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双金属衍生材料电催化还原二氧化碳的研究进展

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摘 要

研发高效的CO_2电还原催化剂对减少碳排放、实现碳中和具有重要意义。单一金属催化剂如单原子催化剂因其良好的催化性能在CO_2电还原领域得到广泛研究。然而，单一金属催化剂存在活性位点单一、反应动力学慢、产物选择性低和稳定性不足等缺点。双金属催化剂因其独特的结构和优异的性能而受到极大关注。通过引入另一种金属，可以改变催化剂的电子结构，促进新的活性位点的形成，从而优化中间体与活性位点之间的相互作用。文章从衍生材料的制备策略、双金属材料的优势剂在电催化二氧化碳领域的应用等角度具体阐述了双金属衍生材料在电催化碳还原领域的研究进展。

关键词

电催化，双金属衍生材料，二氧化碳还原

Research Progress on Electrocatalytic Reduction of Carbon Dioxide by Bimetallic Derived Materials

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Abstract

Developing efficient CO_2 electroreduction catalysts is of great significance for reducing carbon

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emissions and achieving carbon neutrality. Single metal catalysts such as single atom catalysts have been widely studied in the field of CO_2 electroreduction due to their excellent catalytic performance. However, single metal catalysts have disadvantages such as single active sites, slow reaction kinetics, low product selectivity, and insufficient stability. Bimetallic catalysts have attracted great attention due to their unique structure and excellent performance. By introducing another metal, the electronic structure of the catalyst can be altered, promoting the formation of new active sites and optimizing the interaction between intermediates and active sites. This article presents the research progress of bimetallic-derived materials in the field of electrocatalytic carbon reduction, focusing on the preparation strategies of derived materials and the application of dominant agents of bimetallic materials in the field of electrocatalytic carbon dioxide reduction.

Keywords

Electrocatalysis, Bimetallic Derived Material, Carbon Dioxide Reduction

1. 引言

截至 2022 年，全球二氧化碳排放量接近 368 亿吨，其中化工制造业贡献了近四分之一的排放量[1]。因此，减少碳排放迫在眉睫。各种二氧化碳转化技术已被广泛研究，包括光催化[2]、生物催化[3]和电催化等[4]。现代化工过程中，80%以上涉及催化反应，极大地促进了现代化工的发展，其中电催化技术的广泛应用将降低工业对化石燃料的依赖，缓解环境危机[5]。电催化 CO_2 还原反应(CO_2RR)可将 CO_2 转化为高附加值化学品，且被认为是减少 CO_2 排放的环保方法，特别是与可再生能源结合使用时[6]。探索催化剂的构效关系，将反应物、反应中间体和真实活性位点联系起来，对于催化剂的合理设计和催化理论的发展具有至关重要的意义。但识别催化剂表面上的真实活性位点仍然具有挑战性，因为催化界面是动态的，并且在催化反应过程中是非常复杂的[7]。

在过去的十年中，已经开展了大量关于催化剂的开发工作，用于将二氧化碳电催化还原为 C1 产物[4] [8] [9]。在各种催化剂中，基于 Pd、Ag 和 Au 的金属材料表现出良好的催化性能[10]-[12]。然而，这些金属催化剂仍然面临许多问题，如稳定性低、产物选择性差等[13] [14]。近年来，双金属材料是电化学还原二氧化碳最有前途的催化剂之一，但在工业化道路上仍需克服诸多挑战[15] [16]。例如，何老师课题组通过电纺丝技术和热解过程设计构建了一系列碳纳米纤维支撑的双金属钴－铜催化剂(CoxCu/CFs)，通过调节 CoxCuy/CFs 中的金属比例，在二氧化碳还原反应中获得了不同的产物分布和催化性能[17]。侯老师课题组通过水热法制备了 CuSn 合金纳米颗粒，随后在氮气气氛下进行热解，实现合金纳米颗粒均匀分散在氮掺杂石墨烯(NG)上。在较宽的电位范围内，实现了近 93%的 C1 产物法拉第效率(FE)，显著高于 Cu 和 Sn 的单独 FE 值(32%和 58%) [18]。

2. 双金属衍生材料的制备策略及其在电催化还原二氧化碳中的应用

2.1. 电化学原位重构法

原位重建方法可用于合成具有高活性和高选择性的 CO_2 电还原催化剂[19]。如图 1 所示为电化学重构的策略以及优化的策略。例如，吕老师课题组制备了掺杂铱的 $Sr_2Fe_{1.45}Ir_{0.05}Mo_{0.5}O_6^{-\delta}$ (SFIrM)钙钛矿在

CO_2 电解过程中表现出动态电化学重建的特征，SFIrM 表面上高度分散的 IrFe 合金纳米粒子大量出溶。由于活性金属/氧化物界面的构建可有效提高电催化活性，但通过渗透沉积的金属纳米粒子不可避免地会因烧结而失活，导致在高温下性能下降，因此想到通过钙钛矿氧化物晶格到表面的原位溶出来操纵活性金属纳米粒子。原为重构的 IrFe@SFIrM 界面具有 1.46 $A \cdot cm^{-2}$ 的电流密度，同时保持了 99%以上的 CO 法拉第效率，与 $Sr_2Fe_{1.5}Mo_{0.5}O_6^{-\delta}$ (SFM)对应物相比提高了 25.8%。铜基催化剂在 CO_2 还原反应中产生高活性的多碳产物，但铜基催化剂的选择性和稳定性仍然存在巨大挑战。[20]顾老师课题组合成了 Cu-N 配位的 MOF 材料作为前体，通过原位电化学重建，制备了高活性的 Cu/Cu_2O 纳米簇，在−1.03 V vs RHE 下，对 C_2H_4 的法拉第效率为 70.2% ± 1.7%，部分电流密度为 12.38 $mA \cdot cm^{-2}$。通过观察相关中间体的原位红外光谱证实了 C_2H_4 的形成途径，而原位拉曼光谱、原位 XPS 和 HRTEM 证明共存的 Cu_2O 和 Cu 纳米簇是活性位点。[21]

具有多功能活性位点的异质结构氧化物作为一类高效的 CO_2 电化学还原催化剂，在工作条件下容易发生结构的重构，这给理解反应机理和合理设计催化剂带来了挑战。姜老师课题组首次阐明了 CuO/SnO_2 在电化学电位下的结构重建，揭示了二氧化碳电还原产物选择性与原位演化异质结构之间的内在关系。实验数据表明，原始的 CuO/SnO_2 重建为 Cu_2O/SnO_2，其中含有少量的氧空位。对 HCOOH 具有高选择性(法拉第效率为 54.81%)。有趣的是，在−1.05 V 下重建为 Cu/SnO_{2-x}，对乙醇的法拉第效率显著提高到 39.8%。[22]

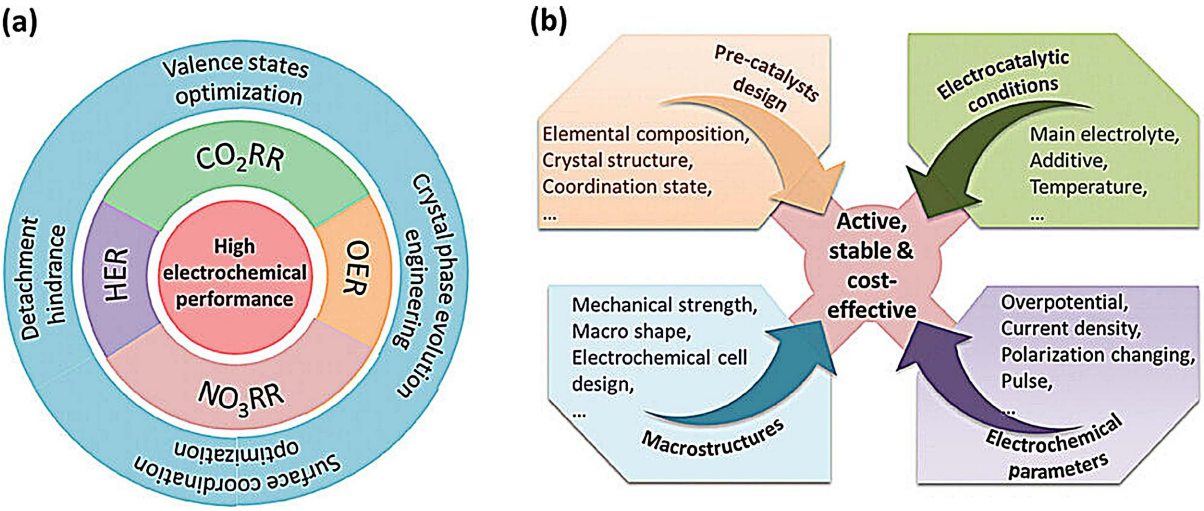

Figure 1. (a) Summary of the reconstruction control strategies; (b) Strategies of the reconstruction optimization.
图 1. (a) 重构控制策略的总结；(b) 重构优化策略

2.2. 热解前驱体法

多孔碳基材料及其与金属氧化物纳米粒子的复合材料被视为重要的催化材料，这是因为它们具有出色的电化学活性、较高的化学稳定性和热稳定性，而且能够根据特定的需求进行合理设计[23]。如图 2 所示是金属有机框架衍生催化剂的典型问题和设计思路。金属有机框架(MOFs)是一类由金属离子或团簇作为节点、多齿有机化合物作为连接体组成的多孔材料。由于其特殊的结构和组成，MOFs 及其复合材料具备诸多优势，包括高结晶度、高孔隙率和比表面积、可机械调控的孔表面、可设计的框架以及多样化的结构等，它们已在发光、主客体识别、吸附/分离、磁性材料、能量转换/存储、催化等诸多领域得到了广泛应用[24]。一般来说，金属有机框架(MOFs)可直接煅烧以获得功能性的 MOF 衍生材料，无需模板以及

复杂的合成步骤。由于其操作简便且耗时短，直接热解法被广泛用于各类 MOF 衍生材料的合成，例如多孔碳材料、单/多金属化合物、单活性位催化剂及其复合材料等。[25]-[28]

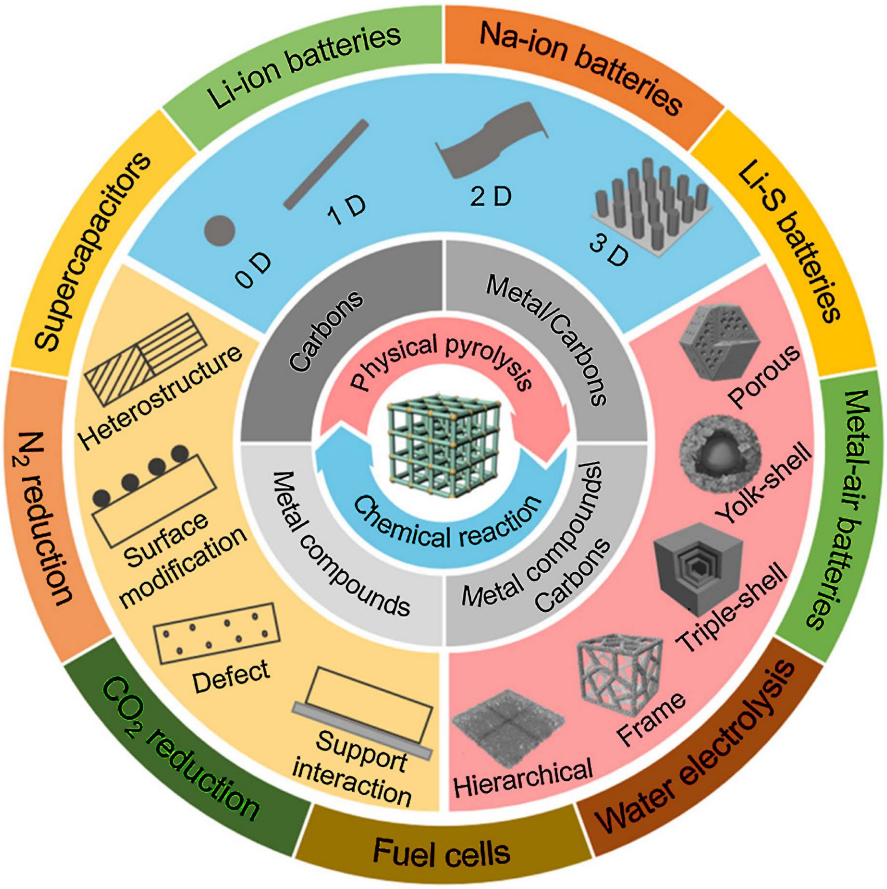

Figure 2. Synthetic technique of MOF derivatives and the corresponding regulations of composition, structure, and performance
图 2. MOF 衍生物的合成技术及其组成、结构和性能的相应规定

3. 双金属材料的优势及其在电催化还原二氧化碳中的应用

3.1. 双金属合金材料

双金属合金电催化剂是一类由两种金属元素组成的催化材料。这类催化剂在电化学领域具有重要应用，尤其是在电催化和燃料电池技术中[29]。双金属合金材料通过引入第二种金属，来调节电子结构，从而优化电催化性能[30]；能够形成新的活性位点，提高反应的选择性和效率[31]；优化中间体与活性位点之间的相互作用，降低反应能垒[32]。刘老师课题组通过两种聚合物模板和金属前驱体的界面自组装，制备了具有两种不同孔隙(~320 和~20 nm)和可调合金组成的 HMMP Cu/Zn 合金。HMMP Cu/Zn 合金催化剂显著促进了 CO_2 的深度电还原为液体 C2 产物，同时抑制了竞争性的质子。其中，HMMP Cu5Zn8 表现出最佳的电催化选择性(在−0.8 V 时乙醇产量高达 6.6%)和优异的稳定性[33]。因此，双金属合金材料电催化剂是由两种金属元素组成的复合材料，通过优化电子结构和表面特性，在电催化领域展现出卓越的性能。通过有效降低反应的极限电势和活化势垒，使得它们在多种电催化反应中表现出更高的活性和选择性。双金属合金材料因其高活性、良好的选择性和稳定性而受到广泛关注。它们能够在较低的过电位下驱动多种重要的电催化反应。然而，尽管双金属合金材料电催化剂具有诸多优点，但其大规模应用仍面

临一些挑战，如成本较高、制备过程复杂以及长期稳定性等问题需要进一步研究和解决。

3.2. 双金属氧化物材料

双金属氧化物在电催化二氧化碳还原中的优势主要体现在以下几个方面：1) 协同增强性能：促进二氧化碳活化，打破中间体的吸/脱附线性关系[34]；2) 形貌效应：不同的纳米结构展现出不同优势[17] [35]；3)电场效应：高曲率诱导的强电场效应可以促进二氧化碳还原[36]；4) 界面工程：双金属非均相界面可调节中间吸附、电子转移、避免催化剂中毒等[37]；5) 电子效应：促进 C-C 偶联[38]；6) 串联效应：耦合多步反应提高催化剂性能[39]。这些优势使得双金属氧化物在 CO_2RR 领域展现出巨大潜力，特别是实现碳中和方面。例如，Aarthi Pandiarajan 课题组制备了双金属 CuZnO-45 纳米结构催化剂，该双金属氧化物能够产生 88.3%的最大甲酸法拉第效率，在−0.86 V vs RHE 的电势下实现了 35.3 mA·cm^{-2} 的部分电流密度，并同时提高了*CO_2·−生成甲酸的选择性[40]。同样，刘老师课题组设计了在部分还原的金/氧化锌纳米阵列(NRs)中(AuZn/ZnO)，通过双金属金/锌位点，可以实现二氧化碳－合成气的转换。与纳米颗粒(NPs)不同，一维 NRs 结构具有优先暴露反应晶面、高结构稳定性、较快的电子转移速率等独特特征，有效地解决了 NPs 活性和稳定性有限的问题，进一步提高了催化剂的催化性能。Zn/ZnO 的费米能级(EF)位于 Zn/ZnO 的导带最小(CBM)和价带最大(VBM)能级的区间，表明具有半导体特性。相比之下，AuZn/ZnO 在 EF 上表现出裂波 DOS，表明其金属性质，反映了其较高的价电子密度，有利于提高其在 AuZn/氧化锌中的催化性能。[41]

因此，双金属氧化物电催化剂是由两种不同金属元素通过氧桥连接形成的化合物，这种结构赋予了它们独特的电子和几何特性。这类催化剂通常展现出比单一金属氧化物更高的活性、选择性和稳定性。这是因为两种金属元素的相互作用可以优化电荷分布，改善了反应物的吸附和活化过程。

3.3. 双金属衍生材料

双金属衍生催化剂在电催化二氧化碳还原领域有着显著优势，它具有高效的催化活性：双金属衍生催化剂通过独特的电子结构和合理的吸附/解吸二氧化碳和中间体，极大提升了催化性能[42]；优化二氧化碳的吸附和调节能垒[43]；调节价态和拓扑结构：优化催化剂结构[44]；提高催化剂的稳定性：通过导向还原或氧化过程，避免过度反应导致活性位暴露受阻来提高稳定性[45]；深入理解催化机制：通过原位光谱学表征进一步理解反应的发生[46]。例如，程老师课题组制备了由金属有机框架(MOF)衍生的 Ag 修饰的 Cu 氧化物催化剂(CuO/Ag@C)，能够有效地将 CO_2 转化为乙烯。MOF 衍生的多孔碳限制了金属纳米颗粒的大小，确保了活性位点的充分暴露。值得注意的是，CuO/Ag@C 催化剂在−0.7 V 下对 C_2H_4 的法拉第效率达到了 48.6%，表现出了出色的稳定性。实验结果和理论计算均表明，Ag 位点促进了 CO 的生成[47]。张老师课题组报道了 CuS-Bi_2S_3 异质结前驱体在 CO_2RR 过程中可以原位重构为 Cu 掺杂铋(CDB)电催化剂。CDB 的工业兼容电流密度为−1.1 A·cm^{-2}，与 CO_2RR 可逆氢电极相比，在−0.86 V 下甲酸生成速率为 21.0 mmol·h^{-1}·cm^{-2}，显著优于目前报道的催化剂。重要的是，还可以实现 1050 mV 的超宽电位区域，具有超过 90%的甲酸法拉第效率和在−400 mA·cm^{-2} 下超过 100 小时的优异长期稳定性[48]。

综上，双金属－有机框架衍生电催化剂是一类通过将两种不同的金属元素结合在金属－有机框架(MOF)结构中，并通过后续处理得到的复合材料。双金属 MOF 衍生材料因其较大的比表面积、孔隙率和结构可调节而受到广泛关注。然而，MOF 材料固有的低导电性大大阻碍了它们在电催化领域的进一步应用。由于 MOFs 主要由有机配体和金属离子或金属簇组成，其电子传导能力较弱，这限制了其在电催化反应中的效率。其次，MOF 及其衍生物的合成过程通常较为复杂，需要精确控制反应条件如温度、压力、溶剂等。此外，MOF 的后处理过程也可能涉及多个步骤，增加了制备难度和成本。尽管 MOF 具有高比

表面积和可调节的结构，但在实际应用中，对活性位点的精确调控仍然是一个挑战。表 1 是近年来应用于电催化二氧化碳还原领域的一些双金属材料性能的比较。

Table 1. Summary of the electrocatalytic performance of bimetallic materials for CO_2
表 1. 双金属材料电催化二氧化碳性能的总结

序号	催化剂	还原产物	法拉第效率	参考文献
1	Cu-Ag/NC	CH_4等	55.3%	[49]
2	M-CuCo/C	C2	79.2%	[50]
3	Pb@Cu	CO	80.3%	[51]
4	Cu-In	CO	90.0%	[52]
5	BiCu/CP	HCOOH	85.0%	[53]
6	$Cu_{20}Sn_1$	CO	95.3%	[54]

4. 总结

综上所述，双金属材料作为近些年来的热门电催化材料被许多研究人员重视。本文综述了各种不同的双金属材料在电催化碳还原领域的研究进展。首先，由于衍生的电催化材料有着不可比拟的优势，因而本文综述了双金属衍生材料的制备策略。其次，综述了不同种类双金属材料的优势及其在电催化还原二氧化碳中的应用。尽管截至目前已经有大量的文献报道双金属材料在电催化碳还原领域的应用，但还未应用于实际生产生活，有必要对其可实施性和工业化进行进一步的研究，让电催化还原二氧化碳造福全人类。

参考文献

[1] Zhang, C., Gu, Y., Jiang, Q., Sheng, Z., Feng, R., Wang, S., *et al*. (2024) Exploration of Gas-Dependent Self-Adaptive Reconstruction Behavior of Cu_2O for Electrochemical CO_2 Conversion to Multi-Carbon Products. *Nano-Micro Letters*, **17**, Article No. 66. https://doi.org/10.1007/s40820-024-01568-1

[2] Xu, Q., Jiang, J., Sheng, X., Jing, Q., Wang, X., Duan, L., *et al*. (2023) Understanding the Synergistic Effect of Piezoelectric Polarization and the Extra Electrons Contributed by Oxygen Vacancies on an Efficient Piezo-Photocatalysis CO_2 Reduction. *Inorganic Chemistry Frontiers*, **10**, 2939-2950. https://doi.org/10.1039/d3qi00405h

[3] Shi, H., Fu, M., Yuan, S., Lu, Y., Yang, Z., Yue, C., *et al*. (2024) Engineered *Escherichia coli* Whole Cell-Mediated Electro-Biocatalysis for Carbon Dioxide to Formic Acid Conversion. *ACS Sustainable Chemistry & Engineering*, **12**, 5544-5554. https://doi.org/10.1021/acssuschemeng.3c08129

[4] Tran, D.S., Vu, N., Nemamcha, H., Boisvert, C., Legrand, U., Fink, A.G., *et al*. (2025) Design of Electrocatalysts and Electrodes for CO_2 Electroreduction to Formic Acid and Formate. *Coordination Chemistry Reviews*, **524**, Article 216322. https://doi.org/10.1016/j.ccr.2024.216322

[5] Xiong, B., Yang, Y., Liu, J., Hua, Z. and Yang, Y. (2022) Electrocatalytic Reduction of CO_2 to C1 Products over Bimetal Catalysts: A DFT Screening Study. *Fuel Processing Technology*, **233**, Article 107315. https://doi.org/10.1016/j.fuproc.2022.107315

[6] Xu, Z., Tan, X., Chen, C., Wang, X., Sui, R., Zhuang, Z., *et al*. (2024) Recent Advances in Microenvironment Regulation for Electrocatalysis. *National Science Review*, **11**, nwae315. https://doi.org/10.1093/nsr/nwae315

[7] Tang, T., Bai, X., Wang, Z. and Guan, J. (2024) Structural Engineering of Atomic Catalysts for Electrocatalysis. *Chemical Science*, **15**, 5082-5112. https://doi.org/10.1039/d4sc00569d

[8] Lü, F., Qi, G., Liu, X., Zhang, C., Guo, R., Peng, X., *et al*. (2019) Selective Electrolysis of CO_2 to CO on Ultrathin In_2Se_3 Nanosheets. *Electrochemistry Communications*, **103**, 127-132. https://doi.org/10.1016/j.elecom.2019.05.020

[9] Zhang, C., Follana-Berná, J., Dragoe, D., Halime, Z., Gotico, P., Sastre-Santos, Á., *et al*. (2024) Cobalt Tetracationic 3,4-pyridinoporphyrazine for Direct CO_2 to Methanol Conversion Escaping the CO Intermediate Pathway. *Angewandte Chemie International Edition*, **63**, e202411967. https://doi.org/10.1002/anie.202411967

[10] Liu, Y., Deng, C., Liu, F., Dai, X., Yang, X., Chen, Y., *et al*. (2024) Coupling Electron Donors with Proton Repulsion via Pt-N_3-S Sites to Boost CO_2 Reduction in CO_2/H_2 Fuel Cell. *Nano Energy*, **126**, Article 109667. https://doi.org/10.1016/j.nanoen.2024.109667

[11] Zeng, L., Shi, J., Chen, H. and Lin, C. (2021) Ag Nanowires/C as a Selective and Efficient Catalyst for CO_2 Electroreduction. *Energies*, **14**, Article 2840. https://doi.org/10.3390/en14102840

[12] Fu, J., Zhu, W., Chen, Y., Yin, Z., Li, Y., Liu, J., *et al*. (2019) Bipyridine-Assisted Assembly of Au Nanoparticles on Cu Nanowires to Enhance the Electrochemical Reduction of CO_2. *Angewandte Chemie International Edition*, **58**, 14100-14103. https://doi.org/10.1002/anie.201905318

[13] Wang, G., Li, X., Yang, X., Liu, L., Cai, Y., Wu, Y., *et al*. (2022) Metal-Based Aerogels Catalysts for Electrocatalytic CO_2 Reduction. *Chemistry—A European Journal*, **28**, e202201834. https://doi.org/10.1002/chem.202201834

[14] He, J., Dettelbach, K.E., Salvatore, D.A., Li, T. and Berlinguette, C.P. (2017) High-Throughput Synthesis of Mixed-Metal Electrocatalysts for CO_2 Reduction. *Angewandte Chemie International Edition*, **56**, 6068-6072. https://doi.org/10.1002/anie.201612038

[15] Cao, X., Chen, C., Min, Y., Yuan, H., Chen, S. and Xu, L. (2021) Prediction of Bimetal Embedded in Two-Dimensional Materials for CO_2 Reduction Electrocatalysis with a New Integrated Descriptor. *Physical Chemistry Chemical Physics*, **23**, 26241-26249. https://doi.org/10.1039/d1cp03805b

[16] Shao, Q., Wang, P. and Huang, X. (2018) Opportunities and Challenges of Interface Engineering in Bimetallic Nanostructure for Enhanced Electrocatalysis. *Advanced Functional Materials*, **29**, Article 1806419. https://doi.org/10.1002/adfm.201806419

[17] He, C., Wang, S., Jiang, X., Hu, Q., Yang, H. and He, C. (2022) Bimetallic Cobalt-Copper Nanoparticle-Decorated Hollow Carbon Nanofibers for Efficient CO_2 Electroreduction. *Frontiers in Chemistry*, **10**, Article 904241. https://doi.org/10.3389/fchem.2022.904241

[18] Xiong, W., Yang, J., Shuai, L., Hou, Y., Qiu, M., Li, X., *et al*. (2019) CuSn Alloy Nanoparticles on Nitrogen-Doped Graphene for Electrocatalytic CO_2 Reduction. *Chem Electro Chem*, **6**, 5951-5957. https://doi.org/10.1002/celc.201901381

[19] Feng, J., Wang, X. and Pan, H. (2024) In-Situ Reconstruction of Catalyst in Electrocatalysis. *Advanced Materials*, **36**, Article 2411688. https://doi.org/10.1002/adma.202411688

[20] Shen, Y.X., Liu, T.F., Li, R.T., Lv, H.F., Ta, N., Zhang, X.M., *et al*. (2023) *In Situ* Electrochemical Reconstruction of $Sr_2Fe_{1.45}Ir_{0.05}Mo_{0.5}O_{6-\Delta}$ Perovskite Cathode for CO_2 Electrolysis in Solid Oxide Electrolysis Cells. *National Science Review*, **10**, nwad078. https://doi.org/10.1093/nsr/nwad078

[21] Liu, C., Zhang, X., Huang, J., Guan, M., Xu, M. and Gu, Z. (2022) *In Situ* Reconstruction of Cu-N Coordinated MOFs to Generate Dispersive Cu/Cu_2O Nanoclusters for Selective Electroreduction of CO_2 to C_2H_4. *ACS Catalysis*, **12**, 15230-15240. https://doi.org/10.1021/acscatal.2c04275

[22] Guo, Z., Yu, Y., Li, C., Campos dos Santos, E., Wang, T., Li, H., *et al*. (2024) Deciphering Structure-Activity Relationship towards CO_2 Electroreduction over SnO_2 by a Standard Research Paradigm. *Angewandte Chemie International Edition*, **63**, e202319913. https://doi.org/10.1002/anie.202319913

[23] Singh, C., Mukhopadhyay, S. and Hod, I. (2021) Metal-Organic Framework Derived Nanomaterials for Electrocatalysis: Recent Developments for CO_2 and N_2 Reduction. *Nano Convergence*, **8**, Article No, 1. https://doi.org/10.1186/s40580-020-00251-6

[24] Mukherjee, S., Hou, S., Watzele, S.A., Garlyyev, B., Li, W., Bandarenka, A.S., *et al*. (2022) Avoiding Pyrolysis and Calcination: Advances in the Benign Routes Leading to MOF-Derived Electrocatalysts. *Chem Electro Chem*, **9**, e202101476. https://doi.org/10.1002/celc.202101476

[25] Li, J., Luo, H., Li, B., Ma, J. and Cheng, P. (2023) Application of MOF-Derived Materials as Electrocatalysts for CO_2 Conversion. *Materials Chemistry Frontiers*, **7**, 6107-6129. https://doi.org/10.1039/d3qm00835e

[26] Xiao, J., Zhang, T. and Wang, Q. (2022) Metal-Organic Framework Derived Single-Atom Catalysts for CO_2 Conversion to Methanol. *Current Opinion in Green and Sustainable Chemistry*, **37**, Article 100660. https://doi.org/10.1016/j.cogsc.2022.100660

[27] Huang, J., Zhang, X., Huang, J., Zheng, D., Xu, M. and Gu, Z. (2023) MOF-Based Materials for Electrochemical Reduction of Carbon Dioxide. *Coordination Chemistry Reviews*, **494**, Article 215333. https://doi.org/10.1016/j.ccr.2023.215333

[28] Kharissova, O.V., Kharisov, B.I. and González, L.T. (2020) Recent Trends on Density Functional Theory-Assisted Calculations of Structures and Properties of Metal-Organic Frameworks and Metal-Organic Frameworks-Derived Nanocarbons. *Journal of Materials Research*, **35**, 1424-1438. https://doi.org/10.1557/jmr.2020.109

[29] van den Berg, D., Izelaar, B., Fu, S. and Kortlever, R. (2024) The Effect of Surface Conditions on the Electrochemical CO_2 Reduction Performance of Bimetallic AuPd Electrocatalysts. *Catalysis Science & Technology*, **14**, 555-561.

https://doi.org/10.1039/d3cy01411h

[30] Wang, Y., Niu, C. and Zhu, Y. (2019) Copper-Silver Bimetallic Nanowire Arrays for Electrochemical Reduction of Carbon Dioxide. *Nanomaterials*, **9**, Article 173. https://doi.org/10.3390/nano9020173

[31] Śliwa, M., Zhang, H., Gao, J., Stephens, B.O., Patera, A.J., Raciti, D., *et al*. (2024) Selective CO_2 Reduction Electrocatalysis Using AgCu Nanoalloys Prepared by a "Host-Guest" Method. *Nano Letters*, **24**, 13911-13918. https://doi.org/10.1021/acs.nanolett.4c02638

[32] Rasul, S., Anjum, D.H., Jedidi, A., Minenkov, Y., Cavallo, L. and Takanabe, K. (2014) A Highly Selective Copper-Indium Bimetallic Electrocatalyst for the Electrochemical Reduction of Aqueous CO_2 to CO. *Angewandte Chemie International Edition*, **54**, 2146-2150. https://doi.org/10.1002/anie.201410233

[33] Su, X., Sun, Y., Jin, L., Zhang, L., Yang, Y., Kerns, P., *et al*. (2020) Hierarchically Porous Cu/Zn Bimetallic Catalysts for Highly Selective CO_2 Electroreduction to Liquid C_2 Products. *Applied Catalysis B*: *Environmental*, **269**, Article 118800. https://doi.org/10.1016/j.apcatb.2020.118800

[34] Mo, C., Yang, C., Hu, Y. and Peng, J. (2024) Bimetallic Bi-In Nanoparticles for Efficient Production of Formate via Electrocatalytic Conversion of CO_2. *Journal of Solid State Electrochemistry*, **28**, 4235-4246. https://doi.org/10.1007/s10008-024-06042-x

[35] Merino-Garcia, I., Albo, J., Krzywda, P., Mul, G. and Irabien, A. (2020) Bimetallic Cu-Based Hollow Fibre Electrodes for CO_2 Electroreduction. *Catalysis Today*, **346**, 34-39. https://doi.org/10.1016/j.cattod.2019.03.025

[36] Luo, M., Fu, X., Geng, S., Li, Z. and Li, M. (2023) Efficient Electrochemical CO_2 Reduction via CuAg Doped CeO_2. *Fuel*, **347**, Article 128470. https://doi.org/10.1016/j.fuel.2023.128470

[37] Li, Y., Zhou, L., Han, G., Cui, W., Li, W. and Hu, T. (2024) ZIF-Derived Catalyst with Inverse ZnO/Co Structure for Efficient CO_2 Methanation. *International Journal of Hydrogen Energy*, **51**, 452-461. https://doi.org/10.1016/j.ijhydene.2023.10.094

[38] Wang, P., Li, T., Wu, Q., Du, R., Zhang, Q., Huang, W., *et al*. (2022) Molecular Assembled Electrocatalyst for Highly Selective CO_2 Fixation to C^{2+} Products. *ACS Nano*, **16**, 17021-17032. https://doi.org/10.1021/acsnano.2c07138

[39] Xue, Y., Li, C., Zhou, X., Kuang, Z., Zhao, W., Zhang, Q., *et al*. (2022) MOF-Derived Cu/Bi Bi-Metallic Catalyst to Enhance Selectivity toward Formate for CO_2 Electroreduction. *Chem Electro Chem*, **9**, e202101648. https://doi.org/10.1002/celc.202101648

[40] Yang, Z., Wang, H., Bi, X., Tan, X., Zhao, Y., Wang, W., *et al*. (2023) Bimetallic In_2O_3/Bi_2O_3 Catalysts Enable Highly Selective CO_2 Electroreduction to Formate within Ultra-Broad Potential Windows. *Energy & Environmental Materials*, **7**, e12508. https://doi.org/10.1002/eem2.12508

[41] Zhao, R., Zhu, Z., Ouyang, T. and Liu, Z. (2023) Selective CO_2-to-Syngas Conversion Enabled by Bimetallic Gold/Zinc Sites in Partially Reduced Gold/Zinc Oxide Arrays. *Angewandte Chemie International Edition*, **63**, e202313597. https://doi.org/10.1002/anie.202313597

[42] Yang, X., Wang, Q., Chen, F., Zang, H., Liu, C., Yu, N., *et al*. (2023) In-Situ Electrochemical Restructuring of Cu_2BiS_x Solid Solution into Bi/Cu_XS_y Heterointerfaces Enabling Stabilization Intermediates for High-Performance CO_2 Electroreduction to Formate. *Nano Research*, **16**, 7974-7981. https://doi.org/10.1007/s12274-022-5337-8

[43] Xue, Y., Guo, Y., Cui, H. and Zhou, Z. (2021) Catalyst Design for Electrochemical Reduction of CO_2 to Multicarbon Products. *Small Methods*, **5**, Article 2100736. https://doi.org/10.1002/smtd.202100736

[44] Li, J., Chen, W., Lin, R., Huang, M., Wang, M., Chai, M., *et al*. (2021) Thermally Evaporated Ag-Au Bimetallic Catalysts for Efficient Electrochemical CO_2 Reduction. *Particle & Particle Systems Characterization*, **38**, Article 2100148. https://doi.org/10.1002/ppsc.202100148

[45] Li, W., Zhang, Z., Liu, W., Gan, Q., Liu, M., Huo, S., *et al*. (2022) ZnSn Nanocatalyst: Ultra-High Formate Selectivity from CO_2 Electrochemical Reduction and the Structure Evolution Effect. *Journal of Colloid and Interface Science*, **608**, 2791-2800. https://doi.org/10.1016/j.jcis.2021.11.002

[46] Wang, W., Wang, Z., Yang, R., Duan, J., Liu, Y., Nie, A., *et al*. (2021) *In Situ* Phase Separation into Coupled Interfaces for Promoting CO_2 Electroreduction to Formate over a Wide Potential Window. *Angewandte Chemie International Edition*, **60**, 22940-22947. https://doi.org/10.1002/anie.202110000

[47] Sun, B., Cheng, H., Shi, C., Guan, J., Jiang, Z., Ma, S., *et al*. (2025) Metal-Organic Framework-Derived Silver/Copper-Oxide Catalyst for Boosting the Productivity of Carbon Dioxide Electrocatalysis to Ethylene. *Journal of Colloid and Interface Science*, **679**, 615-623. https://doi.org/10.1016/j.jcis.2024.10.014

[48] Shen, H., Zhao, Y., Zhang, L., He, Y., Yang, S., Wang, T., *et al*. (2022) In-Situ Constructuring of Copper-Doped Bismuth Catalyst for Highly Efficient CO_2 Electrolysis to Formate in Ampere-Level. *Advanced Energy Materials*, **13**, Article 2202818. https://doi.org/10.1002/aenm.202202818

[49] Zou, X., Li, A., Ma, C., Gao, Z., Zhou, B., Zhu, L., *et al*. (2023) Nitrogen-Doped Carbon Confined Cu-Ag Bimetals for

Efficient Electroreduction of CO_2 to High-Order Products. *Chemical Engineering Journal*, **468**, Article 143606. https://doi.org/10.1016/j.cej.2023.143606

[50] He, A., Yang, Y., Zhang, Q., Yang, M., Zou, Q., Du, J., *et al*. (2022) The Enhanced Local CO Concentration for Efficient CO_2 Electrolysis towards C_2 Products on Tandem Active Sites. *Chemical Engineering Journal*, **450**, Article 138009. https://doi.org/10.1016/j.cej.2022.138009

[51] Xiong, B., Liu, J., Yang, Y., Yang, Y. and Hua, Z. (2022) Effect Mechanism of NO on Electrocatalytic Reduction of CO_2 to CO over Pd@Cu Bimetal Catalysts. *Fuel*, **323**, Article 124339. https://doi.org/10.1016/j.fuel.2022.124339

[52] Xiang, H., Rasul, S., Hou, B., Portoles, J., Cumpson, P. and Yu, E.H. (2019) Copper-Indium Binary Catalyst on a Gas Diffusion Electrode for High-Performance CO_2 Electrochemical Reduction with Record CO Production Efficiency. *ACS Applied Materials & Interfaces*, **12**, 601-608. https://doi.org/10.1021/acsami.9b16862

[53] Liu, B., Xie, Y., Wang, X., Gao, C., Chen, Z., Wu, J., *et al*. (2022) Copper-Triggered Delocalization of Bismuth P-Orbital Favours High-Throughput CO_2 Electroreduction. *Applied Catalysis B*: *Environmental*, **301**, Article 120781. https://doi.org/10.1016/j.apcatb.2021.120781

[54] Zhang, M., Zhang, Z., Zhao, Z., Huang, H., Anjum, D.H., Wang, D., *et al*. (2021) Tunable Selectivity for Electrochemical CO_2 Reduction by Bimetallic Cu-Sn Catalysts: Elucidating the Roles of Cu and Sn. *ACS Catalysis*, **11**, 11103-11108. https://doi.org/10.1021/acscatal.1c02556