Double-Extended Reticular Framework via Localized Covalent Cross-Linking in a Mercaptoaldehydate-Based Metal-Organic Framework for Redox-Modulated Electrochemical Carbon Dioxide Reduction to Ethylene

Karam, Saif (School: RQ Science &amp
Technology)

Electrochemical CO2 reduction (CO2RR) has emerged as a foremost strategy for commercial-scale production of carbon-based derivatives via proton-coupled electron transfers, yet overcoming the energetic constraints of the initial C-C coupling step and managing subsequent branching of multi-carbon intermediates remain exceedingly challenging, necessitating atomically modular and tunable electrocatalysts. Reticular frameworks exhibit unique potential, although each variant encounters inherent limitations undermining the core motivation to harness their properties in electrochemical applications. Herein, an unexplored class of materials, termed double-extended reticular framework (DERF), emerges from localized covalent cross-linking in a de novo introduced mercaptoaldehydate-based MOF, resulting in the first continuous reticular architecture bridging coordinative and covalent linkages. Guided by an iterative first-principles mechanistic process, an original reaction scheme was devised to direct synthetic trials, physicochemical characterization, and electrochemical measurements augmented by atomic-scale theoretical analysis. Unlike previous MOF-COF hybrids, DERF exhibits a controlled heterophase morphology, redox stability, synergistic extended-lattice conjugation for enhanced charge transport, and accessible metal sites for catalysis. Consequently, DERF enables the first CO2RR under pulsed electrolysis in a reticular framework, where a redox-breathing transition tunes lattice topology and metal valence to yield ethylene at low overpotentials with Faradaic efficiencies surpassing benchmarks. This work overcomes longstanding challenges in reticular frameworks, enabling their use as high-performance electrocatalysts and broadening their energy and sensing applications.

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