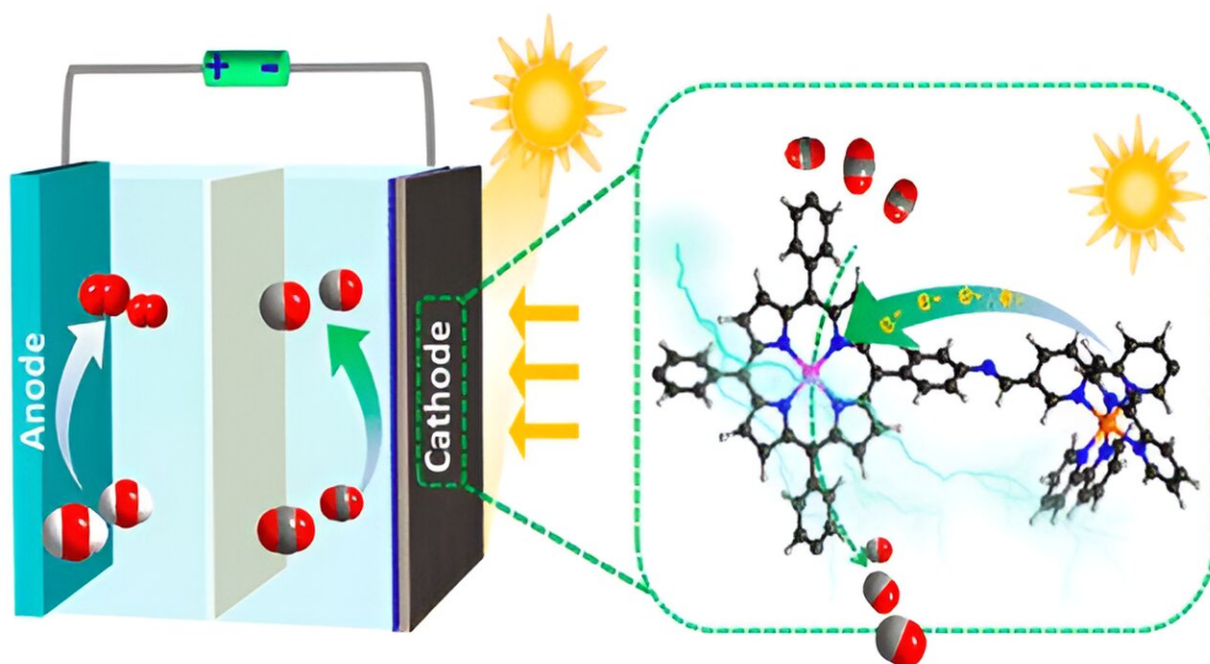


Photocoupled electroreduction of CO₂ over photosensitizer decorated covalent organic frameworks

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Electrocatalytic CO₂ reduction reaction (CO₂RR) is thought to be an ecologically favorable technique for using CO₂ as a cheap and abundant C1 feedstock for the production of value-added chemicals such as CO.

However, the thermodynamically stable nature of the CO₂ molecule featuring high C=O bond energy frequently leads to sluggish kinetics of CO₂→CO and high energy inputs.

Introducing an additional [visible-light](#) field would be a potential way to explore the optimized reaction conditions and develop effective catalysts for efficient CO₂RR toward CO, as the highly energetic photo-induced excited state of light-sensitive electrocatalysts can effectively optimize the formation barrier of reactive intermediates and lower the energy of the rate determining steps (RDS) of electrocatalytic CO₂RR. The efficient excited state lifetime of the active site is an important influencing factor in visible photocoupled electrocatalysis.

In a study published in the [Journal of the American Chemical Society](#), a group led by Prof. Cao Rong and Prof. Huang Yuanbiao from Fujian Institute of Research on the Structure of Matter of the Chinese Academy of Sciences incorporated Ru(bpy)₃Cl₂ photosensitive donors into a 2,2'-bipyridine functionalized Co-porphyrin-based COF (Co-Bpy-COF) by a post-synthetic method (PSM), providing Co-Bpy-COF-Ru_x (X is the molar ratio of Ru and Co species, X = 1/2 and 2/3) with longer excited state lifetime for CO₂ reduction under photo-electric conditions. Donor–acceptor characteristic and giant built-in electric field in Co-Bpy-COF-Ru_x efficiently accelerate the photo-induced electron transfer from Ru(bpy)₃Cl₂ to the cobalt porphyrin under the external light.

The researchers found that compared with the unmodified counterpart Co-Bpy-COF, the optimal Co-Bpy-COF-Ru_{1/2} displays a high CO Faradaic efficiency of 96.7% at -0.7 V vs. reversible hydrogen electrode (RHE) and CO partial current density of 16.27 mA cm⁻² at -1.1 V vs. RHE under the assistance of light, both of which far surpassed the values observed in the dark. Nonetheless, for Co-Bpy-COF, the values of FE_{CO} and j_{CO} tested in the light displayed no significant improvement than those recorded in the dark, which could be attributed to the rapid

relaxation of the excited state in the mono-photosensitive unit system.

In addition, the researchers revealed the trend of excited-electron transfer from $\text{Ru}(\text{bpy})_3\text{Cl}_2$ to cobalt porphyrin by highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the building units. The fluorescence quenching experiment and X-ray photoelectron spectroscopy (XPS) under visible light further confirmed the real existence of excited-electron transfer from $\text{Ru}(\text{bpy})_3\text{Cl}_2$ to cobalt porphyrin.

Furthermore, the researchers verified the formation of the giant built-in electric field in Co-Bpy-COF-Ru_x by electrochemical impedance spectroscopy (EIS) and conductivity measurements. Ultrafast transient absorption (TA) spectra indicated that the powerful donor ($\text{Ru}(\text{bpy})_3\text{Cl}_2$) and the giant built-in electric field dramatically extend the excited state lifetime of cobalt-porphyrins up to 3.4 times higher than the unmodified counterpart Co-Bpy-COF . The effect of external light irradiation lowering the [energy barrier](#) to the formation of CO was verified by Tafel slopes and density function theory (DFT) calculations.

This study focuses on extending the long, excited state lifetime of photo-coupled electrocatalysts for efficient CO_2RR to CO products and provides a guideline for the development of efficient photocoupled electrocatalysts.

More information: Qiu-Jin Wu et al, Photocoupled Electroreduction of CO_2 over Photosensitizer-Decorated Covalent Organic Frameworks, *Journal of the American Chemical Society* (2023). [DOI: 10.1021/jacs.3c06113](https://doi.org/10.1021/jacs.3c06113)

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