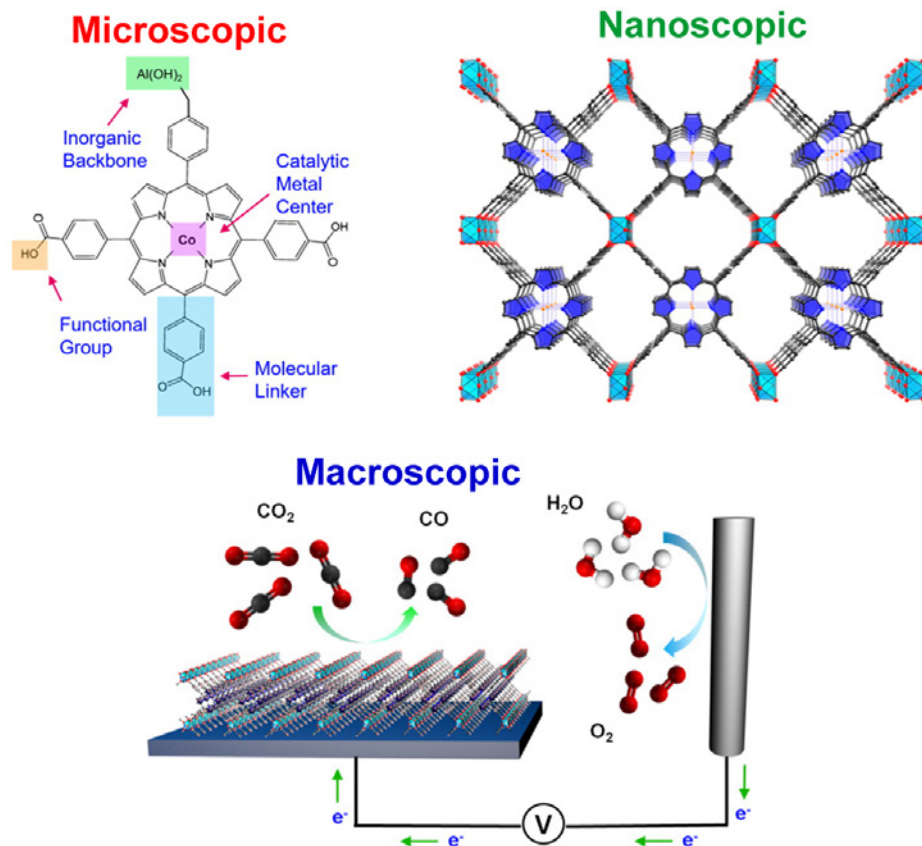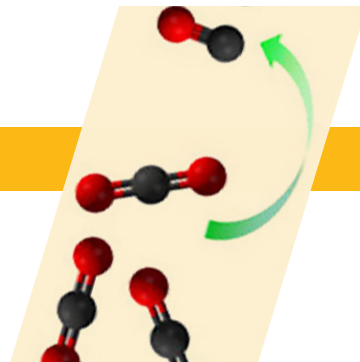**ENERGY SCIENCES**

Porous Framework Electrocatalysts Are Key to Carbon Dioxide Conversion

The catalyst design follows the principles of reticula chemistry, in which each building block is designed, then linked together in a predetermined fashion. Shown here are cobalt porphyrin units linked together with alumina nodes in a porous structure, which is grown on a conductive substrate.

Soaking up Carbon Dioxide

The ability to convert a waste product like CO_2 into useful fuels or chemical precursors will enable further utilization of renewable energy. Currently, photovoltaic (PV) cells can efficiently convert sunlight into electricity, but this technology can only be used when the sunlight is immediately available. Converting solar power, either directly or in multiple steps, into something that can be stored and transported is necessary. Today, most fuels that power our cities and vehicles come from the ground (e.g., coal, oil). This is a finite energy source that is simultaneously environmentally damaging. The end goal of these research efforts and many others is to create a closed carbon cycle in which greenhouse gasses can be captured and turned back into usable fuels via renewable energy sources. While many advances are still necessary to achieve this, the development of efficient CO_2-reduction catalysts is a significant step in the right direction.

The burning of fossil fuels and the consequent rising levels of atmospheric CO_2 has led to a number of negative environmental consequences, including global warming and ocean acidification. Converting CO_2 to fuels or chemical feedstock, ideally through the use of renewable energy, can reduce atmospheric CO_2 and decrease fossil fuel consumption. The principal difficulty is the rarity of earth-abundant catalysts that can do this with high efficiency and selectivity. Recently, researchers have made headway by utilizing super-porous molecular

structures—metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs)—as a new class of CO_2-reduction catalysts. This work, which incorporates structural and electronic studies at the ALS, gives rise to an entirely new basis on which to develop electrocatalysts for converting captured CO_2 into valuable chemical products such as fuels, pharmaceuticals, and plastics.

Finding electrocatalysts that can convert captured CO_2 into fuels such carbon monoxide, methanol, or methane with high efficiency and selectivity has

been a longstanding challenge. The principal difficulty is that the CO_2 reduction reaction is kinetically sluggish. Also, the reduction reaction generates a wide variety of products, and it's difficult to find a catalyst that's selective for a specific one. Homogeneous molecular catalysts offer high selectivity through precise molecular-level tuning but typically suffer from issues of stability and solubility. Heterogeneous catalysts like metals are more stable but cannot be modified easily on a molecular level and therefore don't
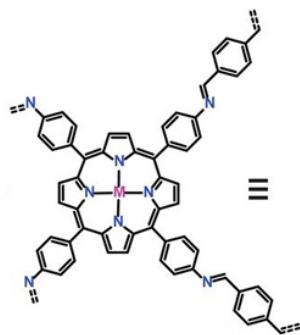
COF-366-M

M = Co   COF-366-Co

23.5 Å
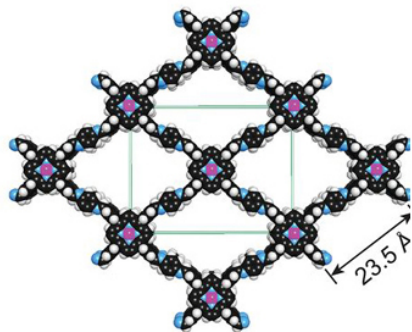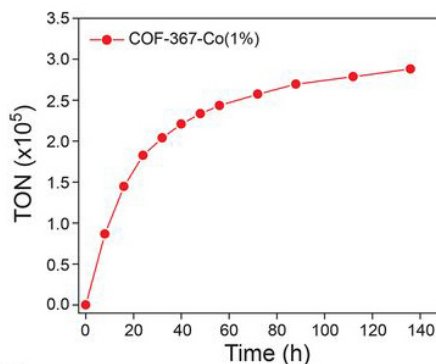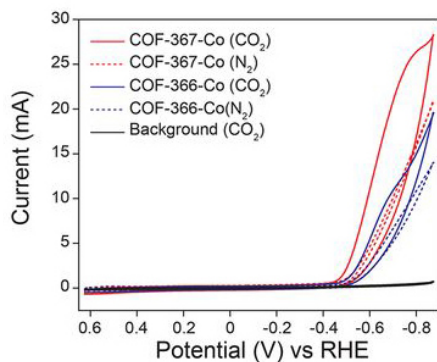
COF catalysts incorporated cobalt porphyrin active sites within a conductive framework. Highly efficient CO_2-to-CO conversion was achieved with upwards of 90% selectivity and turnover numbers of up to 300,000.

The development of this new class of electrocatalysts is especially promising because the nature of MOFs and COFs allows for precise control of the active site, degree of porosity, and framework composition. Further research efforts, such as establishment of structure-function relationships and the exploration of additional frameworks, active sites, and functional groups are underway. This research could lead to a viable way to transform captured CO_2 on a lab and industrial scale.

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offer product selectivity or routes for systematic improvement.

Researchers have used ALS capabilities to develop a new class of CO_2 reduction catalysts. By linking organic catalytic units in an ordered, three-dimensional structure, MOFs and COFs effectively heterogenize a tunable molecular catalyst and stabilize it within the framework structure. MOF- and COF-based catalysts can also be modified to exquisitely balance the concentration of active sites with mass and charge transport for a truly mesoscopic material design across multiple length scales: the atomic (the active site itself), nanoscopic (the framework and porosity), and mesoscopic (the overall device functioning).

MOF catalysts were synthesized using nanometer-thick films of metal oxides deposited onto substrates by atomic layer deposition (ALD), allowing for precise variation of MOF thickness. Grazing-incidence wide-angle x-ray scattering (GIWAXS) measurements at ALS Beamline 7.3.3 showed that the MOF films were crystalline and preferentially oriented, with cobalt porphyrin units perpendicular to the

substrate. MOFs can be created using almost any organic linker, but in this case the porphyrin acted as both the catalyst and the linker. The final MOF catalyst consisted of cobalt-metallated porphyrins in an aluminum oxide inorganic skeleton and converted CO_2 to CO at a rate of 76%, among the highest ever reported in aqueous electrolytes.

COF catalysts feature a conductive framework that allows charges to easily move throughout the structure. Surprisingly, the cobalt porphyrin active sites embedded within the COF framework were 26 times more active than the molecular analogue. X-ray absorption measurements at ALS Beamline 10.3.2 provided evidence that the electronic structure of the cobalt in the COF framework may be different than that of the cobalt in the molecular linker. Within the COF, the electronic structure of the catalyst is actually modified by the framework. With a small catalyst loading to push the limits of intrinsic catalytic activity, the cobalt porphyrin-functionalized COF attained a per-site turnover rate of 300,000.