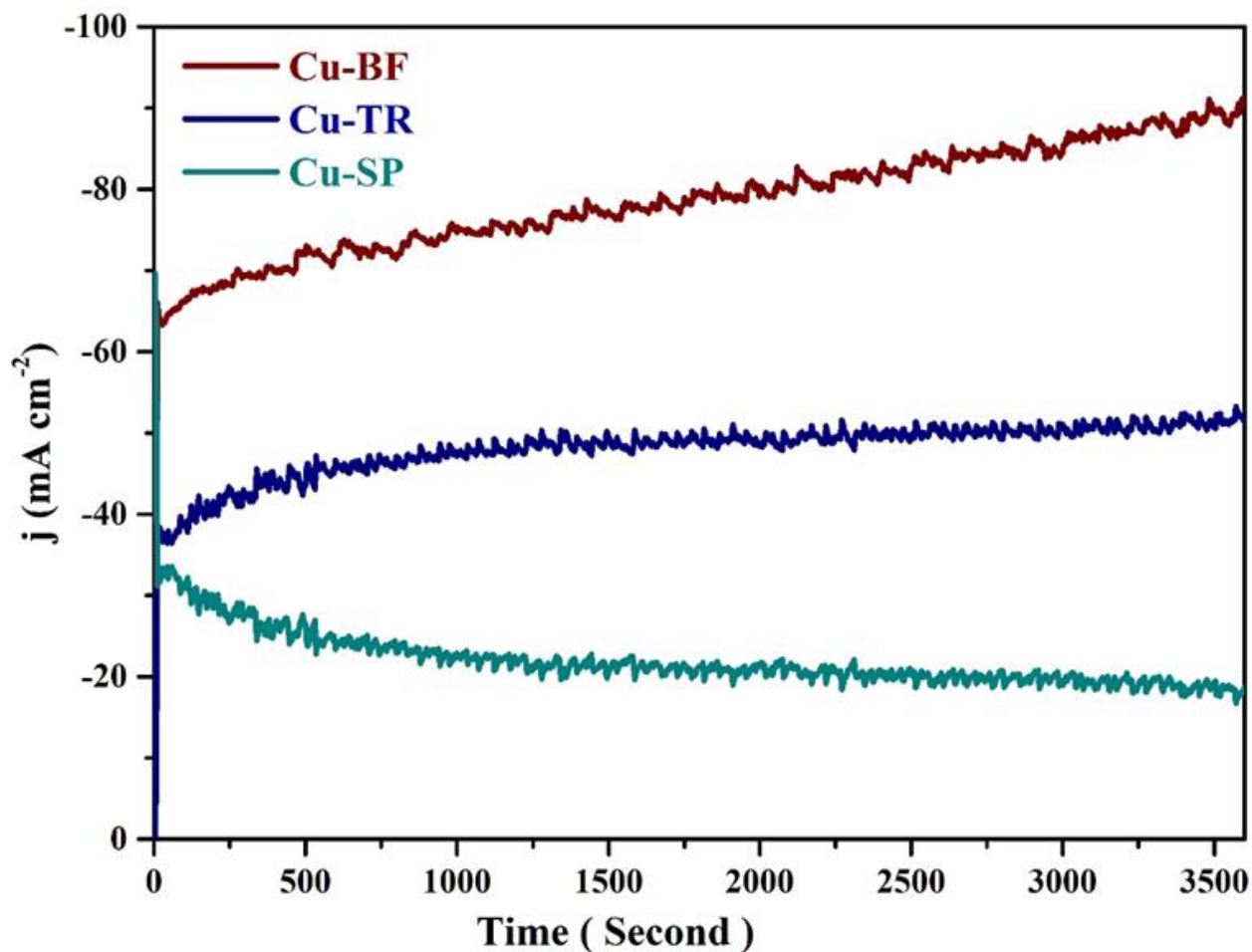


Figure 36: i-t plot of three catalysts Cu-BF, Cu-TR and Cu-SP for 1 h in 1 M KHCO₃ at -1.2 V (vs. RHE) with CO₂ flow rate 5 ml.min⁻¹.

The secondary products included 10% ethanol, 15% carbon monoxide, and 13% hydrogen, as shown in **Figure 4 (a)**. In **Figure S4** panel (a), which represents the process in 1 M KOH on BF catalyst, the results show a slight variation: the FE for ethylene was 50%, ethanol was 10%, carbon monoxide increased to 25%, and hydrogen recorded a slight increase 13.5% at -1.2 V (vs. RHE) with the same carbon dioxide flow rate and a J of 90 mA.cm⁻². In **Figure 34 (b)** and **Figure 35 (b)**, which focus on the TR catalyst with a balance of {100} and {111} faces, the applied potential range of -0.8 to -1.2 V vs. RHE in 1 M KHCO₃. Panel b reveals the highest FE for HCOO⁻ at -1.02 V, reaching 85% with a J of 39 mA.cm⁻², along with 10% carbon

monoxide and 3% hydrogen. In the 1 M KOH electrolyte **Figure 35** (panel b), there is a slight difference: the carbon monoxide percentage increases to 20%, HCOO^- decreases to 75%, while hydrogen remains at the same percentage, and the J stays consistent. Both experiments were conducted under a CO_2 flow rate of $5 \text{ mL}\cdot\text{min}^{-1}$. In **Figure 34 (c)** and **Figure 35 (c)**, which examine the SP catalyst with {111} faces, the potential range of -0.8 to -1.2 V vs. RHE in 1 M KHCO_3 . Panel c shows the highest FE for CO at -1.14 V, achieving 78% with a J of $35 \text{ mA}\cdot\text{cm}^{-2}$, alongside 10% HCOO^- and 10 % hydrogen. In the 1 M KOH electrolyte **Figure 35 (c)**, there is a slight variation: the CO percentage decreases to 77%, hydrogen increases to 11%, while HCOO^- remains at 10%, with the J remaining constant. Both sets of experiments were conducted with a carbon dioxide flow rate of $5 \text{ mL}\cdot\text{min}^{-1}$.

Among the electrochemical activity measurements, the CO_2 flow rate emerges as a critical parameter. Findings have shown that, at lower CO_2 flow rates, the faradaic efficiency for both C_1 and C_{2+} compounds decreased, mainly as a result of the increased generation of H_2 [415]. This happens because a limited CO_2 supply promotes the HER over CO_2 reduction. As a result, increasing the CO_2 flow rate to 20 milliliters per minute led to a noticeable improvement in the faradaic efficiency for both C_1 and C_{2+} products in the flow system [416]. The increased flow rate ensures a greater concentration of CO_2 molecules at the catalyst surface, which helps in maintaining a steady supply of CO_2 molecules for the reduction reaction in flow system. In contrast, as observed in (**Figure 34 (d-f)**), increasing the carbon dioxide flow rate in an H-cell configuration significantly decreases the FE for both C_1 and C_2 product compounds across all three catalysts. Our findings show that a flow rate of 5 mL min^{-1} is optimal for achieving high FE. Beyond this flow rate, efficiency declines notably. This phenomenon occurs because increasing the CO_2 flow rate reduces the dissolution of CO_2 in

the electrolyte, which leads to an increase in the acidity of the solution. As a result, there is less CO₂ available to adsorb on the surface of the catalyst, decreasing the efficiency of CO₂ reduction reactions. This imbalance favors (HER) due to the higher proton concentration in the electrolyte, resulting in more hydrogen production in the system. This can result in insufficient CO₂ adsorption and reduced formation of desired products. Furthermore, the increased turbulence and faster gas flow can disrupt the localized environment at the electrode surface, potentially hindering the reaction kinetics. Additionally, (Figure 38 (c)) illustrates the effect of varying CO₂ flow rates on HCOO⁻ formation as detected by NMR. At a 5 mL min⁻¹ flow rate, the maximum formation of HCOO⁻ is observed. As the flow rate increases, a noticeable decline in FE for HCOO⁻ is evident. This further supports the idea that maintaining an optimal flow rate is crucial for maximizing the production of desired CO₂ reduction products. Thus, our study underscores the importance of precisely controlling the CO₂ flow rate to optimize electrochemical performance and product selectivity.

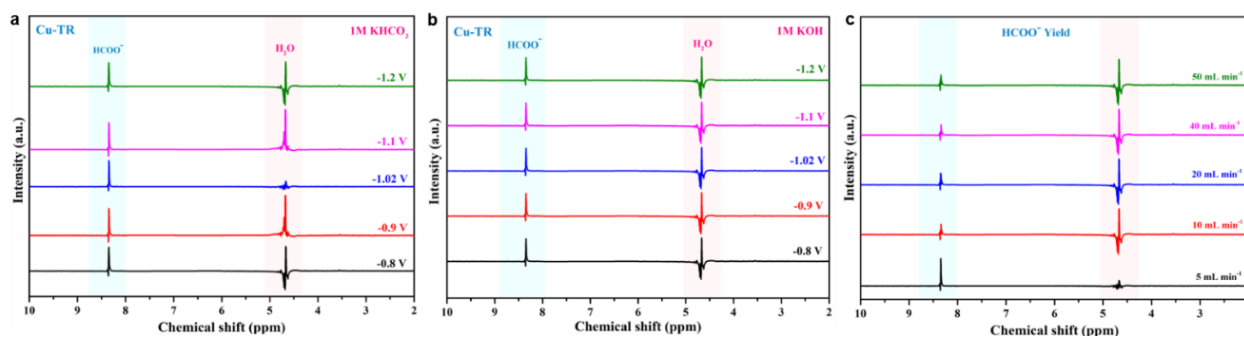


Figure 37: ¹H NMR spectra of electrolytes after 1 h electrolysis for CO₂ER at -1.1V on Cu-TR catalyst; (a) in 1 M KHCO₃, (b) in 1 M KOH, (c) with different CO₂ flow rate {5,10,20,40,50} mL.min⁻¹.

We further adjusted the formation rates of C₁ plus C₂₊ products by normalizing them based on electrochemical surface area (ECSA), which was calculated via the double-layer capacitance (C_{dl}) technique as shown in Figure 27 (a). For the BF catalyst, an improvement

in the formation rate of C_{2+} compounds such as C_2H_4 and C_2H_5OH was observed, alongside a decrease in C_1 products like CO. Conversely, the TR and SP catalysts demonstrated a trend of increasing C_1 products, with $HCOO^-$ reaching $85 \mu\text{mol h}^{-1}$ and CO at $78 \mu\text{mol h}^{-1}$, all conducted in 1 M $KHCO_3$. **Figure 39** displays the GC peaks for gas products over the three catalysts BF, SP, and TR from (a-i) at potential range of (-0.8 to -1.2 V vs. RHE). While for liquid compounds, **Figure 37 (a-b)** illustrates the $HCOO^-$ production over the TR catalyst after 1 h at a potential range from -0.8 to -1.2 V (vs. RHE) in 1 M $KHCO_3$ and KOH electrolytes, respectively. To further understand the CO_2RR over our different catalysts, we conducted electrochemical characterization of the three catalysts in 1 M $KHCO_3$ using H-cell reactor with a CO_2 flow rate of $5 \text{ mL}\cdot\text{min}^{-1}$. The three nanoparticle catalysts were subjected to linear sweep voltammetry (LSV) in both carbon dioxide and argon atmospheres. Each catalyst exhibited a rise in J under the carbon dioxide environment, with the cathodic J surpassing that under argon, as shown in **Figure 38 (a)** and **Figure 40**. According to these findings, the copper BF catalyst demonstrates the highest activity for the CO_2RR , reaching $850 \text{ mA}\cdot\text{cm}^{-2}$ in contrast to $600 \text{ mA}\cdot\text{cm}^{-2}$ when operating in argon environment. The copper TR catalyst demonstrate a J of $300 \text{ mA}\cdot\text{cm}^{-2}$ in the CO_2 environment and approximately $200 \text{ mA}\cdot\text{cm}^{-2}$ in Ar environment, whereas the copper SP catalyst revealed a J of $200 \text{ mA}\cdot\text{cm}^{-2}$ in the carbon dioxide environment and around $100 \text{ mA}\cdot\text{cm}^{-2}$ in Ar.

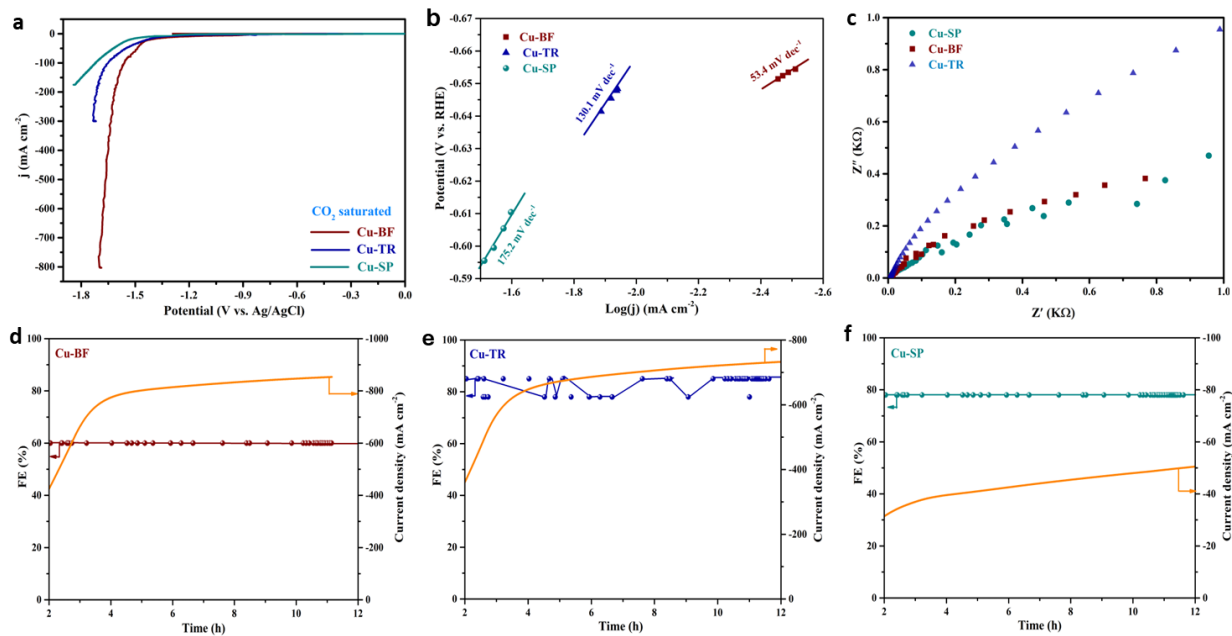


Figure 38: Electrocatalytic CO₂RR characterizations. (a) linear sweep voltammetry plot for catalysts in CO₂ in 1 M KHCO₃; (b) Tafel plot of three catalysts for {C₂H₄, CH₃COO⁻, CO}; (c) EIS (Electrochemical impedance spectroscopy) of Cu catalysts. (d-f) stability test of the prepared catalysts over 12h at -1.2 v for Cu-BF, -1.12 v for Cu-TR, and -1.1 v for Cu-SP (vs. RHE) in 1M KHCO₃.

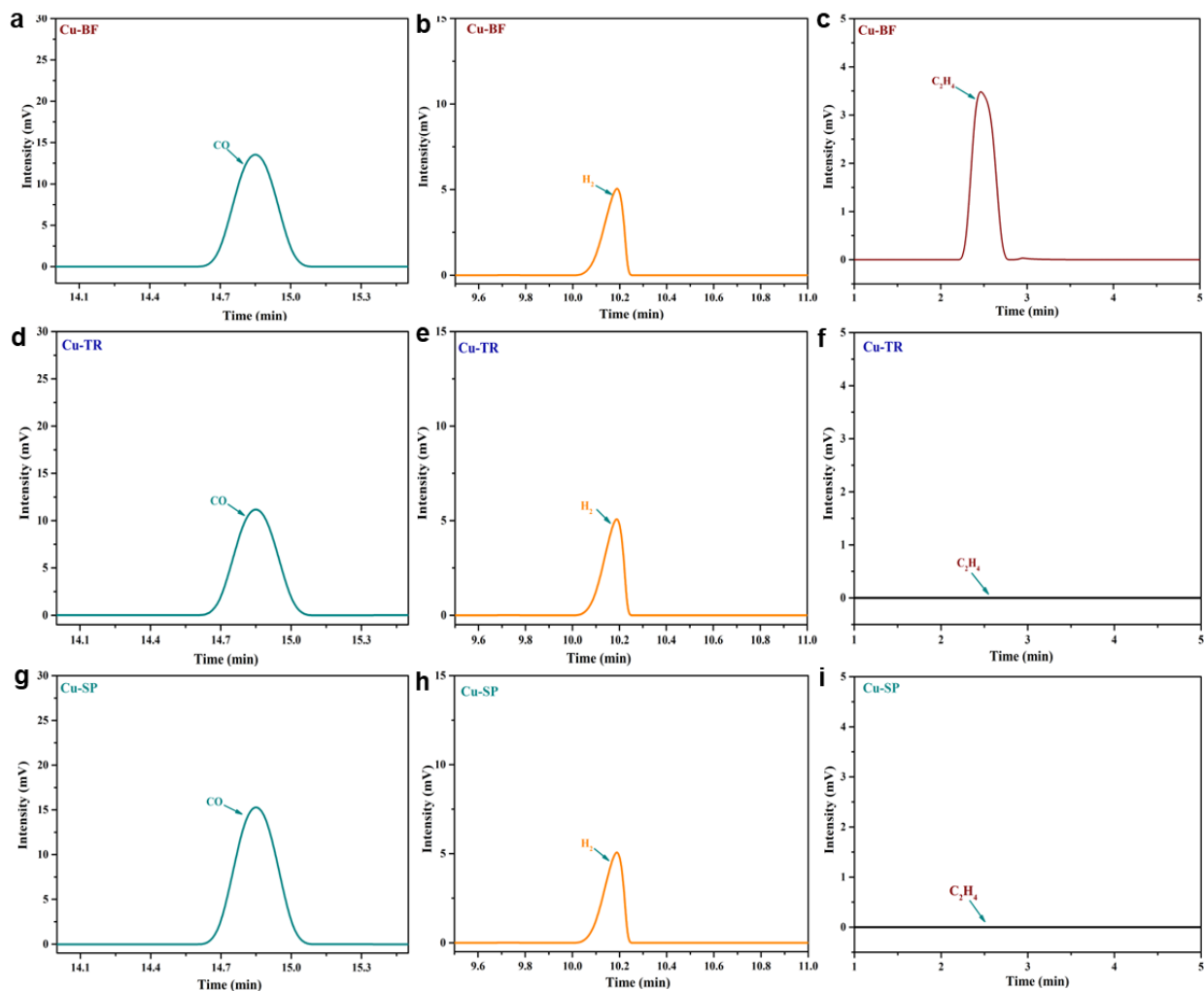


Figure 39: Representative gas chromatographic spectra in CO₂-saturated 1 M KHCO₃ electrolyte at -1.1 V. (a,c) FID area for Cu-BF catalyst and (b) is TCD area. (d,f) FID area for Cu-TR catalyst and (e) is TCD area. (g,i) FID area for Cu-SP catalyst and (h) is TCD area.

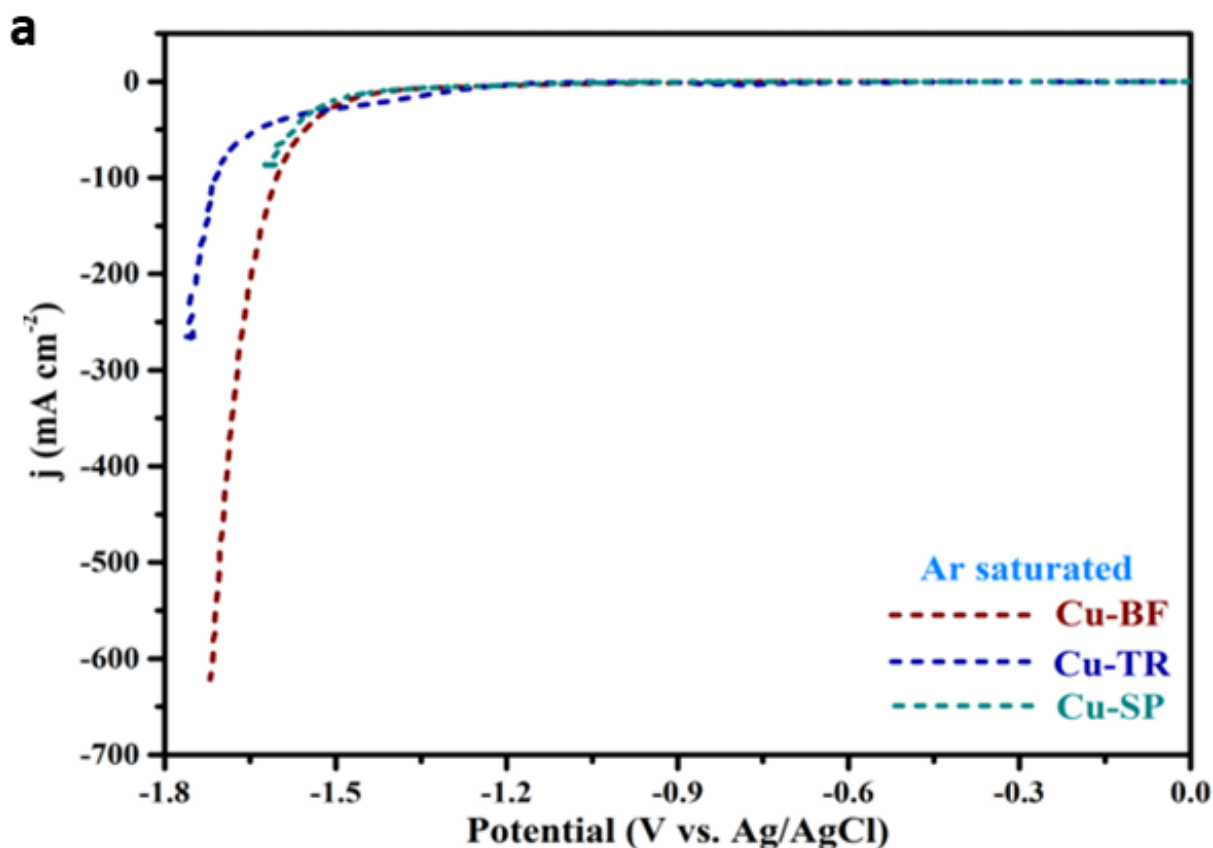


Figure 40: (a) linear sweep voltammetry plot for catalysts in Ar in 1 M KHCO_3 .

Tafel analyses for electrocatalytic CO_2RR to the C_1 and C_{2+} products on Cu-NPs catalysts shows that the slope decreases for the BF catalyst [Figure 39 \(b\)](#), indicating that the RDS for C_{2+} formation occurs in this catalyst. The Tafel slope seen in the copper catalysts suggests that electron transport might be the step that determines the rate. A Tafel slope of about 53.4 mV dec^{-1} related to the BF-Cu catalyst suggests a faster electron transfer rate and a step that determines the rate of the subsequent chemical reaction. For the TR catalyst, the Tafel slope is 130 mV dec^{-1} , and for the SP catalyst, it is 175 mV dec^{-1} , both promoting the production of C_1 products. To further elucidate the electron transfer capabilities, electrochemical impedance spectroscopy (EIS) was achieved for the three catalysts in an H-cell with 1 M

KHCO₃ at -0.9 V (vs. RHE) as displayed in **Figure 39 (c)**. The findings suggest that the BF catalyst, with a low EIS value of 0.8 kΩ, exhibits the greatest electrical conductivity and carrier density. This explains its remarkable high J of 850 mA.cm⁻² in LSV, thereby accelerating the CO₂RR process. In contrast, the SP catalyst, with a J of 200 mA.cm⁻², shows the highest EIS value at 10 kΩ (**Figure 38 (d)**). The TR catalyst, with a moderate EIS value of approximately 1 kΩ, falls in among the two values of the other catalysts.

The outstanding performance of the three catalysts can be explained mechanistically as follows: during the CO₂RR, a CO₂ molecule first absorbs onto an available catalyst site. This is followed by electron transfer, leading to the formation of multiple intermediates, which eventually result in the production of the desired products, as depicted in **Figure 40**. Enhancing CO adsorption is crucial for achieving high C₂⁺ selectivity on BF catalyst, as it allows for appropriate *CO coverage necessary for subsequent C–C coupling instead of carbon monoxide desorbing away from the surface of the catalyst and act as final product [417],[418],[419]. Our findings elucidate that the capacity to adsorb carbon monoxide rises in direct relationship with particular morphologies that include crystal faces, like {100}. The inclusion of Cu⁺ sites on Cu catalysts is expected to improve the adsorption of *CO. Our XPS analysis indicated a higher fraction of Cu⁺ sites on Cu BF, as shown in (**Figure 23 (g)**). This increased presence of Cu⁺ sites explain why the BF catalyst more effectively promotes C₂⁺ product formation.

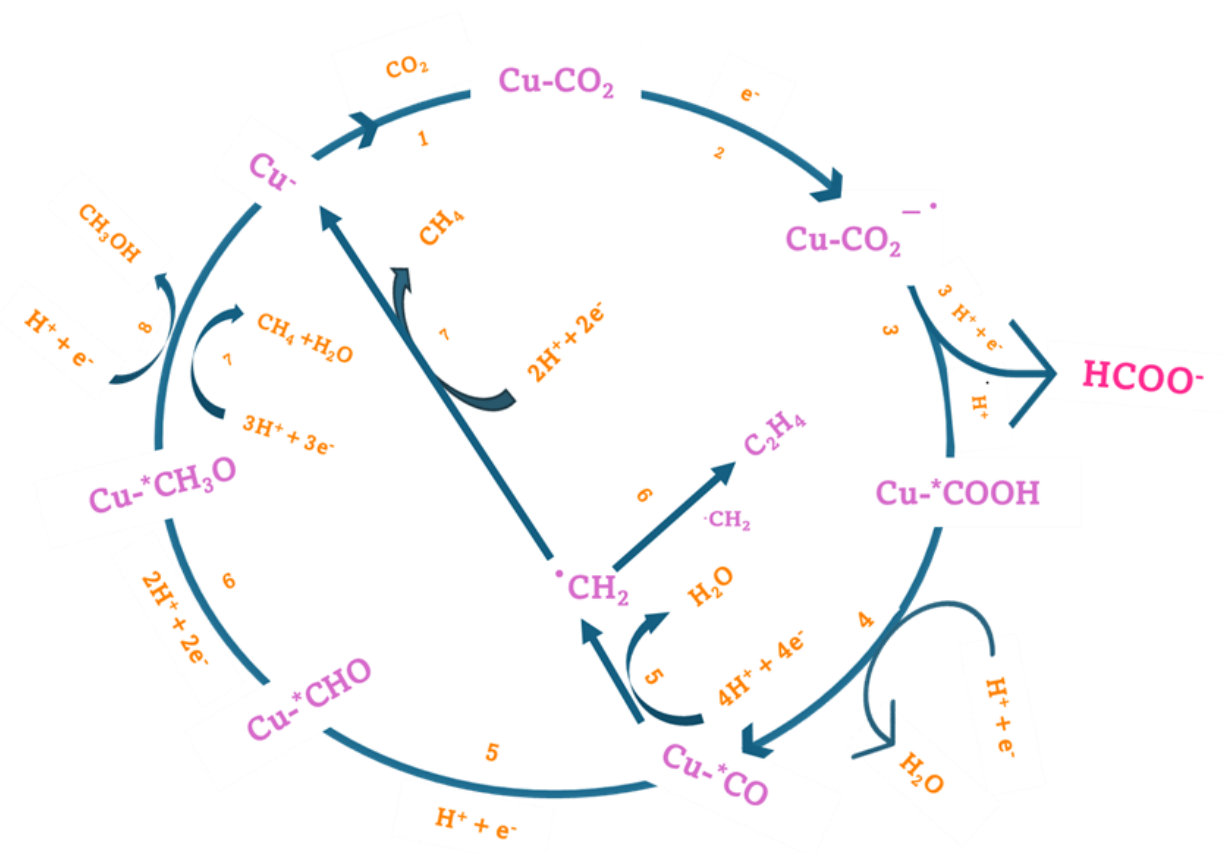


Figure 41: Electrochemical reaction pathways of CO₂ reduction in aqueous electrolyte system on a Cu Catalyst surface.

The ECSA of the catalysts was assessed by measuring the Cdl through cyclic voltammetry (CV) at diverse scanning rates ranging from 50 to 100 mV s⁻¹ at -0.9 V (vs. RHE) using platinum foil as the counter electrode and Ag/AgCl act as the reference electrode. As shows in **Figure 42 (a-d)**, the BF catalyst showed a Cdl of 6 mF cm⁻², which is significantly better compared to the TR catalyst with 4 mF cm⁻² and the SP catalyst with 3 mF cm⁻². This higher Cdl amount for the BF catalyst indicates a larger ECSA. It is advantageous for catalytic activity to have a larger ECSA because it provides a greater number of active sites enabling the electrochemical reactions to take place [420]. In CO₂RR, improved amount of active sites can enhance the adsorption process and activation of CO₂ molecules, enabling a higher reaction

rate and improved product selectivity [421]. The higher ECSA of the BF catalyst implies that it has more surface area available for the reaction, which contributes to its superior performance in CO₂RR to C₂₊ products, achieving a higher *J* and better catalytic efficiency. The substantial difference in ECSA among the catalysts underscores the importance of surface area in electrochemical processes. The BF catalyst's larger ECSA, indicated by its higher Cdl, correlates with its enhanced ability to facilitate electron transfer, and accommodate more reactive intermediates, thereby accelerating the CO₂RR process and resulting in higher C₂₊product yields. We further conducted in situ electrochemical characterization to gain deeper insights into the CO₂RR mechanisms. Raman spectroscopy was employed as an operando characterization tool, providing real-time analysis during the CO₂RR as in **Figure 43 (b)**. To rationally develop highly effective catalytic materials for the electrochemical CO₂RR, it is required to have a high level of awareness and precision regarding the reaction processes [422], As shown in **Figure 44 (a)**, the low-frequency bands seen at 280 and 362 cm⁻¹ are associated with the distinctive vibrations of *CO on copper surfaces. These vibrations are notably the Cu–CO frustrated rotation plus the Cu–CO stretch (ν Cu–CO), respectively.

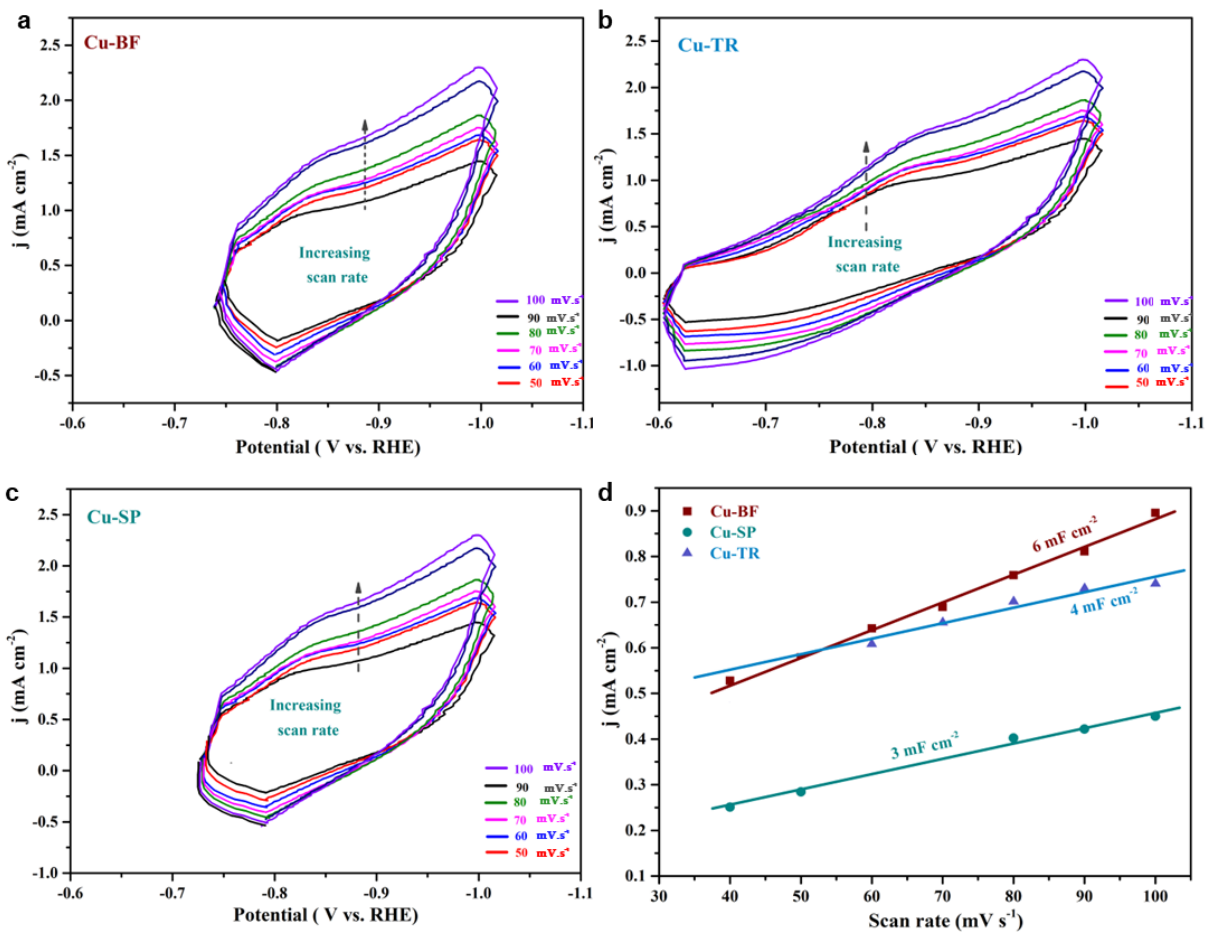


Figure 42: Cyclic voltammograms of (a) Cu-BF, (b) Cu-TR, (c) Cu-SP at different sweep rates of 50, 60, 70, 80, 90 and 100 mV s⁻¹; (d) Double-layer capacitance C_{dl} of Cu catalysts.

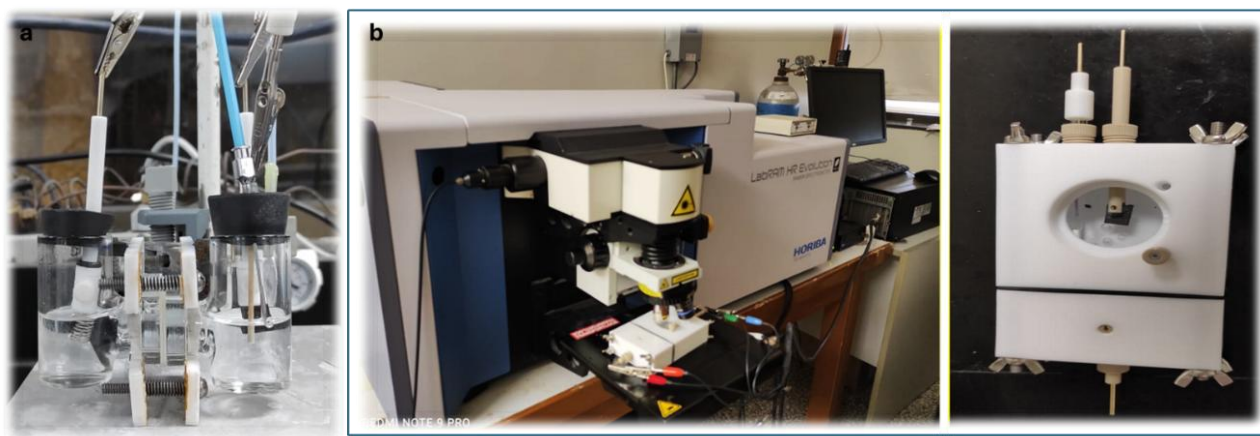


Figure 43: (a) H-cell CO₂RR experimental setup; (b) In situ electrochemical cell for Real time analysis (Raman spectroscopy and flow cell).

These bands are observed across all three catalysts. However, for the BF catalyst, these peaks are particularly pronounced, indicating a higher yield of $^*\text{CO}$, which is crucial for subsequent reactions. In **Figure 44 (b)**, the spectrum ranges from 1300 to 2300 cm^{-1} , revealing various intermediates and their associated vibrations. Between 1400 and 1500 cm^{-1} , the presence of carboxylate or carbonyl groups is detected. At around 1600 cm^{-1} , a peak indicated to the HO-H bending vibration is observed, while at 1540 cm^{-1} , the presence of $^*\text{COOH}$ intermediates indicates the occurrence of C-C coupling, An essential stage in the formation of multi-carbon products. Moreover, the broad range from 2000 cm^{-1} indicates a significant presence of CO on the Cu BF catalyst. This high yield of CO is particularly notable at an applied potential of -1.2 V (vs. RHE), where it contributes to a FE of 60% for ethylene (C_2H_4) production. The high $^*\text{CO}$ coverage on the BF catalyst facilitates C-C coupling, leading to the development of C_{2+} product compounds. The ability to generate high yields of $^*\text{CO}$ and its subsequent involvement in C-C coupling is critical for achieving greater selectivity for multicarbon products such as ethylene [423]. For the TR catalyst, we observed a distinct range of 1400-1500 cm^{-1} in the Raman spectra (panel b), which corresponds to the presence of $^*\text{OCHO}$, a crucial intermediate in formate production. This indicates that the TR catalyst facilitates the formation of formate through this intermediate, highlighting its unique pathway in the CO_2RR . In contrast to the BF catalyst, the TR catalyst does not show a significant trend for CO formation in the low-frequency bands at 280 and 362 cm^{-1} , as depicted in panel (a). This lack of prominent CO peaks suggests that the TR catalyst does not favor CO generation and subsequent C-C coupling to the same extent as the BF catalyst.

The absence of a significant CO trend in the TR catalyst, as observed in panel a, aligns with its lower activity for C₂+ products and higher selectivity towards formate. This differentiation offers valuable understandings into the design and application of Cu-based electrocatalysts, demonstrating how tailored surface properties can steer the CO₂RR towards desired products by influencing the formation and stability of specific reaction intermediates. For the SP catalyst, which produces a high percentage of CO as a major product, we observe distinct features in the Raman spectra. In panel a, there are prominent peaks at 280 and 362 cm⁻¹, indicative of strong Cu-CO binding. These peaks suggest that the SP catalyst assists the initial adsorption with activation of carbon dioxide molecules, leading to the development of CO on the surface of the catalyst.

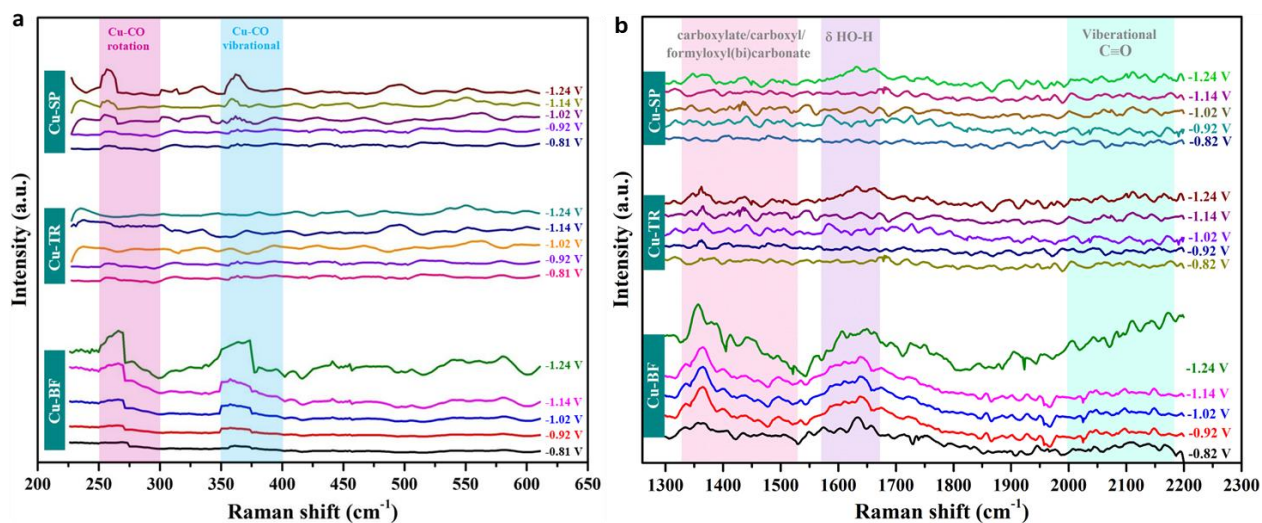


Figure 44: In situ Raman spectroscopy characterizations. (a) the first range from 200 to 650 cm⁻¹ at different applied potential along 10 mins for three catalysts in 1 M KHCO₃. b) the second range from 1300 to 2300 cm⁻¹ at different applied potential along 10 mins for three catalysts in 1 M KHCO₃.

Furthermore, in panel b, there is a notable observation related to CO vibration. The low trend of CO vibration in the range of 2000 cm⁻¹ indicates that CO, once produced on the surface of

the SP catalyst, is efficiently released as the major product. This efficient release of CO is consistent with the high FE for CO observed in electrochemical studies. The high tendency of peaks at 280 and 362 cm^{-1} in panel (a) underscores the effectiveness of the SP catalyst in binding CO, which is a key step in the reduction process. The ability of the SP catalyst to bind and subsequently release CO is a key factor in its high selectivity for CO as a major product. This behavior contrasts with the BF and TR catalysts, which show different intermediate behaviors and product selectivity. For further characterization, we performed ex-situ Raman analyses on the three catalyst electrodes to elucidate the changes on the gas diffusion layer (GDL) before and after the reaction. As indicated in **Figure 45**, panels (a, c, and e) illustrate the Raman spectra of the BF, SP, and TR catalyst electrodes, respectively, prior to any reaction. In these panels, we observe a prominent peak at 250 cm^{-1} , indicative of Cu^{+2} species, along with peaks at 600 and 900 cm^{-1} , which are characteristic of the initial state of the catalysts. In contrast, panels (b, d, and f) reveal the post-reaction Raman spectra for each catalyst, highlighting the structural transformations that occurred during the CO_2RR . For the BF catalyst, as shown in **Figure 45** panel (b), there are significant shifts in peaks within the range of 400 to 650 cm^{-1} . These shifts are characteristic fingerprints of Cu_2O , indicating that the BF catalyst undergoes substantial reduction throughout the reaction, leading to the development of Cu_2O . **Figure 45** Panel (d) shows the post-reaction Raman spectrum for the TR catalyst. Here, the peaks indicative of Cu_2O are present but less pronounced compared to the BF catalyst. This suggests that while some Cu_2O formation occurs, it is not as extensive, indicating a different reaction pathway or product distribution. The reduced intensity of Cu_2O -related peaks in the TR catalyst implies a lesser degree of reduction or a more balanced coexistence of different oxidation states of copper. For the SP catalyst, as depicted in **Figure**

45 panel (f), the post-reaction Raman spectrum shows even fewer Cu₂O-related peaks. This suggests that the SP catalyst primarily retains its original oxidation state, with minimal formation of Cu₂O. The stability of the Cu⁺² species in the SP catalyst is consistent with its observed high selectivity for carbon monoxide production, as the abundance of Cu⁺² sites likely facilitates the efficient adsorption and subsequent desorption of CO. The ex-situ Raman characterizations offer important insights into the structural modifications of the catalysts throughout the carbon dioxide reduction reaction.

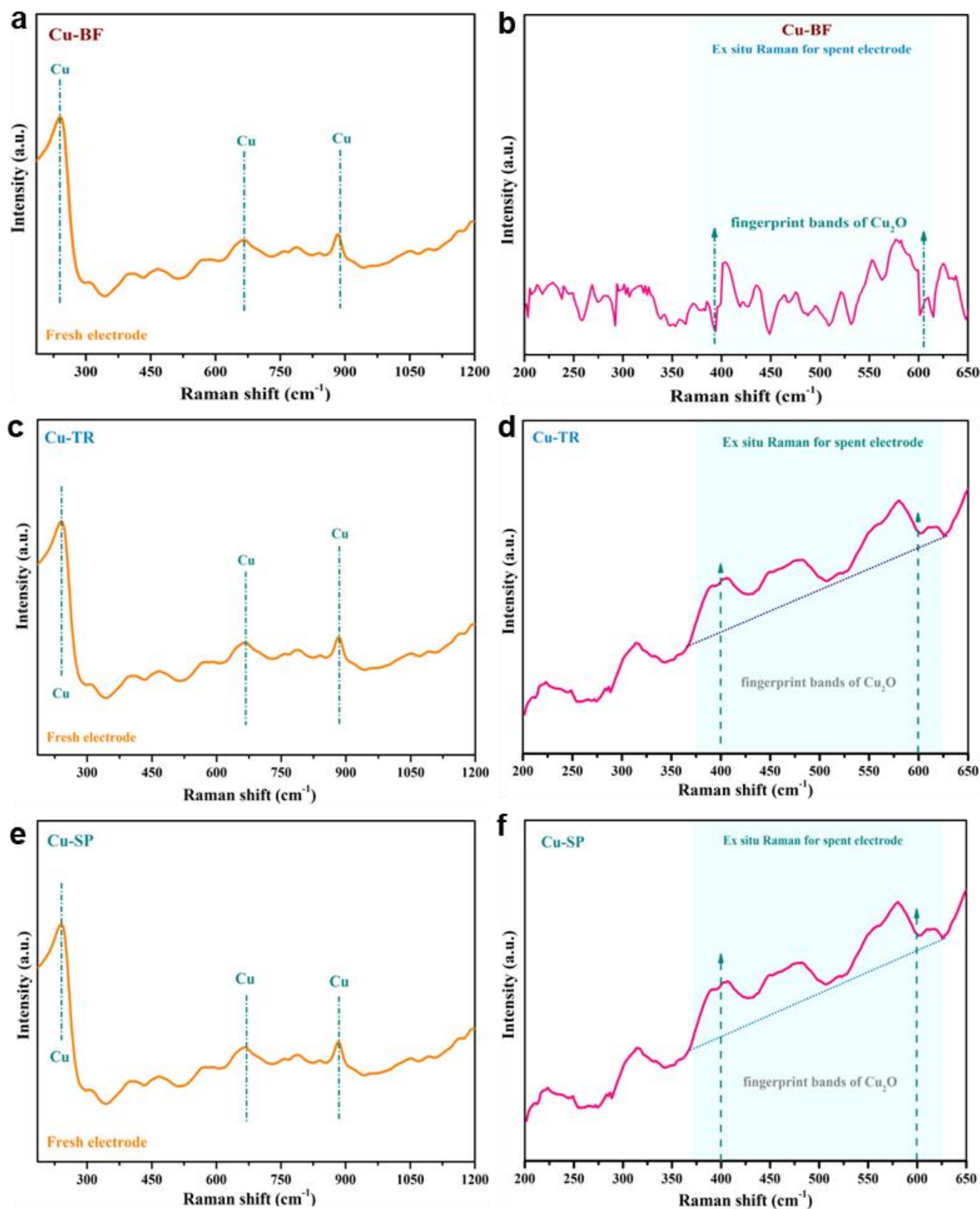


Figure 45: Ex situ Real time characterizations. (a, c, e) fresh electrodes of Cu-BF, Cu-TR and Cu-SP, respectively before any reaction in 0.5 KHCO₃. (b, d, f) Ex situ Raman characterization for spent electrodes of Cu-BF, Cu-TR and Cu-SP, respectively after electrochemical reaction in 0.5 KHCO₃. c) complete reduction for Cu-BF catalyst at -0.8 v (vs. RHE) at different time(s).

To further investigate the performance of the three catalysts, we conducted stability tests under specific conditions over a period of 12 h. The experiments were done at -1.2 V for Cu-BF, -1.12 V for Cu-TR, and -1.1V for Cu-SP (vs. RHE) in 1M KHCO₃, because they are the optimal potential that yield the highest FE%. The results are depicted in **Figure 40 (d-f)**, illustrating the FE and *J* for each catalyst. For the Cu-BF catalyst, shown in panel (c), the stability test over 11 h at -1.2 V demonstrated a consistent FE of 60% for C₂H₄ production. The *J* remained stable at about 600 mA.cm⁻² throughout the testing period. This indicates that the Cu-BF catalyst maintains its high activity and selectivity for ethylene over an extended duration, highlighting its robustness under continuous operation. Panel (d) presents the stability test results for the Cu-TR catalyst at -1.12 V. Over the 12-h period, the TR catalyst demonstrated a *J* of around 700 mA.cm⁻². The FE for formate production remained consistently high at 85%. These findings indicated that the Cu-TR catalyst is highly effective and stable for formate production, maintaining its performance without significant degradation over time. For the Cu-SP catalyst, shown in panel (e), the stability test at -1.1 V revealed a stable FE of 78% for carbon monoxide production. The *J* stayed at around 80 mA.cm⁻² during the 12h testing period. This indicates that the Cu-SP catalyst efficiently produces carbon monoxide and retains its activity and selectivity under prolonged electrochemical conditions. As detailed in **Tabel 2**, we have compared the electrocatalytic performances of our catalysts for CO₂ reduction to C₁ and C₂₊ compounds with those of recently reported catalysts. This comparison underscores the novelty and achievements of our work relative to recent advancements in the field.

Table 2: Electrocatalytic performances for CO₂ to C₁, C₂₊ products over typical catalysts reported recently]

No.	Cu catalyst	Potential (V vs. RHE)	CO	C ₂ H ₄	C ₂ H ₅ OH	HCOO ⁻	j (mA.cm ⁻²)	Ref.
1	Cu-BF	-1.2 V	15%	60%	10%	0	-800	This work
	Cu-TR	-1.02	10%	0	0	85%	-300	
	Cu-SP	-1.1	78%	0	0	10%	-200	
2	Cu/CNS	-1.2	0	0	63%	0	-2	12
3	Dendritic Cu	-1.2	0	39%	7.8%	0	-60	13
4	Cu nanowire arrays	-1.1	0	17.4%	3.8%	0	-4.5	14
5	Cu nanocubes	-1.1	0	41%	3.7%	0	-4	15
6	B-doped Cu	-1.1 V	0	52%	27%	0	-70	16
7	SS-Cu PEM Flow Cell	-1.2 V	0	28%	0	0	-101	17
8	CuSn	-1.13 V	92%	0	0	0	-120	18
9	Cu ₂ Cd/Cd/Cu	-1 V	83%	0	0	0	-8	19
10	Cu foil with the presence of halide ions (Cl, Br, I)	-1 V	0	25%	25%	0	-2.8	20
11	Prism-shaped Cu Nanocatalysts	-1 V	0	28%	28%	0	-2.8	21

3.5 Conclusions

In conclusion, this study underscores the transformative potential of Cu-based catalysts, meticulously engineered through innovative synthesis methods, to significantly enhance the efficiency of electrocatalytic carbon dioxide reduction reactions (CO₂RR). By strategically varying the NaBH₄ percentages during synthesis, we successfully developed catalysts with distinct morphologies, crystal phases, and particle sizes, each tailored to optimize CO₂ reduction at industrial-scale current densities. Our results demonstrated that the blood flow morphology catalyst achieved an impressive 60% selectivity for C₂H₄ at a J of over -90 mA/cm², highlighting its capacity for high-yield hydrocarbon production under rigorous industrial conditions. Additionally, the trigonal morphology catalyst achieved an exceptional 85% selectivity for formate at a J of -39 mA/cm², showcasing its potential for producing valuable oxygenates with high efficiency. Meanwhile, the spherical morphology catalyst delivered a remarkable 78% selectivity for carbon monoxide at a J of -35 mA/cm², demonstrating its suitability for selective syngas production. These outcomes not only validate the effectiveness of our tailored catalyst designs but also pave the way for scalable, sustainable CO₂ conversion processes that align with industrial demands. The ability to achieve high selectivity and efficiency for different products by simply tuning the catalyst morphology opens up new avenues for the development of versatile CO₂RR systems. This breakthrough in catalyst design not only advances the field of electrocatalysis but also holds significant promise for addressing global challenges related to carbon emissions and renewable energy, moving us closer to a more sustainable and economically viable future.

CHAPTER 4

Conclusions and Recommendations

4.1 Conclusions

The electrochemical conversion of CO₂ into value-added C₂ products represents a crucial step toward sustainable carbon utilization. This process not only mitigates CO₂ emissions but also provides a viable pathway for producing chemicals and fuels with high economic and environmental benefits. Significant progress has been made in catalyst design, particularly in **Cu-based catalysts**, which have demonstrated promising selectivity for C₂ products. Advances in **nanostructuring, alloying, and defect engineering** have improved catalytic activity, while **in situ characterization techniques** have provided deeper insights into reaction mechanisms. Computational modeling and **machine learning-driven approaches** have further accelerated catalyst discovery and optimization. Despite these advancements, several challenges remain, including **low selectivity, high overpotentials, catalyst degradation, and scalability limitations**. To overcome these hurdles, future efforts should focus on **developing more stable and efficient catalysts, optimizing reaction conditions, and improving reactor designs**. The integration of **CO₂ electroreduction with renewable energy sources** will be essential for achieving a truly sustainable and economically viable process. With continued interdisciplinary research and technological innovation, CO₂ electrochemical conversion has the potential to play a key role in carbon-neutral energy systems, transforming waste CO₂ into valuable products and contributing to a more sustainable future.

4.2 Future recommendations

The electrochemical conversion of CO₂ presents a promising pathway for mitigating carbon emissions while producing valuable C₂ products, such as ethylene, ethanol, and acetate. However, several challenges remain in improving selectivity, energy efficiency, and catalyst stability. Future research should focus on the following key areas to advance the field and enable industrial-scale implementation:

1. Catalyst Design and Optimization

- Develop advanced **Cu-based catalysts** with improved selectivity for C₂ products through surface engineering, alloying, and nanostructuring.
- Explore **single-atom catalysts (SACs) and bimetallic systems** that can facilitate C–C coupling while minimizing side reactions.
- Investigate **ligand-modified and defect-engineered catalysts** to optimize electronic properties and enhance catalytic activity.

2. Operando Characterization and Mechanistic Insights

- Utilize **in situ and operando techniques** (e.g., X-ray absorption spectroscopy, Raman spectroscopy, and electrochemical STM) to understand reaction pathways and intermediate formations in real time.
- Employ **computational modeling and density functional theory (DFT)** to predict optimal catalyst compositions and reaction mechanisms.

- Apply **machine learning and AI-based approaches** to accelerate catalyst screening and optimization.

3. **Process Optimization and Reactor Design**

- Improve **electrolyzer designs** by integrating gas diffusion electrodes (GDEs) and membrane electrode assemblies (MEAs) to enhance mass transport and minimize overpotentials.
- Optimize **electrolyte compositions** to stabilize intermediates and promote selective CO₂ reduction to C₂ products.
- Implement **flow-cell and high-pressure systems** to scale up CO₂ electroreduction while maintaining high product yields.

4. **Renewable Energy Integration and Sustainability**

- Develop **photoelectrochemical (PEC) systems** that couple CO₂ electroreduction with solar energy harvesting for a self-sustaining process.
- Explore **earth-abundant and non-toxic materials** as alternatives to conventional metal catalysts for long-term sustainability.
- Investigate **electrode durability and catalyst regeneration strategies** to enhance long-term stability and commercial feasibility.

By addressing these challenges, future research can pave the way for efficient, scalable, and sustainable CO₂ electrochemical conversion technologies, contributing to carbon-neutral energy systems and a circular carbon economy.

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S/ N	Journal	IF	Q- Rank
1	Esraa Kotoba , Mohammed Mosaad Awada, Mustapha Umarb, Ismail Abdulazeezc, Omer Ahmed Taiallaa, Khalid Alhooshania,d, Shehu Mohammeda, Abdul Waheedc, Abdulaziz A. Al-Saadia,d, Saheed A. Ganiyua,d* “Interplay of morphology and facet orientation of Cu nanocrystals directing CO ₂ electroreduction to value-added products” (submitted to Energy technology).		
2	Esraa Kotoba , Yousef A. Alsunib,c, Ahmed H. Bibyd, Omer Ahmed Taiallaa, Ijaz Hussainc, Khalid Alhooshania,c, Saheed A. Ganiyua,c*, Munzir H. Sulimane, Muhammad Usmane.” Electrochemical Production of n-Butanol via CO ₂ Reduction: Insights into CO*		Q1

	Dimerization on Cu-cubic Nanocrystals for High Faradaic Efficiency” (submitted to Chemical engineering)		
3	Esraa Kotob ^a , Mohammed Mosaad Awad ^a , Mustapha Umar ^c , Omer Ahmed Taialla ^a , Ijaz Hussain ^b , Shaima’ Ibrahim Alsabbahen ^a , Khalid Alhooshani ^{a,b} , Saheed A. Ganiyu.” Overcoming CO ₂ Utilization Challenges: Boosting Valuable Product Formation with Single-Atom Catalysts and Machine Learning” (published in I science Cell press)		Q1
4	Awad MM, Hussain I, Taialla OA , Ganiyu SA, Alhooshani K, "Recent developments and current trends on catalytic dry reforming of Methane: Hydrogen Production, thermodynamics analysis, techno feasibility, and machine learning(Energy Conversion and Management 304, 118252)		
5	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”. in Coordination Chemistry Reviews	20.6	Q1
6	Mohammed Mosaad Awad, Ijaz Hussain, Umar Mustapha, Omer Ahmed Taialla, Aliyu Musa Alhassan, Esraa Kotob, AbdulHakam Shafiu Abdullahi, Saheed A Ganiyu, Khalid Alhooshani” A critical review of recent advancements in catalytic dry reforming of methane: physicochemical properties, current challenges, and informetric insights” (in International Journal of Hydrogen Energy)	11.5	Q1
7	AS Abdelrazik, Mostafa AM Sayed, Asmaa MA Omar, Fatma Ayman FM, HE Alshimaa, Abdeladim Oulguidoum, Esraa Kotob, Mohamed HM Helmy” Potential of molecular dynamics in the simulation of nanofluids properties and stability” in Journal of Molecular Liquids		Q1
8	Basiru O Yusuf, Mustapha Umar, Esraa Kotob, Abdullahi Abdulhakam, Taialla OA , Mohammed Mosaad Awad, Ijaz Hussain, Khalid R Alhooshani, Saheed A Ganiyu “Recent Advances in Bimetallic Catalysts for Methane Steam Reforming in Hydrogen Production: Current Trends, Challenges, and Future Prospects” Chemistry – An Asian Journal, 2023	4.1	Q1
9	AS Abdelrazik, Mostafa AM Sayed, H Hashim, Asmaa MA Omar, Mohamed HM Helmy, Abdeladim Oulguidoum, Rehab Abubakr, Esraa Kotob” A guide to the preparation techniques of six classes of metal-, metal oxide-, and carbon-based nanofluids and the implications for their stability” in Journal of Thermal Analysis and Calorimetry.		
