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Researchers have developed a porous material that converts CO2 into carbon monoxide (CO) and oxygen.

# Designer material clears hurdle for turning carbon dioxide into fuel



By Robert F. Service (/author/robert-f.-service) | 20 August 2015 6:30 pm | 13 Comments (/chemistry/2015/08/designer-material-clears-hurdle-turning-carbon-dioxide-fuel#disqus_thread)

Plants are great at pulling carbon dioxide out of the air. But they are slow, and researchers would love to speed up the removal of carbon dioxide ($CO_2$)—a key greenhouse gas—from the atmosphere. Today, researchers in California report that they've taken the first step to doing just that, by developing a porous material that converts $CO_2$ into carbon monoxide (CO) and oxygen. Not only could the new material clean our skies, but it might also serve as the starting point for making fuel from renewable power sources.

Chemists have been trying to do something useful with $CO_2$ for decades. But $CO_2$ is a very stable, unreactive molecule. To split it into CO and oxygen, researchers have to add energy, typically electricity. That's not done now, because it's far cheaper to make fuel by refining oil. But some catalysts—substances that speed up chemical reactions—could make the process cheaper by reducing the amount of energy that needs to be pumped in.

One promising catalyst is a ring-shaped organic molecule with a cobalt atom at its core, called a porphyrin. When added to a solution with two electrodes, an electrolyte, and some dissolved $CO_2$, the porphyrin nuzzles up close to the negatively charged electrode and ferries electrons to the $CO_2$, splitting it into CO and oxygen that bubble away. But the setup works only when the porphyrins are dissolved in an environmentally questionable organic solvent. And there are other problems: Porphyrins tend to clump together over time, destroying their electron-ferrying abilities.

To get around these problems, researchers at the University of California, Berkeley, led by chemists Omar Yaghi and Chris Chang, found a way to link porphyrins together into a porous solid material called a covalent organic framework (COF) (http://www.sciencemag.org/content/early/2015/08/19/science.aac8343) . Yaghi and his colleagues have developed a variety of COFs as filters for separating different gases from one another. But in hopes of taking a first step to making renewable fuels, they wanted to see if their cobalt COF could split $CO_2$ as well. Porphyrins seemed like a natural choice, because they're not only good at ferrying electrons to $CO_2$, but they can also conduct electricity. In theory, using a porphyrin COF as a catalyst would allow the material to conduct electrons from an electrode to porphyrin components throughout a thick film of the material. And the COF's porous nature would allow $CO_2$ to percolate through and gain access to the catalytically active cobalt atoms at the porphyrin's core.

After synthesizing their new COF, Yaghi, Chang, and their colleagues placed a layer atop an electrode. Because their catalyst was already in contact with the electrode, they didn't need the organic solvent that's required for the molecular porphyrin catalyst, and they could use a simple water-based electrolyte instead. When they applied an electric current, they found that the porphyrin COF did a better job than the molecular

version of splitting $CO_2$ into CO and oxygen.

The key to the molecular splitting process is when $CO_2$ molecules bind to the cobalt atoms at a porphyrin's core. But Yaghi's team found that in their cobalt porphyrin COF not all of the $CO_2$ molecules found their cobalt targets. So they rebuilt their COF frameworks so they had slightly larger pores to ease the passage of $CO_2$. They also added a bit of copper. $CO_2$molecules tend to avoid copper in favor of cobalt, and adding copper caused the $CO_2$ molecules to crowd around the remaining cobalt atoms, like groupies swarming a rock star. That increased the likelihood that $CO_2$ molecules would make actual contact with a cobalt atom and be split.

The upshot—which the Berkeley team reports online today in *Science*—was that the dual-metal COF split $CO_2$ molecules 60 times as well as the free-floating cobalt porphyrin molecules. The COFs also proved highly efficient, using 90% of the electrons to split $CO_2$ molecules into CO. Finally, the catalysts were extremely active, fracturing some 240,000 $CO_2$ molecules per hour, 25 times as fast as the cobalt-only COFs. That makes the material among the best $CO_2$-splitting catalysts out there.

"This is very nice work," says Paul Kenis, a chemist at the University of Illinois, Urbana-Champaign. He notes that lots of groups are trying to improve their $CO_2$-to-CO conversions by using porous electrode materials. But this work makes the electrode itself out of a catalytically active material. "So you get two for one," Kenis says.

Ultimately, the CO created could be combined with hydrogen (made by splitting water into hydrogen and oxygen) to produce hydrocarbon fuels from renewable energy sources like wind and solar, Kenis and Yaghi say. That's not economical today, because it's still far cheaper to refine oil. But if countries ever want to make fuels from renewable energy only, and avoid dumping more fossil fuel $CO_2$ into the air, catalysts such as this one could be an essential component.

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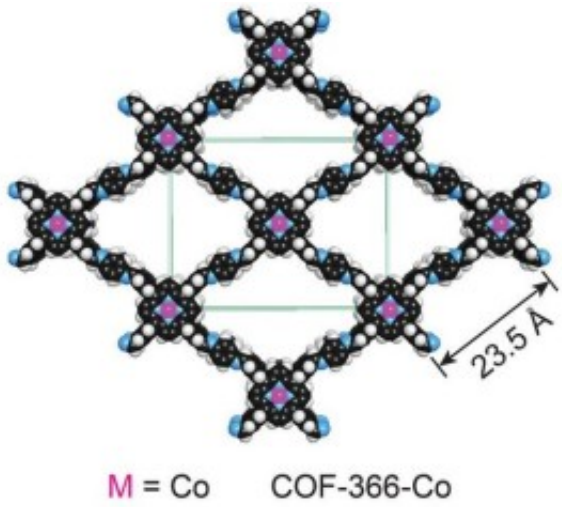
*Science* | DOI: 10.1126/science.aad1655

# Soaking Up Carbon Dioxide and Turning it into Valuable Products

## Berkeley Lab Researchers Double Down on a Good Thing by Incorporating Catalysts into Crystalline Sponges

News Release Lynn Yarris (510) 486-5375 • **AUGUST 27, 2015**

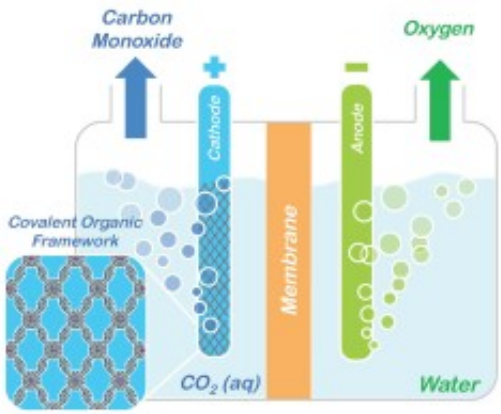
A molecular system that holds great promise for the capture and storage of carbon dioxide has been modified so that it now also holds great promise as a catalyst for converting captured carbon dioxide into valuable chemical products. Researchers with the U.S. Department of Energy (DOE)'s Lawrence Berkeley National Laboratory (Berkeley Lab) have incorporated molecules of carbon dioxide reduction catalysts into the sponge-like crystals of covalent organic frameworks (COFs). This creates a molecular system that not only absorbs carbon dioxide, but also selectively reduces it to carbon monoxide, which serves as a primary building block for a wide range of chemical products including fuels, pharmaceuticals and plastics.




*Structural model showing a covalent organic framework (COF) embedded with a cobalt porphyrin.*

"There have been many attempts to develop homogeneous or heterogeneous catalysts for carbon dioxide, but the beauty of using COFs is that we can mix-and-match the best of both worlds, meaning we have molecular control by choice of catalysts plus the robust crystalline nature of the COF," says Christopher Chang, a chemist with Berkeley Lab's Chemical Sciences Division, and a co-leader of this study. "To date, such porous materials have mainly been used for carbon capture and separation, but in showing they can also be used for carbon dioxide catalysis, our results open up a huge range of potential applications in catalysis and energy."

Chang and Omar Yaghi, a chemist with Berkeley Lab's Materials Sciences Division who invented COFs, are the corresponding authors of a paper in *Science* that describes this research in detail. The paper is titled "Covalent organic frameworks comprising cobalt porphyrins for catalytic CO2 reduction in water." Lead authors are Song Lin, Christian Diercks and Yue-Biao Zhang. Other co-authors are Nikolay Kornienko, Eva Nichols, Yingbo Zhao, Aubrey Paris, Dohyung Kim and Peidong Yang.

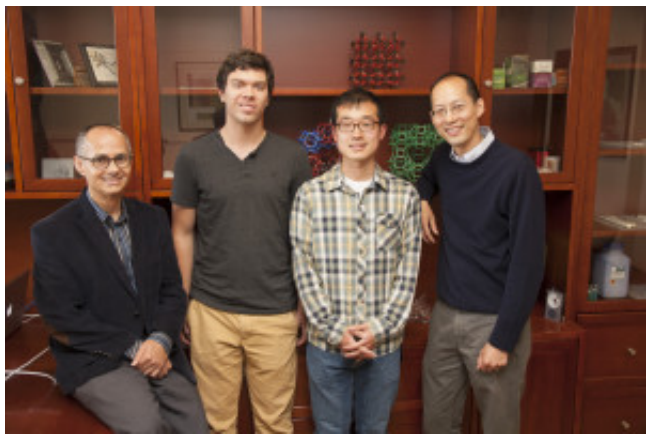



*Conceptual model showing how porphyrin COFs could be used to split CO2 into CO and oxygen . (courtesy of Omar Yaghi)*

Chang and Yaghi both hold appointments with the University of California (UC) Berkeley. Chang is also a Howard Hughes Medical Institute (HHMI) investigator. Yaghi is co-director of the Kavli Energy NanoScience Institute (Kavli-ENSI) at UC Berkeley.

The notoriety of carbon dioxide for its impact on the atmosphere and global climate change has overshadowed its value as an abundant, renewable, nontoxic and nonflammable source of carbon for the manufacturing of widely used chemical products. With the reduction of atmospheric carbon dioxide emissions in mind, Yaghi and his research group at the University of Michigan in 2005 designed and developed the first COFs as a means of separating carbon dioxide from flue gases. A COF is a porous three-dimensional crystal consisting of a tightly folded, compact framework that features an extraordinarily large internal surface area – a COF the size of a sugar cube were it to be opened and unfolded would blanket a football field. The sponge-like quality of a COF's vast internal surface area enables the system to absorb and store enormous quantities of targeted molecules, such as carbon dioxide.

Now, through another technique developed by Yaghi, called "reticular chemistry," which enables molecular systems to be "stitched" into netlike structures that are held together by strong chemical bonds, the Berkeley Lab researchers were able to embed the molecular backbone of COFs with a porphyrin catalyst, a ring-shaped organic molecule with a cobalt atom at its core. Porphyrins are electrical conductors that are especially proficient at transporting electrons to carbon dioxide.



*From left, , Omar Yaghi, Christian Diercks, Song Lin and Chris Chang,. (Photo by Michael Barnes, UC Berkeley)*

"A key feature of COFs is the ability to modify chemically active sites at will with molecular-level control by tuning the building blocks constituting a COF's framework," Yaghi says. "This affords a significant advantage over other solid-state catalysts where tuning the catalytic properties with that level of rational design remains a major challenge. Because the porphyrin COFs are stable in water, they can operate in aqueous electrolyte with high selectivity over competing water reduction reactions, an essential requirement for working with flue gas emissions."

In performance tests, the porphyrin COFs displayed exceptionally high catalytic activity – a turnover number up to 290,000, meaning one porphyrin COF can reduce 290,000 molecules of carbon dioxide to carbon monoxide every second. This represents a 26-fold increase over the catalytic activity of molecular

cobalt  porphyrin catalyst and places porphyrin COFs among the fastest and most efficient catalysts of all known carbon dioxide reduction agents. Furthermore, the research team believes there's plenty of room for further improving porphyrin COF performances.

"We're now seeking to increase the number of electroactive cobalt centers and achieve lower over-potentials while maintaining high activity and selectivity for carbon dioxide reduction over proton reduction," Chang says. "In addition we are working towards expanding the types of value-added carbon products that can be made using COFs and related frameworks."

This research was supported by the DOE Office of Science in part through its Energy Frontier Research Center (EFRC) program. The porphyrin COFs were characterized through X-ray absorption measurements performed at Berkeley Lab's Advanced Light Source, a DOE Office of Science User Facility.

**Additional Information**

For more about the research of Christopher Chang go here

For more about the research of Omar Yaghi go here

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Updated: August 27, 2015

TAGS: Advanced Light Source, chemical sciences, Chemical Sciences Division, clean air, clean energy, energy, materials, materials sciences, Materials Sciences Division, renewable energy, solar energy

# Smithsonian.com

# Could a New Nanomaterial Reduce Greenhouse Gases?

## Berkeley researchers have developed a way to split carbon dioxide into oxygen and carbon monoxide using a nano-mesh

(Spectral-Design/iStock)

By Emily Matchar
smithsonian.com
August 28, 2015

Most methods of fighting climate change are about reducing greenhouse gas emissions: inventing cleaner power plants, engineering greener cars. Then, there's the camp of researchers who focus on drawing gases from the atmosphere once they've already been released.

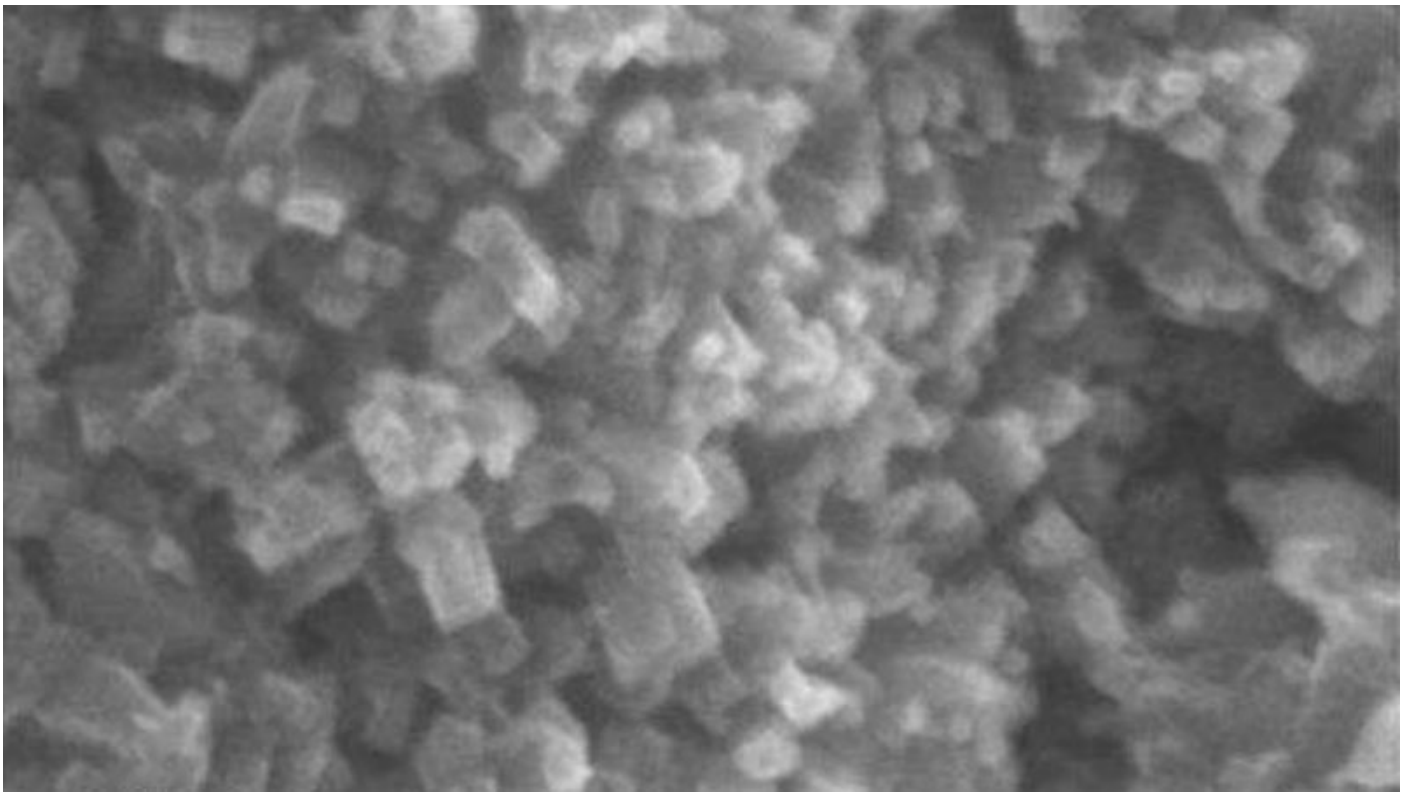
So-called "carbon dioxide capture" has been controversial, often dismissed as impractical or inadequate. Yet as global efforts to reduce emissions have proven difficult and sometimes disappointing, the approach seems increasingly alluring.

A new invention, from scientists at University of California, Berkeley, offers a novel take on carbon capture. The researchers have created a nanomaterial that destroys carbon dioxide by splitting it into oxygen and carbon monoxide.

Scientists have long tried to get rid of carbon dioxide by splitting its molecule. These splitting attempts can be energy-intensive, which defeats the environmental purpose. So reseachers have used various catalysts to speed up the reaction, reducing the amount

of electricity needed to split the molecules. Many scientists have focused on porphyrins, ring-shaped organic molecules, to make these reactions happen. Though porphyrins can have various atoms at their centers, the ones used for this purpose are cobalt porphyrins, which are especially catalytically active. When these porphyrins are added to a solution with two electrodes, an electrolyte and some dissolved carbon dioxide, the porphyrins are attracted to the electrolyte. This causes the electrons to move to the carbon dioxide, splitting it into carbon monoxide and oxygen. But this approach has not been perfect. The porphyrins clump together and lose effectiveness over time, and the solutions used to make the process happen are environmentally questionable themselves.

The Berkeley researchers seem to have found a new way to deal with this by creating a porous nanomaterial linking porphyrins together into a mesh-like substance. This is called a covalent organic framework (COF). The carbon dioxide percolates through the COF, splitting into carbon monoxide and oxygen with very little added energy. It works about 60 times more efficiently than splitting the carbon dioxide using free-floating porphyrins. The research was reported in the journal *Science*.



A magnified image of the COF (Science)

So what can be done with the oxygen and carbon monoxide created by the process?

“Carbon monoxide is important because it’s one of the feedstocks of the chemical industry, which makes fuels based on carbon monoxide,” says Christian Diercks, one of the lead researchers on the study. “The idea is basically to use carbon dioxide, which is a waste, and turn it into fuel.”

In the future, factories could use sheets of these nanomaterials around carbon dioxide-producing areas, such as smokestacks, turning it directly into carbon monoxide for fuel. But this is a long way down the road.

"If you really want to get something like carbon dioxide reduction to happen on a large scale, I think you always need government incentives," Diercks says, "because it always takes industry a long time to pick up new ideas like this."

So far, the lab has only made the material in tiny amounts, 30 milligrams at a time. It takes multiple days to produce, so the process will need to become more efficient to be implemented at an industrial level. The researchers' next step is to look into ways to more efficiently transform the carbon monoxide into fuel.



**About Emily Matchar**

Emily Matchar is a writer based in Hong Kong and Chapel Hill, North Carolina. Her work has appeared in *The New York Times*, *The Atlantic*, *The New Republic*, *The Washington Post* and other publications. She is the author of .

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THE DAILY CALIFORNIAN
Tuesday, September 1, 2015



RESEARCH & IDEAS

TUESDAY, SEPTEMBER 1, 2015

# Campus researchers improve conversion of carbon dioxide into useful products

BY MADELEINE PAUKER | STAFF

LAST UPDATED 2 MINS AGO

A group of UC Berkeley researchers has found ways to better reduce carbon dioxide into carbon monoxide in order to make chemical products, such as fuel and plastics.

The group, led by campus chemistry professors Christopher Chang and Omar Yaghi, published a study earlier this month in which the team explained how incorporating catalysts into crystals allows them to convert carbon dioxide into carbon monoxide more efficiently. Using these sponge-like crystals — which exist in covalent organic frameworks and are visible to the naked eye as a fine, brown or reddish powder — is one of the most efficient ways to reduce carbon dioxide into carbon monoxide.

"The conversion is a big deal since it opens a new route to making interesting materials," said campus chemistry and earth and planetary sciences professor Ronald Cohen. "That is an important accomplishment, independent of whether it leads to ideas for addressing the greenhouse gas issue."

Carbon-capturing materials are already being explored by scientists to improve solutions related to greenhouse gases in the atmosphere, and similar materials are in development at UC Berkeley. The Lawrence Berkeley National Laboratory research group published its August paper in Science with lead authors Song Lin, Christian Diercks and Yue-Biao Zhang.

"We have a choice of burying carbon dioxide at a cost of about $50 per ton (with) current technology ... or recycling carbon dioxide into fuels," Cohen said in an email. "If the cost of converting to fuels becomes low enough, then this idea would be important to controlling climate change."

The crystals' structure has a very high internal surface area like a sponge, allowing them to absorb larger amounts of carbon dioxide than ever before.

Carbon monoxide can already be turned into fuel using several processes. One such technology, known as the Fischer-Tropsch process, has been employed on a large scale in South Africa.

The group sought to make the process cheaper and more efficient than previous experiments. The team used cobalt, a naturally abundant and relatively inexpensive material that makes the process more environmentally friendly. The reaction is also done in water instead of "environmentally questionable" organic solvents, Diercks said.

"There have been many attempts to develop homogeneous or heterogeneous catalysts for carbon



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dioxide, but the beauty of using (these frameworks) is that we can mix-and-match the best of both worlds," Chang said in a press release.

The catalysts, which are organic molecules containing cobalt, are suspended in the porous structure, preventing them from contacting one another and deactivating.

Researchers can also manipulate the structure of the framework to better understand how it influences the chemical reaction, Diercks said.

Diercks said the material could potentially work in power plants to absorb carbon dioxide and convert it into carbon monoxide.

The researchers are still working with milligrams of material, according to Diercks, but they plan to optimize the material to be able to make large quantities at low costs. The team has already shown the initial results of optimizing the amount of cobalt in the catalysts and will continue to focus on making the process more efficient.

*Contact Madeleine Pauker at mpauker@dailycal.org and follow her on Twitter at @powkur.*



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