

REVIEW ARTICLE

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Oxide-derived metals and alloys: from dynamic reconstruction to function across electrocatalytic reactions

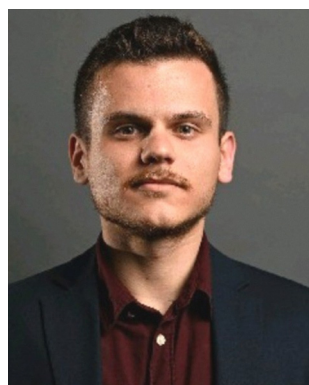
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Oxide-derived (OD) metals and alloys have emerged as a distinct class of electrocatalysts whose unique structural and electronic characteristics enable precise control over activity, selectivity, and stability across electrochemical reactions. Originating from the controlled reduction of metal oxides—first demonstrated in copper—these catalysts retain structural imprints of their oxide precursors, forming defect-rich metallic frameworks with abundant grain boundaries, residual oxygen, lattice strain, and metastable oxidation states that stabilize key intermediates and lower barriers for C–O and C–C coupling. The OD concept has since expanded to metals such as Ag, Sn, Zn, Bi, and their alloys (e.g., Cu–Zn, Cu–Sn, Cu–Ag), achieving high faradaic efficiencies for CO, formate, and multicarbon products under industrially relevant conditions. Advances in *operando* spectroscopy and density functional theory have revealed that oxide precursor chemistry and reduction kinetics govern reconstruction dynamics, oxygen retention, and electronic structure; yet, a unified understanding connecting these features to catalytic function remains incomplete. This review integrates experimental and theoretical advances to establish mechanistic descriptors—such as oxygen coordination, grain-boundary density, and oxophilicity—that connect oxide precursor design, dynamic structural evolution, and catalytic performance. Building on these insights, we formulate design principles and a predictive roadmap for engineering next-generation oxide-derived catalysts across CO₂RR and other electrochemical and thermal transformations.

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1. Introduction

The accelerating accumulation of atmospheric CO₂ underscores the urgent need for technologies that can close the carbon cycle through integrated capture, conversion, and utilization. Among the available approaches, the electrochemical reduction of CO₂ (CO₂RR) has emerged as a particularly promising route, enabling the transformation of CO₂ into fuels and chemical feedstocks using renewable electricity under mild conditions.^{1,2} Despite significant progress, achieving industrially relevant CO₂RR performance—high current densities, high selectivity, and long-term operational stability—remains challenging.^{3,4} A central limitation is the intrinsically dynamic nature of catalytic interfaces, where oxidation states, surface structure, and local reaction environments evolve continuously under bias. Rational catalyst design requires not only an understanding of equilibrium material properties but also of how active sites reconstruct, adapt, and function under *operando* conditions.⁵

Within the diverse landscape of CO₂RR catalysts—including transition metals, metal oxides, chalcogenides, carbides, molecular complexes, and atomically dispersed systems—oxide-derived (OD) metals and alloys have gained attention as a particularly distinctive and versatile class.⁶ These materials originate from the controlled electrochemical or thermal reduction of metal oxides, yielding metallic frameworks enriched with grain boundaries, lattice strain, defect sites, subsurface oxygen, and mixed-valence metal centers. Such features embody a form of “oxide memory,” whereby structural and electronic motifs inherited from the parent oxide persist in the reduced metal.⁷ This non-equilibrium character strongly modulates adsorption energetics, intermediate stabilization, electron transfer, and local pH, imparting catalytic behaviors markedly different from those of conventionally prepared metallic surfaces.^{8,9}

Following their initial development for copper, OD concepts have rapidly expanded across multiple metals and alloys. OD-

Cu has become the prototypical platform for C₂₊ product generation owing to its ability to stabilize the *CO and *OCCO intermediates at defect-rich, oxygen-coordinated sites.¹⁰ OD-Ag and -Au display exceptional selectivity toward CO, whereas OD-Sn, -Bi, and -In favor the *OCHO pathway and achieve high formate efficiencies.¹¹ Binary and ternary OD alloys—including Cu-Sn, Cu-Zn, Cu-Ag, and Cu-Zn-Ag—further broaden the design space by enabling tailored hetero-interfaces, controlled oxygen retention, and coupled multi-site reaction pathways.^{12–14} The principles underlying oxide derivation extend well beyond CO₂RR: analogous reconstruction-driven enhancements have been observed in nitrate and CO reduction, nitrogen reduction, and even classical thermal reactions such as CO oxidation, hydrogenation, and methanol synthesis. This convergence suggests that oxide derivation constitutes a generalizable materials design strategy applicable across reaction families where catalysis is governed by dynamic metal–oxygen interactions.^{15–17}

Despite significant progress, a comprehensive understanding of OD-catalysts remains incomplete. The literature is highly fragmented—many studies focus on single metals such as copper or isolate specific correlations between precursor chemistry, reconstruction conditions, and catalytic performance—making it difficult to extract general mechanistic principles.^{8,18–20} Fundamental questions therefore remain unresolved: how variations in oxide precursor composition and reduction kinetics dictate the structural motifs ultimately embedded in the reconstructed catalyst; how grain boundaries, subsurface oxygen, mixed-valence states, and multimetal interfaces quantitatively influence intermediate energetics in CO₂ reduction; which structural and electronic features are universal across electrochemical and thermochemical reactions, and which are system-specific; and how OD-catalysts activate, evolve, degrade, or self-regenerate under operational conditions.²¹ Existing reviews typically address only isolated aspects of this landscape—highlighting performance trends,



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reaction, catalytic combustion, and desulfurization technologies. Since 2020, Joachim Pasel has headed a department at Forschungszentrum Jülich that specialises in heterogeneous catalysis for the synthesis of higher alcohols from methanol/ethanol mixtures. This includes catalyst characterization, evaluation of catalytic performance, and novel technologies for catalyst synthesis.



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structural studies, or mechanistic insights—yet fall short of providing an integrated framework.^{22,23} What is critically needed is a unifying perspective that links oxide precursor chemistry, non-equilibrium reconstruction pathways, and the structural fingerprints of OD-materials to their electronic structure, reaction mechanisms, catalytic selectivity, and long-term stability.

This review aims to establish such an integrated framework by systematically connecting oxide precursor chemistry, reconstruction dynamics, and the non-equilibrium structural fingerprints of OD-catalysts to their resulting electronic structure, reaction mechanisms, and stability. We classify major OD-material families—from monometallic to multi-metallic and hierarchically structured architectures—and analyze how diverse precursor pathways, including thermal oxidation, electrochemical cycling, precursor-derived frameworks & synthesis, and mixed-metal oxides, imprint defect networks, strain fields, oxygen retention, and nanoscale heterogeneity during reconstruction. We then examine how these physicochemical motifs govern CO₂ reduction mechanisms by modulating: intermediates formation & binding, C–C coupling, hydrogen evolution, and extend these principles to other electrochemical and thermal reactions to demonstrate the broader generality of OD-catalysts behavior across nitrate and CO reduction, nitrogen fixation, and classical gas-phase catalysis. Finally, we discuss activation, degradation, and long-term evolution of OD-structures and propose design principles and a forward-looking roadmap for next-generation catalysts. By synthesizing insights from *operando* spectroscopy, advanced microscopy, theory, and cross-reaction comparisons, this review moves oxide derivation from an empirical concept to a predictive materials-engineering paradigm capable of guiding rational catalyst development across a broad spectrum of electrocatalytic and thermo-catalytic processes. Seemingly competing descriptors—Cu⁺ species, subsurface oxygen, and defect-driven activity—are herein unified as coupled manifestations of a non-equilibrium oxygen-defect-electronic structure continuum. This enables a transition from descriptive correlations to a predictive descriptor framework.

Unlike previous reviews that primarily summarize catalyst performance trends, individual OD-material systems, or isolated mechanistic aspects, this review establishes a descriptor-based cross-system framework linking oxide precursor chemistry, reconstruction dynamics, *operando* structural evolution, and catalytic function. By integrating monometallic, multimetallic, electrochemical, and thermocatalytic OD-systems within a unified mechanistic framework, the present work transitions oxide derivation from a descriptive materials concept toward a predictive catalyst-engineering paradigm.

2. Formation of OD metals and alloys: pathways, reconstruction chemistry, and structural signatures

Oxide-derived metals and alloys form through reduction-induced structural collapse of metal-oxide precursors, producing nano-crystalline metallic frameworks enriched in grain boundaries, strain, and oxygen-modified electronic environments. *Operando*

diffraction and spectroscopy studies reveal that oxide-to-metal conversion proceeds *via* spatially heterogeneous nucleation and coalescence processes, during which residual oxygen and defect networks can be retained. These reconstruction pathways, rather than equilibrium metal structures, define the catalytic identity of OD-materials across Cu-, Ag-, Sn-, Zn-, and Bi-based systems.^{24–26}

2.1 Fabrication methods for oxide-derived metals and alloys

Oxide-derived metals and alloys are produced by first generating a metal-oxide precursor and then reducing it under conditions that induce substantial structural reorganization (Fig. 1a). The decisive step is the oxide-to-metal transformation, during which the oxide collapses into a nano-crystalline, defect-rich metallic framework, a phenomenon documented repeatedly for Cu-, Ag-, Zn-, Sn-, and Bi-based systems.^{27–30} In all cases, the catalytic behavior of the resulting material is dictated more by this reduction-driven reconstruction than by the details of oxide precursor synthesis.

Thermal reduction of oxides in H₂, CO, or forming gas is one of the earliest and most general OD-materials fabrication routes. For CuO/Cu₂O, ZnO, SnO₂, and Bi₂O₃, thermal reduction produces metallic nuclei whose growth is accompanied by oxygen-vacancy formation, voiding, and lattice contraction.^{31–33} Slow low-temperature reduction tends to preserve coarser grains, while rapid high-temperature reduction enhances porosity and defect densities.⁸ In mixed-metal oxide systems such as CuO–ZnO, reduction yields coupled Cu-rich and Zn-rich domains whose composition reflects the relative reduction potentials of each metal; these alloy-like OD frameworks are well documented in *operando* studies.³⁴

Electrochemical reduction is the most widely used method for producing OD-catalysts. When oxide-coated electrodes (Cu₂O/CuO, ZnO, SnO_x, BiO_x, Ag₂O) are polarized at negative potentials, the oxide reduces rapidly, collapses structurally, and reorganizes into a porous, nano-crystalline metal network.^{24,35–37} As reported by Cavalca *et al.*,²⁵ implementing in-*operando* XRD, Raman, and X-ray photoelectron spectroscopy shows that oxygen removal typically precedes or overlaps with the onset of catalytic turnover,¹¹ and that the resulting OD-surfaces are rich in grain boundaries, amorphous–crystalline interfaces, and undercoordinated metal sites.³⁸ Subsurface oxygen and mixed-valence states (*e.g.*, Cu^{+/}Cu⁰ or Zn^{+/}Zn⁰) frequently persist well into the catalytic potential region,³⁹ giving rise to the distinctive electrocatalytic activity of the different OD-materials.⁴⁰ Similarly, in multimetal OD-systems, co-reduction of mixed-metal oxides precursors generates OD-alloyed frameworks.^{34,41,42} The emerged defect-rich, metallic frameworks enable, under reaction conditions, rational tuning of interfacial ensembles that couple *CO formation, CO adsorption, and C–C coupling steps.⁴³

Chemical (liquid-phase) reduction using reductive agents (*e.g.*, NaBH₄, hydrazine, and ascorbate) provides a mild and tunable pathway towards OD-catalysts. Liquid-phase reduction can preserve oxide-imprinted morphologies and enables controlled reduction kinetics, often producing sub-stoichiometric metal/oxide composites analogous to electrochemically generated OD-structures.^{44–46} This strategy is widely employed in the fabrication of multi-metallic systems. It exploits differences in

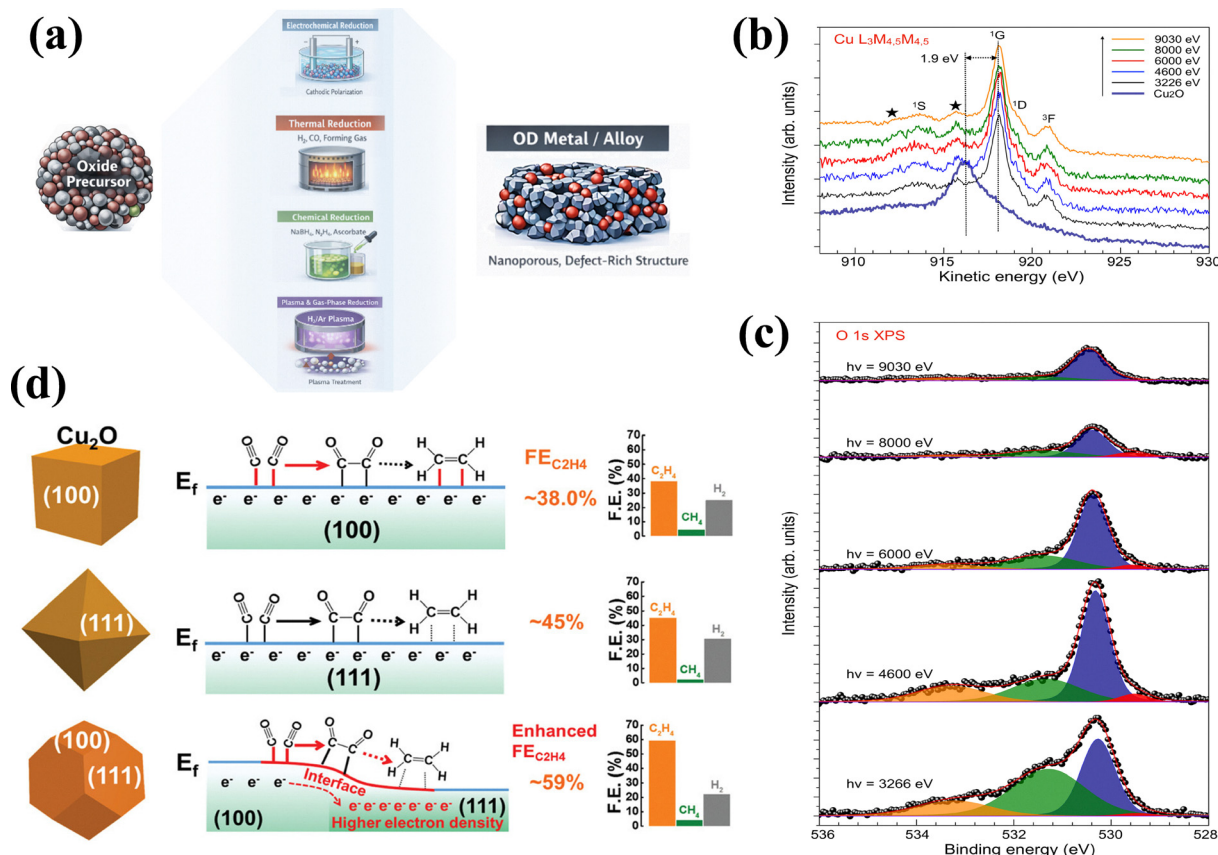


Fig. 1 Formation and properties of oxide-derived (OD) metals and alloys. (a) Summary of the different formation processes towards OD-materials, (b) Auger Cu-spectra, showcasing the shift of Cu–O interactions through the OD–Cu evolution, (c) high-resolution O 1s XPS with various beam penetration depths of OD–Cu. Reproduced with permission from ref. 38, Copyright (2022), Wiley-VCH GmbH, (d) dependence of the CO₂RR selectivity towards multi-carbon products, from the facet orientation of catalyst material. Reproduced with permission from ref. 68, Copyright (2020), Wiley-VCH GmbH.

reducibility to generate heterogeneous interfaces or segregated metal/oxide domains, which remain partially oxidized and catalytically active under operating conditions.⁴⁷

Gas-phase and plasma reduction offer an alternative non-equilibrium route for OD-catalyst production. Hydrogen or Ar/H₂ plasmas remove oxygen extremely rapidly—even at modest temperatures, which yield heavily defected, oxygen-deficient OD-metallic frameworks.^{48–50} Plasma-reduced d-block metal-oxides exhibit high concentrations of oxygen vacancies, enhanced surface charge density, and persistent sub-oxide motifs, all of which are known to lower energy barriers for CO₂ activation. A behavior also observed by Mistry *et al.*⁵¹ for plasma-treated Ag oxides, where rapid reduction produces OD-like Ag with enhanced *CO adsorption and CO₂RR activity.

2.2 General principles of oxide-to-metal reconstruction

During the production of OD-materials, oxides (MO_x) undergo collapse, nucleation, atomic reorganization, and selective oxygen retention, transferred into metallic state (M⁰) non-equilibrium structures, which are rich in grain boundaries, strain, hetero-interfaces, and mixed-valence motifs that cannot be replicated by conventional metallurgical or electrochemical methods.

The transformation of an oxide (MO_x) into its metallic state (M⁰) is a spatially heterogeneous, non-equilibrium process that proceeds

through sequential oxygen removal, metallic nucleation, and framework collapse. Metallic nuclei typically emerge first at vacancy-rich or defect-rich regions, after which coalescence and volumetric contraction generate pervasive strain and vacancy networks.⁵² As illustrated in the work of Gunathunge *et al.*⁵³ by *operando* XAS and Raman studies of Cu₂O and CuO demonstrate that portions of Cu⁺ and Cu–O coordination persist during and after reduction, becoming embedded as subsurface oxygen or mixed-valence C⁺/Cu⁰ motifs within the reconstructed metal. These features modulate local electronic structure and stabilize CO₂RR intermediates such as *COOH and *CO.⁵⁴ Comparable behavior was also reported by Wang *et al.*⁵⁵ for Ag, where the reduction of Ag₂O produces metallic Ag retaining defect-enriched domains. Similarly, for Zn systems, where ZnO reduction yields Zn⁰ nano-crystallites with persistent Zn–O interfacial coupling.^{56,57} The general principle is that OD reconstruction does not follow equilibrium metallurgical pathways—oxygen migration, pH gradients, and field-driven ion mobility imprint non-equilibrium structural fingerprints that define OD catalytic behavior across metals.^{58,59}

2.3 Reduction kinetics, M–O bond strength, and oxygen mobility

Reduction kinetics determine the extent of structural stability introduced into the OD-catalysts. High overpotentials promote

rapid oxygen removal, leading to grain refinement, enhanced porosity, and extensive grain-boundary networks. By comparison, moderate potentials maintain long-range structural order while limiting the formation of low-coordination sites.⁶⁰ The metal–oxygen bond strength sets the effective reduction window: Cu–O and Zn–O bonds are sufficiently weak to allow reduction under CO₂RR-relevant potentials (−0.5 to −1.2 V vs. RHE), enabling partial oxygen retention and mixed-valence states (Fig. 1b).^{61,62} Conversely, stronger Sn–O and Bi–O bonds preserve oxidized motifs even under more negative bias, explaining the persistence of SnO_x and BiO_x domains in OD-Sn and OD-Bi catalysts.⁶³

Oxygen mobility is equally crucial: oxygen may be expelled, redistributed, or trapped (Fig. 1c) depending on diffusion rates, local pH, and oxide morphology.⁶⁴ For OD-Cu, subsurface oxygen can persist for several minutes to hours during steady-state CO₂RR, shaping *CO coverage and C–C coupling behavior. In OD-Zn catalysts, hydrogen pretreatment and vacancy-rich structures create strong internal electric fields that enhance activation of C=O bonds.⁶⁵

While reduction kinetics are often discussed in terms of structural evolution, their catalytic implications are equally critical. Rapid reduction conditions typically generate high defect densities and enhanced porosity, which correlate with increased *CO coverage and improved C₂₊ selectivity in OD-Cu systems.⁶⁶ Conversely, slower or partial reduction can stabilize oxidized motifs, which are beneficial in systems such as OD-Sn or OD-Bi for formate production. Thus, reduction kinetics act as a governing parameter that links precursor transformation directly to catalytic selectivity by controlling the resulting descriptor landscape.

2.4 Facet- and orientation-dependent reconstruction

Crystallographic orientation critically influences how oxide precursors reconstruct into the oxide-derived state, as different facets possess distinct surface energies, M–O coordination environments, and vacancy-formation energetics.⁵⁴ These parameters dictate both reduction kinetics and the defect patterns that emerge during oxide collapse.⁶⁷ As illustrated in the work of Gao *et al.*,⁶⁸ for Cu-based single-crystal studies and shape-controlled Cu₂O nanoparticles consistently show that {100}, {111}, and high-index surfaces undergo markedly different reduction trajectories. Cu₂O cubes ({100}) reduce rapidly and develop OD-Cu architectures enriched in steps, kinks, and dense grain-boundary networks, which enhance *CO binding and facilitate C–C coupling (Fig. 1c). By contrast, {111}-dominated precursors reconstruct into smoother, less defective frameworks with weaker multicarbon selectivity, even though both facets ultimately evolve into complex OD-structures under bias.⁶⁹

These facet-dependent signatures are partially retained after extensive electrochemical restructuring: electrodes initially enriched in Cu(100)-like domains consistently yield higher ethylene and ethanol selectivity than Cu(111)-rich surfaces, demonstrating that precursor orientation imprints long-lived structural and electronic biases into the OD-state.⁷⁰ Similar orientation-governed reduction behavior is observed beyond Cu.^{37,71} As shown by Geng *et al.*,⁴⁸ polar ZnO nanosheets and

nano-rods generate higher oxygen-vacancy densities and more pronounced Zn–ZnO hetero-interfaces upon reduction than non-polar facets, correlating with improved CO₂-to-CO activity in OD-Zn catalysts.⁷² Facet effects have also been documented by Goris *et al.*⁷³ in CeO_{2–x}, where valence-mapping reveals orientation-specific Ce³⁺ distributions and reduction shells, demonstrating that facet-controlled redox and defect chemistry is a general phenomenon in oxide-derived materials.⁷⁴

2.5 Mixed-valence and multimetal oxide precursors

Mixed-valence oxides provide a tunable platform for generating OD-catalysts with heterogeneous but functionally coordinated active motifs. For example, OD-Cu derived from Cu₂O/CuO mixtures contains coexisting Cu⁺/Cu⁰ domains that stabilize *CO and promote C–C coupling.⁶⁴ In contrast, OD-Sn derived from SnO/SnO₂ mixtures forms Sn²⁺/Sn⁴⁺ ensembles that promote *OCHO stabilization and improve formate selectivity.⁷¹

Multimetal oxide precursors extend this concept into a higher-dimensional design space. When metals with different M–O bond strengths and reduction potentials are combined—for instance, in CuO–ZnO, CuO–SnO₂, or CuO–Ag₂O—reduction typically proceeds asynchronously.^{74–76} The more easily reducible component nucleates metallic domains first, while the more stable oxide lags, leading to spatial segregation of metallic and oxy-metallic regions, the formation of alloy gradients, and embedded oxide pockets.^{77,78} The work of Peerlings *et al.*⁷⁴ focused on the *operando* investigation of OD Cu–Zn catalysts, showing that Zn-rich regions retain ZnO_x character over a broad potential range, while Cu-rich domains become metallic. ZnO_x sites act as efficient CO-forming centers *via* *COOH stabilization,⁵⁷ whereas neighboring Cu domains provide high *CO coverage and C–C coupling capability, resulting in improved CO and C₂₊ alcohol production relative to mono-metallic OD-Cu. Sarfraz *et al.*,⁷⁹ further demonstrated multi-site cooperation in oxide-derived Cu–Sn systems. In this configuration, SnO_x motifs stabilize the *OCHO intermediate and promote formate formation, whereas neighboring Cu domains facilitate CO generation and subsequent hydrogenation. Similarly, OD Cu–Ag⁸⁰ and Cu–Au⁸¹ architectures often function as tandem catalysts: noble-metal domains generate CO at low overpotential, which then spills over to Cu-rich OD-sites for C–C coupling into C₂ products. In all of these systems, the composition, connectivity, and oxidation state distribution in the multimetal oxide precursor determine the hetero-interfaces and mixed-valence ensembles that emerge after reduction.⁸² Rather than being passive remnants of synthesis, these embedded motifs define multi-site reaction networks in which different structural units sequentially activate CO₂, convert it to CO or *OCHO, and then drive C–C or C–H bond formation.⁸³

Across the diverse synthesis routes and reconstruction pathways described above, a consistent set of physicochemical descriptors emerges that governs the catalytic behavior of OD-materials. These descriptors can be grouped into three categories, as seen in Table 1. Across the diverse synthesis routes and reconstruction pathways described above, a consistent set of physicochemical descriptors emerges that governs the catalytic

Table 1 Summary of the analyzed reconstruction-derived descriptors that define the formation and properties of the OD-metals and alloys

Primary descriptors (define the electronic structure and active-site distribution)	• Oxygen coordination (subsurface O, M–O motifs) • Defect density (grain boundaries, low-coordination sites)
Secondary descriptors (influence adsorption energetics, surface accessibility, and structural stability)	• Strain (arises from the kinetics of oxide-to-metal transformation) • Porosity (arises from the kinetics of oxide-to-metal transformation)
System-level descriptors (strongly modulate catalytic performance under realistic operation)	• Local pH • Mass-transport confinement

behavior of OD-materials. These descriptors can be grouped into three categories, as summarized in Table 1. Importantly, they should not be interpreted as independent variables, but as intrinsically coupled features generated through reconstruction dynamics, forming a multidimensional descriptor space that governs OD-catalyst function.

3. Physicochemical characteristics and structural evolution of oxide-derived metals and alloys

Oxide-derived metals and alloys display a set of distinctive physicochemical features, like: nano-porosity, elevated grain-boundary density, residual and subsurface oxygen, mixed-valence centers, lattice strain, and hetero-metallic interfaces.^{84–86} As highlighted in recent works on oxide-mediated CO₂RR catalysis and dynamic catalyst reconstruction, such features strongly influence adsorption energetics, intermediate stabilization, charge-transfer behavior, and the balance between productive pathways and competing reactions.⁸⁷

3.1 Nano-porosity and hierarchical morphology

Reduction of metal oxides to their metallic state is accompanied by substantial changes in molar volume, oxygen loss, lattice collapse, and redistribution of cations and anions.³⁰ These transformations proceed non-uniformly and commonly generate nano-pores, interconnected channels, and hierarchical void networks rather than compact metallic layers. Such morphology is well documented for several oxide-derived systems.⁸⁸ In OD-Cu formed from Cu₂O or CuO, *operando* and *ex situ* microscopy reveal bi-continuous, sponge-like frameworks with pore diameters spanning a few to several tens of nanometers, depending on oxide crystallinity, film thickness, and reduction conditions.^{89,90} Comparable porous architectures have been observed in OD-Ag,^{91,92} OD-Au,^{93,94} and OD-Zn, where reduction of thick oxide-films or nanoporous ZnO yields 3D-networks of nano-scale grains and channels. For Zn-based systems, the structural evolution from nanoporous ZnO to OD-Zn dendrites during CO₂RR produces a high roughness surface, enabling high CO partial current densities that scale with the degree of porosity and branching.^{95,96}

In mixed-metal OD alloys, porosity formation follows similar principles but is additionally shaped by the different reduction behaviors of the constituent oxides. Studies on OD-Cu–Zn⁹⁷ and

OD-Cu–Ag show that their precursors undergo asynchronous reduction, giving rise to multimetal porous architectures with Cu-rich and secondary-metal-rich regions embedded within a continuous network of nano-grains.⁹⁸ These porous, compositionally heterogeneous frameworks create spatially distributed catalytic environments—such as CO-generating sites in Zn- or Ag-rich regions adjacent to Cu domains capable of further CO reduction—though the extent and mechanistic impact of such partitioning depend on the specific alloy system.^{65,99}

Beyond structural effects, nano-porosity also contributes to the formation of localized microenvironments, including elevated local pH and intermediate confinement, which further couple structural descriptors with system-level catalytic behavior. As shown by Goyal *et al.*¹⁰⁰ nano-porosity contributes overall to the catalytic behavior through several experimentally supported mechanisms. First, it increases the electrochemical surface area (ECSA) and the density of accessible active sites. Second, confined pore environments can develop local chemical conditions (*e.g.*, elevated pH or enriched CO₂/CO concentrations) that differ from the bulk electrolyte, influencing selectivity. Third, interconnected channels facilitate mass transport and enable higher current densities without compromising reaction pathways. Thus, nano-porosity in OD metals and alloys (Fig. 2a) is a functional feature that shapes catalytic performance across multiple length scales.^{101,102}

3.2 Grain boundaries, low-coordination sites, and defect topologies

A second defining characteristic of oxide-derived catalysts is their unusually high density of crystallographic defects—grain boundaries (GBs), twin boundaries, stacking faults, step edges, and low-coordination surface atoms—generated during the fragmentation and grain refinement that accompany oxide reduction.^{103,104} For OD-Cu, Kanan *et al.*¹⁰⁵ identified the grain sizes to commonly fall in the 2–20 nm range, giving rise to GB densities far exceeding those in annealed polycrystalline Cu. Similar defect-rich nano-crystalline domains are observed in OD-Ag, OD-Au, OD-Zn, and in the reduced states of several multimetal oxide precursors.^{92,93,95}

A significant amount of evidence shows that these defective structures are directly linked to catalytic performance.^{106,107} Kanan *et al.*¹⁰⁸ reported a nearly linear relationship between CO formation activity and surface GB density, with oxide-derived Au made from thick Au₂O layers showing significantly higher CO partial current and lower overpotential than polished Au. In nanostructured and OD-Ag, methods that increase GB density also boost CO production at the same potentials.³⁷ For OD-Cu, atomistic modeling and *operando* spectroscopy reveal that GBs, twin boundaries, and under-coordinated step motifs favor the stabilization of *OCCO and similar C₂ intermediates, which explains the higher selectivity for ethylene and ethanol of OD-Cu compared to smooth Cu facets. These grain-boundary environments also play a critical role in stabilizing subsurface oxygen and oxygen-coordinated motifs, thereby coupling structural defects with electronic effects that are often attributed to Cu⁺-like species.¹⁰⁹ Likewise, Guo *et al.*¹¹⁰ indicated that for Sn-based OD-catalysts, disordered Sn–Sn and Sn–O motifs at grain

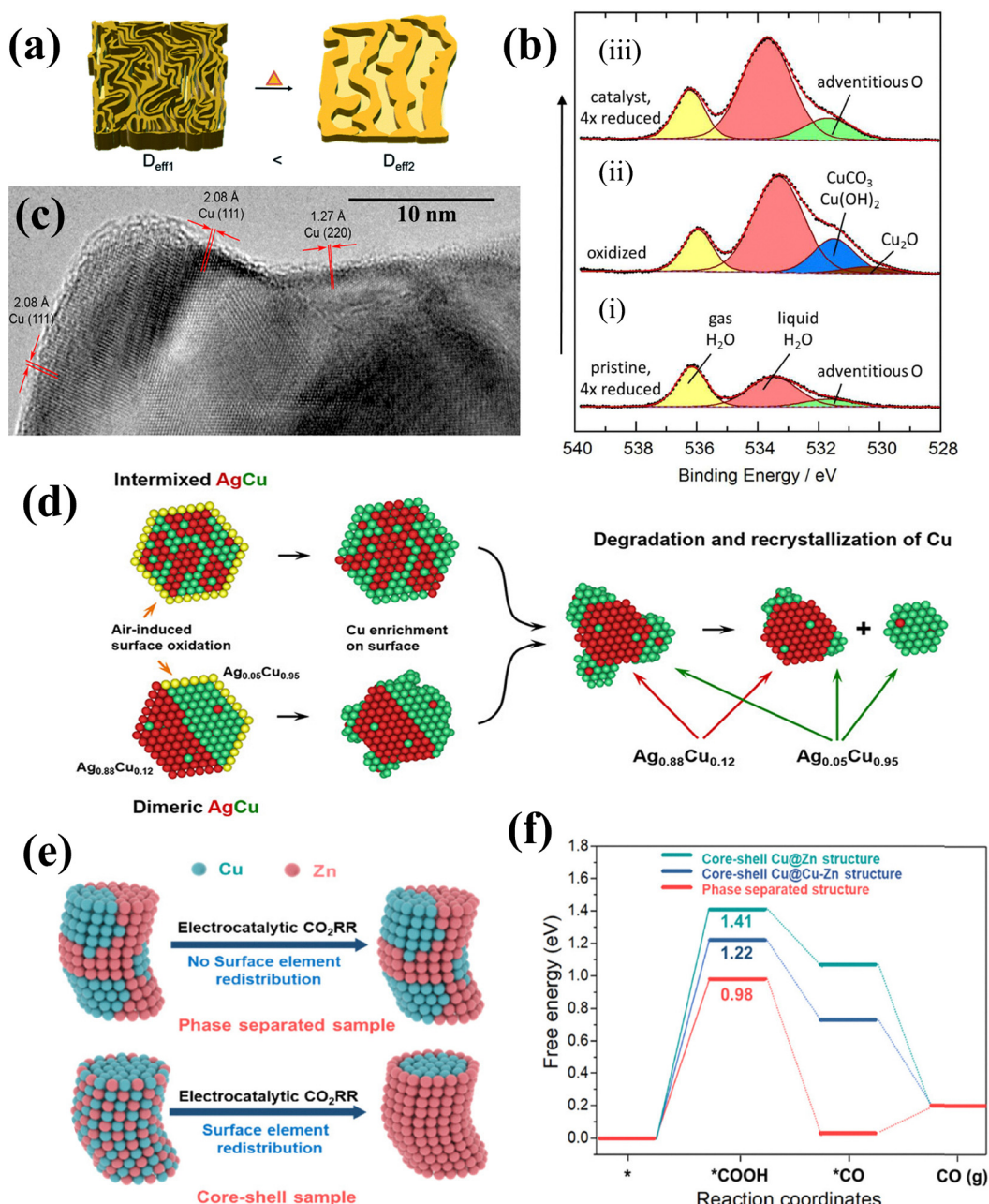


Fig. 2 Structural and physico-chemical characteristics adopted from the evolved OD-metals and alloys. (a) Schematic illustration of pore structure evolution from the pristine catalyst to the OD-catalyst. Reproduced with permission from ref. 100, Copyright (2022), The Royal Society of Chemistry (b) high-resolution O 1s XPS of OD-Cu catalyst, indicating the existence of sub-surface oxygen throughout the different oxidation states of the catalyst. Reproduced with permission from ref. 118, Copyright (2017), American Chemical Society (c) HRTEM of OD-Cu showcasing high-strain grain boundaries as an effect of trapped subsurface oxygen and low-coordination sites. Reproduced with permission from ref. 25, Copyright (2017), American Chemical Society (d) structural and chemical evolution of OD-AgCu alloy catalyst, through its evolution under cathodic potential. Reproduced with permission from ref. 98, Copyright (2023), American Chemical Society (e) structural and chemical evolution of OD-ZnCu alloy catalyst, through its evolution under cathodic potential, (f) discrepancies in the free energy values of the OD-ZnCu as a result of the morphological differences occurring during its evolution. Reproduced with permission from ref. 128, Copyright (2022), American Chemical Society.

boundaries and amorphous regions stabilize the $^*\text{OCHO}$ intermediate and promote the formation of formate. Experimental and theoretical research shows that under-coordinated Sn and Sn-oxide sites reduce the energy barrier for $^*\text{OCHO}$ formation and decrease $^*\text{CO}$ binding, leading to high faradaic efficiencies for formate.¹¹¹ These defect-controlled mechanisms extend

naturally to oxide-derived alloys, where asynchronous reduction of mixed-metal oxides produces multicomponent grain-boundary networks.¹¹² In OD-Cu-Zn, Herzog *et al.*¹¹³ showed through *operando* XAS distinct Cu-rich and Zn-rich nano-domains separated by strained GBs that modulate $^*\text{CO}$ binding and facilitate CO spillover from Zn-derived sites to Cu ensembles. OD-Cu-Ag

systems display similar behavior: Ag domains generate CO efficiently, while GB-rich Cu regions—with mixed Cu^+/Cu^0 character—enable C–C coupling, and interfacial GBs mediate rapid intermediate transfer between the two metals.^{98,99} While Pere *et al.*¹¹⁴ showed for OD-Cu–Sn catalysts, that grain boundaries frequently host adjacent Cu and Sn–O sites, enabling tandem pathways in which Sn-oxide motifs form $^*\text{OCHO}$ while neighboring Cu sites hydrogenate or further reduce C_1 intermediates. Across these alloy systems, GBs do not merely accommodate structural strain—they create heterogeneous reaction zones where complementary catalytic functions coexist within nano-scale distances.

Taken together, the defect architectures of oxide-derived metals and alloys constitute chemically and electronically unique catalytic ensembles. Their high densities of low-coordination metal atoms, metal–oxygen motifs, and heterometallic boundary sites act as catalytic “hot spots” that cannot be reproduced in equilibrium metal surfaces or homogeneous alloy phases.¹¹⁵

3.3 Residual and subsurface oxygen

Residual oxygen—whether as subsurface species, interfacial O, or persistent oxide fragments—is one of the most characteristic structural motifs of oxide-derived catalysts. Even after extensive electrochemical reduction, significant oxygen populations remain trapped within the metallic lattice, at grain boundaries, or as ultrathin oxide clusters. *Operando* AP-XPS, XAS, and EELS have confirmed the persistence of such oxygen species in OD-Cu, OD-Ag, OD-Au, OD-Zn, and in a range of mixed-metal oxide-derived systems.^{116,117}

For OD-Cu, Eilert *et al.*¹¹⁸ demonstrated that although crystalline Cu_2O disappears under steady-state CO_2RR , diffusion-trapped subsurface oxygen persists, producing Cu^+ -like spectral signatures (Fig. 2b). Molecular-dynamics simulations and *operando* spectroscopy further show that this oxygen forms metastable Cu–O ensembles whose lifetime depends on potential, local structure, and grain boundaries. In OD-Zn, nanoporous ZnO retains ZnO-like domains and oxygen vacancies, producing Zn–ZnO heterojunctions that facilitate CO_2 adsorption and CO formation. Mechanistically, these oxygen species shift the local d-band center, redistribute charge, and generate interfacial electric fields that favor activation of polar intermediates such as $^*[\text{CO}_2]^-$ and $^*\text{COOH}$. For OD-Cu, subsurface O and Cu^+/Cu^0 ensembles lower the barrier for $^*\text{COOH}$ formation and increase $^*\text{CO}$ surface coverage, enhancing C–C coupling. In OD-Ag and OD-Au, ultrathin oxide remnants and subsurface O modestly strengthen $^*\text{COOH}$ binding while maintaining weak $^*\text{H}$ binding, enabling highly selective CO formation.²⁶ In Zn-based systems, oxygen vacancies and ZnO-like motifs appear to constitute the active phase, acting as electron-donor sites for CO_2 activation. These oxygen-mediated effects extend directly to oxide-derived alloys.^{96,119} In OD-Cu–Zn, asynchronous reduction of CuO and ZnO produces interfacial Cu–ZnO regions where residual oxygen and O-vacancies persist under CO_2RR , supporting CO formation on Zn-derived domains while Cu sites carry out deeper reduction.⁹⁷ OD-Cu–Ag systems similarly retain Ag–O and Cu–O interfacial motifs that subtly tune CO generation on Ag and facilitate its subsequent transfer to Cu

regions rich in low-coordination Cu^+/Cu^0 sites. In OD-Cu–Sn, Sn–O species remain thermodynamically stable even at strongly cathodic potentials, producing persistent Sn–O/Cu interfaces that stabilize $^*\text{OCHO}$ and modulate the selectivity between formate and CO pathways. Across these alloy systems, residual oxygen functions not as an artifact of incomplete reduction but as an integral structural element that shapes electronic structure, interfacial charge distribution, and intermediate stabilization across multiple catalytic sites.¹²⁰

A critical aspect often overlooked is the transient nature of subsurface oxygen under reaction conditions. While subsurface oxygen is frequently invoked as a key descriptor, its stability is highly sensitive to applied potential, local structure, and reaction environment. Under strongly cathodic conditions, bulk oxide phases are thermodynamically unstable; however, oxygen can persist dynamically within defect-rich regions, grain boundaries, and confined geometries. Subsurface oxygen should therefore be considered a kinetically stabilized and continuously evolving species, rather than a static structural component. Its interaction with defect sites and local strain fields further modulates its lifetime and catalytic influence.¹²¹ Residual oxygen is therefore a functional design parameter of oxide-derived metals and alloys—one that directly influences reaction energetics, selectivity, and the cooperative behavior of multimetal active sites.¹²²

3.4 Strain, lattice distortion, and structural disorder

Reduction of metal oxides to metals generates substantial lattice distortion in oxide-derived catalysts due to volume contraction, non-uniform oxygen removal, and localized collapse of the oxide framework.¹²³ These processes introduce compressive and tensile strain, particularly at grain boundaries, remnant oxide–metal interfaces, and regions that undergo asynchronous reduction.¹²⁴ Molecular-dynamics simulations on OD-Cu reveal broad distributions of local atomic strain, with highly strained motifs preferentially stabilizing adsorbates such as $^*\text{CO}$ and $^*\text{OCCO}$, consistent with their proposed role in promoting C_2 pathways. Jacques *et al.*¹²⁵ in their *operando* XAS studies showed that OD-materials contain nano-crystalline domains with expanded and contracted lattice spacing coexisting with amorphous or partially ordered regions. Such displacement disorder broadens electronic bands, modifies orbital overlap, and perturbs the local d-band center, collectively influencing the binding and activation of key intermediates. In OD-Cu, theoretical studies indicate that compressive strain can strengthen binding of $^*\text{CO}$ and $^*\text{OCCO}$, while tensile strain may facilitate $^*\text{CO}$ desorption—effects that qualitatively align with observed shifts between C_2 and CO selectivity in strained or defect-rich Cu environments.⁸⁴

In oxide-derived alloys such as Cu–Zn and Cu–Ag, lattice mismatch and asynchronous metal-oxide reduction amplify interfacial strain and generate compositionally heterogeneous, strain-stabilized domains.^{98,99,114} These regions exhibit altered electronic structure and intermediate adsorption behavior relative to homogeneous alloys, and *operando* studies correlate such strained hetero-interfaces with enhanced CO formation (Zn-derived sites), CO spillover (Ag/Cu interfaces), and deeper reduction on Cu-rich domains. Across OD metals and alloys,

structural disorder—amorphous pockets, short-range order, and mixed metal–oxygen coordination—coexist with strain, and further diversifies the local chemical environments that underpin their catalytic performance.^{84,126}

3.5 Alloying behavior and multi-metal OD architectures

Multimetal OD architectures are of great significance because their reduction from mixed oxides generates hetero-interfaces, segregated phases (Fig. 2d), and multi-metal coordination environments that are difficult to access by conventional alloying methods.¹²⁷ In Cu–Zn OD-systems, mixed CuO–ZnO or ZnO-decorated Cu precursors reduce asynchronously: Cu-oxide domains convert to metallic Cu at milder potentials, while ZnO persists longer and only partially reduces under CO₂RR (Fig. 2e). The resulting OD-Cu–Zn catalysts feature Cu-rich nano-grains interfaced with ZnO or Zn-rich domains, supporting tandem CO₂ → CO → C₂₊ pathways where Zn-based sites generate CO and Cu-based OD-sites perform C–C coupling.¹²⁸

Similarly, OD Cu–Sn systems derived from CuO–SnO₂ or mixed hydroxides yield phase-segregated architectures in which Sn-oxide-rich motifs suppress HER and C₂ formation but strongly promote *OCHO formation and formate production, while adjacent Cu domains can still produce CO or C₂ products depending on composition and potential.^{74,98,129,130} Bolívar *et al.*¹³¹ Bi–Sn and Bi–Sn–Sb OD alloys exhibit similar behavior. It achieved high formate selectivity at industrially relevant current densities by combining Bi-rich domains that favor formate with Sn-containing domains that enhance conductivity and structural stability. These examples illustrate a general principle: OD alloying enables spatial separation and coupling of functional roles—CO₂ activation, CO generation, C–C coupling, and HER suppression—within a single, reconstruction-derived architecture.¹³²

3.6 Surface chemistry, adsorption energetics, and active-site diversity

The defect-rich, oxygen-modified, and multimetal nature of OD-catalysts produces a broad spectrum of active sites. On OD-Cu, reduced metallic terraces coexist with low-coordination Cu atoms at steps and GBs, Cu⁺–O ensembles near subsurface oxygen, and alloy-modified sites in multimetal systems.^{60,105} These different environments host distinct binding geometries and energetics for *CO₂, *COOH, *CO, *CHO, *OCHO, and *H. Atomistic modeling of OD-Cu and OD-CuZn surfaces indicates that C₂₊ formation is favored at specific clusters of under-coordinated Cu atoms adjacent to subsurface oxygen, where *CO is moderately bound and *OCCO formation barriers are minimized (Fig. 2f).¹³³

For OD-Zn, nanoporous and dendritic architectures with under-coordinated Zn sites and ZnO-like domains show strong CO selectivity, with formate and hydrogen largely suppressed.¹³⁴ In OD-Sn and OD-Bi, oxide-rich surfaces and mixed Sn²⁺/Sn⁴⁺ or Bi³⁺ states strongly stabilize *OCHO, consistent with the near-unity formate faradaic Efficiencies reported at moderate overpotential. These materials exhibit higher *H adsorption energies

than their metallic counterparts, resulting in intrinsically low HER activity.^{135,136}

The diversity of sites in OD-catalysts also facilitates “intermediate channeling” between neighboring sites. CO produced at one site (*e.g.*, ZnO or Ag-rich domains) can migrate and re-adsorb onto adjacent Cu-rich OD-sites optimized for C–C coupling. This spatial cooperation, combined with suppressed HER on oxygen-rich or p-block domains, underpins the unusually high C₂₊ formation rates and formate selectivity observed for OD-catalysts.^{17,74,137}

3.7 Comparison with conventional metallic catalysts

Relative to conventional polycrystalline or electrodeposited metals, OD-catalysts differ not only in quantitative performance but in the qualitative nature of their active states and mechanisms.¹³⁸ Structurally, OD materials are nano-crystalline, contain high densities of grain boundaries and under-coordinated sites, and exhibit pervasive nano-porosity arising from oxide collapse—features rarely achievable in thermally reduced or electrodeposited metals.⁸⁶ Electronically, OD-catalysts host mixed-valence metal centers, locally perturbed d-band structures, and residual or subsurface oxygen, together with strain-modified domains that strongly influence intermediate binding.¹³⁸ Chemically, OD-surfaces contain metal–oxygen motifs, heterometallic interfaces, and dynamic metal/oxide equilibria, all of which are minimal or absent on classical metallic surfaces. These structural and electronic distinctions translate into mechanistic differences during CO₂RR. On metallic Cu, the selectivity towards C₂₊ products is limited by the difficulty of sustaining high *CO coverage and suppressing competing hydrogen evolution reaction.¹³⁹ OD-Cu circumvents this restriction through pore-confined microenvironments, defect-rich grains, and Cu⁺/Cu⁰–O structure ensembles that sustain higher local *CO concentrations and stabilize *OCCO and related C₂ intermediates, thus enhancing C₂₊ product selectivity.¹⁴⁰ For Ag and Au, oxide-derived forms exhibit lower overpotential and higher CO partial currents compared to their metallic counterparts, attributable to increased grain-boundary density and oxygen-modified electronic structure that facilitate *COOH formation.^{92,141} In Sn- and Bi-based systems, OD-catalysts maintain stable oxide motifs that preferentially stabilize *OCHO and greatly suppress *H adsorption, enabling higher formate selectivity at lower overpotential, where metallic Sn or Bi exhibits significant HER or mixed product formation.^{142–144}

Importantly, these physicochemical features should not be viewed as independent descriptors, but as interdependent outcomes of reconstruction kinetics. During oxide-to-metal transformation, heterogeneous reduction concurrently generates grain boundaries, lattice strain, subsurface oxygen, and nanoporosity, yielding coupled descriptor ensembles defined by non-equilibrium dynamics. Within this framework, descriptor influence is strongly condition-dependent. Oxygen coordination and defect density act as primary descriptors, governing electronic structure and active-site distribution, while strain and porosity serve as secondary modifiers and enable system-level effects. Subsurface oxygen is a transient, kinetically stabilized species

whose presence depends on potential, morphology, and oxygen mobility. As Wu *et al.*¹²¹ showed, its continuous evolution under reaction conditions, while defect-rich environments—especially grain boundaries—can stabilize oxygen coordination and generate Cu⁺-like electronic signatures without stable oxidized phases.¹⁴⁵ Together, these results establish grain boundaries, strain, porosity, and oxygen coordination as a coupled, dynamic descriptor network, where catalytic activity and selectivity arise from their interplay rather than any single feature.

4. Mechanistic function of OD metals and alloys in CO₂RR

Oxide-derived metals and alloys express catalytic behavior that diverges fundamentally from conventional metallic systems, not simply in activity or selectivity, but in the very mechanisms through which CO₂ is activated, reduced, coupled, and stabilized.²¹ Their function emerges from a convergence of non-equilibrium structural features—including residual oxygen, high defect and grain-boundary densities, lattice strain, nanoscale confinement, and mixed-valence metal centers—which collectively reshape adsorption energetics and reshape reaction landscapes.¹⁴⁶ These structural motifs are not static: under *operando* conditions, OD-catalysts continuously evolve, yielding a metastable ensemble of active motifs whose cooperative action defines their performance. While intrinsic surface energetics provide a useful mechanistic framework, they do not fully capture catalytic behavior under realistic operating conditions.

4.1 Activation pathways and formation of the active OD-surface under *operando* conditions

During early reduction of oxide precursors, OD-catalysts do not transition into pure metallic phases but instead form a metastable mixture of metallic and partially oxidized environments.³⁸ As shown through the *operando* X-ray absorption study of Cheng *et al.*,⁶⁰ ambient-pressure XPS, and *in situ* diffraction consistently show that Cu₂O and CuO reduce into Cu⁰ while retaining substantial subsurface oxygen and Cu⁺-like spectral signatures, even at strongly cathodic potentials. Slow oxygen diffusion and blocked migration pathways preserve this oxidic character across extended reaction times, giving OD-Cu a hybrid metal–oxide identity that persists throughout CO₂RR. Silver oxides reduce more completely, producing nearly oxygen-free metallic OD-Ag surfaces,^{147–149} whereas SnO₂ and Bi₂O₃ maintain mixed-valence states (Sn⁴⁺/Sn²⁺ and Bi³⁺) under most CO₂RR conditions.^{150–152} These differences in oxygen retention define the resulting electronic structure and CO₂RR selectivity for each OD-system.

Oxide reduction universally drives the collapse of the parent oxide lattice into a nanoporous metal framework, producing strong grain refinement and a high density of grain boundaries. In the work of Kanan *et al.*,¹⁰⁵ OD-Cu formed from the reduction of CuO/Cu₂O yields nanoporous networks of sub-10–20 nm grains with GB densities rising above $\sim 20 \mu\text{m}^{-1}$.^{25,118,153} While OD-Ag structures, studied by Xie *et al.*,¹⁵⁴ exhibited similar restructuring: compact foil transforms during CO₂RR into porous ligaments

with ~ 50 – 200 nm grains and abundant GBs and twin boundaries. Zn-based and Cu–Zn systems also undergo oxide-to-metal collapse, forming coupled Cu-rich and Zn-rich nano-domains within porous, defect-rich frameworks.^{40,65,155} Across OD-Cu, OD-Ag, OD-Zn, and multimetal OD alloys, these transformations significantly increase the concentration of low-coordination sites and interfacial motifs relative to bulk metals.

Operando characterizations from the work of Dattila *et al.*,¹⁴⁶ indicated that OD metals are not static reduced phases. Instead, as shown by Ruiter *et al.*,¹⁵⁶ they remain structurally dynamic: OD-Cu forms and dissolves nanoclusters and vacancy islands during CO₂RR, with ongoing facet rearrangement, subsurface oxygen persistence, and Cu⁺/Cu⁰ cycling (Fig. 3a). OD-Ag continues to refine its grain structure in early electrolysis,¹⁴⁷ while OD-Zn and Cu–Zn alloys show time-dependent redistribution of Cu and Zn and partial re-oxidation under bias.^{74,85,97} Thus, the active phase in OD-metals and alloys—across Cu, Ag, Zn, Sn, Bi, and multimetal systems—is a non-equilibrium, continuously reconstructed ensemble of nano-grains, grain boundaries, residual oxides, and subsurface oxygen that responds dynamically to electrolyte, local pH gradients, and adsorbate coverage.^{61,103,153,157}

4.2 Elementary CO₂RR steps for C₁ products reshaped by OD-structural motifs

CO₂ reduction to C₁ products generally involves CO₂ adsorption and activation on the OD-catalyst's active site, followed by proton-coupled electron transfer steps that generate key surface intermediates (*COOH or *OCHO), which are further transformed to CO or formate product. OD-catalysts fundamentally modify the reaction's energetics by introducing grain boundary electronic states, subsurface oxygen, and nano-confined micro-environments (Fig. 3b). From a mechanistic standpoint, oxide-derived catalysts modify key reaction descriptors including *COOH formation energy, *CO binding strength, interfacial electric-field distribution, and local proton availability. These effects arise from oxygen-modified electronic structure, GB-induced coordination diversity, and nanoscale confinement, collectively enabling deviations from conventional scaling relationships governing CO₂RR selectivity.

CO₂ adsorption. CO₂ adsorption is an energetically challenging step on most pure metal catalysts, because the linear CO₂ molecule interacts weakly with unperturbed metallic surfaces. OD-catalysts overcome this by providing polarization fields at grain boundaries and metal–oxygen interfaces.⁵⁵ Spectroscopic analyses reveal that bent [CO₂]* species form at lower overpotential on OD-Cu than on polycrystalline Cu, owing to the presence of Cu⁺ adjacent to subsurface oxygen.¹⁵⁸ These electrophilic sites inject charge into the CO₂ antibonding LUMO, enabling early activation and bending of the linear molecule. Similar effects occur on OD-Sn and OD-Bi, where Sn⁴⁺ and Bi³⁺ motifs polarize CO₂ and lower activation overpotential.⁵²

Formation of the *COOH intermediate. The formation of *COOH, the first proton–electron transfer step toward CO production, is significantly facilitated on OD-surfaces.¹⁵⁹ As shown by Qu *et al.*,¹⁶⁰ subsurface oxygen in OD-Cu downshifts the local d-band and enhances the density of states near the

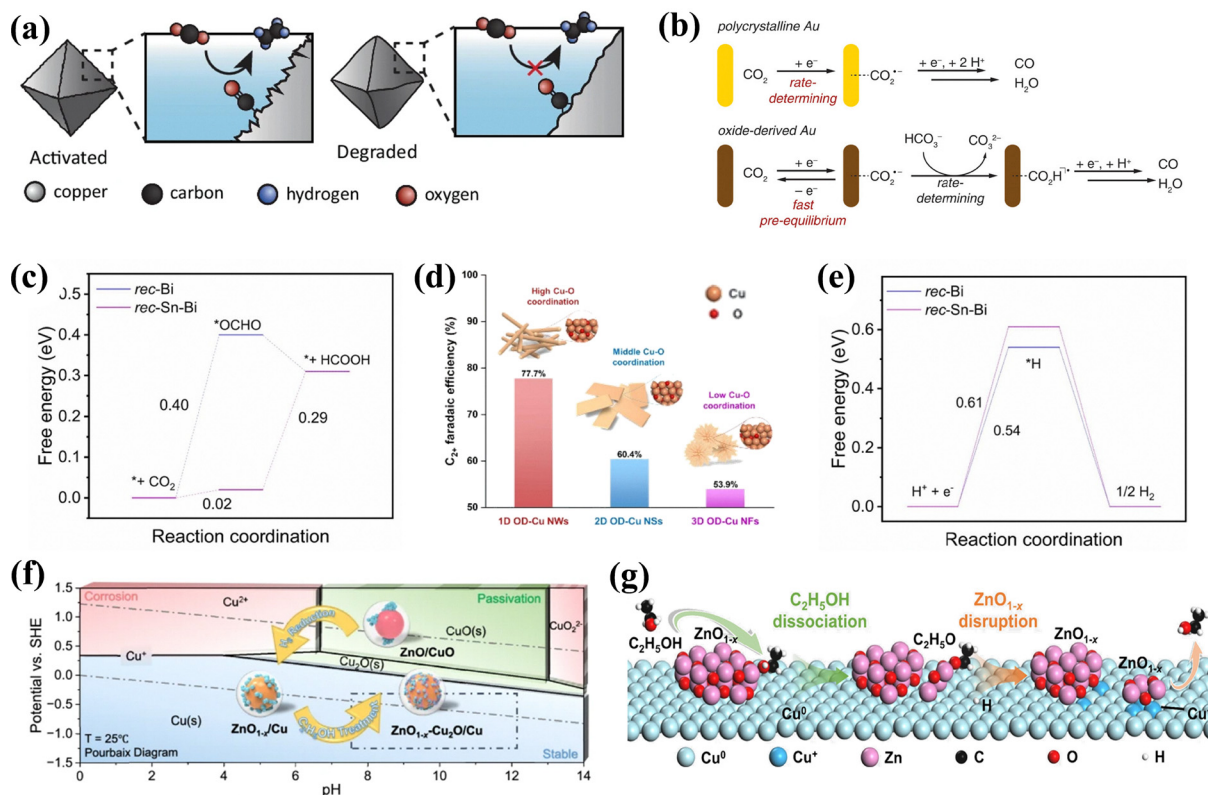


Fig. 3 Function of the OD-catalysts during the CO₂RR. (a) Morphological changes and active sites formation on OD-Cu. Reproduced with permission from ref. 156, Copyright (2025), *Nature Communications* (b) changes in the CO₂RR mechanism over OD-Au versus a typical metallic Au surface. Reproduced with permission from ref. 29, Copyright (2012), American Chemical Society (c) Differences in the free energy *OCHO formation pathway over OD-Bi and OD-SnBi catalysts,¹⁶⁴ (d) OD-Cu catalyst having a direct impact on the CO₂RR product selectivity, as a result of direct alterations of the surface micro-environment coordination. Reproduced with permission from ref. 168, Copyright (2024), Elsevier (e) free energy differences in the *H intermediate formation, for the parasitic HER, over OD-Bi and OD-SnBi catalysts. Reproduced with permission from ref. 164, Copyright (2025), Elsevier (f) schematic illustration of the morphological and physico-chemical alterations of OD-CuZn catalysts, as a function of the reaction environment (pH) and potential, (g) schematic diagram of the dynamic catalyst structural evolution during catalysis. Reproduced with permission from ref. 177, Copyright (2025), *Nature Communications*.

Fermi level, lowering the *COOH formation energy on metallic Cu. *Operando* characterization and DFT studies show that Cu⁺/Cu⁰ interfacial pairs cooperate to stabilize *COOH through bifunctional binding: Cu⁺ stabilizes the oxygen end of the intermediate while Cu⁰ delivers electron density to the carbon site. This synergy is absent on purely metallic surfaces and explains why OD-Cu activates CO₂ at a lower overpotential.¹⁶¹

CO Formation on OD-Ag and OD-Au. OD-Ag and OD-Au produce CO with unusually high selectivity because oxygen-modified Ag or Au sites enhance *COOH stabilization but maintain weak *CO binding.^{29,148} As shown by Eilert *et al.*,¹¹⁸ this energetic alignment lowers the overpotential for CO formation and minimizes HER. Because OD-Ag retains some subsurface oxygen but loses bulk Ag₂O, it presents an ideal electronic configuration where *H binding is energetically disadvantaged, leading to near-quantitative CO faradaic efficiencies at modest potentials.^{154,162}

The *OCHO Pathway on OD-Sn and OD-Bi. In Sn- and Bi-derived OD-catalysts, oxygen-rich surface motifs drive the *OCHO pathway.¹⁶³ Lai *et al.*,¹⁶⁴ showed through *operando* studies the persistence of Sn⁴⁺/Sn²⁺ and Bi³⁺ motifs. Sn⁴⁺ stabilizes oxygen-

bound *OCHO through electrostatic attraction, while Sn²⁺ improves electron transfer (Fig. 3c). This dual-valence configuration explains why OD-Sn and OD-Bi outperform their metallic counterparts in formate selectivity and HER suppression.¹⁶⁵

4.3 Multicarbon product formation via C-C coupling mechanisms on OD-Cu

Among all oxide-derived catalyst systems, OD-Cu occupies a uniquely prominent position due to its unmatched ability to generate multicarbon (C₂₊) products such as ethylene, ethanol, and propanol.¹⁶⁶ Although metallic Cu is already capable of catalyzing the C-C coupling reactions, its efficiency is limited by insufficient *CO coverage, strong competition from HER, and the difficulty of stabilizing dimeric intermediates at terrace sites.¹⁶⁷ In contrast, OD-Cu overcomes these limitations through a synergy of structural, electronic, and chemical effects that emerge after oxide reconstruction. The distinctive catalytic behavior of OD-Cu is best understood as the combined consequence of three mechanisms that reinforce one another: nano-confined accumulation of *CO, grain boundary stabilization of the *OCCO

intermediate, and the persistent involvement of Cu^+ species generated and sustained through subsurface oxygen.⁶²

Early interpretations of OD-Cu activity emphasized the role of residual Cu^+ species as the primary origin of enhanced C–C coupling. However, subsequent *operando* studies have challenged the existence of stable Cu^+ under strongly cathodic conditions, instead pointing to dynamically stabilized subsurface oxygen and defect-rich environments as the key contributors to catalytic behavior. As shown by Mistry *et al.*⁶⁶ OD-Cu exhibits enhanced C_{2+} selectivity linked to its nanostructured morphology and high density of grain boundaries rather than persistent bulk Cu^+ phases. Complementary insights from the work of Lei *et al.*¹⁴⁵ further indicate that electronic perturbations associated with defect-rich environments and transient oxygen coordination can reproduce the spectroscopic signatures often attributed to Cu^+ .

Taken together, these findings suggest that Cu^+ , subsurface oxygen, and defect density should not be interpreted as independent descriptors, but rather as interdependent features arising from reconstruction dynamics. Within this unified picture, subsurface oxygen stabilizes local electronic perturbations, grain boundaries provide structurally flexible active sites, and their combined effect governs $\ast\text{CO}$ coverage and $\ast\text{OCCO}$ stabilization, ultimately controlling C_{2+} formation.

4.3.1 Nano-confined $\ast\text{CO}$ environments and their consequences for C–C bond formation. The porous framework of OD-Cu produced during the reduction of Cu_2O and CuO provides a microenvironment different from that of polycrystalline Cu. In the work of Wu *et al.*¹⁶⁸ OD-Cu contains interlinked channels and sub-10 nm grains that serve as nanometer-scale reaction compartments. Within these confined regions, $\ast\text{CO}$ produced from CO_2 reduction does not diffuse away from the surface as efficiently as on a flat metallic terrace, leading to distinct variations in the product selectivity profile, with the micro-environment coordination (Fig. 3d). *Operando* vibrational spectroscopies and computational mass-transport studies consistently show substantially elevated $\ast\text{CO}$ coverages within OD architectures. In some cases, the effective local $\ast\text{CO}$ concentration has been estimated to be several-fold higher than that achievable on planar Cu electrodes under identical macroscopic conditions.¹⁶⁹ Such nano-confined behavior has two profound mechanistic implications. First, high local $\ast\text{CO}$ activity increases the statistical likelihood that two $\ast\text{CO}$ molecules occupy adjacent sites simultaneously—an essential prerequisite for forming the $\ast\text{OCCO}$ dimer, the key intermediate in all major C_{2+} pathways. Second, $\ast\text{CO}$ -rich nano-cavities influence local proton availability: the consumption of protons inside narrow channels outpaces replenishment from the bulk, creating localized alkaline micro-domains.¹⁶⁰ This alkaline environment suppresses the HER and promotes subsequent C–C coupling steps. Thus, nano-porosity and nano-confinement do not merely increase surface area—they fundamentally alter the kinetic landscape of $\ast\text{CO}$ handling and contribute to C–C bond formation.¹⁷⁰ Importantly, the effectiveness of these mechanisms is strongly influenced by local microenvironmental conditions, particularly $\ast\text{CO}$ accumulation and local pH gradients within porous OD-structures, highlighting the interplay between intrinsic catalytic properties and system-level effects.

4.3.2 Stabilizing effect of defect-rich sites towards the $\ast\text{OCCO}$ intermediate. C–C coupling on Cu proceeds through the formation of a $\ast\text{OCCO}$ bridging dimeric intermediate, requiring spatial flexibility and a sufficiently electron-rich environment at the adsorption site.¹⁰³ While terrace atoms on metallic Cu bind $\ast\text{CO}$ reasonably well, they do not strongly stabilize $\ast\text{OCCO}$, which explains why smooth Cu surfaces rarely deliver high C_{2+} selectivity.¹⁷¹ For the case of OD-Cu, Yeo *et al.*¹⁷² showed that GBs, twin boundaries (defects), and regions of high local strain provide electronically and geometrically favorable environments for stabilizing $\ast\text{OCCO}$ and other dimeric intermediates. Grain boundaries in OD-Cu contain low-coordination Cu atoms whose electronic structure deviates from the d-band profile of bulk Cu.¹⁰⁴ Fang *et al.*,¹⁷³ through their DFT work, showed that these coordinatively unsaturated sites lower the activation barrier for forming $\ast\text{OCCO}$ by providing both stronger $\ast\text{CO}$ binding and a more flexible adsorption geometry that accommodates the bending and re-hybridization associated with dimer formation. While Zhen *et al.*¹⁷⁴ provided additional spectroscopic evidence supporting this model, *operando* Raman measurements have directly detected vibrational features attributed to $\ast\text{OCCO}$ species specifically at defect-rich OD-Cu surfaces, whereas such features are weak or absent on smooth Cu films. Furthermore, GBs act as charge-accumulation zones, particularly when adjacent to subsurface oxygen. This increases the extent of electron donation into antibonding orbitals of the $\ast\text{CO}$ moieties, promoting the formation and subsequent reduction of the $\ast\text{OCCO}$ intermediate. In this way, GBs serve not merely as structural irregularities but as highly specialized catalytic motifs that enable reaction pathways inaccessible on pristine Cu terraces.¹⁷⁵

4.3.3 The function of Cu^+ and subsurface oxygen in steering C_{2+} pathways. *Operando* investigations of Wang *et al.*³⁸ showed that subsurface oxygen remains trapped within OD-Cu even at potentials where bulk Cu_2O is thermodynamically unstable. This retained oxygen stabilizes dynamic Cu^+/Cu^0 ensembles that are continuously regenerated through interaction with adsorbates such as $\ast\text{COOH}$ and $\ast\text{CHO}$. These mixed-valence motifs influence C_{2+} formation through two principal effects.²⁵ First, Cu^+ binds $\ast\text{CO}$ more strongly and directionally than Cu^0 , enriching $\ast\text{CO}$ near Cu^+/Cu^0 interfaces and increasing the likelihood of $\ast\text{OCCO}$ formation. Second, the partially oxidized electronic environment of Cu^+ stabilizes polar intermediates ($\ast\text{CHO}$, $\ast\text{COH}$), which are essential for the ethanol and higher-alcohol pathways. Crucially, Cu^+ does not need to exist as a static phase or in large abundance to be catalytically decisive.¹⁷⁶ The *operando* studies of Zhang *et al.*¹⁷⁷ indicate that Cu^+ forms and disappears dynamically during CO_2RR , with its local concentration governed by subsurface oxygen, intermediate coverage, and transient redox cycling. This continual regeneration ensures that electronically favorable Cu^+ -like sites persist at reaction-relevant regions—even when the macroscopic surface appears metallic. Within the OD framework, nano-confinement maintains high $\ast\text{CO}$ activity, grain boundaries provide geometrically flexible sites that lower the $\ast\text{OCCO}$ activation barrier, and Cu^+-O ensembles tune electronic structure to stabilize both

*OCCO and downstream intermediates.^{178,179} By simultaneously enhancing *CO retention, lowering dimerization energy barriers, and stabilizing key intermediates, OD-Cu circumvents scaling limitations inherent to metallic Cu and consistently delivers superior C₂₊ selectivity across diverse operating conditions.^{146,180}

4.4 Suppression of the hydrogen evolution reaction (HER)

A key advantage of OD-catalysts is their natural ability to suppress the HER, a result that stems directly from the unique geometric and electronic structures formed during oxide-to-metal reconstruction.³⁰ Unlike metallic surfaces, where terrace atoms offer stable, low-energy sites for *H binding. OD-catalysts feature extensive networks of defect sites, strained grain boundaries, and oxygen-coordinated metal ensembles. These features disrupt the *H adsorption step in ways that hinder HER.²⁴ The geometric distortions at GBs and step edges create environments where *H adsorption is less thermodynamically favorable, breaking the usual scaling relationship between *H and other intermediates that typically influence HER activity on pristine metal surfaces.¹⁸¹

As seen in Section 3.3, residual oxygen plays a crucial role by generating subsurface oxygen, vacancies, and metal–oxygen motifs that shift electron density, render surface metal atoms more positively polarized, and thereby weaken proton adsorption. In systems such as OD-Sn, OD-Bi, and OD-Ag, metal–oxygen groups remain stable under strongly cathodic conditions, indicating that partially oxidized states like Sn²⁺/Sn⁴⁺ or Bi³⁺ persist throughout CO₂RR.^{29,182,183} These motifs weaken M–H interactions to such an extent that HER becomes significantly inhibited, even in acidic or near-neutral electrolytes (Fig. 3e).^{184,185} This stands in sharp contrast to metallic Sn or Bi, where reductive potentials rapidly eliminate surface oxides, restoring coordination environments that allow HER to dominate.^{186,187} Nano-porosity further amplifies these effects by generating confined microenvironments where the local pH rises during catalysis.¹⁸⁸ Within nanoporous OD frameworks, protons are consumed more rapidly than they can diffuse from the bulk electrolyte, creating alkaline pockets in which the activity of HER is intrinsically limited. Meanwhile, key CO₂RR intermediates such as *COOH and *OCHO remain strongly stabilized at oxygen-modified sites, enabling selective multi-electron transformations that outcompete proton reduction. The combined action of weakened hydrogen adsorption, oxygen-induced electronic perturbations, and nano-confined alkalinity explains why OD-catalysts exhibit remarkable HER suppression without requiring bulk pH engineering or specialized buffers.^{143,189}

4.5 Dynamic restructuring and *operando* activity

A hallmark of OD-catalysts is that their active state is not static. As shown by Löffler *et al.*,¹⁹⁰ oxides undergo continuous restructuring during CO₂RR, driven by redox cycling, electrolyte interactions, and the dynamical behavior of reaction intermediates. *Operando* studies consistently show that OD-Cu, for example, does not remain purely metallic during catalysis; rather, it experiences periodic, reaction-induced partial re-oxidation through interactions with adsorbed *COOH, dissolved CO₂, and water.¹²¹ These re-oxidation episodes reintroduce oxygen

into subsurface regions or at GBs, regenerating Cu⁺ sites even under potentials where metallic Cu would ordinarily remain fully reduced. Consequently, OD-Cu maintains an ensemble of mixed Cu⁺/Cu⁰ states that fluctuates with time but never collapses into a purely metallic phase.¹⁹¹ While, as previously discussed in part 4.1, beyond Cu several OD metals like Sn and Bi exhibit similar behavior. These oxygenated domains are not residual precursor fragments but are maintained or partially renewed through electrolyte interactions and proton–electron transfer processes. OD-Ag and OD-Zn display related behavior. The *operando* EXAFS investigations from Firet *et al.*,⁹² revealed that trace oxygen remains associated with OD-Ag during CO₂RR, while the ligament network continues to reconstruct under bias.¹⁴⁷ For Zn-based catalysts, *operando* XAS and electrochemical investigations show Zn/ZnO interconversion, with oxygenated Zn species reappearing during operation and sustaining the electronic environment needed for selective CO production.^{95,134}

These findings show that OD-catalysts operate not through a single static active structure, but through a metastable, dynamically sustained ensemble shaped by ongoing chemical fluxes (Fig. 3f). This continuous interplay of oxidation, reduction, and atom migration allows them to maintain active metal sites, oxygen-modified regions, and defect-rich boundaries that together enhance CO₂ activation, intermediate stabilization, and C–C coupling (Fig. 3g).

4.6 Mechanistic trends across OD alloy systems

While monometallic OD-catalysts derive their mechanistic function from defect-rich architectures and oxygen-stabilized states, OD alloys extend these behaviors by introducing cooperative, multi-site catalytic pathways that transcend the capabilities of homogeneous metallic alloys.^{34,74} As shown by Jeon *et al.*,¹²⁶ mixed-metal oxide precursors reduce asynchronously—each metal undergoing reduction at different potentials and rates—resulting in nanoscale segregation, phase boundaries, and interfacial domains that function as coupled catalytic units.

For OD Cu–Ag alloys, silver domains serve as highly efficient CO-generation sites owing to their optimized *COOH formation energetics.¹⁹² The CO released from Ag sites can diffuse and re-adsorb onto adjacent OD-Cu grains, where the high density of grain boundaries and Cu⁺–O ensembles facilitates C–C coupling. This “tandem spillover mechanism”—in which one element handles CO generation and another handles further reduction—is a powerful route to enhancing C₂₊ product yields.¹⁹³ OD-Cu–Zn systems operate *via* complementary chemistry. ZnO or Zn-rich domains preferentially activate CO₂ and suppress HER due to weak *H binding. Meanwhile, Cu-rich OD regions retain high *CO coverage and offer suitable binding geometry for C–C coupling.¹⁹⁴ Thus, Zn-derived sites mediate CO production and HER suppression, whereas Cu-derived sites perform the multicarbon steps.¹⁹⁵ OD-Cu–Sn further illustrates the multi-functionality of alloy OD-catalysts. Sn-oxide domains stabilize the *OCHO intermediate and promote formate formation, while neighboring Cu sites can perform hydrogenation or CO formation depending on potential.¹⁹⁶ Through dynamic

electronic communication and intermediate exchange, OD alloys act as nanoscale reaction cascades, enabling multi-pathway selectivity tuning that is inaccessible to conventional alloy systems with homogeneous surfaces.¹¹⁴

Across oxide-derived metals and alloys, three mechanistic determinants consistently emerge: (i) oxygen-modified electronic structure that tunes intermediate stabilization, (ii) defect-mediated active-site diversity enabling cooperative multi-site reaction pathways, and (iii) nano-confinement effects that reshape local reaction microenvironments. The interplay of these factors decouples catalytic performance from classical scaling relationships and enables selectivity regimes that are difficult to access on conventional metallic catalysts. These principles provide the mechanistic foundation for interpreting performance trends discussed in the following sections.

4.7 System-level effects: mass transport, local pH, and confinement

While the preceding discussion focuses on intrinsic surface energetics and intermediate stabilization, catalytic performance in OD-systems is fundamentally governed by the interplay between these intrinsic descriptors and system-level effects, including mass transport, local pH gradients, and nano-scale confinement. These effects are particularly critical for OD-catalysts, where reconstruction-induced nano-porosity, high defect density, and heterogeneous architectures create spatially non-uniform reaction environments that deviate significantly from bulk electrolyte conditions.¹⁹⁷

In porous OD-structures, restricted diffusion of reactants, intermediates, and ions leads to the formation of confined microenvironments, in which local concentrations and reaction conditions differ markedly from the bulk. In particular, the accumulation of *CO within nanoporous domains has been shown to significantly increase local surface coverage, thereby enhancing the probability of bimolecular interactions such as *CO-*CO coupling. This effect is especially relevant for OD-Cu systems, where C₂₊ formation exhibits a second-order dependence on *CO coverage and is therefore highly sensitive to local intermediate accumulation.¹⁹⁸ Simultaneously, the consumption of protons during CO₂ reduction, combined with limited mass transport in confined geometries, leads to the development of localized alkaline conditions at the catalyst interface. These local pH gradients can substantially alter reaction pathways by suppressing proton-dependent reactions such as the HER, while favoring CO₂ reduction pathways that are less sensitive to proton availability. The importance of pH and electrolyte environment in governing CO₂RR selectivity has been widely demonstrated, with both experimental and theoretical studies showing that reaction rates and product distributions depend strongly on local proton activity and electrolyte composition.¹⁹⁹

The magnitude of these microenvironmental effects depends strongly on reactor configuration and operating regime. In conventional H-cell measurements, current densities are typically low, and catalyst behavior is often interpreted primarily through intrinsic surface kinetics. However, in flow cells, gas-diffusion electrodes (GDEs), and membrane-electrode assemblies (MEAs),

CO₂RR is increasingly operated at technologically relevant current densities, where local CO₂ availability, water activity, ionic transport, carbonate/bicarbonate equilibria, product removal, and proton transport become coupled performance-limiting variables. Recent reviews on CO₂ mass-transport engineering emphasize that electrode architecture, catalyst-layer thickness, wetting state, gas-liquid interface stability, and operating conditions directly determine the local CO₂ concentration and therefore the competition between CO₂RR and HER.²⁰⁰ This is especially relevant for OD-catalysts, where reconstruction-derived nano-porosity enhances intermediate retention but can also impose transport limitations. In OD-Cu, confined domains increase local *CO coverage and promote C-C coupling; however, excessive tortuosity or flooding can restrict CO₂ supply and accelerate HER. Thus, porosity is not inherently beneficial, but an architecture-dependent descriptor governed by the balance between intermediate confinement and reactant depletion. This aligns with recent studies showing that selectivity in high-rate CO₂ electrolysis is dictated by coupled reaction-transport effects rather than adsorption energetics alone.²⁰¹

MEA-type CO₂ electrolyzers further illustrate this coupling. While MEAs reduce ohmic losses and enable high-rate operation, recent work highlights persistent challenges associated with CO₂ utilization, carbonate formation/crossover, water management, and local ionic transport. Studies of MEA systems show that bicarbonate/carbonate transport, membrane properties, and local ion distributions can regulate the availability of regenerated CO₂ near the catalyst layer and strongly affect selectivity and carbon efficiency.²⁰² Therefore, catalytic behavior in OD-systems should be interpreted as the outcome of an integrated catalytic environment, where intrinsic descriptors such as oxygen coordination, defect density, and electronic structure interact with microenvironmental descriptors such as local pH, CO₂ availability, wetting state, ion transport, and intermediate confinement.²⁰³ This view extends the classical perspective summarized by Nitopi *et al.*¹⁹⁷ for Cu-based CO₂RR, in which selectivity depends not only on surface structure and binding energetics but also on electrolyte composition, local pH, mass transport, and operating conditions.

5. Performance landscape of OD metals & alloys in CO₂RR

High GB density and defect-rich topologies provide geometries favorable for *COOH, *OCHO, and *OCCO formation.²⁰⁴ Concurrently, nano-porosity and confinement modify the local reaction environment—elevating pH, suppressing HER, and sustaining high *CO coverage—while continuous reconstruction under bias maintains a metastable catalytic state distinct from both oxide and bulk metal phases. Together, these attributes decouple adsorption energetics from conventional scaling relations, enabling OD-materials to achieve activity and selectivity profiles inaccessible to equilibrium metallic catalysts.⁸⁴ Representative quantitative performance metrics

Table 2 Cross-material benchmarking of oxide-derived catalysts, exhibiting major application potential for the electrochemical CO₂RR. Performance metrics depend on reactor configuration, electrolyte composition, and reporting protocols; values are included for representative benchmarking rather than direct comparison

Catalyst	Electrolyzer	Electrolyte	Partial current densities	FE (%)	Key Active motifs	Stability	Ref.
OD-Cu	Flow-cell	1 M KOH	300–700 mA cm ⁻²	80%, C ²⁺	Oxygen retention/reconstructed Cu, defect-rich OD-state	7 h	231
OD-Cu layers	MEA	0.1 M KHCO ₃	360 mA cm ⁻²	72%, C ₂ H ₄	Reconstructed OD-Cu, defect-rich/oxygen-related stabilization	> 100 h@ 500 mA cm ⁻²	232
OD-Zn dendrites	Flow-cell	2 M KHCO ₃	266 mA cm ⁻²	70%, CO	OD-Zn with high undercoordinated sites from ZnO precursor	6 h	95
OD-Zn	H-Cell	0.1 M KHCO ₃	450 mA cm ⁻²	90%, CO	ZnO-derived reconstruction towards stable high-surface-area Zn	18 h	215
OD-Ag	H-Cell	0.1 M KHCO ₃	3 mA cm ⁻²	80%, CO	OD-Ag from Ag ₂ O shifted the CO selectivity to a N/N lower overpotential		37
OD-Ag, anodic etching	H-Cell	0.1 M KHCO ₃	3 mA cm ⁻²	90%, CO	OD-Ag from an anodic etched Ag ₂ CO ₃ precursor, a robust catalyst due to high active sites concentration	100 h	233
OD-Bi clusters	MEA	0.1 M KHCO ₃	500 mA cm ⁻²	90%, Formate	Oxygen-modified Bi motifs/oxide clusters under operation	10 h	234
OD-AgZn dendrites	H-Cell	0.1 M KHCO ₃	10 mA cm ⁻²	90%, CO	High-surface-area alloy; interface-defined CO selectivity	100 h	235
OD-Au	H-Cell	0.5 M NaHCO ₃	15 A g ⁻¹	95%, CO	Grain-boundary density dependency of CO activity descriptor on Au	12 h	108
OD-Au nanoparticles	H-Cell	0.5 M NaHCO ₃	10 mA cm ⁻²	100%, CO	OD-Au surface stabilizes *CO ₂ intermediate leading to fast reaction kinetics	8 h	29
OD-Au nanoporous	H-Cell	0.5 M KHCO ₃	15 mA cm ⁻²	90%, CO	OD-Au surface adopts a high porosity structure, leading to fast reaction kinetics	12 h	93
OD-In	H-Cell	0.5 M KHCO ₃	20 mA cm ⁻²	95%, formate	The formed In–O hetero-interface promotes the catalysis rate.	12 h	224
OD-CuZn	H-Cell	0.1 M KHCO ₃	55 mA cm ⁻²	70%, C ₂ H ₄	Cu–Zn interactions in the evolved brass alloy steer selectivity	5 h	126
OD-CuSn	H-Cell	0.1 M KHCO ₃	5 mA cm ⁻²	90%, CO	Evolved OD-CuSn surface promotes the CO ₂ RR pathway over the HER.	2 h	79

across major OD-catalyst families are summarized in Table 2 to enable cross-system benchmarking.

5.1 OD-catalysts for C₂₊ product formation (Cu and Cu-based alloys).

Copper (Cu) remains the only practical monometallic electrocatalyst that can convert CO₂ to C₂₊ products at meaningful rates, and OD-Cu often increases C₂H₄/C₂₊ selectivity relative to smooth polycrystalline Cu by combining defect-rich structure, oxygen-modified electronic states, and microenvironment confinement (Fig. 4a).³⁰ Across many OD-Cu preparations (oxide films, Cu₂O/CuO-derived foams, reduced nanocubes), improvements are commonly reported as (i) higher C₂H₄/C₂₊ faradaic efficiencies (often in the ~40–60% range under optimized conditions), (ii) earlier onset and higher partial current densities for C₂ formation, and (iii) reduced apparent HER competitiveness compared with non-porous metallic Cu under similar mass-transport regimes.^{54,205,206} While absolute values depend strongly on electrolyte, pressure, cell architecture, and transport, three recurring determinants rationalize why OD-Cu performs differently from equilibrium Cu surfaces.

As shown in the work of Ligt *et al.*,²⁰⁷ a defining OD-Cu attribute is the persistence of oxygen-containing motifs (sub-surface O, interfacial Cu–O, or kinetically stabilized Cu⁺-like states) after reduction. Spectroscopic (XAS, XPS/EELS) studies showed that OD-Cu can exhibit Cu⁺ signatures under CO₂RR-

relevant cathodic potentials, even when crystalline Cu₂O is absent. Subsurface or interfacial oxygen is widely invoked as a stabilizing reservoir that enables transient Cu⁺/Cu⁰ ensembles, which can tune adsorption of *COOH and *CO and bias the surface toward CO accumulation without fully “poisoning” the surface. Mechanistically, the catalytic consequence is best framed as an ensemble effect: Cu⁺-like motifs can locally polarize adsorbates and alter the binding geometry/electronics of neighboring Cu⁰ sites, increasing the probability of generating C–C coupling-competent *CO configurations that precede *OCCO formation.¹³⁹ Oxide-derived Cu typically reconstructs into nano-crystalline, defect-rich, and nanoporous frameworks, in which grain boundaries, steps, and confined pore networks jointly promote C–C coupling. As illustrated by Wang *et al.*,²⁰⁸ High densities of under-coordinated Cu atoms at grain boundaries and defect sites stabilize *CO-rich ensembles and lower effective barriers for *CO–*CO coupling relative to terrace-dominated Cu, increasing the statistical likelihood of C–C bond formation under reaction-relevant coverages. Simultaneously, nanoporous architectures create confined microenvironments that deviate from bulk conditions, sustaining elevated local *CO activity and higher local pH under high current densities. This combination suppresses proton-driven HER and further favors C₂ pathways. Importantly, the contribution of porosity is most pronounced when it measurably alters local transport and reaction conditions, underscoring that defect topology and

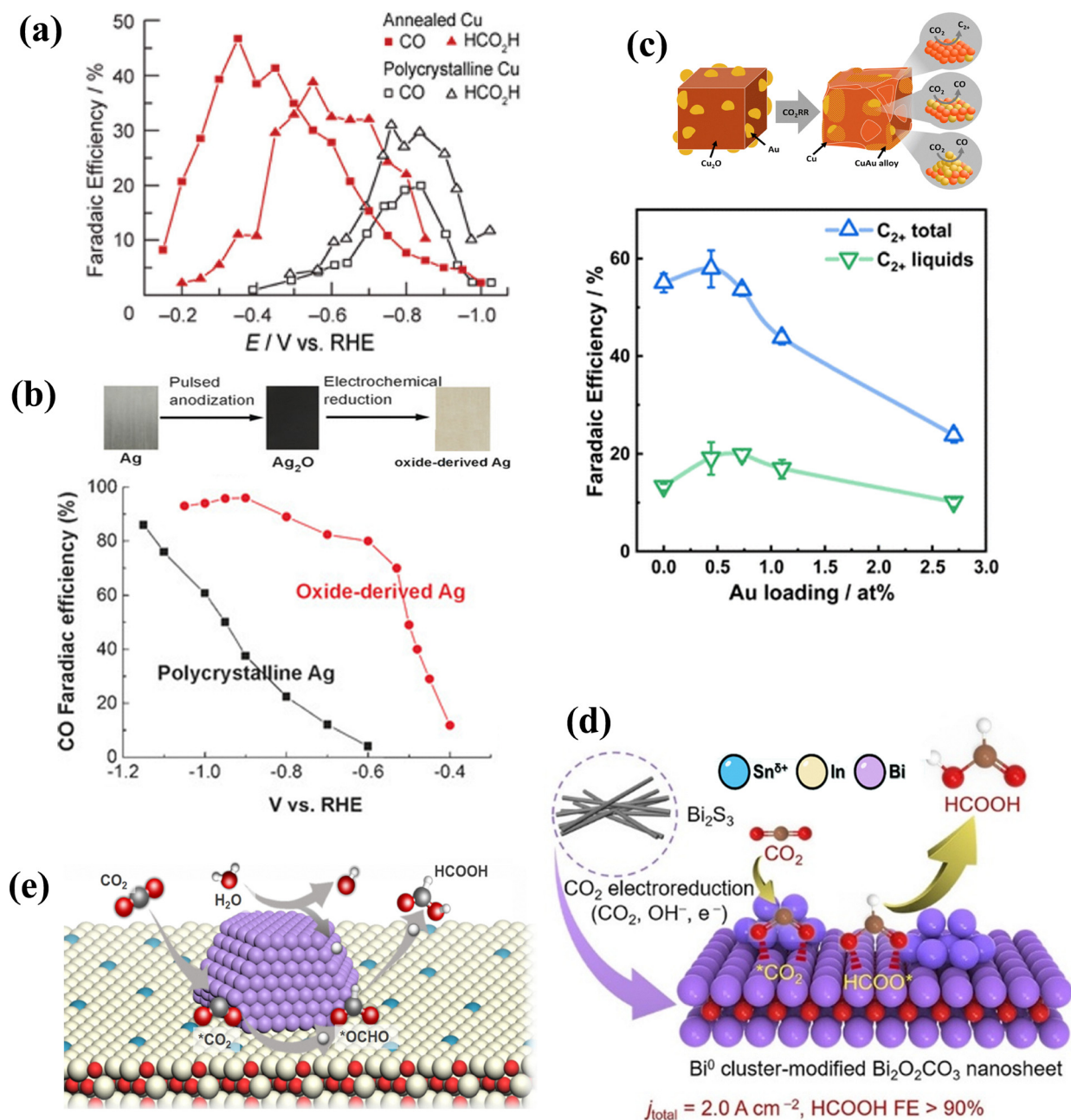


Fig. 4 Performance trends of the oxide-derived (OD) metals and alloys for the electrochemical CO₂RR. (a) Differences in the product selectivity of typical Cu-metallic and OD-Cu nanoparticles. Reproduced with permission from ref. 30, Copyright (2012), American Chemical Society (b) formation pathway of the OD-Ag and its performance metrics for the CO formation versus the typical metallic polycrystalline Ag. Reproduced with permission from ref. 37, Copyright (2016), Wiley-VCH GmbH. (c) Structural evolution of the OD-CuAu alloy during evolution and the dependence of CO₂RR selectivity on alloy composition. Reproduced with permission from ref. 211, Copyright (2024), The Royal Society of Chemistry. (d) Function of OD-SnBi catalyst towards formate and its underlying carbonate-based phases. Reproduced with permission from ref. 223, Copyright (2023), Wiley-VCH GmbH. (e) Robust function of composite OD-SnInBi towards formic acid formation. Reproduced with permission from ref. 227 Copyright (2025), American Chemical Society.

confinement act synergistically rather than independently in enhancing C_{2+} selectivity on OD-Cu.²⁰⁹

Beyond monometallic OD-Cu, oxide-derived Cu-based alloys offer a second design lever: spatially partitioned chemistry arising from asynchronous reduction and phase segregation in mixed-metal oxides. The resulting catalysts contain Cu-rich OD domains that interface with a second metal (or its oxide),

enabling tandem pathways to selectively suppress competing reactions.²¹⁰

Cu-Ag (and, analogously, Cu-Au) systems often function as tandem catalysts: Ag-rich regions favor CO production (via $*COOH$ formation and weak $*H$ binding), while Cu-rich OD regions convert CO to C_{2+} products.⁹⁹ Under conditions where CO supply limits Cu's C_{2+} productivity, placing an efficient CO-

generating phase in proximity to Cu can increase local CO availability and elevate C_{2+} rates. In OD architectures, the same defect/oxygen motifs that benefit OD-Cu can remain relevant. Still, the dominant additional benefit is intermediate channeling (CO transfer) across short diffusion lengths at heterointerfaces.^{211–213}

5.2 OD-catalysts & alloys for CO production.

OD Ag, Au, and Zn-based catalysts are among the most selective platforms for converting CO_2 to CO because OD reconstruction can stabilize the $*COOH$ (or CO_2^-) intermediate without driving excessive CO adsorption, while simultaneously maintaining weak $*H$ binding that suppresses HER. In these systems, the key structure–function motif is typically oxygen-modified, defect-rich metal (residual/interfacial O, trace Ag–O/Au–O coordination, or Zn/ZnO heterojunctions with oxygen vacancies), which perturbs local electronic structure and increases the density of catalytically relevant low-coordination sites.^{214,215}

OD-Ag is the most widely demonstrated OD benchmark for CO formation (Fig. 4b). Oxide-derived nanostructured Ag shifts CO production to substantially lower overpotential than untreated Ag while maintaining high selectivity, consistent with improved stabilization of the $*COOH$ intermediate.²¹⁶ Fiet *et al.*,⁹² showed through their *operando* XAS/EXAFS that OD-Ag can retain trace oxygen-containing coordination under reaction conditions, with oxygen content correlating with improved CO_2 -to-CO activity. At high-rate electrolysis, Ag-based electrodes (including OD-inspired nanostructured variants) routinely reach high formation rates of CO, positioning Ag as the practical reference catalyst for CO production at scale.³⁷

OD-Au exhibits analogous behavior: reduction of thick Au oxide films forms OD-Au nanoparticles that catalyze CO formation at very low overpotential while preserving Au's inherently weak $*H$ binding.²⁹ Grain-boundary-rich Au also shows a strong activity–GB correlation for CO formation, supporting the broader OD principle that defect topologies can elevate intrinsic CO_2RR activity by stabilizing early intermediates (*e.g.*, $*COOH$) without compromising CO desorption.¹⁰⁸

OD-Zn differs mechanistically in that CO selectivity often arises from a hybrid metallic–oxide steady state (Zn^0/ZnO) featuring oxygen vacancies and interfacial Zn–O motifs that favor CO_2 activation while keeping $*H$ binding weak. Studies of ZnO-derived and reconstructed Zn catalysts identify oxygen-vacancy rich ZnO motifs as key contributors to high CO selectivity and stability. Rather than requiring a fully metallic surface, OD-Zn performance is frequently associated with persistent Zn–ZnO hetero-interfaces and dynamic re-oxidation/reconstruction under operating conditions.^{134,215}

Finally, OD Cu–Ag and Cu–Au alloys connect selective CO generation to downstream chemistry through tandem catalysis: Ag/Au-rich domains generate CO efficiently, and CO is locally transferred to adjacent Cu-rich domains where it can be further reduced at more cathodic potentials (Fig. 4c).^{193,217}

The principal OD advantage in these alloys is architectural: mixed-oxide precursors reconstruct into short diffusion-length hetero-domains that enhance intermediate channeling (CO supply) while retaining the defect/oxygen-derived features

that promote high CO selectivity on the noble-metal component.

5.3 OD-catalysts for formate production (Sn, Bi, In & OD alloys)

Oxide-derived Sn, Bi, and In catalysts are among the most formate-selective CO_2RR materials because their active states commonly retain oxygen-containing motifs (sub-oxides, oxycarbonates, oxygen vacancies, and metal–oxygen coordination) that stabilize the $*OCHO$ intermediate while maintaining weak $*H$ binding and thus suppressing HER. In contrast to Cu-type OD-systems, where metallic sites dominate, formate-selective OD-catalysts frequently operate as hybrid metal/oxide ensembles in which partial reduction, interfacial oxygen, and dynamic surface re-oxidation can persist under cathodic bias and continuously regenerate the oxygen-modified active environment.^{218,219}

For OD-Sn, a consistent mechanistic picture is that SnO_x -derived surfaces (often SnO_2 with oxygen vacancies or mixed Sn^{4+}/Sn^{2+} character) preferentially stabilize $*OCHO$ (bidentate coordination through O atoms) and disfavor $*CO$ pathways, yielding high formate selectivity over broad potential windows.²²⁰ *Operando* studies and structure–function analyses show that maintaining an oxygenated SnO_x -like surface (rather than fully metallic Sn) is crucial; when SnO_2 is over-reduced to Sn^0 at very negative potentials, formate activity can decline, motivating strategies that stabilize oxygenated motifs under operating conditions.¹³⁵

OD-Bi catalysts often exhibit exceptional formate selectivity through Bi–O motifs and bismuth oxy-/sub-carbonate phases that form and persist under CO_2RR (Fig. 4e).²²¹ *Operando* Raman and studies of Dutta *et al.*,²²² directly observe carbonate incorporation and the evolution of Bi–O– CO_3 environments during reaction, consistent with $*OCHO$ stabilization and strong HER suppression. More broadly, the active state in many high-performing Bi systems is best described as a dynamically sustained, oxygen-containing Bi phase rather than purely metallic Bi.²²³ Likewise, as shown by Wulan *et al.*²²⁴ indium-oxide-derived catalysts (*e.g.*, In_2O_{3-x} and In/ In_2O_3 heterostructures) favor formate formation when oxygen vacancies and interfacial oxygen are stabilized, thereby enhancing CO_2 activation and supporting $*OCHO$ -type pathways while limiting HER. High formate selectivity and stability have been reported for oxygen-stabilized In/ In_2O_3 architectures and conductive In_2O_{3-x} composites designed to maintain an oxide-like active surface under reaction conditions.²²⁵

Recent advancements in OD multimetal Bi–Sn–Sb architectures have established a robust framework for high-rate CO_2 reduction to formate through the stabilization of oxygen-modified motifs.²²⁶ As indium-oxide systems, the same principles, regarding catalysis functionality, are extended in heterostructured Bi–Sn(In)O systems (Fig. 4d), where local charge redistribution and high-valence $Sn^{\delta+}$ species enhance $*OCHO$ adsorption, enabling integrated electrodes faradaic efficiencies (FE) for HCOOH exceeding 83%.²²⁷ For practical scalability and stable electrolysis, Wen *et al.*²²⁸ have proven the transformative integration of antimony in Bi–Sn-based alloy compositions. These architectures utilize short

diffusion-length hetero-domains to sustain industrially relevant current densities in gas diffusion electrode (GDE) configurations.²²⁹ Notably, Sb-Bi alloy films further push performance limits, with the work of Yang *et al.*²³⁰ demonstrating record activities in flow cells with current densities up to 500–734 mA cm⁻² and an exceptional 95.8% FE for formate.¹²⁹

The performance trends summarized in Table 2 reveal clear structure–function relationships across oxide-derived catalyst families. Cu-based OD-systems dominate C₂₊ formation due to their ability to sustain high *CO coverage and stabilize C–C coupling intermediates, whereas OD-Ag, OD-Au, and OD-Zn exhibit near-quantitative CO selectivity arising from optimal *COOH binding combined with weak *H adsorption. In contrast, OD-Sn, OD-Bi, and OD-In favor formate production through stabilization of the *OCHO intermediate on oxide-rich or mixed-valence surfaces.

Reported performance metrics for OD-catalysts depend strongly on reactor architecture. Gas-diffusion electrode and membrane-electrode assembly configurations enable substantially higher partial current densities and improved selectivity relative to H-cell measurements by mitigating CO₂ mass-transport limitations and stabilizing favorable interfacial environments. Many of the highest activity demonstrations for OD-Cu, OD-Ag, and OD-Sn systems have therefore been achieved in gas-fed flow cells or MEA devices, where sustained partial current densities exceeding 200–1000 mA cm⁻² have been reported. These findings highlight that intrinsic catalyst activity and reactor engineering are inseparable factors in evaluating OD-catalyst performance under application-relevant conditions.^{236–238}

6. Stability and deactivation pathways of OD metals and alloys

In practical electrochemical CO₂ conversion systems, catalyst stability is typically assessed over operational timescales ranging from tens to hundreds of hours at industrially relevant current densities (>200–500 mA cm⁻²). For OD-catalysts, maintaining performance over such durations requires preserving the metastable structural motifs that underpin catalytic function.^{239,240} Unlike conventional metallic catalysts, whose stability is primarily governed by dissolution or poisoning, OD-systems must be evaluated in terms of their ability to sustain dynamic reconstruction while retaining defect density, oxygen-modified active states, and functional hetero-interfaces.²⁴¹

6.1 Structural relaxation, coarsening, and loss of the OD framework

OD-catalysts are generated through rapid, spatially heterogeneous reduction of metal oxides, producing nanoporous architectures composed of small crystallites, high GB densities, and strained or disordered domains. These features are kinetically trapped rather than thermodynamically stable, making structural relaxation inevitable during extended CO₂RR.³⁰ In the work of Eren *et al.*,²⁰⁵ *operando* and quasi-*operando* studies

consistently show grain growth, defect annihilation, and pore collapse as dominant long-term evolution pathways.

As shown by Lee *et al.*,⁸⁵ in OD-Cu, crystallite sizes commonly increase from the initial 5–20 nm range to >50–100 nm after hours of operation at high current density, accompanied by a marked reduction in GB density and loss of interconnected porosity (Fig. 5a).^{22,121} This coarsening correlates directly with declining C₂₊ selectivity, as the stabilization of *OCCO intermediates and maintenance of high local *CO coverage depend on the persistence of low-coordination Cu sites and confined reaction environments.²⁴² Similar relaxation phenomena are observed in OD-Ag and OD-Au, though at slower rates, reflecting lower surface and lattice mobility in noble metals.^{29,92} Structural relaxation is strongly potential- and environment-dependent.²⁴³ Higher cathodic potentials are commonly associated with accelerated surface diffusion and defect relaxation, while elevated local temperatures—arising from ohmic losses and gas evolution in gas diffusion electrodes—further promote coarsening.²⁴⁴ Together, these effects define a practical “meta-stability window” in which OD frameworks retain sufficient defect density and porosity to sustain enhanced catalytic performance. Outside this window, OD-catalysts progressively evolve toward morphologies and electronic structures resembling conventional polycrystalline metals, resulting in performance decay even in the absence of chemical degradation or dissolution.⁹⁹

6.2 Loss of subsurface oxygen and degradation of mixed valence state

Residual oxygen and mixed-valence metal states are central to the catalytic function of OD-materials, yet they are among the most vulnerable non-equilibrium features. Subsurface O²⁻, metal–oxygen clusters, and partially oxidized cations (*e.g.*, Cu⁺/Cu⁰, Sn⁴⁺/Sn²⁺, Bi³⁺) modify local electronic structure by perturbing d-band centers and stabilizing key intermediates such as *COOH and *OCHO, while introducing electronic asymmetry that facilitates multi-electron pathways.^{118,146,205,209} These oxygen-modified ensembles underpin the enhanced selectivity of OD-catalysts relative to fully metallic surfaces. Under sustained cathodic polarization, however, these motifs progressively decay. Strongly reducing potentials drive out-diffusion and consumption of subsurface oxygen, while mixed-valence states collapse toward the metallic phase.¹⁴⁶ *Operando* XAS studies of Yue *et al.*¹⁷⁶ on OD-Cu show that catalysts initially containing substantial Cu⁺ fractions (≈20–40%) evolve toward predominantly Cu⁰ during prolonged CO₂RR, accompanied by reduced *CO coverage and a shift in selectivity from C₂₊ products toward CO and H₂. As similar degradation behavior was also reported by Tian *et al.*,²⁴⁵ for Bi-based electrodes. This behavior reflects the gradual erasure of oxygen-stabilized Cu⁺/Cu⁰ ensembles that favor C–C coupling.²⁴⁶

For formate-selective OD-systems, oxidation-state loss has an even more immediate impact. In OD-Sn and OD-Bi, partially oxidized SnO_x and BiO_x motifs are required to stabilize the *OCHO intermediate *via* bidentate and electrostatic interactions (Fig. 5b).²⁴⁵ Ko *et al.*,²¹⁹ through their *operando* spectroscopic

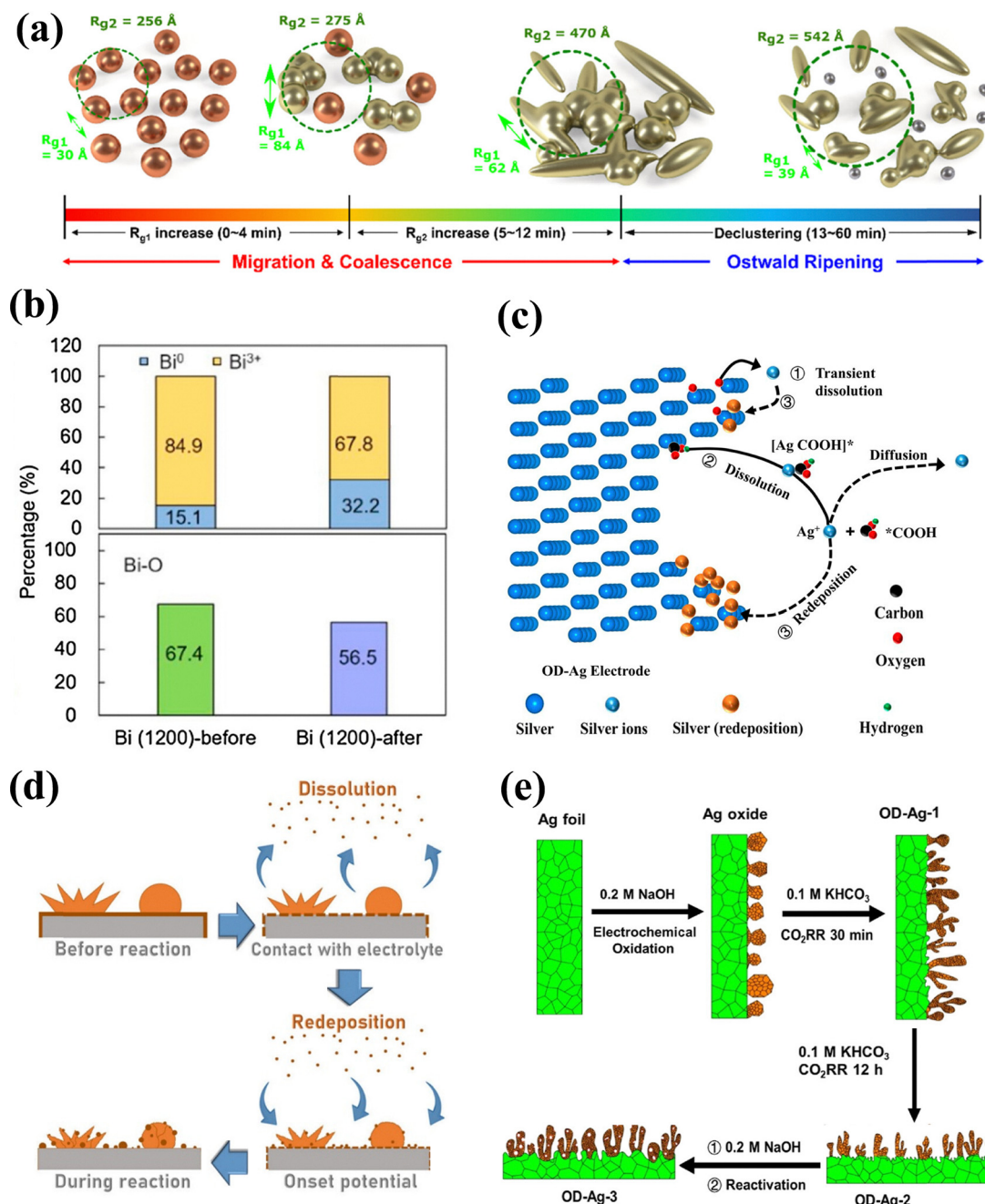


Fig. 5 Deactivation phenomena of OD metals and alloys during the electrochemical CO_2RR , due to structural and physicochemical changes of the active catalyst materials. (a) Structural transformation of Cu-catalysts during electrolysis. Reproduced with permission from ref. 85, Copyright (2025), American Chemical Society. (b) Proportion of Bi^0 , Bi^+ , and $Bi-O$ with XPS analysis of OD-Bi catalysts before and after electrolysis. Reproduced with permission from ref. 245, Copyright (2021), Elsevier. (c) Degradation mechanism of OD-Ag in long-term electrolysis. Reproduced with permission from ref. 147, Copyright (2024), American Chemical Society. (d) Degradation mechanism of OD-Cu in long-term electrolysis. Reproduced with permission from ref. 264, Copyright (2025), American Chemical Society. (e) Schematic representation of the structural evolution of OD-Ag during electrolysis and its reactivation for prolonged catalysis. Reproduced with permission from ref. 147, Copyright (2024), American Chemical Society.

studies, showed that when these sites are reduced to metallic Sn or Bi, *OCHO binding weakens, HER competitiveness increases, and formate selectivity drops sharply. Sustained formate production, therefore, relies on maintaining a hybrid metal/oxide active state rather than a fully reduced surface. In some OD-catalysts, dynamic redox cycling—enabled by local pH gradients, adsorbate-induced oxidation, or kinetically hindered oxygen removal—can

partially regenerate oxygen-containing motifs during operation, producing a quasi-steady active state.²⁴⁷ However, this balance is highly sensitive to potential, electrolyte composition, and mass-transport conditions. Once oxygen loss outpaces regeneration, the catalyst undergoes irreversible loss of “oxide memory”, converging toward a metallic surface with fundamentally different adsorption energetics and reaction pathways.²⁴⁸ This loss of oxide

memory constitutes a distinct deactivation mechanism in OD-catalysts, separate from coarsening or dissolution, and directly undermines the structure–function relationships responsible for their enhanced performance.²⁴⁹

6.3 Dissolution, leaching, and composition drift

Dissolution is a critical deactivation pathway for OD-catalysts, arising from their high density of under-coordinated atoms, defect-stabilized oxidized species, and non-equilibrium surface states. These motifs, while central to OD catalytic performance, are thermodynamically susceptible to solvation and complexation under electrochemical conditions,¹⁴⁷ leading to the selective removal of the most active sites (Fig. 5c).²⁵⁰

In OD-Cu, dissolution proceeds predominantly through Cu⁺ stabilization by carbonate and bicarbonate species, forming soluble Cu(I) complexes even under mildly cathodic CO₂RR conditions.²⁵¹ *Operando* and post-mortem analyses of Ais *et al.*,⁶⁷ show that dissolution preferentially targets oxygen-stabilized Cu sites at defect regions, progressively eroding motifs responsible for enhanced C–C coupling and contributing to long-term losses in C₂₊ selectivity.^{170,252} In OD Cu–Zn systems, dissolution is strongly element-selective: Zn—particularly when present as ZnO or Zn–O–Cu interfacial motifs—leaches preferentially due to its higher solubility and tendency to form hydroxide or carbonate complexes.^{17,253} The loss of Zn-derived motifs removes HER-suppressing and *COOH-stabilizing sites, driving composition drift and diminishing the synergistic behavior that distinguishes OD Cu–Zn catalysts from monometallic Cu.²⁵⁴ In OD Cu–Sn, Sn present as SnO_x or mixed Sn²⁺/Sn⁴⁺ states can dissolve or migrate under cathodic bias, disrupting the dual-site architecture in which Sn–O motifs stabilize *OCHO while adjacent Cu sites mediate *CO chemistry.^{114,255,256} Loss or redistribution of Sn breaks this synergy, reducing formate selectivity and increasing competition from HER or CO pathways.²⁵⁷ For OD CuAg (and CuAu) alloys, dissolution-driven degradation often manifests as surface segregation and enrichment rather than bulk material loss.²⁵⁸ Preferential Cu dissolution or migration leaves Ag-rich surfaces that retain high CO selectivity but no longer support efficient CO spillover or C–C coupling on Cu, effectively reversing the tandem mechanism that initially enhanced C₂₊ formation.^{98,259}

Overall, dissolution and leaching in OD-catalysts drive composition drift and irreversible loss of oxygen-modified and interfacial active ensembles, collapsing the OD-specific electronic structure even in the absence of catastrophic corrosion. As such, dissolution must be considered alongside structural relaxation and oxidation-state evolution as a central determinant of catalyst lifetime.⁹⁷

6.4 Electrochemical and electrolyte-driven dynamic transformations

OD-catalysts operate within a narrow dynamic balance between reduction, re-oxidation, and surface reorganization. While sustained cathodic bias generally promotes loss of oxidized motifs, electrolyte composition, potential fluctuations, and local mass-

transport limitations can induce partial or excessive re-oxidation, fundamentally reshaping the OD active state.^{260,261}

In OD-Cu, controlled partial re-oxidation can transiently regenerate Cu⁺ species and restore C–C coupling activity; however, uncontrolled re-oxidation leads to the formation of thick or amorphous Cu₂O layers with slow reduction kinetics, suppressing C₂₊ selectivity.²⁶² While the studies of Lian *et al.*,²⁶³ further showed that Cu₂O can re-form even at strongly negative potentials (Fig. 5d), driven by oxygen generated during CO₂ activation or retained within confined pore networks when oxygen removal cannot keep pace.²⁶⁴ Analogous sensitivity is observed in OD-Sn and OD-Bi systems, where catalytic performance depends on maintaining a finely balanced population of mixed-valence metal–oxygen motifs.^{222,265} Excessive re-oxidation disrupts this balance, driving the surface toward inactive or HER-competitive phases. These transformations are strongly electrolyte-dependent: bicarbonate buffers can stabilize oxidized motifs but also accelerate carbonate-mediated dissolution; chloride promotes pitting corrosion and uncontrolled oxide growth; and alkali cations modulate surface charge, oxygen mobility, and redox kinetics.^{266–268} Collectively, as also illustrated by Magnussen *et al.*,²⁶⁹ these effects underscore that OD-catalysts are not static materials, but electrochemically adaptive systems whose active ensembles continuously evolve in response to local chemical and electrical environments.

Beyond oxidation-state changes, OD-catalysts undergo pronounced morphological and compositional reorganization due to their defect-rich microstructures.²⁷⁰ *Operando* microscopy reveals surface re-orientation of the facets, grain-boundary migration, and step-edge redistribution in OD-Cu during prolonged operation, altering the density and geometry of *CO and *OCCO binding sites.¹⁵³ In OD alloys, these dynamics are amplified: Zn migrates in OD-Cu–Zn in response to local pH gradients,¹²⁶ Sn redistributes in OD-Cu–Sn disrupting dual-site architectures, and Ag segregates to the surface in OD-Cu–Ag systems, progressively flattening tandem catalytic interfaces. Such reorganizations follow gradients in surface energy, adsorbate coverage, and local electric fields, often driving the catalyst toward morphologies and electronic structures resembling equilibrium polycrystalline metals (Fig. 5e).^{89,98,271}

6.5 Mechanical stress, gas evolution, and adaptive regeneration at high rates

At industrially relevant current densities (> 300–500 mA cm^{−2}), gas evolution introduces a second, equally critical axis of OD-catalyst degradation. Rapid generation of CO, H₂, and hydrocarbons produces mechanical stress through bubble nucleation, growth, and detachment, which can fracture fragile nanoporous frameworks, collapse pore networks, and accelerate detachment of catalyst grains or films.²⁷² These effects are particularly severe in OD materials, where interconnected pores trap gas and sustain extreme local pressure and pH gradients.²⁷³ Baumgartner *et al.*,²⁷⁴ illustrated that within bubble-affected regions, localized alkalinity and electrolyte depletion promote secondary degradation pathways, including enhanced dissolution, carbonate precipitation, and uncontrolled re-oxidation. In OD-Cu gas-diffusion electrodes,

gas-driven mechanical stress is now recognized as a dominant contributor to long-term performance decay, and similar mechanical–chemical coupling accelerates coarsening and active-site loss in OD-Sn and OD-Bi catalysts operated in MEA architectures.^{275–278}

Despite these vulnerabilities, OD-catalysts possess a unique capacity for adaptive regeneration due to their intrinsic redox flexibility. Periodic oxidative pulses, brief potential relaxations, or controlled anodic cycling can reintroduce subsurface oxygen, regenerate mixed-valence motifs, and partially restore defect-rich microstructures.^{279,280} For the case of OD-Cu, Han *et al.*²⁸¹ showed that it can recover Cu⁺ content and porosity following re-oxidation/re-reduction cycles, regaining C₂₊ selectivity lost to coarsening; similar regeneration has been reported for OD-Ag¹⁴⁷ and OD-Bi systems.^{92,186,218} Unlike fully metallic catalysts, OD materials therefore offer a pathway toward redox-assisted self-healing, suggesting that long-term stability may be achieved not by suppressing dynamics, but by engineering electrolysis protocols that deliberately harness and control them.^{243,282}

7. Extension of OD-catalyst principles to other electrochemical and thermal reactions

Although OD metals and alloys were first systematized for CO₂ electroreduction, the physicochemical principles that define their behavior—non-equilibrium reconstruction, defect enrichment, subsurface oxygen retention, mixed-valence metal states, and dynamic redox responsiveness—are broadly applicable across electrochemical and thermal catalysis. Similar OD-like motifs have been identified in reactions such as nitrate and nitrite reduction, CO reduction, oxygen evolution, and thermal processes including CO oxidation, RWGS, and methanol synthesis, where residual oxygen, metal-oxide interfaces, and metastable structures govern activity and selectivity. Viewed collectively, OD-catalysts represent a general class of metastable materials in which redox-driven restructuring and oxygen-mediated electronic tuning are deliberately exploited to access catalytic states unattainable by equilibrium synthesis.^{154,283,284}

7.1 Nitrate and nitrite reduction: defect-mediated activation and oxygen memory

Electrochemical nitrate and nitrite reduction (NO₃RR/NO₂RR) shares key mechanistic features with CO₂ electroreduction, notably the need to mediate multi-electron proton-coupled transfer steps and to stabilize partially reduced, oxygenated intermediates without inducing site poisoning.²⁸⁵ In the work of Wu *et al.*,²⁸⁶ OD-Cu has emerged as one of the most effective catalyst platforms for selective nitrate-to-ammonia conversion, demonstrating NH₃ selectivity exceeding 90%. Cu₂O- or CuO-derived Cu catalysts consistently exhibit substantially higher NH₃ faradaic efficiency and lower onset potentials than metallic Cu. These performance enhancements correlate with the persistence of residual lattice oxygen, Cu⁺ domains, and defect-rich microstructures, which collectively modulate adsorption energetics for

*NO₃[−], *NO₂[−], and *NO intermediates while suppressing competitive hydrogen evolution.^{285,287}

Mechanistically, NO₃RR on OD-Cu proceeds through strongly adsorbed *NO₂[−] and *NO species that require a delicate balance between stabilization and timely conversion.²⁸⁸ *Operando* and theoretical studies show that subsurface oxygen, local strain, and under-coordinated Cu sites in oxide-derived architectures weaken excessively strong *NO₂[−] binding that would otherwise lead to surface poisoning on metallic Cu, while still enabling efficient N–O bond cleavage and subsequent hydrogenation steps toward NH₃ (Fig. 6a and b).²⁸⁹ Grain boundaries, step edges, and amorphous-crystalline interfaces further act as high-density reaction centers for *NO and *NOH, accelerating proton-coupled electron transfer and reducing nitrite accumulation. These structure-function relationships closely parallel those observed in CO₂RR, where OD motifs stabilize *COOH and *OCCO while avoiding overly binding—underscoring the generality of OD design principles across oxygenated reaction networks.²⁹⁰

In the same content, catalyst stability in NO₃RR is governed by many of the same processes as in CO₂RR, but with additional challenges arising from the strongly binding nitrogen–oxygen intermediates.²⁹¹ While OD-Cu's oxygen-modified electronic structure mitigates *NO₂[−] and *NO poisoning relative to metallic Cu, prolonged operation can still lead to Cu⁺ → Cu⁰ reduction, defect annihilation, and grain coarsening, resulting in declining NH₃ selectivity and increased formation of N₂ or H₂.²⁹² In more complex OD-Cu systems derived from layered oxides or metal-organic frameworks, Cu dissolution and loss of Cu₂O-rich domains can further degrade long-term performance.²⁹³ Stabilization strategies such as alloying, support anchoring, and self-supported Cu/Cu₂O frameworks have been shown to retard coarsening and dissolution, enabling sustained nitrate-to-ammonia conversion over extended electrolysis periods.^{294,295}

7.2 Carbon monoxide reduction: C–C coupling in a simplified landscape

Electrochemical carbon monoxide reduction (CORR) provides a direct probe of the intrinsic C–C coupling capability of OD-catalysts by decoupling multicarbon formation from CO₂ activation.²⁹⁶ Under direct CO feed, OD-Cu nanoparticles, nanowires, and nano-crystalline films consistently deliver higher ethylene and oxygenate yields than polycrystalline Cu at comparable potentials, demonstrating that enhanced C₂₊ formation arises from the reconstructed OD framework rather than from CO₂ activation chemistry.²⁹⁷ With the mechanistic origins of this behavior, overall mirroring those identified in CO₂RR. As illustrated by Zhan *et al.*,²⁹⁸ subsurface oxygen and Cu^{+/Cu⁰} mixed-valence ensembles tune *CO adsorption into an optimal regime, enabling high surface coverage without, while grain boundaries, twin boundaries, and under-coordinated Cu sites preferentially stabilize *OCCO and related dimeric intermediates, lowering the kinetic barrier for C–C bond formation. Oxide-derived alloy catalysts further extend these principles. OD Cu–Ag and Cu–Au systems (Fig. 6c) derived from mixed oxides or layered precursors exhibit spatially differentiated active sites: noble-metal-rich domains weakly bind or generate *CO-like intermediates at low

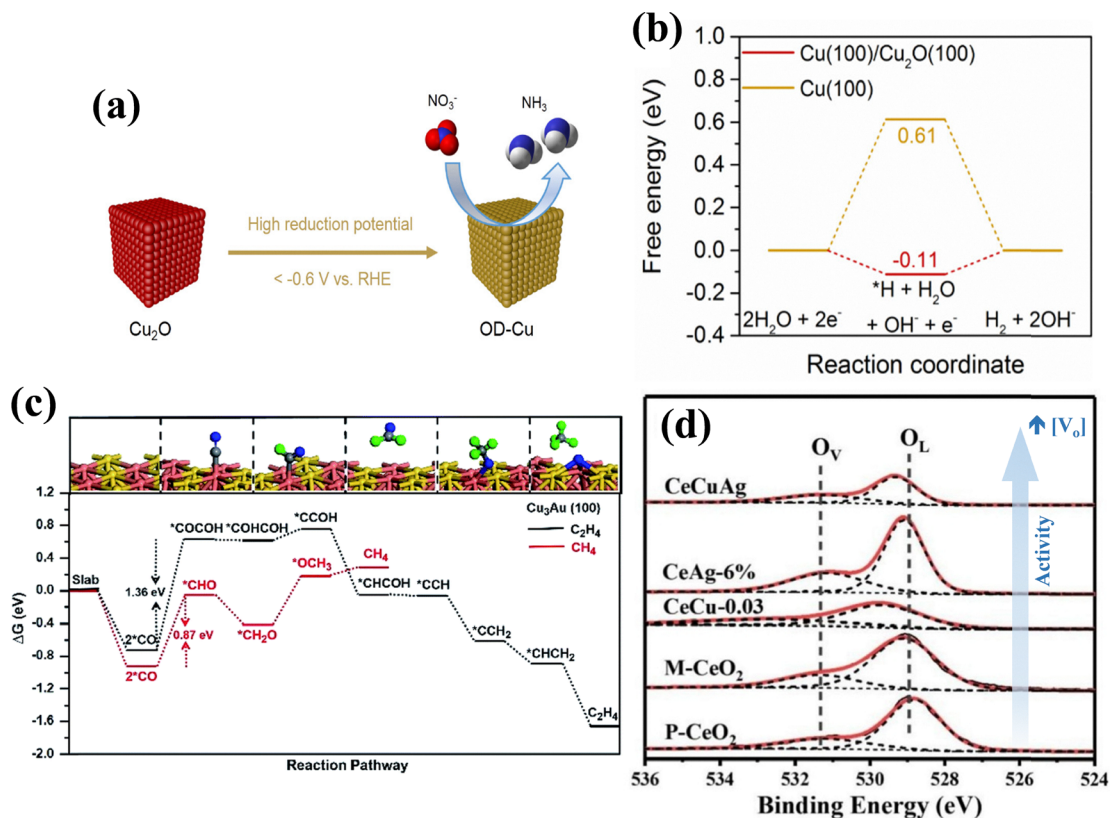


Fig. 6 Characteristics and function of OD metals and alloys for different electrochemical and thermochemical catalytic reactions. (a) Schematic representation of the function of OD-Cu for the electrochemical reduction of nitrate to ammonia, (b) free energy diagrams of the suppressed HER pathway over OD-Cu. Reproduced with permission from ref. 322, Copyright (2023), American Chemical Society. (c) OD-CuAu alloy for the electrochemical reduction of CO to CH₄. Reproduced with permission from ref. 299, Copyright (2021), The Royal Society of Chemistry. (d) Oxygen vacancy concentration (V_O) as a result of synergistic Cu-Ag effects on a composite CuAgCe alloy, for the thermochemical CO oxidation. Reproduced with permission from ref. 312, Copyright (2025), Elsevier.

overpotential, while adjacent Cu-rich OD regions efficiently convert $^*\text{CO}$ into C₂₊ products. The persistence of tandem-like behavior under CORR confirms that engineered hetero-interfaces and residual oxygen are sufficient to sustain multi-carbon pathways.^{99,299}

The stability of OD-catalysts under CORR is generally higher than under CO₂RR due to reduced carbonate formation and smaller pH gradients, but OD-specific degradation modes remain. Loss of Cu⁺, grain coarsening, and compositional drift—such as Ag or Au surface segregation—gradually erode C₂₊ selectivity, shifting products toward CO and H₂.³⁰⁰ Nonetheless, controlled redox pretreatments or periodic oxidative pulses, as shown by Casebolt *et al.*,³⁰¹ can partially regenerate subsurface oxygen and defect-rich microstructures, offering viable routes to maintain CORR performance during prolonged operation.³⁰²

7.3 Oxygen evolution reaction: lattice oxygen redox and OD behavior at the anode

Although OD-catalysts are most often used in cathodic reactions, the oxygen evolution reaction (OER) provides a well-established anodic analogue in which OD-like behavior is central to catalytic function.³⁰³ In NiFe and Fe-containing

oxyhydroxides, Co-oxides, and related systems, high OER activity arises from *in situ* reconstruction into metastable, defect-rich phases governed by dynamic metal-oxygen redox and lattice oxygen participation. *Operando* studies of Bai *et al.*,³⁰⁴ showed that NiFe LDHs and Ni(OH)₂ precursors oxidize under OER conditions to form highly disordered γ-NiOOH-like phases, with Fe incorporation and Ni³⁺/Ni⁴⁺ redox strongly enhancing activity—closely paralleling OD reconstruction from oxide precursors under cathodic bias. Additional mechanistic insights, provided by Strasser *et al.*,³⁰⁵ indicated that the OER on these catalysts proceeds through lattice-oxygen-mediated pathways, where oxygen vacancies, cation disorder, and strong metal-oxygen covalence lower the energy barrier for O-O bond formation. Mixed-valence metal centers cooperate with labile lattice oxygen to form transient M-OOH or M-OO-M intermediates, mirroring the role of subsurface oxygen and mixed-valence ensembles in OD-Cu during CO₂RR. In both cases, catalytic performance is dictated by non-equilibrium surface states rather than by stoichiometric bulk phases. While reductively prepared OD metals (*e.g.*, OD-Cu) are thermodynamically incompatible with OER conditions and re-oxidize under anodic bias, the design principles underlying OD behavior are fully transferable.³⁰⁶ Such approaches, involving oxygen vacancy

engineering, mixed-valence stabilization, metal–oxygen covalence tuning, and controlled reconstruction, underpin the performance of state-of-the-art OER catalysts. The NiFe (oxy)hydroxide system—now the benchmark for alkaline water electrolyzers—exemplifies this paradigm, operating in a continuously reconstructed, non-equilibrium γ -NiOOH phase stabilized by Fe.^{307,308}

7.4 Thermal catalysis: OD principles in CO oxidation, RWGS, and methanol synthesis

Many principles now associated with OD electrocatalysts have long underpinned heterogeneous thermal catalysis.²⁸⁴ Classical systems such as Cu/ZnO-based catalysts for methanol synthesis and RWGS, as well as defective metal oxides used for CO oxidation, rely on partially reduced oxides, defect-rich metal–oxide interfaces, mixed-valence cations, and dynamic redox behavior to achieve high activity and selectivity.³⁰⁹ In CO oxidation, partially reduced CuO_x and AgO_x catalysts often outperform metallic surfaces because oxygen vacancies and sub-stoichiometric oxide phases enable O₂ activation and lattice-oxygen participation through Mars–van Krevelen-type mechanisms (Fig. 6d).^{310–313} Such oxygen-defect networks closely resemble OD electrocatalysts that exploit subsurface oxygen and dynamic reconstruction to activate CO₂ or NO₃[−].³¹⁴

The clearest thermal analogue to OD behavior is found in Cu/ZnO/Al₂O₃ catalysts for methanol synthesis and RWGS, where decades of work identify Cu–Zn interfacial sites as the true active phase.^{315,316} Under reaction conditions, ZnO partially reduces and migrates onto Cu nanoparticles, forming oxygen-deficient Cu⁰-O-Zn^{δ+} motifs that stabilize CO₂/CO-derived intermediates (formate, methoxy) while Cu activates H₂.^{317,318} This interfacial synergy mirrors that of OD Cu–Zn electrocatalysts in CO₂RR, where Cu-rich metallic frameworks decorated with Zn–O clusters tune *COOH binding and suppress HER.^{319,320} Functionally, OD-like thermal catalysts operate through metastable, oxygen-deficient interfaces, rather than ideal metallic or stoichiometric oxide surfaces. Stability is governed by sintering, loss of oxygen vacancies, phase separation, and over-reduction—processes directly analogous to the degradation of OD electrocatalysts.^{317,319} Accordingly, modern thermal-catalyst strategies, as exhibited by Barrow *et al.*,³²¹ including defect engineering, interface confinement, and controlled redox cycling, are essentially thermal implementations of OD design principles, aimed at preserving a non-equilibrium active state over long operation.

8. Design principles and predictive framework for OD-catalysts

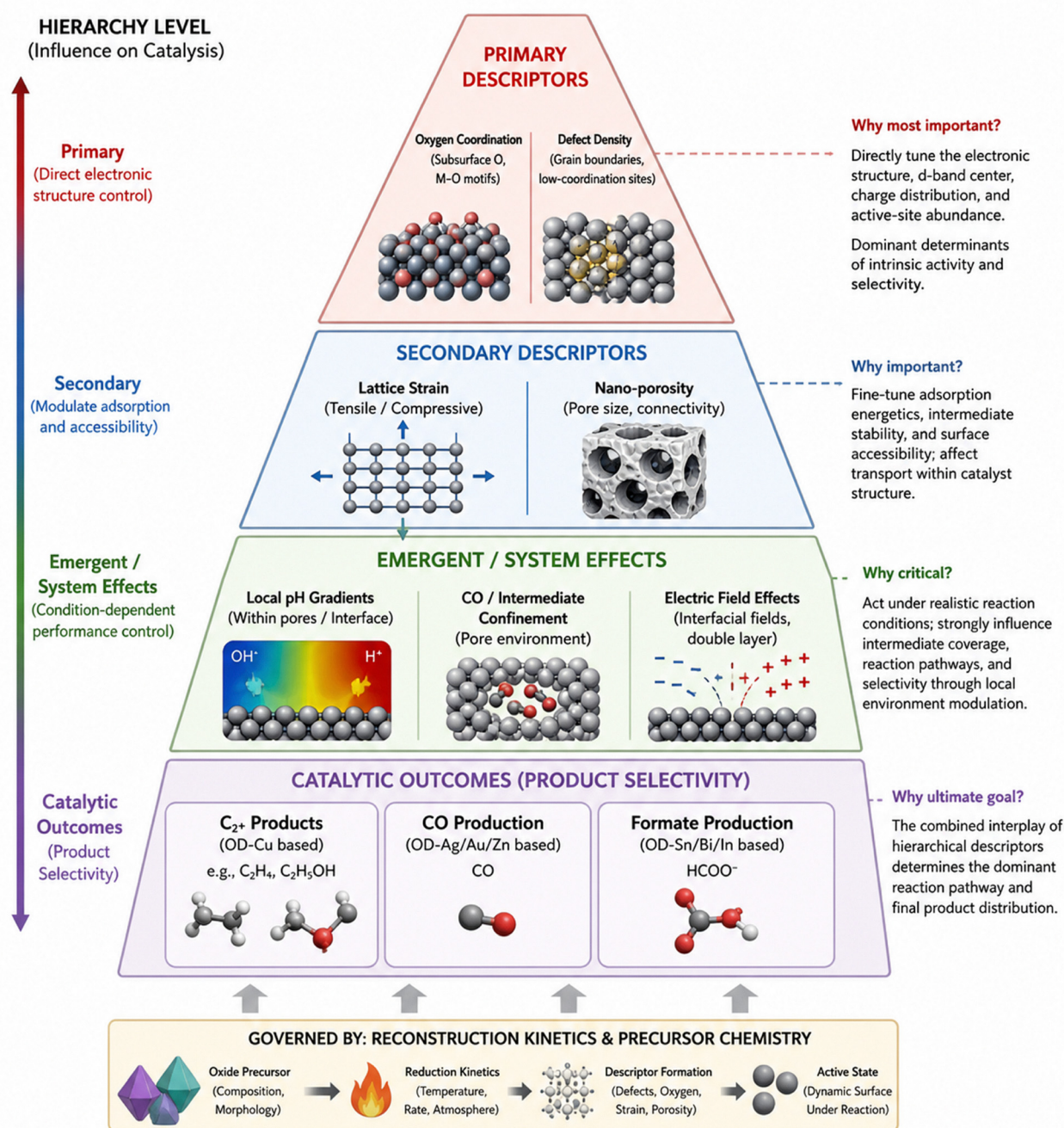
The catalytic behavior of OD metals and alloys arises not from composition alone, but from dynamically evolving, reconstruction-defined active states generated during oxidation, reduction, and operation. Subsurface oxygen, defect-rich nanostructures, lattice strain, nano-confinement, and hetero-interfaces collectively define the non-equilibrium catalytic identity of OD-systems.^{321,323} Unlike conventional catalysts governed primarily by equilibrium surface energetics, OD-catalysts operate through coupled descriptor

networks whose relative importance depends strongly on catalyst composition, reaction pathway, and operating conditions. Consequently, rational OD-catalyst design requires coordinated control over precursor chemistry, reconstruction kinetics, oxygen retention, defect generation, interfacial architecture, electrolyte environment, and *operando* stabilization strategies that sustain favorable metastable states.^{295,324}

8.1 Hierarchical descriptor framework

Across OD-systems based on Cu, Ag, Au, Zn, Sn, Bi (and multimetal variants), a consistent picture has emerged: OD performance is governed less by equilibrium composition than by reconstruction-generated, non-equilibrium motifs created during oxide-to-metal conversion and maintained (often dynamically) under bias.^{84,147,325} As shown by Wang *et al.*,³⁸ recurrently observed signatures include (i) retained subsurface/interfacial oxygen and oxygen-vacancy networks, (ii) nano-crystallinity with high defect densities (GBs & twin boundaries), (iii) local lattice strain and disorder, (iv) mixed-valence metal populations (Mⁿ⁺/M⁰) in near-surface regions, and (v) dynamic metal-oxide/metal-oxide-metal interphases.³²⁶ These motifs are not inferred solely from *ex situ* characterization: they are repeatedly reported using *operando* or quasi-*operando* approaches, particularly in OD-Cu and increasingly in OD noble metals and p-block OD-catalysts.¹¹⁸ Functionally, OD-catalysts behave as spatially heterogeneous active-site ensembles that can decouple adsorption trends constrained on ideal terraces. In Cu-based OD materials, subsurface oxygen and Cu^{δ+} environments have been directly evidenced under reducing bias. They are widely discussed as contributors to altered *CO/*COOH handling, while grain boundaries and defect-rich regions are repeatedly implicated as preferred loci for C–C coupling *via* *OCCO-type intermediates.^{38,174} To transition from descriptive correlations toward predictive catalyst engineering, these reconstruction-derived features can be organized into a hierarchical descriptor framework (Scheme 1). Within this framework, oxygen coordination and defect density emerge as primary descriptors because they directly govern electronic structure, active-site distribution, and intermediate stabilization. Secondary descriptors—including lattice strain and nano-porosity—modulate adsorption energetics, accessibility, and confinement behavior, while emergent system-level descriptors such as local pH gradients, ion transport, and intermediate accumulation become increasingly dominant under high-rate operation. Importantly, the relative influence of these descriptors is catalyst- and condition-dependent, rather than universally beneficial across all OD-systems.

For CO-selective noble-metal systems, GB density is now firmly established as a primary activity descriptor on Au, and OD/defect-engineered Ag surfaces show analogous structure-activity correlations during CO₂RR.^{103,327–329} For formate-selective p-block systems, *operando* studies of SnO₂-derived catalysts and Bi-based pre-catalysts consistently show persistent oxide/oxy motifs and reconstruction-dependent active states, supporting the broader OD theme that oxygen-containing environments can remain catalytically consequential under cathodic operation. Crucially, these OD-signatures are emergent outcomes of precursor-defined reconstruction pathways, not intrinsic properties of the metal



Scheme 1 Rational design framework, stemming from descriptor hierarchy governing catalytic function in oxide-derived (OD) metals and alloys. Primary descriptors—oxygen coordination (subsurface oxygen, metal-oxygen motifs) and defect density (grain boundaries, low-coordination sites)—define the electronic structure and active-site distribution of OD-catalysts. Secondary descriptors, including lattice strain and nano-porosity, emerge from reconstruction kinetics and modulate adsorption energetics and surface accessibility.

alone.^{330–334} *Operando* tracking studies of Zhu *et al.*,³³⁵ of precursor conversion in Cu oxides, show that reduction proceeds through spatially heterogeneous nucleation and coalescence, with concurrent defect generation, and that strain and residual oxygen depend sensitively on the oxide phase, crystallinity, and activation protocol.³³⁶ Accordingly, “precursor engineering” is a primary OD design lever: defect-rich or structurally heterogeneous oxides (mixed phases, partially amorphous frameworks,³³⁷ porous gels,

MOF-derived oxides^{104,338}) tend to reduce *via* percolative nucleation into highly nano-crystalline, grain-boundary-rich networks, whereas defect-poor crystalline oxides more often evolve toward smoother, less OD-like metallic films.^{26,339}

Mixed and doped oxides provide a potent route to programmed non-equilibrium.^{340–342} In Cu-CeO₂ systems, multiple studies support that Ce redox chemistry and oxygen-vacancy buffering at Cu-CeO₂ interfaces can stabilize oxidized Cu^{δ+}-like

states and oxygen-defective interphases that correlate with improved CO₂RR selectivity (Fig. 7a).^{343,344} Similarly, as shown by Go *et al.*,²⁵⁵ heterovalent dopants (*e.g.*, Sn in CuO_x) and vacancy engineering measurably alter oxide–metal transition kinetics, biasing the reconstructed surface toward oxygen-modified states and distinct selectivity regimes.^{345,346} Likewise, in similar multimetal OD-catalysts (*e.g.*, Cu–Zn and Cu–Sn), *operando* studies show that asynchronous reduction and interfacial evolution are common, reinforcing that OD “alloy” behavior is frequently reconstruction-defined heterogeneity rather than a homogeneous equilibrium alloy surface.^{77,155,347,348}

A practical design rule follows: OD-catalysts are best created from oxides intentionally engineered for controlled redox and

structural heterogeneity, such that reduction yields dense defect/interphase networks, while retaining some oxygen-binding character—without forming insulating oxide residue or rapidly relaxing to equilibrium metal morphologies.^{251,349} The core objective is not to eliminate reconstruction, but to steer reconstruction toward a reproducible, sustainable non-equilibrium active ensemble whose regeneration kinetics can compete with defect annihilation and oxygen depletion under operating conditions.³⁵⁰

8.2 Descriptor prioritization across OD-catalyst classes

A key conclusion emerging from the preceding sections is that different OD-catalyst classes are governed by distinct dominant descriptors and mechanistic limitations. Consequently,

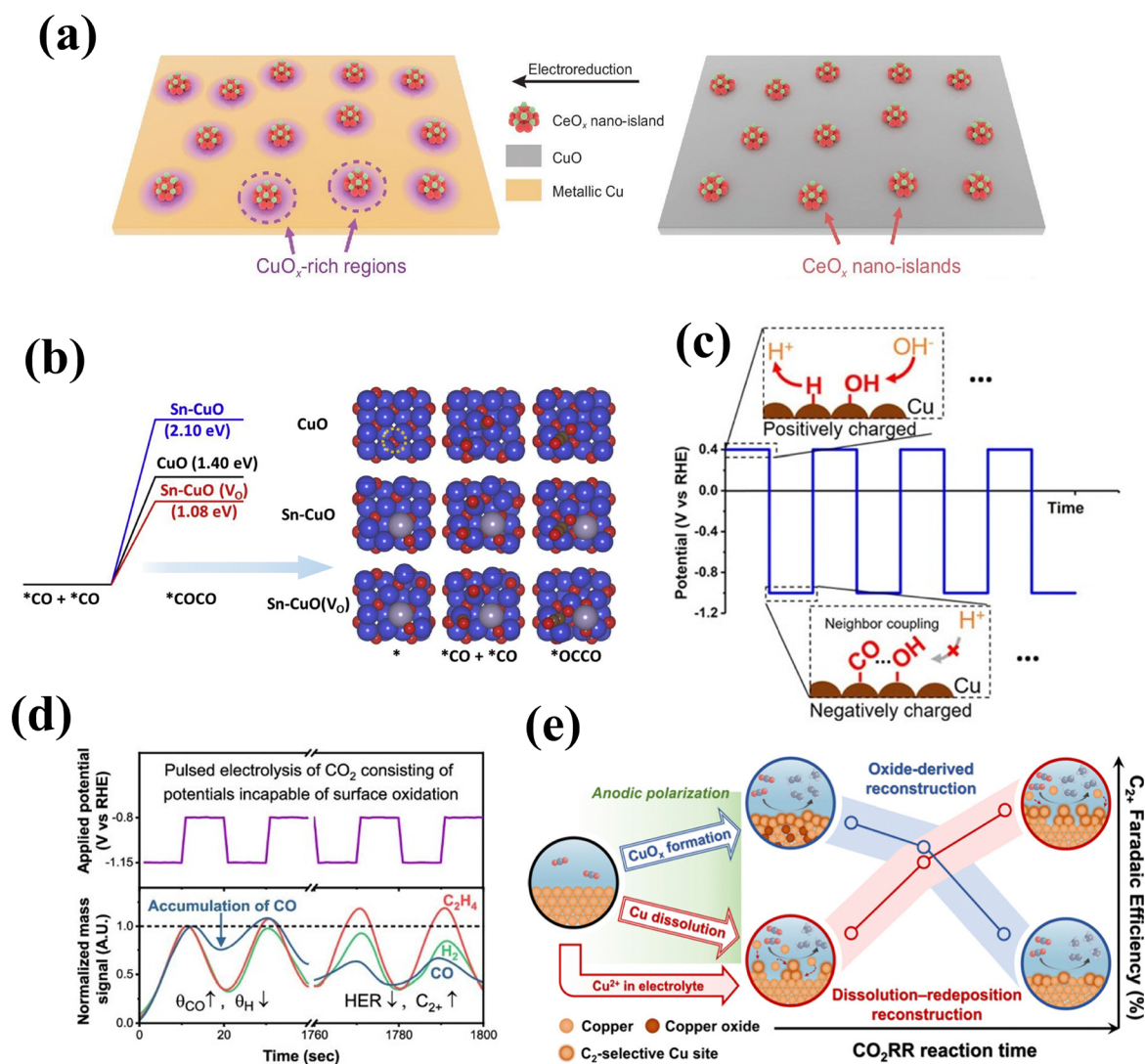


Fig. 7 Performance-determining characteristics and operational strategies of oxide-derived (OD) catalysts for prolonged electrolysis. (a) Allocation of oxygen vacancies (V_O) and active reaction sites over the surface of a composite OD-Cu/CeO_x catalyst. Reproduced with permission from ref. 343, Copyright (2025), Oxford University Press. (b) Free energy diagrams for the *COCO formation of an OD-CuSn catalyst, as a function of its oxygen vacancies (V_O) amount. Reproduced with permission from ref. 356, Copyright (2021), Elsevier. (c) Schematic representation of the reactive species during anodic and cathodic pulse electrolysis, over OD-Cu catalyst. Reproduced with permission from ref. 371, Copyright (2020), American Chemical Society. (d) Real-time monitoring of the CO₂RR during pulsed electrolysis over an OD-Cu catalyst. Reproduced with permission from ref. 372, Copyright (2020), American Chemical Society. (e) Dynamic phases and structural alterations over Cu-based catalysts, as a result of applied polarization during electrolysis. Reproduced with permission from ref. 381, Copyright (2026), American Chemical Society.

generalized optimization strategies are insufficient, and OD-catalyst design must instead follow reaction-specific descriptor prioritization based on the interplay between oxygen coordination, defect density, interfacial structure, confinement effects, and operating conditions. Within this framework, OD-systems should not be interpreted as static catalyst surfaces, but as dynamically evolving catalytic ensembles whose active-state identity depends on reconstruction kinetics and *operando* stabilization. With Scheme 1 summarizing this hierarchical descriptor framework.

For OD-Cu systems, defect density and oxygen-modified local environments emerge as the dominant descriptors governing C_{2+} formation. *Operando* and quasi in-situ studies repeatedly demonstrate that reconstruction-derived grain boundaries, twins, local strain, and subsurface oxygen collectively generate non-equilibrium active ensembles that stabilize high *CO coverage and facilitate *OCCO coupling relative to equilibrium Cu surfaces.^{25,62,118} In particular, the *operando* analysis of Chen *et al.*,³⁵¹ combined with quasi in-situ EELS characterization, showed that subsurface oxygen can persist even in the absence of detectable crystalline Cu_2O , supporting a model in which oxygen is kinetically trapped within defect-rich near-surface regions and dynamically modifies the local electronic structure. Importantly, these descriptors should not be interpreted independently, but rather as coupled manifestations of reconstruction dynamics. Fast or strongly driven reduction generates high densities of grain boundaries and oxygen-modified motifs, yet overly aggressive reduction also accelerates structural relaxation, oxygen depletion, and active-site loss.³⁵² Consequently, optimal OD-Cu performance is increasingly understood as a balance between generating and preserving metastable defect-oxygen ensembles under reaction conditions.³⁵³

Under high-rate operation, however, microenvironmental descriptors become increasingly dominant. Reconstruction-derived nano-porosity promotes local *CO accumulation and localized alkalization, enhancing C-C coupling while suppressing HER. At the same time, excessive tortuosity or flooding can restrict CO_2 transport and destabilize catalytic performance under industrially relevant current densities. Thus, porosity is not universally beneficial, but rather an architecture-dependent descriptor governed by the balance between intermediate confinement and reactant accessibility. In this context, pulsed and redox-cycling protocols are increasingly recognized as practical strategies for periodically regenerating non-equilibrium OD-like surface states and mitigating structural relaxation during prolonged operation.²⁸⁰

In contrast, OD-Ag, OD-Au, and OD-Zn systems are governed primarily by the balance between *COOH stabilization and sufficiently weak *CO binding. Here, oxygen coordination and defect-induced electronic perturbations facilitate CO_2 activation while maintaining rapid CO desorption, thereby promoting selective CO production.³⁵⁴ Unlike OD-Cu systems, excessive confinement or strong intermediate retention is generally less advantageous and may instead promote transport limitations or catalyst poisoning.¹⁸⁰ Consequently, maintaining electronically perturbed but transport-accessible active environments becomes more important than maximizing defect density or confinement

effects. For OD-Sn, OD-Bi, and OD-In catalysts, oxygen coordination acts as the dominant descriptor because partially oxidized motifs stabilize *OCHO intermediates while suppressing competing HER pathways. In these systems, maintaining kinetically stabilized oxide-derived environments is often more beneficial than maximizing metallic character or grain-boundary density.³⁵⁵ Consistent with this behavior, excessive reduction toward fully metallic surfaces frequently decreases formate selectivity and promotes HER. Thus, unlike OD-Cu systems, where dynamic defect generation is highly beneficial, formate-selective OD-catalysts rely more strongly on controlled oxygen retention and stabilization of partially oxidized interfacial motifs. A second, increasingly mature design strategy involves chemically pinning oxygen and defect chemistry using heterovalent dopants or oxide additives that modify reconstruction kinetics and stabilize oxygen-modified active ensembles (Fig. 7b).³⁵⁶ Yang *et al.*³⁵⁷ demonstrated that Sn-doping of CuO_x nanoparticles substantially alters reduction behavior and product selectivity, consistent with dopant-controlled oxygen coordination and reconstruction pathways. More broadly, incorporating redox-active or oxygen-vacancy-forming oxide phases at interfaces can buffer local oxygen chemical potential, retard oxygen depletion, and stabilize non-equilibrium catalytic motifs during operation.^{358,359} These approaches further reinforce that OD-catalyst optimization should focus not on preserving static oxide phases, but on sustaining dynamically reconstructed active ensembles.

In multimetal OD-systems, interfacial coupling becomes the dominant design principle. Increasing *operando* evidence suggests that many OD alloys behave less as homogeneous equilibrium alloys and more as reconstruction-defined heterogeneous architectures generated through asynchronous reduction and dynamic interfacial evolution.³⁶⁰ *Operando* characterization by Zhang *et al.*¹⁷⁷ on Cu-Zn nanoparticles directly linked time-dependent structural and compositional evolution to selectivity changes, indicating that Zn-containing domains evolve differently from Cu-rich regions under CO_2RR conditions. Similarly, the *operando* XAS study of Frisch *et al.*³⁶¹ on Cu-Ag composite catalysts demonstrated that dynamic interface formation and evolving domain interactions are intrinsic to tandem catalytic behavior. Consequently, OD multimetal catalysts are increasingly understood as dynamically evolving interfacial mosaics, in which selective oxidation, asynchronous reduction, and composition redistribution generate transient functional domains that cooperatively regulate intermediate formation, transport, and conversion.

Collectively, these observations demonstrate that predictive OD-catalyst design cannot rely on universally maximizing descriptors such as defects, porosity, or oxygen retention independently. Instead, optimal catalyst architectures require descriptor prioritization (Scheme 1) according to catalyst class, reaction pathway, and operating regime, while balancing catalytic enhancement against transport limitations, conductivity losses, and long-term structural stability.

8.3 Trade-offs and stability constraints in ODcatalyst design

Although reconstruction-derived features such as defect density, oxygen retention, nano-porosity, and interfacial heterogeneity

frequently enhance catalytic activity and selectivity, their effects are not universally beneficial and are often accompanied by important trade-offs. Consequently, predictive design of OD-catalysts requires balancing catalytic enhancement against transport limitations, conductivity losses, structural relaxation, and long-term *operando* stability. In OD-Cu systems, reconstruction-generated defect networks and oxygen-modified environments enhance $\ast\text{CO}$ accumulation and facilitate C-C coupling; however, these metastable motifs are intrinsically dynamic under cathodic operation. *Operando* studies demonstrate that prolonged reduction can induce grain growth, defect relaxation, collapse of porous architectures, and progressive depletion of subsurface oxygen, gradually driving the catalyst toward more equilibrium metallic states with altered selectivity.^{351–353} Excessively aggressive reduction conditions may therefore generate highly active OD-states initially while simultaneously accelerating structural coarsening and active-site loss during long-term operation. Similar trade-offs govern nano-porous OD architectures. While reconstruction-derived porosity enhances local alkalization and intermediate confinement, excessive tortuosity or unstable wetting can restrict CO_2 transport, promote flooding, and generate concentration gradients under industrially relevant current densities. As a result, porosity should not be viewed as a universally beneficial descriptor, but rather as a transport-sensitive architectural parameter whose optimal characteristics depend strongly on catalyst-layer thickness, wettability, electrolyte environment, and reactor configuration.^{197,200,201}

For OD-Ag, OD-Au, and OD-Zn catalysts, oxygen coordination and defect-induced electronic perturbations facilitate $\ast\text{COOH}$ stabilization and selective CO formation while maintaining sufficiently weak $\ast\text{CO}$ binding for rapid desorption. However, excessive oxygen retention or overly confined porous structures may reduce conductivity, hinder reactant accessibility, or promote excessive local $\ast\text{CO}$ accumulation. In these systems, maintaining electronically perturbed but transport-accessible active surfaces is often more advantageous than maximizing defect density or confinement effects.^{214–216}

In OD-Sn, OD-Bi, and OD-In systems, partially oxidized surface environments are frequently associated with enhanced formate selectivity because oxygen-coordinated motifs stabilize $\ast\text{OCHO}$ intermediates while suppressing HER pathways.^{164,239} Nevertheless, these oxygen-modified states remain dynamically sensitive to cathodic polarization. Excessive reduction toward fully metallic surfaces is frequently correlated with decreased formate selectivity, whereas excessive oxide stabilization may reduce conductivity and hinder interfacial charge transfer. Accordingly, optimal catalyst performance requires maintaining kinetically stabilized oxygen-modified environments while preserving sufficient electronic conductivity for sustained operation.^{221–225}

Additional complexity emerges in multimetal OD-systems, where asynchronous reduction and dynamic interface evolution govern catalytic functionality. Although reconstruction-defined interfaces can enhance tandem catalysis and cooperative intermediate transfer, prolonged operation may also induce phase segregation, compositional redistribution, or interfacial

restructuring that alters catalytic behavior over time.^{177,358,359} Consequently, interface density alone is insufficient as a predictive design parameter unless accompanied by strategies that stabilize interfacial functionality under reaction conditions. Importantly, many of these trade-offs become increasingly severe under high-rate operation in GDEs and MEAs. Under industrially relevant current densities, catalyst performance becomes strongly coupled to local pH gradients, ion transport, carbonate formation, wetting stability, and CO_2 availability. Under such conditions, descriptors that appear beneficial under low-current H-cell measurements may become detrimental due to transport limitations, flooding, salt accumulation, or local reactant depletion.²⁰² Indicating that OD-catalyst descriptors cannot be evaluated independently of reactor architecture and operating environment.

Collectively, these observations demonstrate that optimal OD-catalyst engineering should not aim to maximize individual descriptors independently, but rather to balance reconstruction-driven catalytic enhancement against transport, conductivity, and long-term stability constraints. This perspective further reinforces the view that OD-catalysts are best understood as dynamically evolving catalytic systems whose performance emerges from the coupled interaction of structural, electronic, and microenvironmental descriptors under *operando* conditions.

8.4 Dynamic stabilization & *operando* control

OD-catalysts are fundamentally incompatible with purely static potentiostatic operation.^{362,363} The structural and electronic motifs underpinning their enhanced activity—including defect-rich microstructures, subsurface oxygen, mixed-valence metal-oxygen ensembles, and interfacial strain—are intrinsically non-equilibrium and therefore undergo continuous evolution under applied bias.³⁶⁴ Consequently, long-term catalytic performance is governed not by the suppression of reconstruction, but by the ability of the operating conditions to sustain a favorable dynamic steady state in which functionally relevant OD features are regenerated at rates comparable to their loss *via* coarsening, oxygen depletion, dissolution, or compositional segregation.^{365,366}

As hinted before, pulsed electrolysis and redox cycling have emerged as powerful *operando* tools to manage this balance.³⁶⁷ Alternating cathodic bias with brief oxidative or open-circuit intervals has been shown by Burdyny *et al.*,²⁸⁰ to prolong selectivity and activity on OD-Cu by stabilizing Cu^+ populations, preserving grain-boundary networks, and mitigating monotonic grain growth (Fig. 7c).³⁶⁸ Mechanistic studies focused on the OER indicate that pulsing induces controlled dissolution & re-deposition and transient re-oxidation, followed by rapid re-reduction that reintroduces oxygen-modified, defect-rich surface states rather than allowing irreversible relaxation toward equilibrium metallic morphologies.^{369–371} While such protocols generally delay rather than eliminate degradation, they demonstrate that OD active ensembles can be actively refreshed during operation, while the mediated electrolysis rate favors the reagents distribution over the catalyst's active sites. (Fig. 7d).^{26,372} Identical-location microscopy and *operando* impedance studies further support the link between pulsed

operation, surface reshaping, and sustained catalytic function. Dynamic operation is most effective when combined with materials-level strategies that slow the thermodynamic drive toward equilibrium.^{22,373,374} Oxygen-retention engineering—through alloying with oxygen-affine elements, incorporation of oxophilic dopants, or the use of mixed-oxide precursors—can stabilize subsurface oxygen and mixed-valence states.^{358,375} Defect and grain-boundary stabilization *via* alloy anchoring, strong metal-support interactions, or confinement within porous or hierarchical scaffolds reduces defect mobility without eliminating catalytic diversity.^{103,376} Electrolyte composition and local microenvironment further modulate reconstruction kinetics, dissolution, and redox behavior, making electrolyte engineering an integral component of OD-stability.^{377–379}

Operando control is particularly critical for multimetal OD-systems, functioning as reconstruction-defined heterogeneous architectures rather than homogeneous equilibrium alloys. In systems such as Cu–Zn^{77,126,254} and Cu–Ag,^{99,361} asynchronous reduction, interfacial evolution, and composition drift occur on electrochemical timescales, with selectivity governed by the persistence and regeneration of specific interphases that enable tandem or cooperative mechanisms. In this context, dynamic operating protocols can help maintain the balance between distinct functional domains.^{279,280} While, from a practical perspective, the work of Chung *et al.*³⁸⁰ indicates that appropriately optimized dynamic operation can enhance durability—and in some cases overall energy efficiency—offsetting the added complexity of pulsed control. Together, these insights reframe stability in OD-catalysts not as resistance to structural change, but as the capacity to sustain catalytic function through controlled, reversible reconstruction, achieved by coupling precursor and interface design with *operando* exploitation of redox flexibility (Fig. 7e).^{43,62,114,381} The dominant catalytic mechanism in OD-systems depends strongly on the operating regime. Under low current-density conditions, catalytic behavior is often governed primarily by intrinsic adsorption energetics and active-site structure. In contrast, under industrially relevant operation in GDEs and MEAs ($\sim 200\text{--}500\text{ mA cm}^{-2}$), microenvironmental effects—local pH gradients, ion transport, intermediate confinement, wetting stability, and CO₂ availability—become increasingly controlling. This transition is particularly significant for OD-catalysts, where reconstruction-derived porosity intrinsically couples catalytic activity with transport phenomena. Consequently, catalyst descriptors cannot be evaluated independently of reactor architecture and operating conditions.

Importantly, the effectiveness of dynamic operating strategies also depends strongly on catalyst class, reconstruction kinetics, and reactor configuration. In OD-Cu systems, pulsed or periodically oxidizing conditions can partially regenerate defect-rich Cu⁺/Cu⁰ ensembles, stabilize subsurface oxygen, and sustain high *CO coverage, thereby improving long-term C₂₊ selectivity and mitigating structural relaxation during extended electrolysis.^{280,351} In contrast, for OD-Ag and OD-Au systems operating primarily through *COOH stabilization and rapid CO desorption, excessive redox cycling may provide limited benefit and can instead introduce conductivity losses or structural instability without substantially improving selectivity. Similarly, in OD-Sn and OD-Bi catalysts,

where partially oxidized motifs are already intrinsically stable under cathodic conditions, overly aggressive pulsing protocols may destabilize optimized *OCHO-forming environments and reduce formate selectivity. The effectiveness of dynamic operation is further coupled to reactor architecture and operating conditions. Under industrially relevant current densities in GDE and MEA systems, pulsed electrolysis can influence carbonate accumulation, wetting stability, local pH gradients, and reactant/product transport within porous catalyst layers. However, energetic penalties associated with dynamic operation, including capacitive losses and transient inefficiencies, must also be considered when evaluating scalability and overall process efficiency. Consequently, dynamic operating strategies should not be viewed as universally beneficial, but rather as catalyst-specific and reactor-dependent tools for stabilizing metastable OD active states under realistic operating conditions. Recent studies under application-relevant electrolysis conditions further emphasize that optimal OD-catalyst performance emerges from coupled control of reconstruction dynamics, transport behavior, and reactor-level microenvironments rather than intrinsic surface energetics alone.^{202,280}

8.5 Practical design rules for OD-catalyst engineering

Catalyst performance cannot be rationalized through isolated descriptors or equilibrium surface models alone. Instead, catalytic behavior emerges from dynamically coupled interactions between reconstruction kinetics, oxygen coordination, defect topology, interfacial architecture, and local reaction microenvironments. Consequently, predictive OD-catalyst engineering requires descriptor prioritization according to catalyst class, target reaction pathway, and operating regime, rather than universal maximization of reconstruction-derived features.

For OD-Cu systems targeting C₂₊ products, catalyst architectures should prioritize the formation of defect-rich and moderately oxygen-retaining environments capable of sustaining high local *CO coverage and facilitating *OCCO coupling. *Operando* and theoretical studies consistently show that grain boundaries, low-coordination Cu sites, subsurface oxygen, and nano-confined porous structures collectively contribute to enhanced multicarbon selectivity by stabilizing key intermediates and suppressing competing HER pathways.^{25,62,66,103,120,145,167–169,171–179} However, excessive reduction severity or uncontrolled structural disorder can accelerate oxygen depletion, grain coarsening, and collapse of metastable active ensembles during prolonged operation.^{351–353} Accordingly, optimal OD-Cu design should balance defect generation with structural stabilization, while integrating transport-engineered porous architectures that maintain favorable *CO activity without introducing severe diffusion limitations or flooding under high-rate electrolysis.^{168,188,197,200,201}

In OD-Ag, OD-Au, and OD-Zn systems, the dominant design objective differs fundamentally from OD-Cu. Because selective CO production depends primarily on efficient *COOH stabilization combined with sufficiently weak *CO adsorption, catalyst optimization should focus on electronically perturbed but transport-accessible active environments rather than maximal confinement or defect density. *Operando* studies indicate

that oxygen-modified coordination environments, oxygen vacancies, and grain-boundary-rich structures can lower CO₂ activation barriers and enhance CO selectivity, while excessive oxygen retention or highly tortuous porous structures may reduce conductivity and hinder reactant accessibility.^{29,37,55,92,108,118,134,147,148,154,214–216}

Consequently, OD-catalyst engineering in these systems should emphasize controlled oxygen coordination, moderate defect densities, and stable porous architectures that preserve rapid CO desorption and efficient mass transport during operation.

For OD-Sn, OD-Bi, and OD-In catalysts, maintaining kinetically stabilized oxygen-modified motifs is particularly important because partially oxidized surface environments preferentially stabilize *OCHO intermediates while suppressing HER pathways.^{135,142–144,150–152,163–165,218–225}

Unlike OD-Cu systems, where dynamic defect generation strongly promotes catalytic performance, formate-selective OD-catalysts generally benefit from preserving controlled oxide-derived coordination environments under cathodic conditions. Excessive reduction toward fully metallic surfaces frequently correlates with decreased formate selectivity and increased HER activity, whereas excessive oxide stabilization can reduce conductivity and limit charge transfer. Therefore, practical catalyst-engineering strategies for OD formate systems should focus on balancing oxygen retention with sufficient electronic conductivity, while stabilizing partially oxidized interfacial motifs through dopants, heterostructures, or controlled reconstruction pathways.^{354–357}

In multimetal OD-catalysts, interfacial coupling and asynchronous reconstruction emerge as dominant design principles. *Operando* studies of OD Cu–Zn, Cu–Ag, and Cu–Sn systems demonstrate that catalytic performance frequently originates from dynamically evolving interfacial architectures rather than homogeneous alloy phases. In these systems, reconstruction-derived heterogeneity enables spatial separation of catalytic functions—including CO generation, intermediate confinement, C–C coupling, and HER suppression—within nanometer-scale distances.^{74,79,80,97–99,113,114,177,193–196,211,358,359} Consequently, predictive design of multimetal OD-catalysts should prioritize interface density, reconstruction compatibility, and controlled composition gradients rather than equilibrium alloy formation alone. Stabilizing chemically distinct but cooperatively interacting domains is particularly important for sustaining tandem reaction pathways and intermediate spillover under prolonged operation.

Beyond catalyst composition and morphology, the analysis throughout this review further demonstrates that OD-catalyst performance is strongly coupled to reactor architecture and operating environment. Under industrially relevant current densities in GDEs and MEAs, catalyst behavior becomes increasingly governed by local pH gradients, ion transport, carbonate formation, wetting stability, and CO₂ availability.^{188,197–202} Accordingly, catalyst descriptors such as porosity, oxygen retention, and defect density cannot be optimized independently of catalyst-layer thickness, electrolyte composition, membrane properties, and mass-transport conditions. Future OD-catalyst development should therefore integrate catalyst engineering with transport engineering, electrolyte optimization, and reactor-level design

strategies to maintain stable non-equilibrium active states under commercially relevant operating conditions. Collectively, these insights establish OD-catalysis as a dynamically stabilized catalytic paradigm in which reconstruction kinetics, oxygen coordination, interfacial evolution, and microenvironmental effects jointly govern catalytic function. Accordingly, the most effective OD-catalysts are unlikely to correspond to static equilibrium structures, but rather to metastable active states sustained under *operando* conditions. Future progress will therefore rely on integrating *operando* characterization, theory-guided descriptor identification, and reaction-environment engineering to advance OD-catalyst development from empirical optimization toward predictive, application-oriented design.

9. Future perspectives

Future progress in OD-catalysis will depend on moving from retrospective structure–performance correlations toward predictive control of dynamically reconstructed active states. A priority is the development of *operando* and time-resolved characterization methods capable of resolving transient oxygen coordination, defect evolution, phase segregation, and interfacial restructuring under realistic current densities and reactor configurations. Such methods should be coupled with theory and data-driven descriptor identification to distinguish causal descriptors from correlated structural features. A second challenge is the stabilization of metastable OD active states during long-term operation. Strategies such as controlled redox cycling, dopant-mediated oxygen retention, hetero-interface engineering, and electrolyte/microenvironment control offer promising routes, but their effectiveness must be evaluated under application-relevant conditions, including flow cells, GDEs, and MEAs. Future work should explicitly connect catalyst descriptors with transport behavior, wetting stability, carbonate formation, and energy efficiency.

Finally, OD-catalyst development should increasingly integrate catalyst design with reactor and process engineering. The most effective OD-catalysts are unlikely to be static equilibrium materials, but dynamically sustained active states whose performance depends on precursor chemistry, reconstruction kinetics, local microenvironment, and device architecture. Establishing quantitative descriptor–performance–stability relationships will be essential for translating OD-catalysis from empirical materials discovery toward scalable electrochemical and thermochemical energy-conversion technologies.

10. Conclusion

Oxide-derived (OD) catalysts represent a fundamentally distinct catalytic platform in which performance emerges from dynamically sustained, non-equilibrium active states generated through redox-driven reconstruction. Rather than being governed solely by equilibrium surface energetics, catalytic function in OD systems arises from the coupled interplay between oxygen coordination, defect-rich nanostructures, interfacial heterogeneity, and *operando* microenvironments, which collectively reshape

adsorption behavior and enable cooperative reaction pathways inaccessible on conventional metallic surfaces. By integrating mechanistic insights from *operando* characterization, theoretical modeling, and comparative studies of monometallic and multi-metallic systems, this review establishes a descriptor-based framework linking precursor chemistry, reconstruction kinetics, structural evolution, and catalytic function. The recurrence of OD-type phenomena across CO₂RR, CORR, nitrogen- and oxygen-based electrocatalysis, as well as key thermocatalytic reactions, further highlights the broader relevance of dynamic catalyst design strategies beyond individual reaction systems.

Importantly, the analysis presented here demonstrates that OD-catalyst design cannot rely on universally maximizing descriptors such as defect density, oxygen retention, or nanoporosity independently. Instead, catalytic performance depends on condition-dependent balancing of metastable active-state stabilization, transport behavior, conductivity, interfacial coupling, and reactor-level microenvironmental effects. Different catalyst classes are therefore governed by distinct dominant descriptors and mechanistic constraints, emphasizing that predictive OD-catalyst engineering requires catalyst-specific and operating-condition-dependent design strategies rather than generalized optimization approaches. Consequently, future progress will depend on the deliberate engineering of dynamically stabilized catalytic states through controlled reconstruction pathways, oxygen-retention strategies, hetero-interface design, transport-engineered architectures, electrolyte optimization, and adaptive operating protocols. Collectively, these insights position OD-catalysis as a predictive and *operando*-defined catalyst-engineering paradigm, providing a pathway toward robust and scalable electrochemical and thermochemical energy-conversion technologies.

Author contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript. I. Stamatelos made the original draft, the literature review, and wrote & edited. Z. Guo and W. Saei contributed equally to the literature review, analysis writing, and editing. J. Pasel supervised the work and edited the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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References

- 1 O. S. Bushuyev, P. De Luna, C. T. Dinh, L. Tao, G. Saur, J. van de Lagemaat, S. O. Kelley and E. H. Sargent, What Should We Make with CO₂ and How Can We Make It?, *Joule*, 2018, **2**(5), 825–832, DOI: [10.1016/j.joule.2017.09.003](https://doi.org/10.1016/j.joule.2017.09.003).
- 2 R. Peters, N. Wegener, R. C. Samsun, F. Schorn, J. Riese, M. Grünewald and D. Stolten, A Techno-Economic Assessment of Fischer–Tropsch Fuels Based on Syngas from Co-Electrolysis, *Processes*, 2022, **10**(4), 699, DOI: [10.3390/pr10040699](https://doi.org/10.3390/pr10040699).
- 3 M. Spurgeon and J. Kumar, B. A Comparative Technoeconomic Analysis of Pathways for Commercial Electrochemical CO₂ Reduction to Liquid Products, *Energy Environ. Sci.*, 2018, **11**(6), 1536–1551, DOI: [10.1039/C8EE00097B](https://doi.org/10.1039/C8EE00097B).
- 4 T. Zheng, K. Jiang and H. Wang, Recent Advances in Electrochemical CO₂-to-CO Conversion on Heterogeneous Catalysts, *Adv. Mater.*, 2018, **30**(48), 1802066, DOI: [10.1002/adma.201802066](https://doi.org/10.1002/adma.201802066).
- 5 S. Verma, B. Kim, H.-R. “Molly” Jhong, S. Ma and P. J. A. Kenis, A Gross-Margin Model for Defining Technoeconomic Benchmarks in the Electroreduction of CO₂, *ChemSusChem*, 2016, **9**(15), 1972–1979, DOI: [10.1002/cssc.201600394](https://doi.org/10.1002/cssc.201600394).
- 6 J. E. Pander III, D. Ren, Y. Huang, N. W. X. Loo, S. H. L. Hong and B. S. Yeo, Understanding the Heterogeneous Electrocatalytic Reduction of Carbon Dioxide on Oxide-Derived Catalysts, *ChemElectroChem*, 2018, **5**(2), 219–237, DOI: [10.1002/celec.201701100](https://doi.org/10.1002/celec.201701100).
- 7 K. Takehira and T. Shishido, Preparation of Supported Metal Catalysts Starting from Hydrotalcites as the Precursors and Their Improvements by Adopting “Memory Effect.”, *Catal. Surv. Asia*, 2007, **11**(1), 1–30, DOI: [10.1007/s10563-007-9016-2](https://doi.org/10.1007/s10563-007-9016-2).
- 8 F. Ye, Q. Ren, L. Zhang and L. Luo, A Comparative Study of Oxide-Derived Cu Electrocatalysts through Electrochemical vs. Thermal Reduction, *Chem. Commun.*, 2022, **58**(41), 6120–6123, DOI: [10.1039/D2CC01534J](https://doi.org/10.1039/D2CC01534J).
- 9 W. Kwon, D. Kim, Y. Lee, J. Jung and D. Nam, Advancements in Understanding Catalyst Reconstruction During Electrochemical CO₂ Reduction, *Exploration*, 2025, **5**(4), e20240019, DOI: [10.1002/EXP.20240019](https://doi.org/10.1002/EXP.20240019).
- 10 D. Raciti, K. J. Livi and C. Wang, Highly Dense Cu Nanowires for Low-Overpotential CO₂ Reduction, *Nano Lett.*, 2015, **15**(10), 6829–6835, DOI: [10.1021/acs.nanolett.5b03298](https://doi.org/10.1021/acs.nanolett.5b03298).
- 11 A. Bagger, W. Ju, A. S. Varela, P. Strasser and J. Rossmeisl, Electrochemical CO₂ Reduction: A Classification Problem, *ChemPhysChem*, 2017, **18**(22), 3266–3273, DOI: [10.1002/cphc.201700736](https://doi.org/10.1002/cphc.201700736).
- 12 S. Ma, M. Sadakiyo, M. Heima, R. Luo, R. T. Haasch, J. I. Gold, M. Yamauchi and P. J. A. Kenis, Electroreduction

- of Carbon Dioxide to Hydrocarbons Using Bimetallic Cu-Pd Catalysts with Different Mixing Patterns, *J. Am. Chem. Soc.*, 2017, **139**(1), 47–50, DOI: [10.1021/jacs.6b10740](https://doi.org/10.1021/jacs.6b10740).
- 13 I. Stamatelos, G. T. S. T. da Silva, C. Ribeiro and M. Shviro, Exploring Heterostructures of D-Block Metal Oxides Coupled to ZnO for the Electrochemical Reduction of CO₂, *ACS Appl. Energy Mater.*, 2023, **6**(22), 11510–11520, DOI: [10.1021/acsaem.3c01791](https://doi.org/10.1021/acsaem.3c01791).
- 14 I. Stamatelos, F. Scheepers, J. Pasel, C.-T. Dinh and D. Stolten, Ternary Zn-Ce-Ag Catalysts for Selective and Stable Electrochemical CO₂ Reduction at Large-Scale, *Appl. Catal., B*, 2024, 124062, DOI: [10.1016/j.apcatb.2024.124062](https://doi.org/10.1016/j.apcatb.2024.124062).
- 15 Z. Wu, H. Zhu, Z. Wang, Y. Sun, M. Jia, X. Meng, Y. Li, L. Liu, A. Liu and X. Ren, Metal–Organic Framework Derived Co–NC for Electrocatalytic Reduction of Nitrate to Ammonia, *Catal.:Sci. Technol.*, 2025, **15**(11), 3434–3444, DOI: [10.1039/D5CY00159E](https://doi.org/10.1039/D5CY00159E).
- 16 X. Chang, X. Zi, J. Li, F. Liu, X. Han, J. Chen, Z. Hao, H. Zhang, Z. Zhang, P. Gao, M. Li, J. Lv and X. Ma, An Insight into Synergistic Metal-Oxide Interaction in CO₂ Hydrogenation to Methanol over Cu/ZnO/ZrO₂, *Catalysts*, 2023, **13**(10), 1337, DOI: [10.3390/catal13101337](https://doi.org/10.3390/catal13101337).
- 17 M. L. J. Peerlings, K. Han, A. Longo, K. H. Helfferich, M. Ghiasi, P. E. De Jongh and P. Ngene, Synthesis and Catalytic Performance of Bimetallic Oxide-Derived CuO–ZnO Electrocatalysts for CO₂ Reduction, *ACS Catal.*, 2024, **14**(14), 10701–10711, DOI: [10.1021/acscatal.4c01575](https://doi.org/10.1021/acscatal.4c01575).
- 18 D. Karapinar, C. E. Creissen, J. G. Rivera De La Cruz, M. W. Schreiber and M. Fontecave, Electrochemical CO₂ Reduction to Ethanol with Copper-Based Catalysts, *ACS Energy Lett.*, 2021, **6**(2), 694–706, DOI: [10.1021/acsenenergylett.0c02610](https://doi.org/10.1021/acsenenergylett.0c02610).
- 19 J. Zhang, S. Xia, Y. Wang, J. Wu and Y. Wu, Recent Advances in Dynamic Reconstruction of Electrocatalysts for Carbon Dioxide Reduction, *iScience*, 2024, **27**(6), 110005, DOI: [10.1016/j.isci.2024.110005](https://doi.org/10.1016/j.isci.2024.110005).
- 20 Z. Jan, Q. Guo, J. Zhang, X. Li and Y. Su, Dynamic Reconstruction of Electrocatalysts during CO₂ Reduction Reactions, *Sci. China:Chem.*, 2026, **69**(4), 1623–1638, DOI: [10.1007/s11426-025-2965-8](https://doi.org/10.1007/s11426-025-2965-8).
- 21 I. Stamatelos and W. Saei, Function of Catalyst-Material Phases in Low-Temperature Electrolysis, *Advances in Electrocatalysis*, IntechOpen, 2025, DOI: [10.5772/intechopen.1011365](https://doi.org/10.5772/intechopen.1011365).
- 22 W. Lai, Z. Ma, J. Zhang, Y. Yuan, Y. Qiao and H. Huang, Dynamic Evolution of Active Sites in Electrocatalytic CO₂ Reduction Reaction: Fundamental Understanding and Recent Progress, *Adv. Funct. Mater.*, 2022, **32**(16), 2111193, DOI: [10.1002/adfm.202111193](https://doi.org/10.1002/adfm.202111193).
- 23 D. Cheng, Z. Wei, Z. Zhang, P. Broekmann, A. N. Alexandrova and P. Sautet, Restructuring and Activation of Cu(111) under Electrocatalytic Reduction Conditions, *Angew. Chem., Int. Ed.*, 2023, **62**(20), e202218575, DOI: [10.1002/anie.202218575](https://doi.org/10.1002/anie.202218575).
- 24 H. Mistry, A. S. Varela, C. S. Bonifacio, I. Zegkinoglou, I. Sinev, Y.-W. Choi, K. Kisslinger, E. A. Stach, J. C. Yang, P. Strasser and B. R. Cuenya, Highly Selective Plasma-Activated Copper Catalysts for Carbon Dioxide Reduction to Ethylene, *Nat. Commun.*, 2016, **7**(1), 12123, DOI: [10.1038/ncomms12123](https://doi.org/10.1038/ncomms12123).
- 25 F. Cavalca, R. Ferragut, S. Aghion, A. Eilert, O. Diaz-Morales, C. Liu, A. L. Koh, T. W. Hansen, L. G. M. Pettersson and A. Nilsson, Nature and Distribution of Stable Subsurface Oxygen in Copper Electrodes During Electrochemical CO₂ Reduction, *J. Phys. Chem. C*, 2017, **121**(45), 25003–25009, DOI: [10.1021/acs.jpcc.7b08278](https://doi.org/10.1021/acs.jpcc.7b08278).
- 26 Y. Lum and J. W. Ager, Stability of Residual Oxides in Oxide-Derived Copper Catalysts for Electrochemical CO₂ Reduction Investigated with 18O Labeling, *Angew. Chem.*, 2018, **130**(2), 560–563, DOI: [10.1002/ange.201710590](https://doi.org/10.1002/ange.201710590).
- 27 A. Zahid, A. Shah and I. Shah, Oxide Derived Copper for Electrochemical Reduction of CO₂ to C₂+ Products, *Nanomaterials*, 2022, **12**(8), 1380, DOI: [10.3390/nano12081380](https://doi.org/10.3390/nano12081380).
- 28 R. Kas, R. Kortlever, A. Milbrat, M. T. M. Koper, G. Mul and J. Baltrusaitis, Electrochemical CO₂ Reduction on Cu₂O-Derived Copper Nanoparticles: Controlling the Catalytic Selectivity of Hydrocarbons, *Phys. Chem. Chem. Phys.*, 2014, **16**(24), 12194–12201, DOI: [10.1039/C4CP01520G](https://doi.org/10.1039/C4CP01520G).
- 29 Y. Chen, C. W. Li and M. W. Kanan, Aqueous CO₂ Reduction at Very Low Overpotential on Oxide-Derived Au Nanoparticles, *J. Am. Chem. Soc.*, 2012, **134**(49), 19969–19972, DOI: [10.1021/ja309317u](https://doi.org/10.1021/ja309317u).
- 30 C. W. Li and M. W. Kanan, CO₂ Reduction at Low Overpotential on Cu Electrodes Resulting from the Reduction of Thick Cu₂O Films, *J. Am. Chem. Soc.*, 2012, **134**(17), 7231–7234, DOI: [10.1021/ja3010978](https://doi.org/10.1021/ja3010978).
- 31 H.-W. Miao and J.-G. Duh, Microstructure Evolution in Sn–Bi and Sn–Bi–Cu Solder Joints under Thermal Aging, *Mater. Chem. Phys.*, 2001, **71**(3), 255–271, DOI: [10.1016/S0254-0584\(01\)00298-X](https://doi.org/10.1016/S0254-0584(01)00298-X).
- 32 J. A. Rodríguez, J. Y. Kim, J. C. Hanson, M. Pérez and A. I. Frenkel, Reduction of CuO in H₂: *In Situ* Time-Resolved XRD Studies, *Catal. Lett.*, 2003, **85**(3), 247–254, DOI: [10.1023/A:1022110200942](https://doi.org/10.1023/A:1022110200942).
- 33 R. N. C. de Siqueira, E. de Albuquerque Brocchi, P. F. de Oliveira and M. S. Motta, Hydrogen Reduction of Zinc and Iron Oxides Containing Mixtures, *Metall. Mater. Trans. B*, 2014, **45**(1), 66–75, DOI: [10.1007/s11663-013-9951-4](https://doi.org/10.1007/s11663-013-9951-4).
- 34 D. Ren, B. S.-H. Ang and B. S. Yeo, Tuning the Selectivity of Carbon Dioxide Electroreduction toward Ethanol on Oxide-Derived Cu₂Zn Catalysts, *ACS Catal.*, 2016, **6**(12), 8239–8247, DOI: [10.1021/acscatal.6b02162](https://doi.org/10.1021/acscatal.6b02162).
- 35 J. Kim, W. Choi, J. W. Park, C. Kim, M. Kim and H. Song, Branched Copper Oxide Nanoparticles Induce Highly Selective Ethylene Production by Electrochemical Carbon Dioxide Reduction, *J. Am. Chem. Soc.*, 2019, **141**(17), 6986–6994, DOI: [10.1021/jacs.9b00911](https://doi.org/10.1021/jacs.9b00911).
- 36 E. Bertin, S. Garbarino, C. Roy, S. Kazemi and D. Guay, Selective Electroreduction of CO₂ to Formate on Bi and Oxide-Derived Bi Films, *J. CO₂ Util.*, 2017, **19**, 276–283, DOI: [10.1016/j.jcou.2017.04.006](https://doi.org/10.1016/j.jcou.2017.04.006).
- 37 M. Ma, B. J. Trześniewski, J. Xie and W. A. Smith, Selective and Efficient Reduction of Carbon Dioxide to Carbon

- Monoxide on Oxide-Derived Nanostructured Silver Electrocatalysts, *Angew. Chem., Int. Ed.*, 2016, 55(33), 9748–9752, DOI: [10.1002/anie.201604654](https://doi.org/10.1002/anie.201604654).
- 38 H.-Y. Wang, M. Soldemo, D. Degerman, P. Lömker, C. Schlueter, A. Nilsson and P. Amann, Direct Evidence of Subsurface Oxygen Formation in Oxide-Derived Cu by X-Ray Photoelectron Spectroscopy, *Angew. Chem., Int. Ed.*, 2022, 61(3), e202111021, DOI: [10.1002/anie.202111021](https://doi.org/10.1002/anie.202111021).
- 39 A. J. Garza, A. T. Bell and M. Head-Gordon, Is Subsurface Oxygen Necessary for the Electrochemical Reduction of CO₂ on Copper?, *J. Phys. Chem. Lett.*, 2018, 9(3), 601–606, DOI: [10.1021/acs.jpclett.7b03180](https://doi.org/10.1021/acs.jpclett.7b03180).
- 40 H. Hu, Y. Tang, Q. Hu, P. Wan, L. Dai and X. J. Yang, In-Situ Grown Nanoporous Zn-Cu Catalysts on Brass Foils for Enhanced Electrochemical Reduction of Carbon Dioxide, *Appl. Surf. Sci.*, 2018, 445, 281–286, DOI: [10.1016/j.apsusc.2018.03.146](https://doi.org/10.1016/j.apsusc.2018.03.146).
- 41 D. A. Torelli, S. A. Francis, J. C. Crompton, A. Javier, J. R. Thompson, B. S. Brunshawig, M. P. Soriaga and N. S. Lewis, Nickel-Gallium-Catalyzed Electrochemical Reduction of CO₂ to Highly Reduced Products at Low Overpotentials, *ACS Catal.*, 2016, 6(3), 2100–2104, DOI: [10.1021/acscatal.5b02888](https://doi.org/10.1021/acscatal.5b02888).
- 42 K. Liu, M. Ma, L. Wu, M. Valenti, D. Cardenas-Morcoso, J. P. Hofmann, J. Bisquert, S. Gimenez and W. A. Smith, Electronic Effects Determine the Selectivity of Planar Au-Cu Bimetallic Thin Films for Electrochemical CO₂ Reduction, *ACS Appl. Mater. Interfaces*, 2019, 11(18), 16546–16555, DOI: [10.1021/acsami.9b01553](https://doi.org/10.1021/acsami.9b01553).
- 43 C. Long, K. Wan, Y. Chen, L. Li, Y. Jiang, C. Yang, Q. Wu, G. Wu, P. Xu, J. Li, X. Shi, Z. Tang and C. Cui, Steering the Reconstruction of Oxide-Derived Cu by Secondary Metal for Electrosynthesis of n-Propanol from CO, *J. Am. Chem. Soc.*, 2024, 146(7), 4632–4641, DOI: [10.1021/jacs.3c11359](https://doi.org/10.1021/jacs.3c11359).
- 44 J. Xue, X. Jia, Z. Sun, H. Li, Q. Shen, X. Liu, H. Jia and Y. Zhu, Selective CO₂ Photoreduction to C₂ Hydrocarbon via Synergy between Metastable Ordered Oxygen Vacancies and Hydrogen Spillover over TiO₂ Nanobelts, *Appl. Catal., B*, 2024, 342, 123372, DOI: [10.1016/j.apcatb.2023.123372](https://doi.org/10.1016/j.apcatb.2023.123372).
- 45 B. Wang, Y. Wei, H. Fang, X. Qiu, Q. Zhang, H. Wu, Q. Wang, Y. Zhang and X. Ji, Mn-Substituted Tunnel-Type Polyantimonic Acid Confined in a Multidimensional Integrated Architecture Enabling Superfast-Charging Lithium-Ion Battery Anodes, *Adv. Sci.*, 2021, 8(3), 2002866, DOI: [10.1002/advs.202002866](https://doi.org/10.1002/advs.202002866).
- 46 X. Jia, C. Streb and Y.-F. Song, Devisable POM/Ni Foam Composite: Precisely Control Synthesis toward Enhanced Hydrogen Evolution Reaction at High pH, *Chem. – Eur. J.*, 2019, 25(68), 15548–15554, DOI: [10.1002/chem.201903059](https://doi.org/10.1002/chem.201903059).
- 47 T. Wang, J. Hu, R. Ouyang, Y. Wang, Y. Huang, S. Hu and W.-X. Li, Nature of Metal-Support Interaction for Metal Catalysts on Oxide Supports, *Science*, 2024, 386(6724), 915–920, DOI: [10.1126/science.adp6034](https://doi.org/10.1126/science.adp6034).
- 48 Z. Geng, X. Kong, W. Chen, H. Su, Y. Liu, F. Cai, G. Wang and J. Zeng, Oxygen Vacancies in ZnO Nanosheets Enhance CO₂ Electrochemical Reduction to CO, *Angew. Chem., Int. Ed.*, 2018, 57(21), 6054–6059, DOI: [10.1002/anie.201711255](https://doi.org/10.1002/anie.201711255).
- 49 H. Zheng, G. Luo, A. Zhang, X. Lu and L. He, The Synthesis and Catalytic Applications of Nanosized High-Entropy Alloys, *ChemCatChem*, 2021, 13(3), 806–817, DOI: [10.1002/cctc.202001163](https://doi.org/10.1002/cctc.202001163).
- 50 F. Breclj and M. Mozetic, Reduction of Metal Oxide Thin Layers by Hydrogen Plasma, *Vacuum*, 1990, 40(1), 177–181, DOI: [10.1016/0042-207X\(90\)90149-S](https://doi.org/10.1016/0042-207X(90)90149-S).
- 51 H. Mistry, Y.-W. Choi, A. Bagger, F. Scholten, C. S. Bonifacio, I. Sinev, N. J. Divins, I. Zegkinoglou, H. S. Jeon, K. Kisslinger, E. A. Stach, J. C. Yang, J. Rossmeisl and B. Roldan Cuenya, Enhanced Carbon Dioxide Electroreduction to Carbon Monoxide over Defect-Rich Plasma-Activated Silver Catalysts, *Angew. Chem., Int. Ed.*, 2017, 56(38), 11394–11398, DOI: [10.1002/anie.201704613](https://doi.org/10.1002/anie.201704613).
- 52 P. Schlexer, A. Ruiz Puigdollers and G. Pacchioni, Role of Metal/Oxide Interfaces in Enhancing the Local Oxide Reducibility, *Top. Catal.*, 2019, 62(17), 1192–1201, DOI: [10.1007/s11244-018-1056-5](https://doi.org/10.1007/s11244-018-1056-5).
- 53 C. M. Gunathunge, J. Li, X. Li and M. M. Waegle, Surface-Adsorbed CO as an Infrared Probe of Electrocatalytic Interfaces, *ACS Catal.*, 2020, 10(20), 11700–11711, DOI: [10.1021/acscatal.0c03316](https://doi.org/10.1021/acscatal.0c03316).
- 54 R. M. Arán-Ais, F. Scholten, S. Kunze, R. Rizo and B. Roldan Cuenya, The Role of in Situ Generated Morphological Motifs and Cu(i) Species in C₂₊ Product Selectivity during CO₂ Pulsed Electroreduction, *Nat. Energy*, 2020, 5(4), 317–325, DOI: [10.1038/s41560-020-0594-9](https://doi.org/10.1038/s41560-020-0594-9).
- 55 X.-Z. Wang, Q. Hu, M. Gao, S. Liu and J.-L. Luo, Tuning the Subsurface Oxygen of Ag₂O-Derived Ag Nanoparticles to Achieve Efficient CO₂ Electroreduction to CO, *Electrochim. Acta*, 2022, 403, 139656, DOI: [10.1016/j.electacta.2021.139656](https://doi.org/10.1016/j.electacta.2021.139656).
- 56 S. Nayak, P. U. Biedermann and A. Erbe, Superoxide Intermediate in the Oxygen Reduction on a Zinc Hydroxide Model Corrosion Product, *J. Chem. Phys.*, 2022, 157(22), 224702, DOI: [10.1063/5.0130076](https://doi.org/10.1063/5.0130076).
- 57 Y. Song, Y. Wang, J. Shao, K. Ye, Q. Wang and G. Wang, Boosting CO₂ Electroreduction via Construction of a Stable ZnS/ZnO Interface, *ACS Appl. Mater. Interfaces*, 2022, 14(18), 20368–20374, DOI: [10.1021/acscami.1c15669](https://doi.org/10.1021/acscami.1c15669).
- 58 Z. Xiao, X. Tang, F. Gao, J. Xue and X. Wang, Exploring Ni-Based Alkaline OER Catalysts: A Comprehensive Review of Structures, Performance, and in Situ Characterization Methods, *DeCarbon*, 2025, 7, 100097, DOI: [10.1016/j.decarb.2024.100097](https://doi.org/10.1016/j.decarb.2024.100097).
- 59 X. Zhang, Y. Huang, J. Wang, J. Tang, Y. Mei, N. Zhu, Z. Li, L. Li and Y. Wang, Facet-Dependent Transformation and Toxicity of Nanoscale Zinc Oxide in the Synthetic Saliva, *J. Environ. Sci.*, 2024, 139, 170–181, DOI: [10.1016/j.jes.2023.05.033](https://doi.org/10.1016/j.jes.2023.05.033).
- 60 D. Cheng, Z.-J. Zhao, G. Zhang, P. Yang, L. Li, H. Gao, S. Liu, X. Chang, S. Chen, T. Wang, G. A. Ozin, Z. Liu and J. Gong, The Nature of Active Sites for Carbon Dioxide Electroreduction over Oxide-Derived Copper Catalysts, *Nat. Commun.*, 2021, 12(1), 395, DOI: [10.1038/s41467-020-20615-0](https://doi.org/10.1038/s41467-020-20615-0).

- 61 J.-J. Velasco-Vélez, T. Jones, D. Gao, E. Carbonio, R. Arrigo, C.-J. Hsu, Y.-C. Huang, C.-L. Dong, J.-M. Chen, J.-F. Lee, P. Strasser, B. Roldan Cuenya, R. Schlögl, A. Knop-Gericke and C.-H. Chuang, The Role of the Copper Oxidation State in the Electrocatalytic Reduction of CO₂ into Valuable Hydrocarbons, *ACS Sustainable Chem. Eng.*, 2019, 7(1), 1485–1492, DOI: [10.1021/acssuschemeng.8b05106](https://doi.org/10.1021/acssuschemeng.8b05106).
- 62 C. Long, X. Liu, K. Wan, Y. Jiang, P. An, C. Yang, G. Wu, W. Wang, J. Guo, L. Li, K. Pang, Q. Li, C. Cui, S. Liu, T. Tan and Z. Tang, Regulating Reconstruction of Oxide-Derived Cu for Electrochemical CO₂ Reduction toward n-Propanol, *Sci. Adv.*, 2023, 9(43), eadi6119, DOI: [10.1126/sciadv.adi6119](https://doi.org/10.1126/sciadv.adi6119).
- 63 M. Shamsuddin, Reduction of Oxides and Reduction Smelting, in *Physical Chemistry of Metallurgical Processes*, ed. M. Shamsuddin, Springer International Publishing: Cham, 2nd edn, 2021, pp. 149–203, DOI: [10.1007/978-3-030-58069-8_5](https://doi.org/10.1007/978-3-030-58069-8_5).
- 64 C. Chen, X. Yan, Y. Wu, S. Liu, X. Sun, Q. Zhu, R. Feng, T. Wu, Q. Qian, H. Liu, L. Zheng, J. Zhang and B. Han, The *in Situ* Study of Surface Species and Structures of Oxide-Derived Copper Catalysts for Electrochemical CO₂ Reduction, *Chem. Sci.*, 2021, 12(16), 5938–5943, DOI: [10.1039/D1SC00042J](https://doi.org/10.1039/D1SC00042J).
- 65 I. Hjorth, M. Nord, M. Rønning, J. Yang and D. Chen, Electrochemical Reduction of CO₂ to Synthesis Gas on CNT Supported Cu_xZn_{1-x}O Catalysts, *Catal. Today*, 2020, 357, 311–321, DOI: [10.1016/j.cattod.2019.02.045](https://doi.org/10.1016/j.cattod.2019.02.045).
- 66 H. Mistry, A. S. Varela, C. S. Bonifacio, I. Zegkinoglou, I. Sinev, Y.-W. Choi, K. Kisslinger, E. A. Stach, J. C. Yang, P. Strasser and B. R. Cuenya, Highly Selective Plasma-Activated Copper Catalysts for Carbon Dioxide Reduction to Ethylene, *Nat. Commun.*, 2016, 7(1), 12123, DOI: [10.1038/ncomms12123](https://doi.org/10.1038/ncomms12123).
- 67 R. M. Arán-Ais, R. Rizo, P. Grosse, G. Algara-Siller, K. Dembélé, M. Plodinec, T. Lunkenbein, S. W. Chee and B. R. Cuenya, Imaging Electrochemically Synthesized Cu₂O Cubes and Their Morphological Evolution under Conditions Relevant to CO₂ Electroreduction, *Nat. Commun.*, 2020, 11(1), 3489, DOI: [10.1038/s41467-020-17220-6](https://doi.org/10.1038/s41467-020-17220-6).
- 68 Y. Gao, Q. Wu, X. Liang, Z. Wang, Z. Zheng, P. Wang, Y. Liu, Y. Dai, M.-H. Whangbo and B. Huang, Cu₂O Nanoparticles with Both 100 and 111 Facets for Enhancing the Selectivity and Activity of CO₂ Electroreduction to Ethylene, *Adv. Sci.*, 2020, 7(6), 1902820, DOI: [10.1002/adv.201902820](https://doi.org/10.1002/adv.201902820).
- 69 W. Luo, X. Nie, M. J. Janik and A. Asthagiri, Facet Dependence of CO₂ Reduction Paths on Cu Electrodes, *ACS Catal.*, 2016, 6(1), 219–229, DOI: [10.1021/acscatal.5b01967](https://doi.org/10.1021/acscatal.5b01967).
- 70 X. Hong, H. Zhu, D. Du, Q. Zhang and Y. Li, Research Progress of Copper-Based Bimetallic Electrocatalytic Reduction of CO₂, *Catalysts*, 2023, 13(2), 376, DOI: [10.3390/catal13020376](https://doi.org/10.3390/catal13020376).
- 71 S. Zhao, S. Li, T. Guo, S. Zhang, J. Wang, Y. Wu and Y. Chen, Advances in Sn-Based Catalysts for Electrochemical CO₂ Reduction, *Nanomicro Lett.*, 2019, 11, 62, DOI: [10.1007/s40820-019-0293-x](https://doi.org/10.1007/s40820-019-0293-x).
- 72 D. H. Won, H. Shin, J. Koh, J. Chung, H. S. Lee, H. Kim and S. I. Woo, Highly Efficient, Selective, and Stable CO₂ Electroreduction on a Hexagonal Zn Catalyst, *Angew. Chem., Int. Ed.*, 2016, 55(32), 9297–9300, DOI: [10.1002/anie.201602888](https://doi.org/10.1002/anie.201602888).
- 73 B. Goris, S. Turner, S. Bals and G. Van Tendeloo, Three-Dimensional Valency Mapping in Ceria Nanocrystals, *ACS Nano*, 2014, 8(10), 10878–10884, DOI: [10.1021/nn5047053](https://doi.org/10.1021/nn5047053).
- 74 M. L. J. Peerlings, K. Han, A. Longo, K. H. Hellferich, M. Ghiasi, P. E. de Jongh and P. Ngene, Synthesis and Catalytic Performance of Bimetallic Oxide-Derived CuO–ZnO Electrocatalysts for CO₂ Reduction, *ACS Catal.*, 2024, 14(14), 10701–10711, DOI: [10.1021/acscatal.4c01575](https://doi.org/10.1021/acscatal.4c01575).
- 75 A. O. Juma, E. A. A. Arbab, C. M. Muiva, L. M. Lepodise and G. T. Mola, Synthesis and Characterization of CuO–NiO–ZnO Mixed Metal Oxide Nanocomposite, *J. Alloys Compd.*, 2017, 723, 866–872, DOI: [10.1016/j.jallcom.2017.06.288](https://doi.org/10.1016/j.jallcom.2017.06.288).
- 76 Y. Yao, Z. Huang, L. A. Hughes, J. Gao, T. Li, D. Morris, S. E. Zeltmann, B. H. Savitzky, C. Ophus, Y. Z. Finfrook, Q. Dong, M. Jiao, Y. Mao, M. Chi, P. Zhang, J. Li, A. M. Minor, R. Shahbazian-Yassar and L. Hu, Extreme Mixing in Nanoscale Transition Metal Alloys, *Matter*, 2021, 4(7), 2340–2353, DOI: [10.1016/j.matt.2021.04.014](https://doi.org/10.1016/j.matt.2021.04.014).
- 77 S. Dongare, N. Singh, H. Bhunia and P. K. Bajpai, Electrochemical Reduction of CO₂ Using Oxide Based Cu and Zn Bimetallic Catalyst, *Electrochim. Acta*, 2021, 392, 138988, DOI: [10.1016/j.electacta.2021.138988](https://doi.org/10.1016/j.electacta.2021.138988).
- 78 N. Dutta, B. Giri, M. Riyaz, S. Midya, A. Singh, D. Bagchi, S. Mondal, S. Kediya, A. K. Singh, S. Chakraborty, A. K. Singh and S. C. Peter, Confining Reaction Intermediates in Oxide-Derived Hollow Cu–Zn Bimetallic Catalyst Facilitates Selective Formation of C₂₊ Alcohols from Electrochemical Carbon Dioxide Reduction, *Angew. Chem., Int. Ed.*, 2025, e23150, DOI: [10.1002/anie.202523150](https://doi.org/10.1002/anie.202523150).
- 79 S. Sarfraz, A. T. Garcia-Esparza, A. Jedidi, L. Cavallo and K. Takanabe, Cu–Sn Bimetallic Catalyst for Selective Aqueous Electroreduction of CO₂ to CO, *ACS Catal.*, 2016, 6(5), 2842–2851, DOI: [10.1021/acscatal.6b00269](https://doi.org/10.1021/acscatal.6b00269).
- 80 D. Kim, J. Resasco, Y. Yu, A. M. Asiri and P. Yang, Synergistic Geometric and Electronic Effects for Electrochemical Reduction of Carbon Dioxide Using Gold–Copper Bimetallic Nanoparticles, *Nat. Commun.*, 2014, 5(1), 4948, DOI: [10.1038/ncomms5948](https://doi.org/10.1038/ncomms5948).
- 81 F. Jia, X. Yu and L. Zhang, Enhanced Selectivity for the Electrochemical Reduction of CO₂ to Alcohols in Aqueous Solution with Nanostructured Cu–Au Alloy as Catalyst, *J. Power Sources*, 2014, 252, 85–89, DOI: [10.1016/j.jpowsour.2013.12.002](https://doi.org/10.1016/j.jpowsour.2013.12.002).
- 82 G. Zhang, Z.-J. Zhao, D. Cheng, H. Li, J. Yu, Q. Wang, H. Gao, J. Guo, H. Wang, G. A. Ozin, T. Wang and J. Gong, Efficient CO₂ Electroreduction on Facet-Selective Copper Films with High Conversion Rate, *Nat. Commun.*, 2021, 12(1), 5745, DOI: [10.1038/s41467-021-26053-w](https://doi.org/10.1038/s41467-021-26053-w).
- 83 S. Huo, Z. Weng, Z. Wu, Y. Zhong, Y. Wu, J. Fang and H. Wang, Coupled Metal/Oxide Catalysts with Tunable Product Selectivity for Electrocatalytic CO₂ Reduction,

- ACS Appl. Mater. Interfaces*, 2017, 9(34), 28519–28526, DOI: [10.1021/acsami.7b07707](https://doi.org/10.1021/acsami.7b07707).
- 84 Q. Lei, L. Huang, J. Yin, B. Davaasuren, Y. Yuan, X. Dong, Z.-P. Wu, X. Wang, K. X. Yao, X. Lu and Y. Han, Structural Evolution and Strain Generation of Derived-Cu Catalysts during CO₂ Electroreduction, *Nat. Commun.*, 2022, 13, 4857, DOI: [10.1038/s41467-022-32601-9](https://doi.org/10.1038/s41467-022-32601-9).
- 85 S. H. Lee, J. E. Avilés Acosta, D. Lee, D. M. Larson, H. Li, J. Chen, J. Lee, E. Erdem, D. U. Lee, S. J. Blair, A. Gallo, H. Zheng, A. C. Nielander, C. J. Tassone, T. F. Jaramillo and W. S. Drisdell, Structural Transformation and Degradation of Cu Oxide Nanocatalysts during Electrochemical CO₂ Reduction, *J. Am. Chem. Soc.*, 2025, 147(8), 6536–6548, DOI: [10.1021/jacs.4c14720](https://doi.org/10.1021/jacs.4c14720).
- 86 K. Zhao, Y. Liu, X. Quan, S. Chen and H. Yu, CO₂ Electroreduction at Low Overpotential on Oxide-Derived Cu/Carbons Fabricated from Metal Organic Framework, *ACS Appl. Mater. Interfaces*, 2017, 9(6), 5302–5311, DOI: [10.1021/acsami.6b15402](https://doi.org/10.1021/acsami.6b15402).
- 87 H. Tabassum, X. Yang, R. Zou and G. Wu, Surface Engineering of Cu Catalysts for Electrochemical Reduction of CO₂ to Value-Added Multi-Carbon Products, *Chem Catal.*, 2022, 2(7), 1561–1593, DOI: [10.1016/j.checat.2022.04.012](https://doi.org/10.1016/j.checat.2022.04.012).
- 88 P. Grosse, A. Yoon, C. Rettenmaier, A. Herzog, S. W. Chee and B. Roldan Cuenya, Dynamic Transformation of Cubic Copper Catalysts during CO₂ Electroreduction and Its Impact on Catalytic Selectivity, *Nat. Commun.*, 2021, 12(1), 6736, DOI: [10.1038/s41467-021-26743-5](https://doi.org/10.1038/s41467-021-26743-5).
- 89 G. H. Simon, C. S. Kley and B. Roldan Cuenya, Potential-Dependent Morphology of Copper Catalysts During CO₂ Electroreduction Revealed by In Situ Atomic Force Microscopy, *Angew. Chem., Int. Ed.*, 2021, 60(5), 2561–2568, DOI: [10.1002/anie.202010449](https://doi.org/10.1002/anie.202010449).
- 90 A. Dutta, M. Rahaman, M. Mohos, A. Zanetti and P. Broekmann, Electrochemical CO₂ Conversion Using Skeleton (Sponge) Type of Cu Catalysts, *ACS Catal.*, 2017, 7(8), 5431–5437, DOI: [10.1021/acscatal.7b01548](https://doi.org/10.1021/acscatal.7b01548).
- 91 M. S. Jee, H. Kim, H. S. Jeon, K. H. Chae, J. Cho, B. K. Min and Y. J. Hwang, Stable Surface Oxygen on Nanostructured Silver for Efficient CO₂ Electroreduction, *Catal. Today*, 2017, 288, 48–53, DOI: [10.1016/j.cattod.2016.09.026](https://doi.org/10.1016/j.cattod.2016.09.026).
- 92 N. J. Firet, M. A. Blommaert, T. Burdyny, A. Venugopal, D. Bohra, A. Longo and W. A. Smith, Operando EXAFS Study Reveals Presence of Oxygen in Oxide-Derived Silver Catalysts for Electrochemical CO₂ Reduction, *J. Mater. Chem. A*, 2019, 7(6), 2597–2607, DOI: [10.1039/C8TA10412C](https://doi.org/10.1039/C8TA10412C).
- 93 Z. Qi, J. Biener and M. Biener, Surface Oxide-Derived Nanoporous Gold Catalysts for Electrochemical CO₂-to-CO Reduction, *ACS Appl. Energy Mater.*, 2019, 2(11), 7717–7721, DOI: [10.1021/acsaem.9b00355](https://doi.org/10.1021/acsaem.9b00355).
- 94 T. Yu, X. Zhou, Y. Chen, J. Chen, S. Yuan, Z. Zhang, L. Qian and S. Li, Robust Catalysis of Hierarchically Nanoporous Gold for CO₂ Electrochemical Reduction, *Electrochim. Acta*, 2023, 437, 141537, DOI: [10.1016/j.electacta.2022.141537](https://doi.org/10.1016/j.electacta.2022.141537).
- 95 M. P. L. Kang, M. J. Kolb, F. Calle-Vallejo and B. S. Yeo, The Role of Undercoordinated Sites on Zinc Electrodes for CO₂ Reduction to CO, *Adv. Funct. Mater.*, 2022, 32(23), 2111597, DOI: [10.1002/adfm.202111597](https://doi.org/10.1002/adfm.202111597).
- 96 S.-T. Guo, Y.-W. Du, H. Luo, Z. Zhu, T. Ouyang and Z.-Q. Liu, Stabilizing Undercoordinated Zn Active Sites through Confinement in CeO₂ Nanotubes for Efficient Electrochemical CO₂ Reduction, *Angew. Chem., Int. Ed.*, 2024, 63(2), e202314099, DOI: [10.1002/anie.202314099](https://doi.org/10.1002/anie.202314099).
- 97 S. B. Varandili, D. Stoian, J. Vavra, K. Rossi, J. R. Pankhurst, Y. T. Guntern, N. Lopez and R. Buonsanti, Elucidating the Structure-Dependent Selectivity towards Methane and Ethanol of CuZn in the CO₂ Electroreduction Using Tailored Cu/ZnO Precatalysts, *Chem. Sci.*, 2021, 12(43), 14484–14493, DOI: [10.1039/D1SC04271H](https://doi.org/10.1039/D1SC04271H).
- 98 P.-C. Chen, C. Chen, Y. Yang, A. L. Maulana, J. Jin, J. Feijoo and P. Yang, Chemical and Structural Evolution of AgCu Catalysts in Electrochemical CO₂ Reduction, *J. Am. Chem. Soc.*, 2023, 145(18), 10116–10125, DOI: [10.1021/jacs.3c00467](https://doi.org/10.1021/jacs.3c00467).
- 99 D. Wang, H. D. Jung, S. Liu, J. Chen, H. Yang, Q. He, S. Xi, S. Back and L. Wang, Revealing the Structural Evolution of CuAg Composites during Electrochemical Carbon Monoxide Reduction, *Nat. Commun.*, 2024, 15(1), 4692, DOI: [10.1038/s41467-024-49158-4](https://doi.org/10.1038/s41467-024-49158-4).
- 100 A. Goyal, C. J. Bondue, M. Graf and M. T. M. Koper, Effect of Pore Diameter and Length on Electrochemical CO₂ Reduction Reaction at Nanoporous Gold Catalysts, *Chem. Sci.*, 2022, 13(11), 3288–3298, DOI: [10.1039/D1SC05743J](https://doi.org/10.1039/D1SC05743J).
- 101 J. Lim, H. Lim, B. Kim, S. M. Kim, J.-B. Lee, K. R. Cho, H. Choi, S. Sultan, W. Choi, W. Kim and Y. Kwon, Local pH Induced Electrochemical CO₂ Reduction on Nanostructured Ag for Adjustable Syngas Composition, *Electrochim. Acta*, 2021, 395, 139190, DOI: [10.1016/j.electacta.2021.139190](https://doi.org/10.1016/j.electacta.2021.139190).
- 102 A. J. Welch, A. Q. Fenwick, A. Böhme, H.-Y. Chen, I. Sullivan, X. Li, J. S. DuChene, C. Xiang and H. A. Atwater, Operando Local pH Measurement within Gas Diffusion Electrodes Performing Electrochemical Carbon Dioxide Reduction, *J. Phys. Chem. C*, 2021, 125(38), 20896–20904, DOI: [10.1021/acs.jpcc.1c06265](https://doi.org/10.1021/acs.jpcc.1c06265).
- 103 X. Feng, K. Jiang, S. Fan and M. W. Kanan, A Direct Grain-Boundary-Activity Correlation for CO Electroreduction on Cu Nanoparticles, *ACS Cent. Sci.*, 2016, 2(3), 169–174, DOI: [10.1021/acscentsci.6b00022](https://doi.org/10.1021/acscentsci.6b00022).
- 104 S. Kim, D. Shin, J. Park, J.-Y. Jung and H. Song, Grain Boundary-Rich Copper Nanocatalysts Generated from Metal-Organic Framework Nanoparticles for CO₂-to-C₂+ Electroconversion, *Adv. Sci.*, 2023, 10(9), 2207187, DOI: [10.1002/advs.202207187](https://doi.org/10.1002/advs.202207187).
- 105 A. Verdager-Casadevall, C. W. Li, T. P. Johansson, S. B. Scott, J. T. McKeown, M. Kumar, I. E. L. Stephens, M. W. Kanan and I. Chorkendorff, Probing the Active Surface Sites for CO Reduction on Oxide-Derived Copper Electrocatalysts, *J. Am. Chem. Soc.*, 2015, 137(31), 9808–9811, DOI: [10.1021/jacs.5b06227](https://doi.org/10.1021/jacs.5b06227).
- 106 A. Mustafa, B. G. Lougou, Y. Shuai, Z. Wang, S. Razzaq, E. Shagdar, J. Zhao and J. Shan, Recent Progresses in the Mechanism, Performance, and Fabrication Methods of Metal-Derived Nanomaterials for Efficient Electrochemical

- CO₂ Reduction, *J. Mater. Chem. A*, 2021, **9**(8), 4558–4588, DOI: [10.1039/D0TA11111B](https://doi.org/10.1039/D0TA11111B).
- 107 M. Wang, Z. Wang, X. Li, X. Sun, H. Huang, H. Chen, H. Luo, L. Li, X. Zou and X. Zhao, Unconventional High-Entropy Oxide with Inner Metallic Coordination and Surface Medium-Entropy Metal-OH for Durable PEM Water Electrolysis at 2 A Cm⁻², *Adv. Mater.*, 2025, **37**(45), e11461, DOI: [10.1002/adma.202511461](https://doi.org/10.1002/adma.202511461).
- 108 X. Feng, K. Jiang, S. Fan and M. W. Kanan, Grain-Boundary-Dependent CO₂ Electroreduction Activity, *J. Am. Chem. Soc.*, 2015, **137**(14), 4606–4609, DOI: [10.1021/ja5130513](https://doi.org/10.1021/ja5130513).
- 109 S. Chu, X. Yan, C. Choi, S. Hong, A. W. Robertson, J. Masa, B. Han, Y. Jung and Z. Sun, Stabilization of Cu⁺ by Tuning a CuO–CeO₂ Interface for Selective Electrochemical CO₂ Reduction to Ethylene, *Green Chem.*, 2020, **22**(19), 6540–6546, DOI: [10.1039/D0GC02279A](https://doi.org/10.1039/D0GC02279A).
- 110 Z. Guo, T. Wang, H. Liu, X. Jia, D. Zhang, L. Wei, J. Xu and H. Li, Electrochemical CO₂ Reduction on SnO: Insights into C1 Product Dynamic Distribution and Reaction Mechanisms, *ACS Catal.*, 2025, **15**(4), 3173–3183, DOI: [10.1021/acscatal.4c07987](https://doi.org/10.1021/acscatal.4c07987).
- 111 H. Liu, Y. Su, S. Kuang, M. Hensen, E. J. Zhang and S. Ma, X. Highly Efficient CO₂ Electrolysis within a Wide Operation Window Using Octahedral Tin Oxide Single Crystals, *J. Mater. Chem. A*, 2021, **9**(12), 7848–7856, DOI: [10.1039/D1TA00285F](https://doi.org/10.1039/D1TA00285F).
- 112 L. Li, Z.-J. Zhao, G. Zhang, D. Cheng, X. Chang, X. Yuan, T. Wang and J. Gong, Neural Network Accelerated Investigation of the Dynamic Structure–Performance Relations of Electrochemical CO₂ Reduction over SnO_x Surfaces, *Research*, 2023, **6**, 0067, DOI: [10.34133/research.0067](https://doi.org/10.34133/research.0067).
- 113 A. Herzog, M. Rüscher, H. Sang Jeon, J. Timoshenko, C. Rettenmaier, U. Hejral, E. M. Davis, T. Haase, F. Kordus, D. Kühn, S. Frandsen, W. Bergmann, A. Cuenya and B. R. Time-Resolved Operando, Insights into the Tunable Selectivity of Cu–Zn Nanocubes during Pulsed CO₂ Electroreduction, *Energy Environ. Sci.*, 2024, **17**(19), 7081–7096, DOI: [10.1039/D4EE02308K](https://doi.org/10.1039/D4EE02308K).
- 114 L. C. Pardo Pérez, A. Arndt, S. Stojkovic, I. Y. Ahmet, J. T. Arens, F. Dattila, R. Wendt, A. Guilherme Buzanich, M. Radtke, V. Davies, K. Höflich, E. Köhnen, P. Tockhorn, R. Golnak, J. Xiao, G. Schuck, M. Wollgarten, N. López and M. T. Mayer, Determining Structure-Activity Relationships in Oxide Derived Cu–Sn Catalysts During CO₂ Electroreduction Using X-Ray Spectroscopy, *Adv. Energy Mater.*, 2022, **12**(5), 2103328, DOI: [10.1002/aenm.202103328](https://doi.org/10.1002/aenm.202103328).
- 115 Z. Chen, T. Wang, B. Liu, D. Cheng, C. Hu, G. Zhang, W. Zhu, H. Wang, Z.-J. Zhao and J. Gong, Grain-Boundary-Rich Copper for Efficient Solar-Driven Electrochemical CO₂ Reduction to Ethylene and Ethanol, *J. Am. Chem. Soc.*, 2020, **142**(15), 6878–6883, DOI: [10.1021/jacs.0c00971](https://doi.org/10.1021/jacs.0c00971).
- 116 A. Jadon, C. Rossi, M. Djafari-Rouhani, A. Estève and D. Pech, Interaction of Hydrogen with the Bulk, Surface and Subsurface of Crystalline RuO₂ from First Principles, *Phys. Open*, 2021, **7**, 100059, DOI: [10.1016/j.physo.2021.100059](https://doi.org/10.1016/j.physo.2021.100059).
- 117 L. Ma, D. Geng, M. Tan, J. Li, R. Guo, Z. Zhai, X. Liu, J. Chen and Q. Li, Operando Unraveling the Dynamic Correlation between Structure Evolution and Performance Shift during CO₂ Electroreduction on In₂O₃ Electrodes, *Appl. Catal., B*, 2025, **369**, 125153, DOI: [10.1016/j.apcatb.2025.125153](https://doi.org/10.1016/j.apcatb.2025.125153).
- 118 A. Eilert, F. Cavalca, F. S. Roberts, J. Osterwalder, C. Liu, M. Favaro, E. J. Crumlin, H. Ogasawara, D. Friebe, L. G. M. Pettersson and A. Nilsson, Subsurface Oxygen in Oxide-Derived Copper Electrocatalysts for Carbon Dioxide Reduction, *J. Phys. Chem. Lett.*, 2017, **8**(1), 285–290, DOI: [10.1021/acs.jpclett.6b02273](https://doi.org/10.1021/acs.jpclett.6b02273).
- 119 H.-C. Wu, Y.-W. Huang, Y.-C. Lin, C.-H. Yang and T.-C. Liu, Enhanced Zn/ZnO Heterointerfaces via Pulsed-Potential Electrochemical Reconstruction for Highly Selective CO₂ Reduction, *ACS Appl. Mater. Interfaces*, 2025, **17**(41), 56991–57001, DOI: [10.1021/acsami.5c11775](https://doi.org/10.1021/acsami.5c11775).
- 120 C. Liu, M. P. Lourenço, S. Hedström, F. Cavalca, O. Diaz-Morales, H. A. Duarte, A. Nilsson and L. G. M. Pettersson, Stability and Effects of Subsurface Oxygen in Oxide-Derived Cu Catalyst for CO₂ Reduction, *J. Phys. Chem. C*, 2017, **121**(45), 25010–25017, DOI: [10.1021/acs.jpcc.7b08269](https://doi.org/10.1021/acs.jpcc.7b08269).
- 121 Z. Wu, P. Yang and M. Gao, Dynamic Evolution of Copper-Based Catalysts during CO₂ Electroreduction, *Nano Mater. Sci.*, 2026, **8**(3), 687–702, DOI: [10.1016/j.nanoms.2024.01.007](https://doi.org/10.1016/j.nanoms.2024.01.007).
- 122 J. Xu, W. Wang, Y. Shi, H. Li, T. Sun, X. Wan, C. Zhao, R. Hao and W. Wang, Surface Oxygen Coverage-Mediated *OOH Modulation Enables Highly Selective H₂O₂ Electrosynthesis, *Chem. Eng. J.*, 2025, **526**, 171260, DOI: [10.1016/j.cej.2025.171260](https://doi.org/10.1016/j.cej.2025.171260).
- 123 L. Li, Z.-J. Zhao, C. Hu, P. Yang, X. Yuan, Y. Wang, L. Zhang, L. Moskaleva and J. Gong, Tuning Oxygen Vacancies of Oxides to Promote Electrocatalytic Reduction of Carbon Dioxide, *ACS Energy Lett.*, 2020, **5**(2), 552–558, DOI: [10.1021/acsenenergylett.9b02749](https://doi.org/10.1021/acsenenergylett.9b02749).
- 124 W. Zhang, C. Huang, Q. Xiao, L. Yu, L. Shuai, P. An, J. Zhang, M. Qiu, Z. Ren and Y. Yu, Atypical Oxygen-Bearing Copper Boosts Ethylene Selectivity toward Electrocatalytic CO₂ Reduction, *J. Am. Chem. Soc.*, 2020, **142**(26), 11417–11427, DOI: [10.1021/jacs.0c01562](https://doi.org/10.1021/jacs.0c01562).
- 125 S. D. M. Jacques, M. Di Michiel, A. M. Beale, T. Sochi, M. G. O'Brien, L. Espinosa-Alonso, B. M. Weckhuysen and P. Barnes, Dynamic X-Ray Diffraction Computed Tomography Reveals Real-Time Insight into Catalyst Active Phase Evolution, *Angew. Chem.*, 2011, **123**(43), 10330–10334, DOI: [10.1002/ange.201104604](https://doi.org/10.1002/ange.201104604).
- 126 H. S. Jeon, J. Timoshenko, F. Scholten, I. Sinev, A. Herzog, F. T. Haase and B. Roldan Cuenya, Operando Insight into the Correlation between the Structure and Composition of CuZn Nanoparticles and Their Selectivity for the Electrochemical CO₂ Reduction, *J. Am. Chem. Soc.*, 2019, **141**(50), 19879–19887, DOI: [10.1021/jacs.9b10709](https://doi.org/10.1021/jacs.9b10709).
- 127 B. C. Dharmalingam, A. Koushik V, M. Mureddu, L. Atzori, S. Lai, A. Pettinau, N. S. Kaisare, P. Aghalayam and J. J. Varghese, Unravelling the Role of Metal-Metal Oxide Interfaces of Cu/ZnO/ZrO₂/Al₂O₃ Catalyst for Methanol Synthesis from CO₂: Insights from Experiments and DFT-Based Microkinetic Modeling, *Appl. Catal., B*, 2023, **332**, 122743, DOI: [10.1016/j.apcatb.2023.122743](https://doi.org/10.1016/j.apcatb.2023.122743).

- 128 L. Wan, X. Zhang, J. Cheng, R. Chen, L. Wu, J. Shi and J. Luo, Bimetallic Cu–Zn Catalysts for Electrochemical CO₂ Reduction: Phase-Separated versus Core–Shell Distribution, *ACS Catal.*, 2022, **12**(5), 2741–2748, DOI: [10.1021/acscatal.1c05272](https://doi.org/10.1021/acscatal.1c05272).
- 129 Z. Li, Y. Feng, Y. Li, X. Chen, N. Li, W. He and J. Liu, Fabrication of Bi/Sn Bimetallic Electrode for High-Performance Electrochemical Reduction of Carbon Dioxide to Formate, *Chem. Eng. J.*, 2022, **428**, 130901, DOI: [10.1016/j.cej.2021.130901](https://doi.org/10.1016/j.cej.2021.130901).
- 130 C. Chowdhury, F. Studt and J. Jelic, Metal–Support Interactions in Metal/Oxide and Inverse Oxide/Metal Catalysts: A Case Study Using Cu/ZnO and ZnO/Cu Model Catalysts, *J. Phys. Chem. C*, 2025, **129**(12), 5860–5867, DOI: [10.1021/acs.jpcc.4c08821](https://doi.org/10.1021/acs.jpcc.4c08821).
- 131 B. Ávila-Bolívar, V. Montiel and J. Solla-Gullón, Electrochemical Reduction of CO₂ to Formate on Nanoparticulated Bi–Sn–Sb Electrodes, *ChemElectroChem*, 2022, **9**(9), e202200272, DOI: [10.1002/celec.202200272](https://doi.org/10.1002/celec.202200272).
- 132 W. Zhu, K. Zhao, S. Liu, M. Liu, F. Peng, P. An, B. Qin, H. Zhou, H. Li and Z. He, Low-Overpotential Selective Reduction of CO₂ to Ethanol on Electrodeposited Cu₂Au Nanowire Arrays, *J. Energy Chem.*, 2019, **37**, 176–182, DOI: [10.1016/j.jechem.2019.03.030](https://doi.org/10.1016/j.jechem.2019.03.030).
- 133 S. Nilsson, J. N. El Berch, D. Albinsson, J. Fritzsche, G. Mpourmpakis and C. Langhammer, The Role of Grain Boundary Sites for the Oxidation of Copper Catalysts during the CO Oxidation Reaction, *ACS Nano*, 2023, **17**(20), 20284–20298, DOI: [10.1021/acsnano.3c06282](https://doi.org/10.1021/acsnano.3c06282).
- 134 I. Stamatelos, C.-T. Dinh, W. Lehnert and M. Shviro, Zn-Based Catalysts for Selective and Stable Electrochemical CO₂ Reduction at High Current Densities, *ACS Appl. Energy Mater.*, 2022, **5**(11), 13928–13938, DOI: [10.1021/acsaem.2c02557](https://doi.org/10.1021/acsaem.2c02557).
- 135 L. Fang, X. Lyu, J. J. Xu, Y. Liu, X. Hu, B. J. Reinhart and T. Li, Operando X-Ray Absorption Spectroscopy Study of SnO₂ Nanoparticles for Electrochemical Reduction of CO₂ to Formate, *ACS Appl. Mater. Interfaces*, 2022, **14**(50), 55636–55643, DOI: [10.1021/acsami.2c17481](https://doi.org/10.1021/acsami.2c17481).
- 136 G. B. Damas, C. R. Miranda, R. Sgarbi, J. M. Portela, M. R. Camilo, F. H. B. Lima and C. M. Araujo, On the Mechanism of Carbon Dioxide Reduction on Sn-Based Electrodes: Insights into the Role of Oxide Surfaces, *Catalysts*, 2019, **9**(8), 636, DOI: [10.3390/catal9080636](https://doi.org/10.3390/catal9080636).
- 137 F.-M. Li, C. Xia and B. Y. Xia, Exploration and Insight of Dynamic Structure Evolution for Electrocatalysts, *Acc. Mater. Res.*, 2023, **4**(5), 427–437, DOI: [10.1021/accountsmr.2c00261](https://doi.org/10.1021/accountsmr.2c00261).
- 138 Z. Liang, J. Fu, M. B. Vukmirovic and R. R. Adzic, Electrochemical CO₂ Reduction on Oxide-Derived Cu Surface with Various Oxide Thicknesses, *ECS Trans.*, 2018, **85**(12), 195, DOI: [10.1149/08512.0195ecst](https://doi.org/10.1149/08512.0195ecst).
- 139 Y. Zhong, Z. Sun, B. Y. Xia and Y. Su, Structural Reconstruction of Copper-Based Catalysts in CO₂ Electroreduction Reaction: A Comprehensive Review, *Chem. – Eur. J.*, 2025, **31**(27), e202500770, DOI: [10.1002/chem.202500770](https://doi.org/10.1002/chem.202500770).
- 140 S. Chen, F. Farzinpour and N. Kornienko, Dynamic Active Sites behind Cu-Based Electrocatalysts: Original or Restructuring-Induced Catalytic Activity, *Chem*, 2025, **11**(8), DOI: [10.1016/j.chempr.2025.102575](https://doi.org/10.1016/j.chempr.2025.102575).
- 141 X. Liu, A. Wang, L. Li, T. Zhang, C.-Y. Mou and J.-F. Lee, Structural Changes of Au–Cu Bimetallic Catalysts in CO Oxidation: *In Situ* XRD, EPR, XANES, and FT-IR Characterizations, *J. Catal.*, 2011, **278**(2), 288–296, DOI: [10.1016/j.jcat.2010.12.016](https://doi.org/10.1016/j.jcat.2010.12.016).
- 142 K. Xu, S. Liu, Z. Cao, Y. Mao and Q. Mao, Pore-Structure-Enhanced Electrochemical Reduction of CO₂ to Formate on Sn-Based Double-Layer Catalysts, *Electrochem. Commun.*, 2021, **128**, 107056, DOI: [10.1016/j.elecom.2021.107056](https://doi.org/10.1016/j.elecom.2021.107056).
- 143 H. Jiang, Z. Fan, M. Zhang, S. Guo, L. Li, X. Yu, Z. Liu, W. Wang, H. Dong and M. Zhong, Redox-Stabilized Sn/SnO₂ Nanostructures for Efficient and Stable CO₂ Electroreduction to Formate, *ChemElectroChem*, 2023, **10**(8), e202201164, DOI: [10.1002/celec.202201164](https://doi.org/10.1002/celec.202201164).
- 144 Y. Fang, Y. Wen, C. Cai, K. Li, Y. Kuwahara, K. Mori, H. Yamashita, X. Qian and Y. Zhao, Bismuth-Based Catalysts for Electrocatalytic CO₂ Reduction to Formate in Aqueous Media, *Chem Catal.*, 2025, **5**(11), 101540, DOI: [10.1016/j.checat.2025.101540](https://doi.org/10.1016/j.checat.2025.101540).
- 145 Q. Lei, H. Zhu, K. Song, N. Wei, L. Liu, D. Zhang, J. Yin, X. Dong, K. Yao, N. Wang, X. Li, B. Davaasuren, J. Wang and Y. Han, Investigating the Origin of Enhanced C₂₊ Selectivity in Oxide-/Hydroxide-Derived Copper Electrodes during CO₂ Electroreduction, *J. Am. Chem. Soc.*, 2020, **142**(9), 4213–4222, DOI: [10.1021/jacs.9b11790](https://doi.org/10.1021/jacs.9b11790).
- 146 F. Dattila, R. García-Muelas and N. López, Active and Selective Ensembles in Oxide-Derived Copper Catalysts for CO₂ Reduction., *ACS Energy Lett.*, 2020, **5**(10), 3176–3184, DOI: [10.1021/acsenerylett.0c01777](https://doi.org/10.1021/acsenerylett.0c01777).
- 147 M. Yang, J. Wu, Y. Li, H. Pan, H. Cui, X. Lu and X. Tang, Structural Evolution of Oxide-Derived Nanostructured Silver Electrocatalysts during CO₂ Electroreduction, *ACS Catal.*, 2024, **14**(8), 6169–6178, DOI: [10.1021/acscatal.4c00217](https://doi.org/10.1021/acscatal.4c00217).
- 148 F. Mattarozzi, N. van der Willige, V. Gulino, C. Keijzer, R. C. J. van de Poll, E. J. M. Hensen, P. Ngene and P. E. de Jongh, Oxide-Derived Silver Nanowires for CO₂ Electrocatalytic Reduction to CO, *ChemCatChem*, 2023, **15**(22), e202300792, DOI: [10.1002/cctc.202300792](https://doi.org/10.1002/cctc.202300792).
- 149 Y. Mao, Q. Mao, H. Yang, Q. Liu, X. Dong, Y. Li, S. Zhou and B. Liu, Dynamically Stabilizing Oxygen Atoms in Silver Catalyst for Highly Selective and Durable CO₂ Reduction Reaction, *Angew. Chem., Int. Ed.*, 2024, **63**(49), e202410932, DOI: [10.1002/anie.202410932](https://doi.org/10.1002/anie.202410932).
- 150 G. Zhang, B. Tan, D. H. Mok, H. Liu, B. Ni, G. Zhao, K. Ye, S. Huo, X. Miao, Z. Liang, X. Liu, L. Chen, Z. Zhang, W.-B. Cai, S. Back and K. Jiang, Electrifying HCOOH Synthesis from CO₂ Building Blocks over Cu–Bi Nanorod Arrays, *Proc. Natl. Acad. Sci. U. S. A.*, 2024, **121**(29), e2400898121, DOI: [10.1073/pnas.2400898121](https://doi.org/10.1073/pnas.2400898121).
- 151 S. Rasul, A. Pugnant, H. Xiang, J.-M. Fontmorin and E. H. Yu, Low Cost and Efficient Alloy Electrocatalysts for CO₂ Reduction to Formate, *J. CO₂ Util.*, 2019, **32**, 1–10, DOI: [10.1016/j.jcou.2019.03.016](https://doi.org/10.1016/j.jcou.2019.03.016).
- 152 F. Yang, C. Liang, W. Zhou, W. Zhao, P. Li, Z. Hua, H. Yu, S. Chen, S. Deng, J. Li, Y. M. Lam and J. Wang, Oxide-Derived Bismuth as an Efficient Catalyst for

- Electrochemical Reduction of Flue Gas, *Small*, 2023, **19**(30), 2300417, DOI: [10.1002/sml.202300417](https://doi.org/10.1002/sml.202300417).
- 153 Y. Yang, S. Louisia, S. Yu, J. Jin, I. Roh, C. Chen, M. V. Fonseca Guzman, J. Feijóo, P.-C. Chen, H. Wang, C. J. Pollock, X. Huang, Y.-T. Shao, C. Wang, D. A. Muller, H. D. Abruña and P. Yang, Operando Studies Reveal Active Cu Nanograins for CO₂ Electroreduction, *Nature*, 2023, **614**(7947), 262–269, DOI: [10.1038/s41586-022-05540-0](https://doi.org/10.1038/s41586-022-05540-0).
- 154 Y. Xie, Z. Guo, Z. Lang, K. Liu, J. Lv, J. Yan, S. Zhu, Y. Zhou, B. Xu, H. B. Wu, M. Xu and A. Wu, Oxide-Derived Low-Coordination Ag Catalysts Enable Efficient Photovoltaic-Driven Electrochemical CO₂ Reduction in MEA Electrolyzers, *EES Catal.*, 2025, **3**(6), 1391–1399, DOI: [10.1039/D5EY00208G](https://doi.org/10.1039/D5EY00208G).
- 155 D. Giziński, M. Najderek, A. Brudzisz, J. Lee, J. Choi and W. J. Stepniowski, Surface Reorganization of Oxide-Derived Cu-M (M = Zn, Ag) Bimetallic Catalysts in CO₂ Electroreduction Environment, *Surf. Interfaces*, 2024, **44**, 103692, DOI: [10.1016/j.surfin.2023.103692](https://doi.org/10.1016/j.surfin.2023.103692).
- 156 J. de Ruiter, V. R. M. Benning, S. Yang, B. J. den Hartigh, H. Wang, P. T. Prins, J. M. Dorresteyn, J. C. L. Janssens, G. Manna, A. V. Petukhov, B. M. Weckhuysen, F. T. Rabouw and W. van der Stam, Multiscale X-Ray Scattering Elucidates Activation and Deactivation of Oxide-Derived Copper Electrocatalysts for CO₂ Reduction, *Nat. Commun.*, 2025, **16**(1), 373, DOI: [10.1038/s41467-024-55742-5](https://doi.org/10.1038/s41467-024-55742-5).
- 157 T. Kim, D. H. Lee, S. Jo, S. H. Pyun, K.-T. Kim and Y.-H. Song, Cover Picture: Mechanism of the Accelerated Reduction of an Oxidized Metal Catalyst under Electric Discharge (ChemCatChem 4/2016), *ChemCatChem*, 2016, **8**(4), 657, DOI: [10.1002/cctc.201600138](https://doi.org/10.1002/cctc.201600138).
- 158 P. Ghosh, D. Roy, A. Das, R. K. Sharma and B. Pathak, Dynamic Surface Evolution and O Diffusion in High-Index Cu₂O Surfaces for Enhanced Electrochemical CO₂ Reduction, *J. Phys. Chem. C*, 2025, **129**(49), 21622–21633, DOI: [10.1021/acs.jpcc.5c05945](https://doi.org/10.1021/acs.jpcc.5c05945).
- 159 A. Ruiz Puigdollers, P. Schlexer, S. Tosoni and G. Pacchioni, Increasing Oxide Reducibility: The Role of Metal/Oxide Interfaces in the Formation of Oxygen Vacancies, *ACS Catal.*, 2017, **7**(10), 6493–6513, DOI: [10.1021/acscatal.7b01913](https://doi.org/10.1021/acscatal.7b01913).
- 160 Y. Qu, W. Zheng, P. Wang, H. Huang, M. Huang, L. Hu, H. Wang and Q. Chen, Creating Interfaces of Cu⁰/Cu⁺ in Oxide-Derived Copper Catalysts for Electrochemical CO₂ Reduction to Multi-Carbon Products, *J. Colloid Interface Sci.*, 2023, **645**, 735–742, DOI: [10.1016/j.jcis.2023.04.133](https://doi.org/10.1016/j.jcis.2023.04.133).
- 161 A. K. Mishra and N. H. de Leeuw, Mechanistic Insights into the Cu(I) Oxide-Catalyzed Conversion of CO₂ to Fuels and Chemicals: A DFT Approach, *J. CO₂ Util.*, 2016, **15**, 96–106, DOI: [10.1016/j.jcou.2016.02.008](https://doi.org/10.1016/j.jcou.2016.02.008).
- 162 D. Sekiba, H. Nakamizo, R. Ozawa, Y. Gunji and H. Fukutani, Electronic Structure Investigation of Ag(110)p(2 × 1)O Surface, *Surf. Sci.*, 2000, **449**(1), 111–124, DOI: [10.1016/S0039-6028\(99\)01225-X](https://doi.org/10.1016/S0039-6028(99)01225-X).
- 163 X. Zhang, M. Wu, Y. Xu, J. Ji, Y. Chen, W. Wang, N. Mitsuzaki and Z. Chen, Low-Overpotential CO₂ Electroreduction to HCOOH Using Electrodeposited Dendritic Bi-Ce Alloys, *Langmuir*, 2025, **41**(48), 32382–32393, DOI: [10.1021/acs.langmuir.5c03988](https://doi.org/10.1021/acs.langmuir.5c03988).
- 164 X. Lai, Y. Xiao, J. Feng, Y. Li, L. Li, Z. Feng, W. F. Ip and H. Pan, In-Situ Reconstructed Sn-Incorporated Bi for Highly Selective Electrochemical CO₂ Reduction to Formate, *Appl. Catal., B*, 2025, 126222, DOI: [10.1016/j.apcatb.2025.126222](https://doi.org/10.1016/j.apcatb.2025.126222).
- 165 Y. Kong, X. Jiang, X. Li, J. Sun, Q. Hu, X. Chai, H. Yang and C. He, Boosting Electrocatalytic CO₂ Reduction to Formate via Carbon Nanofiber Encapsulated Bismuth Nanoparticles with Ultrahigh Mass Activity, *Chin. J. Catal.*, 2023, **45**, 95–106, DOI: [10.1016/S1872-2067\(22\)64177-9](https://doi.org/10.1016/S1872-2067(22)64177-9).
- 166 Y. Hori, Electrochemical CO₂ Reduction on Metal Electrodes, in *Modern Aspects of Electrochemistry*, ed. C. G. Vayenas, R. E. White and M. E. Gamboa-Aldeco, Springer, New York, NY, 2008, pp. 89–189, DOI: [10.1007/978-0-387-49489-0_3](https://doi.org/10.1007/978-0-387-49489-0_3).
- 167 Y. Liu, H. Huang and X. Peng, Highly Enhanced Capacitance of CuO Nanosheets by Formation of CuO/SWCNT Networks through Electrostatic Interaction, *Electrochim. Acta*, 2013, **104**, 289–294, DOI: [10.1016/j.electacta.2013.04.110](https://doi.org/10.1016/j.electacta.2013.04.110).
- 168 M. Wu, C. Zhu, J. Mao, X. Dong, S. Li, G. Feng, G. Li, G. Wu, Y. Song, W. Wei and W. Chen, Dimensional Effect of Oxide-Derived Cu Electrocatalysts to Reduce CO₂ into Multicarbon Compounds, *Chem. Eng. J.*, 2024, **499**, 156006, DOI: [10.1016/j.cej.2024.156006](https://doi.org/10.1016/j.cej.2024.156006).
- 169 Z. Jiang, C. Clavaguéra, S. A. Denisov, J. Ma and M. Mostafavi, Role of Oxide-Derived Cu on the Initial Elementary Reaction Intermediate During Catalytic CO₂ Reduction, *J. Am. Chem. Soc.*, 2024, **146**(44), 30164–30173, DOI: [10.1021/jacs.4c08603](https://doi.org/10.1021/jacs.4c08603).
- 170 J. Resasco, L. D. Chen, E. Clark, C. Tsai, C. Hahn, T. F. Jaramillo, K. Chan and A. T. Bell, Promoter Effects of Alkali Metal Cations on the Electrochemical Reduction of Carbon Dioxide, *J. Am. Chem. Soc.*, 2017, **139**(32), 11277–11287, DOI: [10.1021/jacs.7b06765](https://doi.org/10.1021/jacs.7b06765).
- 171 J. H. Montoya, C. Shi, K. Chan and J. K. Nørskov, Theoretical Insights into a CO Dimerization Mechanism in CO₂ Electroreduction, *J. Phys. Chem. Lett.*, 2015, **6**(11), 2032–2037, DOI: [10.1021/acs.jpclett.5b00722](https://doi.org/10.1021/acs.jpclett.5b00722).
- 172 A. D. Handoko, C. W. Ong, Y. Huang, Z. G. Lee, L. Lin, G. B. Panetti and B. S. Yeo, Mechanistic Insights into the Selective Electroreduction of Carbon Dioxide to Ethylene on Cu₂O-Derived Copper Catalysts, *J. Phys. Chem. C*, 2016, **120**(36), 20058–20067, DOI: [10.1021/acs.jpcc.6b07128](https://doi.org/10.1021/acs.jpcc.6b07128).
- 173 Q. Fang, Y. Jia, X. Lang, G. Li, T. Zhao, D. Zhong, J. Li and Q. Zhao, Defect-Rich Porous Cu with Abundant Cu(100) for Acidic CO₂ Electroreduction in Membrane Electrode Assembly, *Adv. Sci.*, 2025, **12**(40), e10161, DOI: [10.1002/adv.202510161](https://doi.org/10.1002/adv.202510161).
- 174 C. Zhan, F. Dattila, C. Rettenmaier, A. Bergmann, S. Kühl, R. García-Muelas, N. López and B. R. Cuenya, Revealing the CO Coverage-Driven C–C Coupling Mechanism for Electrochemical CO₂ Reduction on Cu₂O Nanocubes via Operando Raman Spectroscopy, *ACS Catal.*, 2021, **11**(13), 7694–7701, DOI: [10.1021/acscatal.1c01478](https://doi.org/10.1021/acscatal.1c01478).
- 175 M. Sun, D. S. R. Rocabado, J. Cheng, T. G. Noguchi, M. Donoshita, T. Matsuu, M. Higashi, T. Fujigaya,

- T. Ishimoto and M. Yamauchi, In Situ Observation of Post-CO Intermediates to Decode C–C Coupling Pathways in CO₂ Electroreduction, *Angew. Chem., Int. Ed.*, 2025, **64**(30), e202502740, DOI: [10.1002/anie.202502740](https://doi.org/10.1002/anie.202502740).
- 176 K. Yue, Y. Qin, H. Huang, Z. Lv, M. Cai, Y. Su, F. Huang and Y. Yan, Stabilized Cu⁰–Cu⁺ Dual Sites in a Cyanamide Framework for Selective CO₂ Electroreduction to Ethylene, *Nat. Commun.*, 2024, **15**(1), 7820, DOI: [10.1038/s41467-024-52022-0](https://doi.org/10.1038/s41467-024-52022-0).
- 177 F. Zhang, N. Cao, C. Wang, S. Wang, Y. He, Y. Shi, M. Yan, Y. Bao, Z. Li and P. Xie, In Situ Stabilization of Cu⁺ for CO₂ Electroreduction via Environmental-Molecules-Induced ZnO_{1–x} Shield, *Nat. Commun.*, 2025, **16**(1), 6082, DOI: [10.1038/s41467-025-61189-z](https://doi.org/10.1038/s41467-025-61189-z).
- 178 J. Darayen, O. Chailapakul, P. Praserttham, J. Panpranot, D. N. Tungasmita and Y. Boonyongmaneerat, Porous Electrodeposited Cu as a Potential Electrode for Electrochemical Reduction Reactions of CO₂, *Appl. Sci.*, 2021, **11**(23), 11104, DOI: [10.3390/app112311104](https://doi.org/10.3390/app112311104).
- 179 J. Li, F. Che, Y. Pang, C. Zou, J. Y. Howe, T. Burdyny, J. P. Edwards, Y. Wang, F. Li, Z. Wang, P. De Luna, C.-T. Dinh, T.-T. Zhuang, M. I. Saidaminov, S. Cheng, T. Wu, Y. Z. Finfrock, L. Ma, S.-H. Hsieh, Y.-S. Liu, G. A. Botton, W.-F. Pong, X. Du, J. Guo, T.-K. Sham, E. H. Sargent and D. Sinton, Copper Adparticle Enabled Selective Electrosynthesis of N-Propanol, *Nat. Commun.*, 2018, **9**(1), 4614, DOI: [10.1038/s41467-018-07032-0](https://doi.org/10.1038/s41467-018-07032-0).
- 180 C. Hahn, T. Hatsukade, Y.-G. Kim, A. Vailionis, J. H. Baricuatro, D. C. Higgins, S. A. Nitopi, M. P. Soriaga and T. F. Jaramillo, Engineering Cu Surfaces for the Electrocatalytic Conversion of CO₂: Controlling Selectivity toward Oxygenates and Hydrocarbons, *Proc. Natl. Acad. Sci. U. S. A.*, 2017, **114**(23), 5918–5923, DOI: [10.1073/pnas.1618935114](https://doi.org/10.1073/pnas.1618935114).
- 181 T.-T. Zhuang, Z.-Q. Liang, A. Seifitokaldani, Y. Li, P. De Luna, T. Burdyny, F. Che, F. Meng, Y. Min, R. Quintero-Bermudez, C. T. Dinh, Y. Pang, M. Zhong, B. Zhang, J. Li, P.-N. Chen, X.-L. Zheng, H. Liang, W.-N. Ge, B.-J. Ye, D. Sinton, S.-H. Yu and E. H. Sargent, Steering Post-C–C Coupling Selectivity Enables High Efficiency Electroreduction of Carbon Dioxide to Multi-Carbon Alcohols, *Nat. Catal.*, 2018, **1**(6), 421–428, DOI: [10.1038/s41929-018-0084-7](https://doi.org/10.1038/s41929-018-0084-7).
- 182 D. Xia, H. Yu, H. Xie, P. Huang, R. Menzel, M. M. Titirici and G. Chai, Recent Progress of Bi-Based Electrocatalysts for Electrocatalytic CO₂ Reduction, *Nanoscale*, 2022, **14**(22), 7957–7973, DOI: [10.1039/D2NR01900K](https://doi.org/10.1039/D2NR01900K).
- 183 Y. Chen and M. W. Kanan, Tin Oxide Dependence of the CO₂ Reduction Efficiency on Tin Electrodes and Enhanced Activity for Tin/Tin Oxide Thin-Film Catalysts, *J. Am. Chem. Soc.*, 2012, **134**(4), 1986–1989, DOI: [10.1021/ja2108799](https://doi.org/10.1021/ja2108799).
- 184 P. A. Haugg, J. Smyczek, P. Hubert, C. Schröder and S. Schauermaier, Crucial Effect of Subsurface Hydrogen on Low-Barrier Hydrogenation and Keto–Enol Tautomerization of Carbonyl Compounds, *ACS Catal.*, 2024, **14**(13), 10022–10030, DOI: [10.1021/acscatal.4c01441](https://doi.org/10.1021/acscatal.4c01441).
- 185 M. Hellström, Subsurface Hydrogen Bonds at the Polar Zn-Terminated ZnO(0001) Surface, *Phys. Rev. B*, 2016, **94**(24), DOI: [10.1103/PhysRevB.94.245433](https://doi.org/10.1103/PhysRevB.94.245433).
- 186 L. Li, S. Yao, Y. Feng, Z. Gao, J. Wang, P. Yin, H. Liu and Z. Zhang, Grain Boundary-Induced Stabilization of Bi₃₊/Bi₀ Coexistence in β-Bi₂O₃ for Highly Efficient Electrochemical CO₂ Reduction to Formate, *Appl. Catal., B*, 2025, **372**, 125302, DOI: [10.1016/j.apcatb.2025.125302](https://doi.org/10.1016/j.apcatb.2025.125302).
- 187 T. Mahmoudi, W.-Y. Rho, M. Kohan, Y. H. Im, S. Mathur and Y.-B. Hahn, Suppression of Sn₂₊/Sn₄₊ Oxidation in Tin-Based Perovskite Solar Cells with Graphene-Tin Quantum Dots Composites in Active Layer, *Nano Energy*, 2021, **90**, 106495, DOI: [10.1016/j.nanoen.2021.106495](https://doi.org/10.1016/j.nanoen.2021.106495).
- 188 X. Lang, Y. Jia, Q. Fang, Z. Peng, D. Zhong, J. Li and Q. Zhao, Engineering CuIn Microenvironment for Efficient Acidic Electrochemical CO₂ Reduction to CO, *Appl. Catal., B*, 2025, **371**, 125244, DOI: [10.1016/j.apcatb.2025.125244](https://doi.org/10.1016/j.apcatb.2025.125244).
- 189 X. Y. Zhang, Z. X. Lou, J. Chen, Y. Liu, X. Wu, J. Y. Zhao, H. Y. Yuan, M. Zhu, S. Dai, H. F. Wang, C. Sun, P. F. Liu and H. G. Yang, Direct OC–CHO Coupling towards Highly C₂₊ Products Selective Electroreduction over Stable Cu⁰/Cu₂₊ Interface, *Nat. Commun.*, 2023, **14**(1), 7681, DOI: [10.1038/s41467-023-43182-6](https://doi.org/10.1038/s41467-023-43182-6).
- 190 M. Löffler, K. J. J. Mayrhofer and I. Katsounaros, Oxide Reduction Precedes Carbon Dioxide Reduction on Oxide-Derived Copper Electrodes, *J. Phys. Chem. C*, 2021, **125**(3), 1833–1838, DOI: [10.1021/acs.jpcc.0c09107](https://doi.org/10.1021/acs.jpcc.0c09107).
- 191 S. H. Lee, I. Sullivan, D. M. Larson, G. Liu, F. M. Toma, C. Xiang and W. S. Drisdell, Correlating Oxidation State and Surface Area to Activity from Operando Studies of Copper CO Electroreduction Catalysts in a Gas-Fed Device, *ACS Catal.*, 2020, **10**(14), 8000–8011, DOI: [10.1021/acscatal.0c01670](https://doi.org/10.1021/acscatal.0c01670).
- 192 W. Wang, M. Salomone, M. Re Fiorentin, F. Risplendi and G. Cicero, Activating C–C Coupling on Copper during CO₂RR: Charge-Controlled Design of Alloy Catalysts, *ACS Electrochem.*, 2025, **1**(11), 2512–2520, DOI: [10.1021/acselecchem.5c00297](https://doi.org/10.1021/acselecchem.5c00297).
- 193 C. Chen, Y. Li, S. Yu, S. Louisia, J. Jin, M. Li, M. B. Ross and P. Yang, Cu–Ag Tandem Catalysts for High-Rate CO₂ Electrolysis toward Multicarbon, *Joule*, 2020, **4**(8), 1688–1699, DOI: [10.1016/j.joule.2020.07.009](https://doi.org/10.1016/j.joule.2020.07.009).
- 194 B. Sun, H. Hu, J. Guan, Z. Jiang, Y. Wang, S. Ma, K. Song, C. Shi and H. Cheng, Porous-Carbon Confined Cu–O–Zn Heterointerface for Efficient Electroreduction of CO₂ to Syngas with Controllable CO/H₂ Ratios, *Fuel*, 2024, **371**, 132145, DOI: [10.1016/j.fuel.2024.132145](https://doi.org/10.1016/j.fuel.2024.132145).
- 195 C. Azenha, C. Mateos-Pedrero, T. Lagarteira and A. M. Mendes, Tuning the Selectivity of Cu₂O/ZnO Catalyst for CO₂ Electrochemical Reduction, *J. CO₂ Util.*, 2023, **68**, 102368, DOI: [10.1016/j.jcou.2022.102368](https://doi.org/10.1016/j.jcou.2022.102368).
- 196 X. Tan, W. Guo, S. Liu, S. Jia, L. Xu, J. Feng, X. Yan, C. Chen, Q. Zhu, X. Sun and B. Han, A Sn-Stabilized Cu^{δ+} Electrocatalyst toward Highly Selective CO₂-to-CO in a Wide Potential Range, *Chem. Sci.*, 2022, **13**(40), 11918–11925, DOI: [10.1039/D2SC04607E](https://doi.org/10.1039/D2SC04607E).

- 197 S. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, A. K. Engstfeld, S. Horch, B. Seger, I. E. L. Stephens, K. Chan, C. Hahn, J. K. Nørskov, T. F. Jaramillo and I. Chorkendorff, Progress and Perspectives of Electrochemical CO₂ Reduction on Copper in Aqueous Electrolyte, *Chem. Rev.*, 2019, **119**(12), 7610–7672, DOI: [10.1021/acs.chemrev.8b00705](https://doi.org/10.1021/acs.chemrev.8b00705).
- 198 I. E. L. Stephens, K. Chan, A. Bagger, S. W. Boettcher, J. Bonin, E. Boutin, A. K. Buckley, R. Buonsanti, E. R. Cave, X. Chang, S. W. Chee, A. H. M. da Silva, P. de Luna, O. Einsle, B. Endrődi, M. Escudero-Escribano, J. V. Ferreira de Araujo, M. C. Figueiredo, C. Hahn, K. U. Hansen, S. Haussener, S. Hunegnaw, Z. Huo, Y. J. Hwang, C. Janáky, B. S. Jayathilake, F. Jiao, Z. P. Jovanov, P. Karimi, M. T. M. Koper, K. P. Kuhl, W. H. Lee, Z. Liang, X. Liu, S. Ma, M. Ma, H.-S. Oh, M. Robert, B. R. Cuenya, J. Rossmeisl, C. Roy, M. P. Ryan, E. H. Sargent, P. Sebastián-Pascual, B. Seger, L. Steier, P. Strasser, A. S. Varela, R. E. Vos, X. Wang, B. Xu, H. Yadegari and Y. Zhou, 2022 Roadmap on Low Temperature Electrochemical CO₂ Reduction, *J. Phys. Energy*, 2022, **4**(4), 042003, DOI: [10.1088/2515-7655/ac7823](https://doi.org/10.1088/2515-7655/ac7823).
- 199 A. S. Varela, M. Kroschel, N. D. Leonard, W. Ju, J. Steinberg, A. Bagger, J. Rossmeisl and P. Strasser, pH Effects on the Selectivity of the Electrocatalytic CO₂ Reduction on Graphene-Embedded Fe–N–C Motifs: Bridging Concepts between Molecular Homogeneous and Solid-State Heterogeneous Catalysis, *ACS Energy Lett.*, 2018, **3**(4), 812–817, DOI: [10.1021/acseenergylett.8b00273](https://doi.org/10.1021/acseenergylett.8b00273).
- 200 Y. Zhou, K. Wang, S. Zheng, X. Cheng, Y. He, W. Qin, X. Zhang, H. Chang, N. Zhong and X. He, Advancements in Electrochemical CO₂ Reduction Reaction: A Review on CO₂ Mass Transport Enhancement Strategies, *Chem. Eng. J.*, 2024, **486**, 150169, DOI: [10.1016/j.cej.2024.150169](https://doi.org/10.1016/j.cej.2024.150169).
- 201 T. Xu, H. Yang, T. Lu, R. Zhong, J.-J. Lv, S. Zhu, M. Zhang, Z.-J. Wang, Y. Yuan, J. Li, J. Wang, H. Jin, S. Pan, X. Wang, T. Cheng and S. Wang, Microenvironment Engineering by Targeted Delivery of Ag Nanoparticles for Boosting Electrocatalytic CO₂ Reduction Reaction, *Nat. Commun.*, 2025, **16**(1), 977, DOI: [10.1038/s41467-025-56039-x](https://doi.org/10.1038/s41467-025-56039-x).
- 202 E. W. Lees, J. C. Bui, O. Romiluyi, A. T. Bell and A. Z. Weber, Exploring CO₂ Reduction and Crossover in Membrane Electrode Assemblies, *Nat. Chem. Eng.*, 2024, **1**(5), 340–353, DOI: [10.1038/s44286-024-00062-0](https://doi.org/10.1038/s44286-024-00062-0).
- 203 M. Li, E. W. Lees, W. Ju, S. Subramanian, K. Yang, J. C. Bui, H.-P. Iglesias van Montfort, M. Abdinejad, J. Middelkoop, P. Strasser, A. Z. Weber, A. T. Bell and T. Burdyny, Local Ionic Transport Enables Selective PGM-Free Bipolar Membrane Electrode Assembly, *Nat. Commun.*, 2024, **15**(1), 8222, DOI: [10.1038/s41467-024-52409-z](https://doi.org/10.1038/s41467-024-52409-z).
- 204 Z. Chen, Y. Ye and K. Jiang, Metal–Metal Oxide Hybrid Catalysts for Electrocatalytic CO₂ Reduction Reaction, *Chem. Phys. Rev.*, 2024, **5**(4), 041302, DOI: [10.1063/5.0223542](https://doi.org/10.1063/5.0223542).
- 205 B. Eren, D. Zhrebetsky, L. L. Patera, C. H. Wu, H. Bluhm, C. Africh, L.-W. Wang, G. A. Somorjai and M. Salmeron, Activation of Cu(111) Surface by Decomposition into Nanoclusters Driven by CO Adsorption, *Science*, 2016, **351**(6272), 475–478, DOI: [10.1126/science.aad8868](https://doi.org/10.1126/science.aad8868).
- 206 K.-L. C. Nguyen, J. P. Bruce, A. Yoon, J. J. Navarro, F. Scholten, F. Landwehr, C. Rettenmaier, M. Heyde and B. R. Cuenya, The Influence of Mesoscopic Surface Structure on the Electrocatalytic Selectivity of CO₂ Reduction with UHV-Prepared Cu(111) Single Crystals, *ACS Energy Lett.*, 2024, **9**(2), 644–652, DOI: [10.1021/acsenergylett.3c02693](https://doi.org/10.1021/acsenergylett.3c02693).
- 207 B. Ligt, L. B. Donk, F. A. Rollier, J. F. M. Simons, M. C. Figueiredo and E. J. M. Hensen, Restructuring of Shape-Controlled Cu₂O Catalysts during CO₂ Electroreduction, *J. Electroanal. Chem.*, 2026, **1002**, 119742, DOI: [10.1016/j.jelechem.2025.119742](https://doi.org/10.1016/j.jelechem.2025.119742).
- 208 X. Wang, K. Klingan, M. Klingenhof, T. Möller, J. Ferreira de Araújo, I. Martens, A. Bagger, S. Jiang, J. Rossmeisl, H. Dau and P. Strasser, Morphology and Mechanism of Highly Selective Cu(II) Oxide Nanosheet Catalysts for Carbon Dioxide Electroreduction, *Nat. Commun.*, 2021, **12**(1), 794, DOI: [10.1038/s41467-021-20961-7](https://doi.org/10.1038/s41467-021-20961-7).
- 209 F. Calle-Vallejo and M. T. M. Koper, Theoretical Considerations on the Electroreduction of CO to C₂ Species on Cu(100) Electrodes, *Angew. Chem., Int. Ed.*, 2013, **52**(28), 7282–7285, DOI: [10.1002/anie.201301470](https://doi.org/10.1002/anie.201301470).
- 210 T. Zhang, J. C. Bui, Z. Li, A. T. Bell, A. Z. Weber and J. Wu, Highly Selective and Productive Reduction of Carbon Dioxide to Multicarbon Products *via in situ* CO Management Using Segmented Tandem Electrodes, *Nat. Catal.*, 2022, **5**(3), 202–211, DOI: [10.1038/s41929-022-00751-0](https://doi.org/10.1038/s41929-022-00751-0).
- 211 C. Rettenmaier, A. Herzog, D. Casari, M. Rüscher, H. S. Jeon, D. Kordus, M. L. Luna, S. Köhl, U. Hejral, E. M. Davis, S. W. Chee, J. Timoshenko, D. T. L. Alexander, A. Bergmann and B. R. Cuenya, Operando Insights into Correlating CO Coverage and Cu–Au Alloying with the Selectivity of Au NP-Decorated Cu₂O Nanocubes during the Electrocatalytic CO₂ Reduction, *EES Catal.*, 2024, **2**(1), 311–323, DOI: [10.1039/D3EY00162H](https://doi.org/10.1039/D3EY00162H).
- 212 D. Niu, C. Wei, Z. Lu, Y. Fang, B. Liu, D. Sun, X. Hao, H. Pan and G. Wang, Cu₂O–Ag Tandem Catalysts for Selective Electrochemical Reduction of CO₂ to C₂ Products, *Molecules*, 2021, **26**(8), 2175, DOI: [10.3390/molecules26082175](https://doi.org/10.3390/molecules26082175).
- 213 R. van den Berg, G. Prieto, G. Korpershoek, L. I. van der Wal, A. J. van Bunningen, S. Lægsgaard-Jørgensen, P. E. de Jongh and K. P. de Jong, Structure Sensitivity of Cu and CuZn Catalysts Relevant to Industrial Methanol Synthesis, *Nat. Commun.*, 2016, **7**(1), 13057, DOI: [10.1038/ncomms13057](https://doi.org/10.1038/ncomms13057).
- 214 F. Yu, K. Deng, M. Du, W. Wang, F. Liu and D. Liang, Electrochemical CO₂ Reduction: From Catalysts to Reactive Thermodynamics and Kinetics, *Carbon Capture Sci. Technol.*, 2023, **6**, 100081, DOI: [10.1016/j.ccst.2022.100081](https://doi.org/10.1016/j.ccst.2022.100081).
- 215 W. Luo, Q. Zhang, J. Zhang, E. Moiolli, K. Zhao and A. Züttel, Electrochemical Reconstruction of ZnO for Selective Reduction of CO₂ to CO, *Appl. Catal., B*, 2020, **273**, 119060, DOI: [10.1016/j.apcatb.2020.119060](https://doi.org/10.1016/j.apcatb.2020.119060).
- 216 P. Jeanty, C. Scherer, E. Magori, K. Wiesner-Fleischer, O. Hinrichsen and M. Fleischer, Upscaling and Continuous Operation of Electrochemical CO₂ to CO Conversion in

- Aqueous Solutions on Silver Gas Diffusion Electrodes, *J. CO₂ Util.*, 2018, **24**, 454–462, DOI: [10.1016/j.jcou.2018.01.011](https://doi.org/10.1016/j.jcou.2018.01.011).
- 217 T. Zhang, Z. Li, A. K. Ummireddi and J. Wu, Navigating CO Utilization in Tandem Electrocatalysis of CO₂, *Trends Chem.*, 2023, **5**(4), 252–266, DOI: [10.1016/j.trechm.2022.12.003](https://doi.org/10.1016/j.trechm.2022.12.003).
- 218 H. Q. Fu, J. Liu, N. M. Bedford, Y. Wang, J. Wright, P. F. Liu, C. F. Wen, L. Wang, H. Yin, D. Qi, P. Liu, H. G. Yang and H. Zhao, Operando Converting BiOCl into Bi₂O₂(CO₃)_xCl_y for Efficient Electrocatalytic Reduction of Carbon Dioxide to Formate, *Nano-Micro Lett.*, 2022, **14**(1), 121, DOI: [10.1007/s40820-022-00862-0](https://doi.org/10.1007/s40820-022-00862-0).
- 219 Y.-J. Ko, J.-Y. Kim, W. H. Lee, M. G. Kim, T.-Y. Seong, J. Park, Y. Jeong, B. K. Min, W.-S. Lee, D. K. Lee and H.-S. Oh, Exploring Dopant Effects in Stannic Oxide Nanoparticles for CO₂ Electro-Reduction to Formate, *Nat. Commun.*, 2022, **13**(1), 2205, DOI: [10.1038/s41467-022-29783-7](https://doi.org/10.1038/s41467-022-29783-7).
- 220 A. Dutta, A. Kuzume, M. Rahaman, S. Veszteg and P. Broekmann, Monitoring the Chemical State of Catalysts for CO₂ Electroreduction: An In Operando Study, *ACS Catal.*, 2015, **5**(12), 7498–7502, DOI: [10.1021/acscatal.5b02322](https://doi.org/10.1021/acscatal.5b02322).
- 221 S. Liu, B. Hu, J. Zhao, W. Jiang, D. Feng, C. Zhang, W. Yao, S. Liu, B. Hu, J. Zhao, W. Jiang, D. Feng, C. Zhang and W. Yao, Enhanced Electrocatalytic CO₂ Reduction of Bismuth Nanosheets with Introducing Surface Bismuth Subcarbonate, *Coatings*, 2022, **12**, 233, DOI: [10.3390/coatings12020233](https://doi.org/10.3390/coatings12020233).
- 222 A. Dutta, I. Zelocualtecatl Montiel, K. Kiran, A. Rieder, V. Grozovski, L. Gut and P. Broekmann, A Tandem (Bi₂O₃ → Bimet) Catalyst for Highly Efficient Ec-CO₂ Conversion into Formate: Operando Raman Spectroscopic Evidence for a Reaction Pathway Change, *ACS Catal.*, 2021, **11**(9), 4988–5003, DOI: [10.1021/acscatal.0c05317](https://doi.org/10.1021/acscatal.0c05317).
- 223 L. Lin, X. He, X.-G. Zhang, W. Ma, B. Zhang, D. Wei, S. Xie, Q. Zhang, X. Yi and Y. Wang, A Nanocomposite of Bismuth Clusters and Bi₂O₂CO₃ Sheets for Highly Efficient Electrocatalytic Reduction of CO₂ to Formate, *Angew. Chem.*, 2023, **135**(3), e202214959, DOI: [10.1002/ange.202214959](https://doi.org/10.1002/ange.202214959).
- 224 B. Wulan, X. Cao, D. Tan, J. Ma and J. Zhang, To Stabilize Oxygen on In/In₂O₃ Heterostructure via Joule Heating for Efficient Electrocatalytic CO₂ Reduction, *Adv. Funct. Mater.*, 2023, **33**(1), 2209114, DOI: [10.1002/adfm.202209114](https://doi.org/10.1002/adfm.202209114).
- 225 Z. Zhu, Y. Zhao, P. Sun, Y. Sun, X. Ma, Y. Dong, Z. Zhang, A. N. Alodhayb, X. Yi, W. Shi and Z. Chen, Tailoring the Electrolyte Microenvironment of Indium Catalysts for Enhanced Formic Acid Electrosynthesis, *J. Energy Chem.*, 2025, **105**, 54–64, DOI: [10.1016/j.jechem.2025.01.041](https://doi.org/10.1016/j.jechem.2025.01.041).
- 226 G. Díaz-Sainz, K. Fernández-Caso, B. Ávila-Bolívar, V. Montiel, J. Solla-Gullón, M. Alvarez-Guerra and A. Irabien, Advances in the Development of Innovative Bi-Sn-Sb-Based Gas Diffusion Electrodes for Continuous CO₂ Electroreduction to Formate, *J. CO₂ Util.*, 2025, **95**, 103070, DOI: [10.1016/j.jcou.2025.103070](https://doi.org/10.1016/j.jcou.2025.103070).
- 227 Z. Li, Z. Li, H. Lu, B. Song, X. Zhao, H. Zhou, L. Wang, Q. Zou, Y. Yang and M. Wei, Construction of Bi–Sn(In)O Integrated Electrode for Efficient CO₂ Electroreduction to Formate, *ACS Appl. Mater. Interfaces*, 2025, **17**(26), 38112–38121, DOI: [10.1021/acsami.5c07565](https://doi.org/10.1021/acsami.5c07565).
- 228 G. Wen, D. U. Lee, B. Ren, F. M. Hassan, G. Jiang, Z. P. Cano, J. Gostick, E. Croiset, Z. Bai, L. Yang and Z. Chen, Orbital Interactions in Bi-Sn Bimetallic Electrocatalysts for Highly Selective Electrochemical CO₂ Reduction toward Formate Production, *Adv. Energy Mater.*, 2018, **8**(31), 1802427, DOI: [10.1002/aenm.201802427](https://doi.org/10.1002/aenm.201802427).
- 229 X. Li, X. Wu, J. Li, J. Huang, L. Ji, Z. Leng, N. Qian, D. Yang and H. Zhang, Sn-Doped Bi₂O₃ Nanosheets for Highly Efficient Electrochemical CO₂ Reduction toward Formate Production, *Nanoscale*, 2021, **13**(46), 19610–19616, DOI: [10.1039/D1NR06038D](https://doi.org/10.1039/D1NR06038D).
- 230 W. Yang, C. Si, Y. Zhao, Q. Wei, G. Jia, G. Cheng, J. Qin and Z. Zhang, Activating Inert Antimony for Selective CO₂ Electroreduction to Formate via Bimetallic Interactions, *Appl. Catal., B*, 2022, **316**, 121619, DOI: [10.1016/j.apcatb.2022.121619](https://doi.org/10.1016/j.apcatb.2022.121619).
- 231 H. Wang, H. X. Yang, Y. N. Xu, H. Q. Fu, X. Y. Li, J. J. He, Q. Niu, J. C. Wu, H. Y. Yuan, P. F. Liu and H. G. Yang, Retained Oxygen Regulation in Oxide-Derived Copper for Promoted CO₂ Electroreduction Toward Multicarbon Products, *Angew. Chem., Int. Ed.*, 2025, **64**(25), e202423889, DOI: [10.1002/anie.202423889](https://doi.org/10.1002/anie.202423889).
- 232 Y.-C. Zhang, X.-L. Zhang, Z.-Z. Wu, Z.-Z. Niu, L.-P. Chi, F.-Y. Gao, P.-P. Yang, Y.-H. Wang, P.-C. Yu, J.-W. Duanmu, S.-P. Sun and M.-R. Gao, Facet-Switching of Rate-Determining Step on Copper in CO₂-to-Ethylene Electroreduction, *Proc. Natl. Acad. Sci. U. S. A.*, 2024, **121**(25), e2400546121, DOI: [10.1073/pnas.2400546121](https://doi.org/10.1073/pnas.2400546121).
- 233 M. Ma, K. Liu, J. Shen, R. Kas and W. A. Smith, In Situ Fabrication and Reactivation of Highly Selective and Stable Ag Catalysts for Electrochemical CO₂ Conversion, *ACS Energy Lett.*, 2018, **3**(6), 1301–1306, DOI: [10.1021/acsenerylett.8b00472](https://doi.org/10.1021/acsenerylett.8b00472).
- 234 X. Jiang, L. Lin, Y. Rong, R. Li, Q. Jiang, Y. Yang and D. Gao, Boosting CO₂ Electroreduction to Formate via Bismuth Oxide Clusters, *Nano Res.*, 2023, **16**(10), 12050–12057, DOI: [10.1007/s12274-022-5073-0](https://doi.org/10.1007/s12274-022-5073-0).
- 235 S. Lamaison, D. Wakerley, J. Blanchard, D. Montero, G. Rousse, D. Mercier, P. Marcus, D. Taverna, D. Giaume, V. Mougél and M. Fontecave, High-Current-Density CO₂-to-CO Electroreduction on Ag-Alloyed Zn Dendrites at Elevated Pressure, *Joule*, 2020, **4**(2), 395–406, DOI: [10.1016/j.joule.2019.11.014](https://doi.org/10.1016/j.joule.2019.11.014).
- 236 A. Ozden, Y. Wang, F. Li, M. Luo, J. Sisler, A. Thevenon, A. Rosas-Hernández, T. Burdyny, Y. Lum, H. Yadegari, T. Agapie, J. C. Peters, E. H. Sargent and D. Sinton, Cascade CO₂ Electroreduction Enables Efficient Carbonate-Free Production of Ethylene, *Joule*, 2021, **5**(3), 706–719, DOI: [10.1016/j.joule.2021.01.007](https://doi.org/10.1016/j.joule.2021.01.007).
- 237 Z. Zhang, Y. Xie and Y. Wang, What Matters in the Emerging Application of CO₂ Electrolysis, *Curr. Opin. Electrochem.*, 2022, **34**, 101012, DOI: [10.1016/j.coelec.2022.101012](https://doi.org/10.1016/j.coelec.2022.101012).
- 238 C.-T. Dinh, T. Burdyny, M. G. Kibria, A. Seifitokaldani, C. M. Gabardo, F. P. García de Arquer, A. Kiani, J. P. Edwards, P. De Luna, O. S. Bushuyev, C. Zou, R. Quintero-Bermudez, Y. Pang, D. Sinton and E. H. Sargent, CO₂ Electroreduction to Ethylene via Hydroxide-Mediated Copper Catalysis at an Abrupt

- Interface, *Science*, 2018, **360**(6390), 783–787, DOI: [10.1126/science.aas9100](https://doi.org/10.1126/science.aas9100).
- 239 A. Tsoukalou, P. M. Abdala, A. Armutlulu, E. Willinger, A. Fedorov and C. R. Müller, Operando X-Ray Absorption Spectroscopy Identifies a Monoclinic ZrO₂:In Solid Solution as the Active Phase for the Hydrogenation of CO₂ to Methanol, *ACS Catal.*, 2020, **10**(17), 10060–10067, DOI: [10.1021/acscatal.0c01968](https://doi.org/10.1021/acscatal.0c01968).
- 240 L. Hao and Z. Sun, Metal Oxide-Based Materials for Electrochemical CO₂ Reduction, *Acta Phys.-Chim. Sin.*, 2020, **37**(7), 2009033, DOI: [10.3866/PKU.WHXB202009033](https://doi.org/10.3866/PKU.WHXB202009033).
- 241 F.-Y. Chen, Z.-Y. Wu, Z. Adler and H. Wang, Stability Challenges of Electrocatalytic Oxygen Evolution Reaction: From Mechanistic Understanding to Reactor Design, *Joule*, 2021, **5**(7), 1704–1731, DOI: [10.1016/j.joule.2021.05.005](https://doi.org/10.1016/j.joule.2021.05.005).
- 242 Y. Wang, C. Niu, Y. Zhu, D. He and W. Huang, Tunable Syngas Formation from Electrochemical CO₂ Reduction on Copper Nanowire Arrays, *ACS Appl. Energy Mater.*, 2020, **3**(10), 9841–9847, DOI: [10.1021/acsaem.0c01504](https://doi.org/10.1021/acsaem.0c01504).
- 243 J. Timoshenko and B. Roldan Cuenya, *In Situ*/Operando Electrocatalyst Characterization by X-Ray Absorption Spectroscopy, *Chem. Rev.*, 2021, **121**(2), 882–961, DOI: [10.1021/acs.chemrev.0c00396](https://doi.org/10.1021/acs.chemrev.0c00396).
- 244 Y. Yue, Z. Wu, Z. Ye, Z. Li, X. Wang, K. Xie, D. Han, Q.-H. Yang and Z. Weng, Identifying Cu Reconstruction Mechanism in CO₂ and CO Electroreduction *via* Cu⁺ Detection and in Situ Atomic Force Microscopy, *Sci. China Mater.*, 2025, **68**(7), 2381–2387, DOI: [10.1007/s40843-025-3412-2](https://doi.org/10.1007/s40843-025-3412-2).
- 245 Y. Tian, D. Li, J. Wu, J. Liu, C. Li, G. Liu, D. Chen and Y. Feng, Electroreduction of CO₂ to Formate with Excellent Selectivity and Stability on Nano-Dendrite Bi Film Electrode, *J. CO₂ Util.*, 2021, **43**, 101360, DOI: [10.1016/j.jcou.2020.101360](https://doi.org/10.1016/j.jcou.2020.101360).
- 246 S. Lee, D. Kim and J. Lee, Electrocatalytic Production of C₃–C₄ Compounds by Conversion of CO₂ on a Chloride-Induced Bi-Phasic Cu₂O–Cu Catalyst, *Angew. Chem., Int. Ed.*, 2015, **54**(49), 14701–14705, DOI: [10.1002/anie.201505730](https://doi.org/10.1002/anie.201505730).
- 247 T.-D. Nguyen-Phan, L. Hu, B. H. Howard, W. Xu, E. Stavitski, D. Leshchev, A. Rothenberger, K. C. Neyerlin and D. R. Kauffman, High Current Density Electroreduction of CO₂ into Formate with Tin Oxide Nanospheres, *Sci. Rep.*, 2022, **12**(1), 8420, DOI: [10.1038/s41598-022-11890-6](https://doi.org/10.1038/s41598-022-11890-6).
- 248 Y. Jiang, J. Shan, P. Wang, L. Huang, Y. Zheng and S.-Z. Qiao, Stabilizing Oxidation State of SnO₂ for Highly Selective CO₂ Electroreduction to Formate at Large Current Densities, *ACS Catal.*, 2023, **13**(5), 3101–3108, DOI: [10.1021/acscatal.3c00123](https://doi.org/10.1021/acscatal.3c00123).
- 249 C. Liu, B. Mei, Z. Shi, Z. Jiang, J. Ge, W. Xing, P. Song and W. Xu, Operando Formation of Highly Efficient Electrocatalysts Induced by Heteroatom Leaching, *Nat. Commun.*, 2024, **15**(1), 242, DOI: [10.1038/s41467-023-44480-9](https://doi.org/10.1038/s41467-023-44480-9).
- 250 B. Tomc, M. Bele, M. A. Nazrulla, P. Šket, M. Finšgar, A. Kjara Surca, A. Rebeka Kamšek, M. Šala, J. Š. Hudoklin, M. Huš, B. Likozar and N. Hodnik, Deactivation of Copper Electrocatalysts during CO₂ Reduction Occurs via Dissolution and Selective Redeposition Mechanism, *J. Mater. Chem. A*, 2025, **13**(6), 4119–4128, DOI: [10.1039/D4TA006466F](https://doi.org/10.1039/D4TA006466F).
- 251 D. Zhong, D. Cheng, Q. Fang, Y. Liu, J. Li and Q. Zhao, Understanding the Restructuring and Degradation of Oxide-Derived Copper during Electrochemical CO₂ Reduction, *Chem. Eng. J.*, 2023, **470**, 143907, DOI: [10.1016/j.cej.2023.143907](https://doi.org/10.1016/j.cej.2023.143907).
- 252 Y. Lum and J. W. Ager, Sequential Catalysis Controls Selectivity in Electrochemical CO₂ Reduction on Cu, *Energy Environ. Sci.*, 2018, **11**(10), 2935–2944, DOI: [10.1039/C8EE01501E](https://doi.org/10.1039/C8EE01501E).
- 253 A. H. M. Da Silva, S. J. Raaijman, C. S. Santana, J. M. Assaf, J. F. Gomes and M. T. M. Koper, Electrocatalytic CO₂ Reduction to C₂+ Products on Cu and Cu_xZn_y Electrodes: Effects of Chemical Composition and Surface Morphology, *J. Electroanal. Chem.*, 2021, **880**, 114750, DOI: [10.1016/j.jelechem.2020.114750](https://doi.org/10.1016/j.jelechem.2020.114750).
- 254 L. Wang, H. Peng, S. Lamaison, Z. Qi, D. M. Koshy, M. B. Stevens, D. Wakerley, J. A. Zamora Zeledón, L. A. King, L. Zhou, Y. Lai, M. Fontecave, J. Gregoire, F. Abild-Pedersen, T. F. Jaramillo and C. Hahn, Bimetallic Effects on Zn–Cu Electrocatalysts Enhance Activity and Selectivity for the Conversion of CO₂ to CO, *Chem Catal.*, 2021, **1**(3), 663–680, DOI: [10.1016/j.checat.2021.05.006](https://doi.org/10.1016/j.checat.2021.05.006).
- 255 S. Go, W. Kwon, D. Hong, T. Lee, S.-H. Oh, D. Bae, J.-H. Kim, S. Lim, Y.-C. Joo and D.-H. Nam, Thermodynamic Phase Control of Cu–Sn Alloy Electrocatalysts for Selective CO₂ Reduction, *Nanoscale Horiz.*, 2024, **9**(12), 2295–2305, DOI: [10.1039/D4NH00393D](https://doi.org/10.1039/D4NH00393D).
- 256 C. Zhang, G. Zhao, Z. Li, Q. Zhang, Y. Jiang, X. Tang, Z. Lv and T. Zhuang, Sn-Induced Stable Cu⁺ in Cu₂O/Cu₆Sn₅ Interface System for Stabilizing *OCHO in CO₂-to-Formate Electroreduction, *Inorg. Chem.*, 2025, **64**(50), 24910–24919, DOI: [10.1021/acs.inorgchem.5c04804](https://doi.org/10.1021/acs.inorgchem.5c04804).
- 257 S. A. Sanden, A. Schmidt, M. Kożusznik, Y. Haver, Y. Weidemann, K. Pellumbi, S. Rösler, K. J. Puring, A. Mikula and U.-P. Apfel, *In Situ* Generation of Cu- and Ag–Sn Alloys from Metal Sulfides for CO₂ Reduction, *Energy Adv.*, 2025, **4**(5), 657–665, DOI: [10.1039/D4YA00603H](https://doi.org/10.1039/D4YA00603H).
- 258 F. A. Rollier, V. Muravev, N. Kosinov, T. Wissink, D. Anastasiadou, B. Ligt, L. Barthe, M. C. Figueiredo and E. J. M. Hensen, Cu–Ag Interactions in Bimetallic Cu–Ag Catalysts Enhance C₂+ Product Formation during Electrochemical CO Reduction, *J. Mater. Chem. A*, 2025, **13**(3), 2285–2300, DOI: [10.1039/D4TA04263H](https://doi.org/10.1039/D4TA04263H).
- 259 Y. Jiang, C. Lv, B. Lu, Y. Song, T. Liu, X. Zhang, D. Gao, K. Ye and G. Wang, Ag Stabilized Cu⁺/Cu⁰ Interface Catalysts for Enhanced CO₂ Electroreduction to C₂+ Products at Ampere Level Current Density, *ACS Nano*, 2025, **19**(11), 11263–11272, DOI: [10.1021/acsnano.4c18967](https://doi.org/10.1021/acsnano.4c18967).
- 260 J. Osiewacz, M. Löffelholz, B. Ellendorff and T. Turek, Modeling Mass Transfer Limitations Driven by Electrowetting in Electrochemical CO₂ Reduction at Silver Gas Diffusion Electrodes, *J. Power Sources*, 2024, **603**, 234430, DOI: [10.1016/j.jpowsour.2024.234430](https://doi.org/10.1016/j.jpowsour.2024.234430).
- 261 S. Mu, H. Lu, Q. Wu, L. Li, R. Zhao, C. Long and C. Cui, Hydroxyl Radicals Dominate Reoxidation of Oxide-Derived

- Cu in Electrochemical CO₂ Reduction, *Nat. Commun.*, 2022, **13**(1), 3694, DOI: [10.1038/s41467-022-31498-8](https://doi.org/10.1038/s41467-022-31498-8).
- 262 T.-C. Chou, C.-C. Chang, H.-L. Yu, W.-Y. Yu, C.-L. Dong, J.-J. Velasco-Vélez, C.-H. Chuang, L.-C. Chen, J.-F. Lee, J.-M. Chen and H.-L. Wu, Controlling the Oxidation State of the Cu Electrode and Reaction Intermediates for Electrochemical CO₂ Reduction to Ethylene, *J. Am. Chem. Soc.*, 2020, **142**(6), 2857–2867, DOI: [10.1021/jacs.9b11126](https://doi.org/10.1021/jacs.9b11126).
- 263 Z. Lian, F. Dattila and N. López, Stability and Lifetime of Diffusion-Trapped Oxygen in Oxide-Derived Copper CO₂ Reduction Electrocatalysts, *Nat. Catal.*, 2024, **7**(4), 401–411, DOI: [10.1038/s41929-024-01132-5](https://doi.org/10.1038/s41929-024-01132-5).
- 264 B. Tomc, M. Bele, M. Plut, M. Kostelec, S. Popović, M. A. Nazrulla, F. Ruiz-Zepeda, A. R. Kamšek, M. Šala, A. Elbataoui, L. D. Rafailović, Y. B. Pissolitto, F. Trivinho-Strixino, W. J. Stepniowski, L. Suhadolnik and N. Hodnik, Recognizing the Universality of Copper Reconstruction Via Dissolution–Redeposition at the Onset of CO₂ Reduction, *J. Phys. Chem. Lett.*, 2025, **16**(36), 9553–9560, DOI: [10.1021/acs.jpclett.5c01974](https://doi.org/10.1021/acs.jpclett.5c01974).
- 265 L. G. Puppín, L. F. da Silva, M. Carmo, H. Varela and O. F. Lopes, Effect of the Oxidation State and Morphology of SnO_x-Based Electrocatalysts on the CO₂ Reduction Reaction, *J. Mater. Res.*, 2021, **36**(20), 4240–4248, DOI: [10.1557/s43578-021-00250-1](https://doi.org/10.1557/s43578-021-00250-1).
- 266 F. D. Speck and S. Cherevko, Electrochemical Copper Dissolution: A Benchmark for Stable CO₂ Reduction on Copper Electrocatalysts, *Electrochem. Commun.*, 2020, **115**, 106739, DOI: [10.1016/j.elecom.2020.106739](https://doi.org/10.1016/j.elecom.2020.106739).
- 267 G. Marcandalli, M. C. O. Monteiro, A. Goyal and M. T. M. Koper, Electrolyte Effects on CO₂ Electrochemical Reduction to CO, *Acc. Chem. Res.*, 2022, **55**(14), 1900–1911, DOI: [10.1021/acs.accounts.2c00080](https://doi.org/10.1021/acs.accounts.2c00080).
- 268 G. S. Sajadi, V. Saheb, M. Shahidi-Zandi and S. M. A. Hosseini, A Study on Synergistic Effect of Chloride and Sulfate Ions on Copper Corrosion by Using Electrochemical Noise in Asymmetric Cells, *Sci. Rep.*, 2022, **12**(1), 14384, DOI: [10.1038/s41598-022-18317-2](https://doi.org/10.1038/s41598-022-18317-2).
- 269 R. Amirbeigiarab, J. Tian, A. Herzog, C. Qiu, A. Bergmann, B. Roldan Cuenya and O. M. Magnussen, Atomic-Scale Surface Restructuring of Copper Electrodes under CO₂ Electroreduction Conditions, *Nat. Catal.*, 2023, **6**(9), 837–846, DOI: [10.1038/s41929-023-01009-z](https://doi.org/10.1038/s41929-023-01009-z).
- 270 J.-J. Velasco-Vélez, R. V. Mom, L.-E. Sandoval-Díaz, L. J. Falling, C.-H. Chuang, D. Gao, T. E. Jones, Q. Zhu, R. Arrigo, B. Roldan Cuenya, A. Knop-Gericke, T. Lunkenbein and R. Schlögl, Revealing the Active Phase of Copper during the Electroreduction of CO₂ in Aqueous Electrolyte by Correlating In Situ X-Ray Spectroscopy and In Situ Electron Microscopy, *ACS Energy Lett.*, 2020, **5**(6), 2106–2111, DOI: [10.1021/acsenergylett.0c00802](https://doi.org/10.1021/acsenergylett.0c00802).
- 271 W. Zhang, P. He, C. Wang, T. Ding, T. Chen, X. Liu, L. Cao, T. Huang, X. Shen, O. A. Usoltsev, A. L. Bugaev, Y. Lin and T. Yao, Operando Evidence of Cu⁺ Stabilization via a Single-Atom Modifier for CO₂ Electroreduction, *J. Mater. Chem. A*, 2020, **8**(48), 25970–25977, DOI: [10.1039/D0TA08369K](https://doi.org/10.1039/D0TA08369K).
- 272 T. Burdyny and W. A. Smith, CO₂ Reduction on Gas-Diffusion Electrodes and Why Catalytic Performance Must Be Assessed at Commercially-Relevant Conditions, *Energy Environ. Sci.*, 2019, **12**(5), 1442–1453, DOI: [10.1039/C8EE03134G](https://doi.org/10.1039/C8EE03134G).
- 273 K. Yang, R. Kas, W. A. Smith and T. Burdyny, Role of the Carbon-Based Gas Diffusion Layer on Flooding in a Gas Diffusion Electrode Cell for Electrochemical CO₂ Reduction, *ACS Energy Lett.*, 2021, **6**(1), 33–40, DOI: [10.1021/acsenergylett.0c02184](https://doi.org/10.1021/acsenergylett.0c02184).
- 274 L. M. Baumgartner, A. Kahn, M. Hoogland, J. Bleeker, W. F. Jager and D. A. Vermaas, Direct Imaging of Local pH Reveals Bubble-Induced Mixing in a CO₂ Electrolyzer, *ACS Sustainable Chem. Eng.*, 2023, **11**(28), 10430–10440, DOI: [10.1021/acssuschemeng.3c01773](https://doi.org/10.1021/acssuschemeng.3c01773).
- 275 A. Anawati, G. S. Frankel, A. Agarwal and N. Sridhar, Degradation and Deactivation of Sn Catalyst Used for CO₂ Reduction as Function of Overpotential, *Electrochim. Acta*, 2014, **133**, 188–196, DOI: [10.1016/j.electacta.2014.04.057](https://doi.org/10.1016/j.electacta.2014.04.057).
- 276 Z. Chen, Y. Xiao, X. Qiao, H. Ou, C.-F. Lee, H.-T. Wang, Y.-C. Shao and L. Han, Monitoring Chalcogenide Ions-Guided in Situ Transform Active Sites of Tailored Bismuth Electrocatalysts for CO₂ Reduction to Formate, *Proc. Natl. Acad. Sci. U. S. A.*, 2025, **122**(10), e2420922122, DOI: [10.1073/pnas.2420922122](https://doi.org/10.1073/pnas.2420922122).
- 277 D. Takamatsu, N. Fukatani, A. Yoneyama, T. Hirano, K. Hirai, S. Yabuuchi, K. Watanabe, K. Kamiya and S. Nakanishi, Dynamic Relocation of Copper Catalysts in Gas Diffusion Electrodes during CO₂ Electroreduction, *J. Am. Chem. Soc.*, 2025, **147**(27), 24103–24112, DOI: [10.1021/jacs.5c07944](https://doi.org/10.1021/jacs.5c07944).
- 278 F. Bienen, D. Kopljar, A. Löwe, S. Geiger, N. Wagner, E. Klemm and K. A. Friedrich, Revealing Mechanistic Processes in Gas-Diffusion Electrodes During CO₂ Reduction via Impedance Spectroscopy, *ACS Sustainable Chem. Eng.*, 2020, **8**(36), 13759–13768, DOI: [10.1021/acssuschemeng.0c04451](https://doi.org/10.1021/acssuschemeng.0c04451).
- 279 R. Casebolt, K. Levine, J. Suntivich and T. Hanrath, Pulse Check: Potential Opportunities in Pulsed Electrochemical CO₂ Reduction, *Joule*, 2021, **5**(8), 1987–2026, DOI: [10.1016/j.joule.2021.05.014](https://doi.org/10.1016/j.joule.2021.05.014).
- 280 J. Kok, J. de Ruiter, W. van der Stam and T. Burdyny, Interrogation of Oxidative Pulsed Methods for the Stabilization of Copper Electrodes for CO₂ Electrolysis, *J. Am. Chem. Soc.*, 2024, **146**(28), 19509–19520, DOI: [10.1021/jacs.4c06284](https://doi.org/10.1021/jacs.4c06284).
- 281 Z. Han, D. Han, Z. Chen, J. Gao, G. Jiang, X. Wang, S. Lyu, Y. Guo, C. Geng, L. Yin, Z. Weng and Q.-H. Yang, Steering Surface Reconstruction of Copper with Electrolyte Additives for CO₂ Electroreduction, *Nat. Commun.*, 2022, **13**(1), 3158, DOI: [10.1038/s41467-022-30819-1](https://doi.org/10.1038/s41467-022-30819-1).
- 282 S. Alizadehfanaloo, J. Garrevoet, M. Seyrich, V. Murzin, J. Becher, D. E. Doronkin, T. L. Sheppard, J.-D. Grunwaldt, C. G. Schroer and A. Schropp, Tracking Dynamic Structural Changes in Catalysis by Rapid 2D-XANES Microscopy, *J. Synchrotron Radiat.*, 2021, **28**(5), 1518–1527, DOI: [10.1107/S1600577521007074](https://doi.org/10.1107/S1600577521007074).

- 283 A. Yoon, L. Bai, F. Yang, F. Franco, C. Zhan, M. Rüschler, J. Timoshenko, C. Pratsch, S. Werner, H. S. Jeon, M. C. Monteiro, O. de, S. W. Chee and B. Roldan Cuenya, Revealing Catalyst Restructuring and Composition during Nitrate Electroreduction through Correlated Operando Microscopy and Spectroscopy, *Nat. Mater.*, 2025, **24**(5), 762–769, DOI: [10.1038/s41563-024-02084-8](https://doi.org/10.1038/s41563-024-02084-8).
- 284 Z. Fan, F. Gao, J. Zhang, L. Yi, N. Luo, H. Yi and X. Tang, Advances in CO Catalytic Oxidation on Typical Metal Oxide Catalysts: Performance, Mechanism, and Optimization, *J. Mater. Chem. A*, 2025, **13**(32), 26129–26165, DOI: [10.1039/D5TA03067F](https://doi.org/10.1039/D5TA03067F).
- 285 L. Bai, F. Franco, J. Timoshenko, C. Rettenmaier, F. Scholten, H. S. Jeon, A. Yoon, M. Rüschler, A. Herzog, F. T. Haase, S. Kühn, S. W. Chee, A. Bergmann and R. C. Beatriz, Electrocatalytic Nitrate and Nitrite Reduction toward Ammonia Using Cu₂O Nanocubes: Active Species and Reaction Mechanisms, *J. Am. Chem. Soc.*, 2024, **146**(14), 9665–9678, DOI: [10.1021/jacs.3c13288](https://doi.org/10.1021/jacs.3c13288).
- 286 Q. Wu, X. Fan, B. Shan, L. Qi, X. Quan and Y. Liu, Insights into Lattice Oxygen and Strains of Oxide-Derived Copper for Ammonia Electrosynthesis from Nitrate, *Nat. Commun.*, 2025, **16**(1), 3479, DOI: [10.1038/s41467-025-58811-5](https://doi.org/10.1038/s41467-025-58811-5).
- 287 I. Messias, M. E. G. Winkler, G. F. Costa, T. Mariano, J. B. Souza Junior, I. T. Neckel, M. C. Figueiredo, N. Singh and R. Nagao, Role of Structural and Compositional Changes of Cu₂O Nanocubes in Nitrate Electroreduction to Ammonia, *ACS Appl. Energy Mater.*, 2024, **7**(19), 9034–9044, DOI: [10.1021/acsaem.4c02326](https://doi.org/10.1021/acsaem.4c02326).
- 288 J. Geng and S. Ji, Boosting Electrocatalytic Nitrate Reduction to Ammonia via Cu₂O/Cu(OH)₂ Heterostructures Promoting Electron Transfer, *Nano Res.*, 2024, **17**(6), 4898–4907, DOI: [10.1007/s12274-024-6480-1](https://doi.org/10.1007/s12274-024-6480-1).
- 289 G. F. Costa, M. Winkler, T. Mariano, M. R. Pinto, I. Messias, J. B. Souza, I. T. Neckel, M. F. C. Santos, C. F. Tormena, N. Singh and R. Nagao, Identifying the Active Site of Cu/Cu₂O for Electrocatalytic Nitrate Reduction Reaction to Ammonia, *Chem Catal.*, 2024, **4**(1), DOI: [10.1016/j.checat.2023.100850](https://doi.org/10.1016/j.checat.2023.100850).
- 290 X. Guo, R.-T. Gao, Z. Gao and L. Wang, Grain Boundary Engineering on Cu-Based Electrocatalysts Promotes Nitrate Reduction to Ammonia Production, *J. Energy Chem.*, 2025, **106**, 351–359, DOI: [10.1016/j.jechem.2025.01.036](https://doi.org/10.1016/j.jechem.2025.01.036).
- 291 R. V. Mom, L.-E. Sandoval-Díaz, D. Gao, C.-H. Chuang, E. A. Carbonio, T. E. Jones, R. Arrigo, D. Ivanov, M. Hävecker, B. Roldan Cuenya, R. Schlögl, T. Lunkenbein, A. Knop-Gericke and J.-J. Velasco-Vélez, Assessment of the Degradation Mechanisms of Cu Electrodes during the CO₂ Reduction Reaction, *ACS Appl. Mater. Interfaces*, 2023, **15**(25), 30052–30059, DOI: [10.1021/acsaami.2c23007](https://doi.org/10.1021/acsaami.2c23007).
- 292 N. Saafie, N. A. Mohamad, W. S. Koh, X. Zeng, S. Y. Kim and W.-J. Ong, Evolving Electrocatalytic Nitrate-to-Ammonia Conversion on Cu- and Co-Based Catalyst Engineering with Paired Electrolysis Approaches, *Mater. Horiz.*, 2026, **13**(5), 2173–2212, DOI: [10.1039/D5MH02001H](https://doi.org/10.1039/D5MH02001H).
- 293 M. Wei, S. Li, X. Wang, G. Zuo, H. Wang, X. Meng and J. Wang, A Perspective on Cu-Based Electrocatalysts for Nitrate Reduction for Ammonia Synthesis, *Adv. Energy Sustainability Res.*, 2024, **5**(1), 2300173, DOI: [10.1002/aesr.202300173](https://doi.org/10.1002/aesr.202300173).
- 294 Z. You, J. Shen, S. Wang, Y. Wang, Y. Liang and S. Yuan, Constructing High Activity Cu/Cu₂O via Nitrate-Assisted Directed Evolution for Enhanced Electro Catalytic Nitrate-to-Ammonia Conversion, *Sep. Purif. Technol.*, 2025, **369**, 133165, DOI: [10.1016/j.seppur.2025.133165](https://doi.org/10.1016/j.seppur.2025.133165).
- 295 Z. Li, M. Zheng, C. Yan, D. Yang, R. Yang, C. Zhang, H. Liu, P. Song, C. Yin, Z. Qi, D. Liu, X. Zhou, L. Song, C. Lv and G. Yu, Stabilizing Cu⁰-Cu^{δ+} Sites via Ohmic Contact Interface Engineering for Ampere-Level Nitrate Electroreduction to Ammonia, *Nat. Commun.*, 2025, **16**(1), 8940, DOI: [10.1038/s41467-025-63996-w](https://doi.org/10.1038/s41467-025-63996-w).
- 296 Y. Zheng, A. Vasileff, X. Zhou, Y. Jiao, M. Jaroniec and S.-Z. Qiao, Understanding the Roadmap for Electrochemical Reduction of CO₂ to Multi-Carbon Oxygenates and Hydrocarbons on Copper-Based Catalysts, *J. Am. Chem. Soc.*, 2019, **141**(19), 7646–7659, DOI: [10.1021/jacs.9b02124](https://doi.org/10.1021/jacs.9b02124).
- 297 Y. Ji, A. Guan and G. Zheng, Copper-Based Catalysts for Electrochemical Carbon Monoxide Reduction, *Cell Rep. Phys.*, 2022, **3**(10), 101072, DOI: [10.1016/j.xcrp.2022.101072](https://doi.org/10.1016/j.xcrp.2022.101072).
- 298 C. Zhan, F. Dattila, C. Rettenmaier, A. Herzog, M. Herran, T. Wagner, F. Scholten, A. Bergmann, N. López and B. Roldan Cuenya, Key Intermediates and Cu Active Sites for CO₂ Electroreduction to Ethylene and Ethanol, *Nat. Energy*, 2024, **9**(12), 1485–1496, DOI: [10.1038/s41560-024-01633-4](https://doi.org/10.1038/s41560-024-01633-4).
- 299 A. Guan, Q. Wang, Y. Ji, S. Li, C. Yang, L. Qian, L. Zhang, L. Wu and G. Zheng, Steric Effect Induces CO Electroreduction to CH₄ on Cu–Au Alloys, *J. Mater. Chem. A*, 2021, **9**(38), 21779–21784, DOI: [10.1039/D1TA06162C](https://doi.org/10.1039/D1TA06162C).
- 300 K. J. P. Schouten, E. Pérez Gallent and M. T. M. Koper, The Influence of pH on the Reduction of CO and CO₂ to Hydrocarbons on Copper Electrodes, *J. Electroanal. Chem.*, 2014, **716**, 53–57, DOI: [10.1016/j.jelechem.2013.08.033](https://doi.org/10.1016/j.jelechem.2013.08.033).
- 301 R. Casebolt, K. W. Kimura, K. Levine, J. A. Cimada DaSilva, J. Kim, T. A. Dunbar, J. Suntivich and T. Hanrath, Effect of Electrolyte Composition and Concentration on Pulsed Potential Electrochemical CO₂ Reduction, *ChemElectroChem*, 2021, **8**(4), 681–688, DOI: [10.1002/celec.202001445](https://doi.org/10.1002/celec.202001445).
- 302 E. L. Clark and A. T. Bell, Direct Observation of the Local Reaction Environment during the Electrochemical Reduction of CO₂, *J. Am. Chem. Soc.*, 2018, **140**(22), 7012–7020, DOI: [10.1021/jacs.8b04058](https://doi.org/10.1021/jacs.8b04058).
- 303 P. Li, N. Song, N. Wang, Y. He, Z. Zhu and Y. Yan, Enhancement Strategies in Transition Metal Oxides as Efficient Electrocatalysts for the Oxygen Evolution Reaction, *Molecules*, 2026, **31**(1), 147, DOI: [10.3390/molecules31010147](https://doi.org/10.3390/molecules31010147).
- 304 L. Bai, S. Lee and X. Hu, Spectroscopic and Electrokinetic Evidence for a Bifunctional Mechanism of the Oxygen Evolution Reaction, *Angew. Chem., Int. Ed.*, 2021, **60**(6), 3095–3103, DOI: [10.1002/anie.202011388](https://doi.org/10.1002/anie.202011388).
- 305 Y.-J. Ko, M. H. Han, H. Kim, J.-Y. Kim, W. H. Lee, J. Kim, J. Y. Kwak, C.-H. Kim, T.-E. Park, S.-H. Yu, W.-S. Lee,

- C. H. Choi, P. Strasser and H.-S. Oh, Unraveling Ni-Fe 2D Nanostructure with Enhanced Oxygen Evolution via *in Situ* and *Operando* Spectroscopies, *Chem Catal.*, 2022, 2(9), 2312–2327, DOI: [10.1016/j.checat.2022.07.016](https://doi.org/10.1016/j.checat.2022.07.016).
- 306 V. K. Singh, B. Malik, R. Konar, E. S. Avraham, G. D. Nessim, V. K. Singh, B. Malik, R. Konar, E. S. Avraham and G. D. Nessim, The Electrocatalytic Oxygen Evolution Reaction Activity of Rationally Designed NiFe-Based Glycerates, *Electrochem*, 2024, 5(1), 70–83, DOI: [10.3390/electrochem5010005](https://doi.org/10.3390/electrochem5010005).
- 307 Y. Zhang, W. Zhang, X. Zhang, X. Wang, J. Wang, Q. Zhao, Y. Sun, J. Li, G. Liu and X. Han, Activating Lattice Oxygen Based on Energy Band Engineering in Oxides for Industrial Water/Saline Oxidation, *Energy Environ. Sci.*, 2024, 17(10), 3347–3357, DOI: [10.1039/D4EE00214H](https://doi.org/10.1039/D4EE00214H).
- 308 Z. He, J. Zhang, Z. Gong, H. Lei, D. Zhou, N. Zhang, W. Mai, S. Zhao and Y. Chen, Activating Lattice Oxygen in NiFe-Based (Oxy)Hydroxide for Water Electrolysis, *Nat. Commun.*, 2022, 13(1), 2191, DOI: [10.1038/s41467-022-29875-4](https://doi.org/10.1038/s41467-022-29875-4).
- 309 J. S. Rodríguez, J. M. L. Nieto, E. Rodríguez-Castellón, A. Infantes, D. Gómez, P. Concepción, J. S. Rodríguez, J. M. L. Nieto, E. Rodríguez-Castellón, A. Infantes, D. Gómez and P. Concepción, Enhancing Stability of Cu/ZnO Catalysts in the CO₂ Hydrogenation to Methanol by the Addition of MoO₃ and ReO₃ Promoters, *Nanomaterials*, 2025, 15(22), 1730, DOI: [10.3390/nano15221730](https://doi.org/10.3390/nano15221730).
- 310 P. Du, C. Chen, X. Chen, C. Dong, Y. Cao, W. Jia, Z. Guo and S. Liu, Ho-doping Enhanced CuO/CeO₂ Nanorods for Low-temperature Synergistic NH₃-SCR and CO Oxidation under Oxygen-rich Conditions, *J. Environ. Chem. Eng.*, 2025, 13(5), 118432, DOI: [10.1016/j.jece.2025.118432](https://doi.org/10.1016/j.jece.2025.118432).
- 311 T. Tang, L. Ye, Y. Chen, J. Xue, X. Shen, J. Chen, F. H. Quarcoo, V. Rac, V. Rakić, X. Li and X. Du, Diving into the Interface-Mediated Mars-van Krevelen (M–vK) Characteristic of CuO_x-Supported CeO₂ Catalysts, *Appl. Catal., B*, 2024, 342, 123368, DOI: [10.1016/j.apcatb.2023.123368](https://doi.org/10.1016/j.apcatb.2023.123368).
- 312 C. Yin, Y. Lei, H. Wu, Y. Xu, H. Luo and H. Wang, Synergistic Effect of Cu and Ag on Porous (Cu, Ag) Co-Doped CeO₂ Nanosheets for Low-Temperature CO Oxidation, *Inorg. Chem. Commun.*, 2025, 172, 113729, DOI: [10.1016/j.inoche.2024.113729](https://doi.org/10.1016/j.inoche.2024.113729).
- 313 L. Liu, F. Zhou, L. Wang, X. Qi, F. Shi and Y. Deng, Low-Temperature CO Oxidation over Supported Pt, Pd Catalysts: Particular Role of FeO_x Support for Oxygen Supply during Reactions, *J. Catal.*, 2010, 274(1), 1–10, DOI: [10.1016/j.jcat.2010.05.022](https://doi.org/10.1016/j.jcat.2010.05.022).
- 314 H. Du, H. Luo, M. Jiang, X. Yan, F. Jiang and H. Chen, A Review of Activating Lattice Oxygen of Metal Oxides for Catalytic Reactions: Reaction Mechanisms, Modulation Strategies of Activity and Their Practical Applications, *Appl. Catal., A*, 2023, 664, 119348, DOI: [10.1016/j.apcata.2023.119348](https://doi.org/10.1016/j.apcata.2023.119348).
- 315 Y. Zhou, J. Jiang, Y. Wang, R. Liu, S. Zhang and J. Wang, Supercritical CO₂ Activation Enables an Exceptional Methanol Synthesis Activity Over the Industrial Cu/ZnO/Al₂O₃ Catalyst, *Adv. Sci.*, 2025, 12(17), 2500118, DOI: [10.1002/adv.202500118](https://doi.org/10.1002/adv.202500118).
- 316 D. Li, R. Qiu, B. M. Moskowitz, Z. Jiang, H. Gu, Q. Wen, I. E. Wachs and M. Zhu, Nature of the Active Sites and Reaction Mechanism during Methanol Steam Reforming over Cu/ZnO: An Isotopic Modulated Excitation Diffuse Reflectance Infrared Fourier Transform Spectroscopy Study, *J. Am. Chem. Soc.*, 2025, 147(27), 24040–24049, DOI: [10.1021/jacs.5c07628](https://doi.org/10.1021/jacs.5c07628).
- 317 Y. Liu, L. Cui, C. Liu, L. Huang and F. Cao, Enhanced CO₂ Hydrogenation to Methanol over Cu-ZnO-Al₂O₃ Catalyst Modified with Zirconium: Experimental and Theoretical Insights, *Chem. Eng. J.*, 2025, 511, 162221, DOI: [10.1016/j.cej.2025.162221](https://doi.org/10.1016/j.cej.2025.162221).
- 318 E. L. Kunkes, F. Studt, F. Abild-Pedersen, R. Schlögl and M. Behrens, Hydrogenation of CO₂ to Methanol and CO on Cu/ZnO/Al₂O₃: Is There a Common Intermediate or Not?, *J. Catal.*, 2015, 328, 43–48, DOI: [10.1016/j.jcat.2014.12.016](https://doi.org/10.1016/j.jcat.2014.12.016).
- 319 X. Jiang, J. Ke, R. Li, H. Huang, Z. Liu, H. Feng, Q. Ma, X. Gao, G. Liu, X. Feng, T.-S. Zhao and N. Tsubaki, Hydrophobically Modified Cu-ZnO-Al₂O₃ Catalyst for CO₂ Hydrogenation to Methanol, *J. Environ. Chem. Eng.*, 2025, 13(3), 116758, DOI: [10.1016/j.jece.2025.116758](https://doi.org/10.1016/j.jece.2025.116758).
- 320 Y. Sun, C. Huang, L. Chen, Y. Zhang, M. Fu, J. Wu and D. Ye, Active Site Structure Study of Cu/Plate ZnO Model Catalysts for CO₂ Hydrogenation to Methanol under the Real Reaction Conditions, *J. CO₂ Util.*, 2020, 37, 55–64, DOI: [10.1016/j.jcou.2019.11.029](https://doi.org/10.1016/j.jcou.2019.11.029).
- 321 N. Barrow, J. Bradley, B. Corrie, Y. Cui, T. D. Tran, T. E. Erden, A. Fish, M. Garcia, P. Glen, N. Mistry, M. Nicholson, S. Roloff-Standring, D. Sheldon, T. Smith, A. Summer, K. U. Din and N. Macleod, Doubling the Life of Cu/ZnO Methanol Synthesis Catalysts via Use of Si as a Structural Promoter to Inhibit Sintering, *Sci. Adv.*, 2024, 10(3), eadk2081, DOI: [10.1126/sciadv.adk2081](https://doi.org/10.1126/sciadv.adk2081).
- 322 N. Zhou, Z. Wang, N. Zhang, D. Bao, H. Zhong and X. Zhang, Potential-Induced Synthesis and Structural Identification of Oxide-Derived Cu Electrocatalysts for Selective Nitrate Reduction to Ammonia, *ACS Catal.*, 2023, 13(11), 7529–7537, DOI: [10.1021/acscatal.3c01315](https://doi.org/10.1021/acscatal.3c01315).
- 323 H. Deng, T. Liu, W. Zhao, J. Wang, Y. Zhang, S. Zhang, Y. Yang, C. Yang, W. Teng, Z. Chen, G. Zheng, F. Li, Y. Su, J. Hui and Y. Wang, Substituent Tuning of Cu Coordination Polymers Enables Carbon-Efficient CO₂ Electroreduction to Multi-Carbon Products, *Nat. Commun.*, 2024, 15(1), 9706, DOI: [10.1038/s41467-024-54107-2](https://doi.org/10.1038/s41467-024-54107-2).
- 324 A. Li, H. Ooka, S. Kong, K. Adachi, Y. Zhang, K. Fushimi, S. Hamamoto, M. Oura, S. H. Kim, D. Hashizume and R. Nakamura, Oxygen Evolution Electrocatalysis Resilient to Voltage Fluctuations, *Nat. Sustainable*, 2025, 8(12), 1533–1540, DOI: [10.1038/s41893-025-01665-y](https://doi.org/10.1038/s41893-025-01665-y).
- 325 T. Wissink, A. J. W. Man, W. Chen, J. M. J. J. Heinrichs, R. C. J. van de Poll, M. C. Figueiredo and E. J. M. Hensen, Evolution of Bismuth Oxide Catalysts during Electrochemical CO₂ Reduction, *J. CO₂ Util.*, 2023, 77, 102604, DOI: [10.1016/j.jcou.2023.102604](https://doi.org/10.1016/j.jcou.2023.102604).
- 326 S. Louisia, J. Feijóo, Y. Yang, S. Yu, M. V. Fonseca Guzman, Y. Shan, E. Tusini, A. S. Hoffman, S. R. Bare and P. Yang,

- Adapted Cell Design for the Operando X-Ray Absorption Study of a Structurally Evolving Cu Nanoparticle Ensemble during the CO₂ Electroconversion to Multicarbon Products, *J. Phys. Chem. C*, 2026, **130**(1), 426–436, DOI: [10.1021/acs.jpcc.5c06449](https://doi.org/10.1021/acs.jpcc.5c06449).
- 327 X. Zhu, J. Huang and M. Eikerling, Electrochemical CO₂ Reduction at Silver from a Local Perspective, *ACS Catal.*, 2021, **11**(23), 14521–14532, DOI: [10.1021/acscatal.1c04791](https://doi.org/10.1021/acscatal.1c04791).
- 328 B. Zhang, J. Zou, Z. Chen, W. Yan, W. Liu, C. Dong, D. Cai, Q. Zhang, Y. Wang and S. Xie, Defect-Engineered Carbon-Confined Silver for Enhanced CO₂ Electrocatalytic Reduction to CO in Acidic Media, *Next Nanotechnol.*, 2023, **2**, 100014, DOI: [10.1016/j.nxnano.2023.100014](https://doi.org/10.1016/j.nxnano.2023.100014).
- 329 R. G. Mariano, K. McKelvey, H. S. White and M. W. Kanan, Selective Increase in CO₂ Electroreduction Activity at Grain-Boundary Surface Terminations, *Science*, 2017, **358**(6367), 1187–1192, DOI: [10.1126/science.aao3691](https://doi.org/10.1126/science.aao3691).
- 330 A. Kuzume, A. Dutta, S. Veszteg, P. Broekmann, Operando Raman Spectroscopy: Studies on the Reactivity and Stability of SnO₂ Nanoparticles During Electrochemical CO₂ Reduction Reaction, in *Encyclopedia of Interfacial Chemistry*, ed. K. Wandelt, Elsevier: Oxford, 2018, pp. 217–226, DOI: [10.1016/B978-0-12-409547-2.13300-1](https://doi.org/10.1016/B978-0-12-409547-2.13300-1).
- 331 Z. Li, Y. Yang, H. Ding, Z. Li, L. Wang, X. Zhang, J. Li, W. Xie, X. Hu, B. Wang and M. Wei, *In Situ* Investigations on Bi-Based Electrocatalyst Construction and Reaction Dynamic Monitoring toward Efficient CO₂ Reduction, *Chem Catal.*, 2023, **3**(10), 100767, DOI: [10.1016/j.checat.2023.100767](https://doi.org/10.1016/j.checat.2023.100767).
- 332 W. Shan, R. Liu, H. Zhao, Z. He, Y. Lai, S. Li, G. He and J. Liu, In Situ Surface-Enhanced Raman Spectroscopic Evidence on the Origin of Selectivity in CO₂ Electrocatalytic Reduction, *ACS Nano*, 2020, **14**(9), 11363–11372, DOI: [10.1021/acsnano.0c03534](https://doi.org/10.1021/acsnano.0c03534).
- 333 T. Dou, J. He, S. Diao, Y. Wang, X. Zhao, F. Zhang and X. Lei, Dynamic Reconstructing of CuS/SnO₂-S for Promoting CO₂ Electroreduction to Formate, *J. Energy Chem.*, 2023, **82**, 497–506, DOI: [10.1016/j.jechem.2023.03.016](https://doi.org/10.1016/j.jechem.2023.03.016).
- 334 M. A. A. Mahbub, J. R. C. Junqueira, X. Wang, J. Zhang, S. Dieckhöfer, S. Seisel, D. Das and W. Schuhmann, Dynamic Transformation of Functionalized Bismuth to Catalytically Active Surfaces for CO₂ Reduction to Formate at High Current Densities, *Adv. Funct. Mater.*, 2024, **34**(3), 2307752, DOI: [10.1002/adfm.202307752](https://doi.org/10.1002/adfm.202307752).
- 335 Q. Zhu, X. Sun, D. Yang, J. Ma, X. Kang, L. Zheng, J. Zhang, Z. Wu and B. Han, Carbon Dioxide Electroreduction to C₂ Products over Copper-Cuprous Oxide Derived from Electrosynthesized Copper Complex, *Nat. Commun.*, 2019, **10**(1), 3851, DOI: [10.1038/s41467-019-11599-7](https://doi.org/10.1038/s41467-019-11599-7).
- 336 J. Xiao, A. Kuc, T. Frauenheim and T. Heine, CO₂ Reduction at Low Overpotential on Cu Electrodes in the Presence of Impurities at the Subsurface, *J. Mater. Chem. A*, 2014, **2**(14), 4885–4889, DOI: [10.1039/C3TA14755J](https://doi.org/10.1039/C3TA14755J).
- 337 L. Li, Q. Shao and X. Huang, Amorphous Oxide Nanostructures for Advanced Electrocatalysis, *Chem. – Eur. J.*, 2020, **26**(18), 3943–3960, DOI: [10.1002/chem.201903206](https://doi.org/10.1002/chem.201903206).
- 338 K. Yao, Y. Xia, J. Li, N. Wang, J. Han, C. Gao, M. Han, G. Shen, Y. Liu, A. Seifitokaldani, X. Sun and H. Liang, Metal–Organic Framework Derived Copper Catalysts for CO₂ to Ethylene Conversion, *J. Mater. Chem. A*, 2020, **8**(22), 11117–11123, DOI: [10.1039/D0TA02395G](https://doi.org/10.1039/D0TA02395G).
- 339 Y. Meng, J. Ding, Y. Liu, G. Hu, Y. Feng, Y. Wu and X. Liu, Advancements in Amorphous Oxides For Electrocatalytic Carbon Dioxide Reduction, *Mater. Today Catal.*, 2024, **7**, 100065, DOI: [10.1016/j.mtcata.2024.100065](https://doi.org/10.1016/j.mtcata.2024.100065).
- 340 C. Deng, Q. Huang, X. Zhu, Q. Hu, W. Su, J. Qian, L. Dong, B. Li, M. Fan and C. Liang, The Influence of Mn-Doped CeO₂ on the Activity of CuO/CeO₂ in CO Oxidation and NO + CO Model Reaction, *Appl. Surf. Sci.*, 2016, **389**, 1033–1049, DOI: [10.1016/j.apsusc.2016.08.035](https://doi.org/10.1016/j.apsusc.2016.08.035).
- 341 W. Chen, M. Li, Y. Cheng, F. Gao, C. Pan, H. Wang, J. Mao, B. Wang and F. Huang, Eu-Doped Cu₂O for Tailored Cu⁺/Cu⁰ Sites and Enhanced C₂ Selectivity in CO₂ Electroreduction, *Appl. Surf. Sci.*, 2025, **690**, 162633, DOI: [10.1016/j.apsusc.2025.162633](https://doi.org/10.1016/j.apsusc.2025.162633).
- 342 X. Li, H. Eliasson and R. Erni, Impact of Oxidation State on Copper Nanoparticle Stability in Industrial Cu/ZnO/Al₂O₃ Hydrogenation Catalyst, *BIO Web Conf.*, 2024, **129**, 26021, DOI: [10.1051/bioconf/202412926021](https://doi.org/10.1051/bioconf/202412926021).
- 343 M. Wei, J. Li, J. Zhao, S. Hu, Y. Ji, W. Xue, Y. Dai, H. Wang, X. Zhang, K. N. Hui, X. Li, C. Xia, T. Zheng and J. Zeng, Stabilization of Oxidized Cu Species via CeO_x Nano-Islands for Enhanced CO₂ Reduction to C₂₊ Products, *Natl. Sci. Rev.*, 2025, **12**(11), nwaf351, DOI: [10.1093/nsr/nwaf351](https://doi.org/10.1093/nsr/nwaf351).
- 344 H. Zou, S. Chen, Z. Liu and W. Lin, Selective CO Oxidation over CuO–CeO₂ Catalysts Doped with Transition Metal Oxides, *Powder Technol.*, 2011, **207**(1), 238–244, DOI: [10.1016/j.powtec.2010.11.005](https://doi.org/10.1016/j.powtec.2010.11.005).
- 345 Q. Li, M. Li, S. Zhang, X. Liu, X. Zhu, Q. Ge, H. Wang, Q. Li, M. Li, S. Zhang, X. Liu, X. Zhu, Q. Ge and H. Wang, Tuning Sn–Cu Catalysis for Electrochemical Reduction of CO₂ on Partially Reduced Oxides SnO_x–CuO_x-Modified Cu Electrodes, *Catalysts*, 2019, **9**, 476, DOI: [10.3390/catal9050476](https://doi.org/10.3390/catal9050476).
- 346 Q. Li, J. Fu, W. Zhu, Z. Chen, B. Shen, L. Wu, Z. Xi, T. Wang, G. Lu, J. Zhu and S. Sun, Tuning Sn-Catalysis for Electrochemical Reduction of CO₂ to CO via the Core/Shell Cu/SnO₂ Structure, *J. Am. Chem. Soc.*, 2017, **139**(12), 4290–4293, DOI: [10.1021/jacs.7b00261](https://doi.org/10.1021/jacs.7b00261).
- 347 M. Zhang, Z. Zhang, Z. Zhao, H. Huang, D. H. Anjum, D. Wang, J. He and K.-W. Huang, Tunable Selectivity for Electrochemical CO₂ Reduction by Bimetallic Cu–Sn Catalysts: Elucidating the Roles of Cu and Sn, *ACS Catal.*, 2021, **11**(17), 11103–11108, DOI: [10.1021/acscatal.1c02556](https://doi.org/10.1021/acscatal.1c02556).
- 348 B. Li, J. Chen, L. Wang, D. Xia, S. Mao, L. Xi, S. Ying, H. Zhang and Y. Wang, Dynamic Reconstruction of Cu-Doped SnO₂ for Efficient Electrochemical Reduction of CO₂ to Formate, *Appl. Catal., B*, 2025, **363**, 124784, DOI: [10.1016/j.apcatb.2024.124784](https://doi.org/10.1016/j.apcatb.2024.124784).
- 349 S. Wang, T. Kou, S. E. Baker, E. B. Duoss and Y. Li, Recent Progress in Electrochemical Reduction of CO₂ by Oxide-Derived Copper Catalysts, *Mater. Today Nano*, 2020, **12**, 100096, DOI: [10.1016/j.mtnano.2020.100096](https://doi.org/10.1016/j.mtnano.2020.100096).
- 350 J. Jang, K. Lee, H. Shin, H. Seok Lee, B.-H. Lee, J. Jeong, J. Kim, W. Hwang, S. Park, M. S. Bootharaju, S. Back, J. Shim, J. Hyun Kim, T. Hyeon and Y.-E. Sung, Distinct

- Reconstruction of Aluminum-Doped Oxide-Derived Copper Enhances the Selectivity of C₂₊ Products in CO₂ Electroreduction, *J. Mater. Chem. A*, 2023, **11**(35), 19066–19073, DOI: [10.1039/D3TA02375C](https://doi.org/10.1039/D3TA02375C).
- 351 C. Chen, X. Yan, Y. Wu, S. Liu, X. Sun, Q. Zhu, R. Feng, T. Wu, Q. Qian, H. Liu, L. Zheng, J. Zhang and B. Han, The *in Situ* Study of Surface Species and Structures of Oxide-Derived Copper Catalysts for Electrochemical CO₂ Reduction, *Chem. Sci.*, 2021, **12**(16), 5938–5943, DOI: [10.1039/D1SC00042J](https://doi.org/10.1039/D1SC00042J).
- 352 L. Liu, M. Lopez-Haro, C. W. Lopes, S. Rojas-Buzo, P. Concepcion, R. Manzorro, L. Simonelli, A. Sattler, P. Serna, J. J. Calvino and A. Corma, Structural Modulation and Direct Measurement of Subnanometric Bimetallic PtSn Clusters Confined in Zeolites, *Nat. Catal.*, 2020, **3**(8), 628–638, DOI: [10.1038/s41929-020-0472-7](https://doi.org/10.1038/s41929-020-0472-7).
- 353 K. An and G. A. Somorjai, Nanocatalysis I: Synthesis of Metal and Bimetallic Nanoparticles and Porous Oxides and Their Catalytic Reaction Studies, *Catal. Lett.*, 2015, **145**(1), 233–248, DOI: [10.1007/s10562-014-1399-x](https://doi.org/10.1007/s10562-014-1399-x).
- 354 T. Pan, Z. Wu and K. Zhou, In Situ Incorporation of Zn into Hierarchical ZSM-5 Zeolites for Olefin Hydroisomerization, *Ind. Eng. Chem. Res.*, 2020, **59**(27), 12371–12380, DOI: [10.1021/acs.iecr.0c01506](https://doi.org/10.1021/acs.iecr.0c01506).
- 355 J. Heine, B. Peerless, S. Dehnen and C. Lichtenberg, Charge Makes a Difference: Molecular Ionic Bismuth Compounds, *Angew. Chem., Int. Ed.*, 2023, **62**(24), e202218771, DOI: [10.1002/anie.202218771](https://doi.org/10.1002/anie.202218771).
- 356 Y. Jiang, C. Choi, S. Hong, S. Chu, T.-S. Wu, Y.-L. Soo, L. Hao, Y. Jung and Z. Sun, Enhanced Electrochemical CO₂ Reduction to Ethylene over CuO by Synergistically Tuning Oxygen Vacancies and Metal Doping, *Cell Rep. Phys.*, 2021, **2**(3), 100356, DOI: [10.1016/j.xcrp.2021.100356](https://doi.org/10.1016/j.xcrp.2021.100356).
- 357 S. Yang, Z. Liu, H. An, S. Arnouts, J. de Ruiter, F. Rollier, S. Bals, T. Altantzis, M. C. Figueiredo, I. A. W. Filot, E. J. M. Hensen, B. M. Weckhuysen and W. van der Stam, Near-Unity Electrochemical CO₂ to CO Conversion over Sn-Doped Copper Oxide Nanoparticles, *ACS Catal.*, 2022, **12**(24), 15146–15156, DOI: [10.1021/acscatal.2c04279](https://doi.org/10.1021/acscatal.2c04279).
- 358 C. Yan, H. Yuan, X. Wang, R. Hao, G. Liu, W. Luo, Z. Wang, K. Liu, Z. Wang, Y. Lan, D. Cui and Z. Lu, Sn-Doping Stabilizes Residual Oxygen Species to Promote Intermediate Desorption for Enhanced CO₂ to CO Conversion, *Sci. China Mater.*, 2023, **66**(9), 3547–3554, DOI: [10.1007/s40843-023-2511-5](https://doi.org/10.1007/s40843-023-2511-5).
- 359 M. Zhang, G. Qin, P. Li, X. Zhang, H. Chang, Z. Zhou, W. Zhao, X. Huang, K. Tang, Y. Ning, C. Song, P. He, M. Zhang, G. Qin, P. Li, X. Zhang, H. Chang, Z. Zhou, W. Zhao, X. Huang, K. Tang, Y. Ning, C. Song and P. He, Enhanced Catalytic Performance of Sn Single-Atom Doped CuO with Oxygen Vacancies for Efficient Epoxidation of α -Olefins, *Molecules*, 2025, **30**, 1042, DOI: [10.3390/molecules30051042](https://doi.org/10.3390/molecules30051042).
- 360 K. Lin, M. Yang, X. Wang, J. Zhao, Z. Li and Y. Liu, Outstanding OER Performance under Industrial Conditions of Porous Branched High-Entropy Oxides Prepared through Anodization of FeCoNiMnTi Alloy, *J. Alloys Compd.*, 2025, **1038**, 182670, DOI: [10.1016/j.jallcom.2025.182670](https://doi.org/10.1016/j.jallcom.2025.182670).
- 361 M. L. Frisch, L. Wu, C. Atlan, Z. Ren, M. Han, R. Tucoulou, L. Liang, J. Lu, A. Guo, H. N. Nong, A. Arinchtin, M. Sprung, J. Villanova, M.-I. Richard and P. Strasser, Unraveling the Synergistic Effects of Cu-Ag Tandem Catalysts during Electrochemical CO₂ Reduction Using Nanofocused X-Ray Probes, *Nat. Commun.*, 2023, **14**(1), 7833, DOI: [10.1038/s41467-023-43693-2](https://doi.org/10.1038/s41467-023-43693-2).
- 362 K. Feng, J. Zhang, Z. Li, X. Liu, Y. Pan, Z. Wu, J. Tian, Y. Chen, C. Zhang, Q. Xue, L. He, X. Zhang, Y. Wang, B. Yang, D. Su, K. H. Luo and B. Yan, Spontaneous Regeneration of Active Sites against Catalyst Deactivation, *Appl. Catal., B*, 2024, **344**, 123647, DOI: [10.1016/j.apcatb.2023.123647](https://doi.org/10.1016/j.apcatb.2023.123647).
- 363 Q. Li, W. Luo, X. Cui and J. Shi, Rapid and In Situ Active Sites Regeneration for OER Activity Recovery and Greatly Prolonged Water-Splitting Performance, *Angew. Chem., Int. Ed.*, 2025, **64**(21), e202500303, DOI: [10.1002/anie.202500303](https://doi.org/10.1002/anie.202500303).
- 364 H. Chen, L. Wang, M. Na and X. Zou, Reconstruction Chemistry of Electrocatalysts under Working Conditions, *Chem. Sci.*, 2025, **16**(44), 20662–20676, DOI: [10.1039/D5SC06605K](https://doi.org/10.1039/D5SC06605K).
- 365 T. Ito, J. Raj, T. Zhang, S. Roy and J. Wu, Operational Strategies of Pulsed Electrolysis to Enhance Multi-Carbon Product Formation in Electrocatalytic CO₂ Reduction, *EES Catal.*, 2024, **2**(4), 997–1005, DOI: [10.1039/D4EY00039K](https://doi.org/10.1039/D4EY00039K).
- 366 X. Zhang, L. Wang, J. Wei, Z. Guo, X. Liu, L. Duan, H. Zhao and Y. Song, Dynamic Oxygen Vacancy Engineering on CuO via Refreshable Catalytic Surface for High-Efficient Water Decontamination, *Nat. Commun.*, 2026, **17**, 1432, DOI: [10.1038/s41467-025-68180-8](https://doi.org/10.1038/s41467-025-68180-8).
- 367 V.-H. Do and J.-M. Lee, Surface Engineering for Stable Electrocatalysis, *Chem. Soc. Rev.*, 2024, **53**(5), 2693–2737, DOI: [10.1039/D3CS00292F](https://doi.org/10.1039/D3CS00292F).
- 368 W. Chen, X. Jin, M. Wang, A. Bohan, Z. Wei, G. Jiang, H. Shi and L. Zhang, Controlling the Morphology of CuO to Construct Rich Cu⁰/Cu⁺ Interfaces for CO₂ Electroreduction to Multi-Carbon Products, *Adv. Funct. Mater.*, 2026, **36**(32), e26003, DOI: [10.1002/adfm.202526003](https://doi.org/10.1002/adfm.202526003).
- 369 F. Bao, E. Kemppainen, I. Dorbandt, F. Xi, R. Bors, N. Maticiu, R. Wenisch, R. Bagacki, C. Schary, U. Michalczyk, P. Bogdanoff, I. Lauermann, R. van de Krol, R. Schlattmann and S. Calnan, Host, Suppressor, and Promoter—The Roles of Ni and Fe on Oxygen Evolution Reaction Activity and Stability of NiFe Alloy Thin Films in Alkaline Media, *ACS Catal.*, 2021, **11**(16), 10537–10552, DOI: [10.1021/acscatal.1c01190](https://doi.org/10.1021/acscatal.1c01190).
- 370 C. Kuai, Z. Xu, C. Xi, A. Hu, Z. Yang, Y. Zhang, C.-J. Sun, L. Li, D. Sokaras, C. Dong, S.-Z. Qiao, X.-W. Du and F. Lin, Phase Segregation Reversibility in Mixed-Metal Hydroxide Water Oxidation Catalysts, *Nat. Catal.*, 2020, **3**(9), 743–753, DOI: [10.1038/s41929-020-0496-z](https://doi.org/10.1038/s41929-020-0496-z).
- 371 K. W. Kimura, R. Casebolt, J. Cimada DaSilva, E. Kauffman, J. Kim, T. A. Dunbar, C. J. Pollock, J. Suntivich and T. Hanrath, Selective Electrochemical CO₂ Reduction during Pulsed Potential Stems from Dynamic Interface, *ACS Catal.*, 2020, **10**(15), 8632–8639, DOI: [10.1021/acscatal.0c02630](https://doi.org/10.1021/acscatal.0c02630).
- 372 C. Kim, L.-C. Weng and A. T. Bell, Impact of Pulsed Electrochemical Reduction of CO₂ on the Formation of

- C₂+ Products over Cu, *ACS Catal.*, 2020, **10**(21), 12403–12413, DOI: [10.1021/acscatal.0c02915](https://doi.org/10.1021/acscatal.0c02915).
- 373 H. Wang, L. D. B. Mandemaker, J. de Ruiter, X. Yu, W. van der Stam and B. M. Weckhuysen, Identical Grain Atomic Force Microscopy Elucidates Facet-Dependent Restructuring of Copper for CO₂ Electroreduction, *Angew. Chem.*, 2025, **137**(16), e202424530, DOI: [10.1002/ange.202424530](https://doi.org/10.1002/ange.202424530).
- 374 I. Kim, G.-B. Lee, S. Kim, H. D. Jung, J.-Y. Kim, T. Lee, H. Choi, J. Jo, G. Kang, S.-H. Oh, W. Kwon, D. Hong, H. G. Kim, Y. Lee, U. Kim, H. Kim, M. Kim, S. Back, J. Park, Y.-C. Joo and D.-H. Nam, Unveiling the Reconstruction of Copper Bimetallic Catalysts during CO₂ Electroreduction, *Nat. Catal.*, 2025, **8**(7), 697–713, DOI: [10.1038/s41929-025-01368-9](https://doi.org/10.1038/s41929-025-01368-9).
- 375 Z. Ling, Y. Yin, X. Kang, X. Li, R. Duan, S. Zhou, H. Liu, G. Mo, Z. Chen, X. Wu, R. Feng, Z. Wu, B. Han and X. Xing, Enhanced Electrochemical Reduction of CO₂ to CO by ZnO Nanorods Enriched with Oxygen Vacancies, *Chem Catal.*, 2025, **5**(2), DOI: [10.1016/j.checat.2024.101192](https://doi.org/10.1016/j.checat.2024.101192).
- 376 X. Lv, Q. Liu, J. Wang, X. Wu, X. Li, Y. Yang, J. Yan, A. Wu and H. B. Wu, Grain Refining Enables Mixed Cu⁺/Cu⁰ States for CO₂ Electroreduction to C₂+ Products at High Current Density, *Appl. Catal., B*, 2023, **324**, 122272, DOI: [10.1016/j.apcatb.2022.122272](https://doi.org/10.1016/j.apcatb.2022.122272).
- 377 T. Li, C. Yang, J.-L. Luo and G. Zheng, Electrolyte Driven Highly Selective CO₂ Electroreduction at Low Overpotentials, *ACS Catal.*, 2019, **9**(11), 10440–10447, DOI: [10.1021/acscatal.9b02443](https://doi.org/10.1021/acscatal.9b02443).
- 378 J. Vavra, T.-H. Shen, D. Stoian, V. Tileli and R. Buonsanti, Real-Time Monitoring Reveals Dissolution/Redeposition Mechanism in Copper Nanocatalysts during the Initial Stages of the CO₂ Reduction Reaction, *Angew. Chem.*, 2021, **133**(3), 1367–1374, DOI: [10.1002/ange.202011137](https://doi.org/10.1002/ange.202011137).
- 379 L. Wang, Z. Chen, Y. Xiao, L. Huang, X. Wang, H. Fruehwald, D. Akhmetzyanov, M. Hanson, Z. Chen, N. Chen, B. Billinghamurst, R. D. L. Smith, C. V. Singh, Z. Tan and Y. A. Wu, Stabilized Cu^δ + -OH Species on *in situ* Reconstructed Cu Nanoparticles for CO₂-to-C₂H₄ Conversion in Neutral Media, *Nat. Commun.*, 2024, **15**(1), 7477, DOI: [10.1038/s41467-024-52004-2](https://doi.org/10.1038/s41467-024-52004-2).
- 380 Y. L. Chung, S. Kim, Y. Lee, D. T. Wijaya, C. W. Lee, K. Jin and J. Na, Pulsed Electrolysis for CO₂ Reduction: Techno-Economic Perspectives, *iScience*, 2024, **27**(8), 110383, DOI: [10.1016/j.isci.2024.110383](https://doi.org/10.1016/j.isci.2024.110383).
- 381 H. Kim, H. An, J. Kim, H. Park, C. Cha, R. Haaring, H. Lee, K. Han and D. Y. Chung, Dynamic Interface Engineering *via* Mechanistic Understanding of Copper Reconstruction in Electrochemical CO₂ Reduction Reaction, *J. Am. Chem. Soc.*, 2026, **148**(6), 6045–6056, DOI: [10.1021/jacs.5c16244](https://doi.org/10.1021/jacs.5c16244).