



Advancing CO₂RR Through Hybrid Framework Catalysts

Nouraiz Mushtaq^{1*} and Khizzra Aslam²

¹Interdisciplinary Research Center for Hydrogen Technologies and Carbon Management (IRC-HTCM), King Fahd University of Petroleum & Minerals, KFUPM, Box 5040, Dhahran, 31261, Saudi Arabia

²School of Optics and Photonics, Beijing Institute of Technology, Beijing 10081, China

***Corresponding author:** Nouraiz Mushtaq, Interdisciplinary Research Center for Hydrogen Technologies and Carbon Management (IRC-HTCM), King Fahd University of Petroleum & Minerals, KFUPM, Box 5040, Dhahran, 31261, Saudi Arabia.

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Abstract

MOF-COF hybrids combine MOF tunability with COF stability, offering a powerful platform for electrocatalytic CO₂ reduction. Despite synthetic and structural challenges, early results are highly promising. Targeted innovation and advanced characterization could unlock their full CO₂RR potential.

Introduction

The development of metal-organic framework (MOF) and covalent organic framework (COF) hybrid materials has emerged as one of the most promising yet underexplored frontiers in the design of next-generation electrocatalysts. These hybrid assemblies attempt to merge the high tunability, porosity, and structural precision of MOFs with the exceptional stability, π -conjugation, and synthetic versatility of COFs. Although initial demonstrations have shown great promise, the field remains in its early stages, constrained by challenges in atomic precision, synthetic control, structural understanding, and catalytic performance. Nevertheless, these very challenges continue to inspire substantial scientific creativity. In this opinion piece, I argue that MOF-COF hybrids represent one of the most powerful and conceptually fertile platforms for advancing electrocatalytic CO₂ reduction (CO₂RR)—provided that the community confronts their current limitations directly and innovates

aggressively across chemistry, materials science, and in-situ characterization.

The Bottleneck of Atomic Precision and the Need for Rational Design

One of the most formidable obstacles lies in the difficulty of achieving atomically precise structural control when integrating MOFs and COFs. Because both frameworks rely on distinct bonding regimes—coordination interactions in MOFs and covalent linkages in COFs—their controlled co-assembly into single-crystalline structures remains deeply challenging. Yet this challenge is not merely synthetic; it limits our ability to fully understand structure-property relationships. Achieving precise fabrication is not an aesthetic choice but a scientific necessity. The electrocatalytic mechanism of CO₂RR is highly sensitive to active-site environment, local elec-

tronic structures, pore orientation, and heterointerface chemistry. Without precise control, it becomes nearly impossible to correlate catalytic pathways with specific structural motifs. As I see it, the next leap in this field will come from the deliberate selection of building blocks—metal nodes, organic linkers, π -conjugated scaffolds—that are inherently compatible for co-crystallization. Rational design must replace trial-and-error synthesis if the field is to mature into a predictive science.

Hybrid Synthesis Strategies: A Missing Theoretical Framework

Despite the synergy between MOFs and COFs, hybrid synthesis methods remain rudimentary. Current approaches—typically involving either MOF-on-COF or COF-on-MOF growth—are highly system-dependent and rarely generalizable. The field urgently needs a unified conceptual and methodological framework. In my opinion, one of the most promising directions is the development of conjugated combination strategies, in which the hybridization is not merely physical but electronically integrated. By achieving true interfacial conjugation, researchers could simultaneously enhance crystallinity, stability, charge transport, and catalytic activity. Beyond this, alternative bonding strategies—hydrogen bonding, metal-organic coordination, or even metallophilic interactions—could unlock entirely new forms of structural integration. We must push beyond the limited range of current methods and embrace a broader palette of chemical interactions to engineer truly coherent MOF-COF hybrids.

Lack of Mechanistic Understanding: The Case for In-Situ Characterization

A major barrier to progress is the limited understanding of growth mechanisms, interface formation, and heterostructure evolution. Until we can visualize and quantify the construction of MOF-COF architectures, synthesis will remain poorly controlled and largely empirical. Here, advanced in-situ characterization tools offer unprecedented opportunities. Cryogenic TEM, operando XRD, low-dose TEM, and emerging spectroscopic methods can reveal atomic-scale interfaces, intermediate phases, and dynamic structural transformations. These insights are not merely academic—they enable predictive models that allow researchers to intentionally manipulate morphology, defect domains, pore alignment, and electronic coupling. In my view, the integration of experimental observation with theoretical modeling will form the backbone of the next generation of hybrid framework design.

Structural Advantages and Biocompatibility Limitations

MOF-COF hybrid structures offer hierarchical porosity, high surface area, and tunable functionality—traits that make them ideal for catalysis, separations, and sensing. Yet, despite these structural advantages, their application in electrocatalytic CO₂RR remains surprisingly limited. More critically, their rigid structures and tightly packed interlayer interactions often result in poor biocompati-

bility—an issue that restricts potential applications in biosensing, environmental remediation, or catalytic systems interfaced with biological systems. I argue that this limitation is neither fundamental nor unavoidable. Regulating interlayer spacing, incorporating hydrophilic domains, and designing frameworks with non-aromatic units could collectively tune biocompatibility without sacrificing catalytic performance. Such structural modification strategies will become increasingly important as the field strives toward environmental and sustainable applications.

Extending CO₂ Reduction Beyond C₁ and C₂ Products: The Next Grand Challenge

Most MOF, COF, and MOF-COF based catalysts currently produce C₁ (CO, formate, methane) or C₂ (ethylene, ethanol) products. However, the real industrial breakthrough will occur when these materials enable efficient generation of C₃ and C₃⁺ molecules—propanol, butanol, or multicarbon oxygenates. Achieving this requires overcoming a major mechanistic barrier: retaining *C₂ intermediates long enough to enable C-C-C coupling. To date, no MOF- or COF-based catalyst has fully solved this challenge, but tandem catalysis offers a highly promising route. By coupling CO₂-to-CO catalysts with CO-to-C₃⁺ catalysts in a single hybrid structure, synergy between adjacent sites could dramatically improve selectivity and conversion efficiency. In my opinion, tandem catalysis represents one of the most exciting and commercially meaningful directions for MOF-COF hybrids in CO₂RR. Not only does it simplify mechanistic complexity, it also provides a platform for modular catalyst design—precisely the type of design flexibility needed for real-world deployment.

Conclusion

Despite the significant challenges, I believe the future of MOF-COF hybrid materials in electrocatalytic CO₂ reduction is extraordinarily bright. The structural precision, synthetic tunability, and functional diversity of these materials present nearly limitless opportunities. What the field needs now is not incremental improvement, but coordinated global efforts in:

- rational structural design
- unified hybrid synthesis strategies
- in-situ mechanistic characterization
- tandem catalytic engineering
- and translation toward industrial applications

If these efforts converge, MOF-COF hybrids could redefine the boundaries of CO₂ conversion science and catalyze the emergence of sustainable carbon circularity. The challenges are substantial, but so is the transformative potential. With continued innovation, collaboration, and theoretical insight, I am confident that MOF-COF hybrid materials will play a foundational role in the future of electrocatalytic CO₂ reduction technology.