

Novel tin-based metal–organic frameworks for reducing carbon dioxide to formate

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Novel Tin(II)-Based Metal–Organic Framework for Reducing Carbon Dioxide to Formate Under Visible Light

Most metal complexes that reduce carbon dioxide (CO₂) to useful chemicals via photocatalysis utilize rare and precious metals

Metal–organic frameworks (MOFs) made of Earth-abundant and non-toxic elements can act as photocatalysts

Tin (Sn)-based MOF for photocatalytic reduction of CO₂ to formate (HCOO⁻)

[Sn^{II}₂(H₃ttc)₂·MeOH]_n (KGF-10)

Crystal undergoes structural change

C
 H
 N
 O
 S
 Sn1
 Sn2

H₃ttc: trithiocyanuric acid, MeOH: methanol, BIH: 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole

- Visible light-driven photocatalysis
- Additional photosensitizer not required
- High apparent quantum yield of 9.8%
- Excellent selectivity over 99%

The novel non-toxic and highly efficient Sn-MOF opens new possibilities for solar energy-driven photocatalytic reduction of CO₂

Tin(II)-Based Metal–Organic Frameworks Enabling Efficient, Selective Reduction of CO₂ to Formate under Visible Light
 Kamakura et al. (2023) | *Angewandte Chemie International Edition* | 10.1002/anie.202305923

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Graphical abstract. Credit: Tokyo Tech

The never-ending demand for carbon-rich fuels to drive the economy keeps adding more and more carbon dioxide (CO₂) to the atmosphere. While efforts are being made to reduce CO₂ emissions, that alone cannot counter the adverse effects of the gas already present in the atmosphere.

So, scientists have come up with innovative ways to use existing atmospheric CO₂ by transforming it into useful chemicals such as formic acid (HCOOH) and methanol. A popular method for carrying out such conversions is to use [visible light](#) for driving the photoreduction of CO₂ via photocatalysts.

In a recent breakthrough published in *Angewandte Chemie, International Edition*, a team of researchers led by Prof. Kazuhiko Maeda of Tokyo Institute of Technology developed a tin-based metal–organic framework (MOF) that can enable selective photoreduction of CO₂. They reported a novel tin (Sn)-based MOF called KGF-10, with the formula [Sn^{II}₂(H₃ttc)₂.MeOH]_n (H₃ttc: trithiocyanuric acid and MeOH: methanol).

It successfully reduced CO₂ into HCOOH in the presence of visible light. "Most high-performance CO₂ reduction photocatalysts driven by visible light rely on rare, precious metals as principal components. Furthermore, integrating the functions of light absorption and catalysis into a single molecular unit made up of abundant metals has remained a long-standing challenge. Hence, Sn was the ideal candidate as it can overcome both challenges," explains Prof. Maeda.

MOFs, which bring the best of both metals and organic materials, are being explored as the more sustainable alternative to conventional rare-

earth metal-based photocatalysts. Sn, known for its ability to act as both a catalyst and absorber during a photocatalytic reaction, could be a promising candidate for MOF-based photocatalysts. While MOFs composed of zirconium, iron, and lead have been widely explored, not much is known about Sn-based MOFs.

For synthesizing the Sn-based MOF KGF-10, the researchers used H_3tc , MeOH, and tin chloride as the starting materials and chose 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole as the [electron donor](#) and the hydrogen source. The prepared KGF-10 was then subjected to several analysis techniques. They revealed that the material showed moderate CO_2 adsorption ability, had a bandgap of 2.5 eV, and absorbed visible light wavelengths.

Once aware of the physical and chemical properties of the new material, scientists used it for catalyzing the reduction of CO_2 in the presence of visible light. They found that KGF-10 successfully reduced CO_2 into formate ($HCOO^-$) with 99% selectivity without needing any additional photosensitizer or catalyst. It also exhibited a record-high apparent quantum yield—the ratio of the number of electrons involved in the reaction to the total number of incident photons—of 9.8% at 400 nm. Furthermore, [structural analysis](#) carried out during the reactions revealed that KGF-10 underwent structural changes while facilitating photocatalytic reduction.

This study presented for the first time a tin-based high-performance, precious-metal free, and single-component photocatalyst for visible-light-driven reduction of CO_2 to formate. The excellent properties of KGF-10 demonstrated by the team could open new avenues for its application as a photocatalyst in reactions such as solar energy-driven CO_2 reduction.

"The results of our study are a testimony to the fact that MOFs can be a platform for creating outstanding photocatalytic functions, usually

unattainable with molecular metal complexes, using non-toxic, inexpensive, and Earth-abundant metals," concludes Prof. Maeda.

More information: Yoshinobu Kamakura et al, Tin(II)-Based Metal–Organic Frameworks Enabling Efficient, Selective Reduction of CO₂ to Formate under Visible Light, *Angewandte Chemie International Edition* (2023). [DOI: 10.1002/anie.202305923](https://doi.org/10.1002/anie.202305923)

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