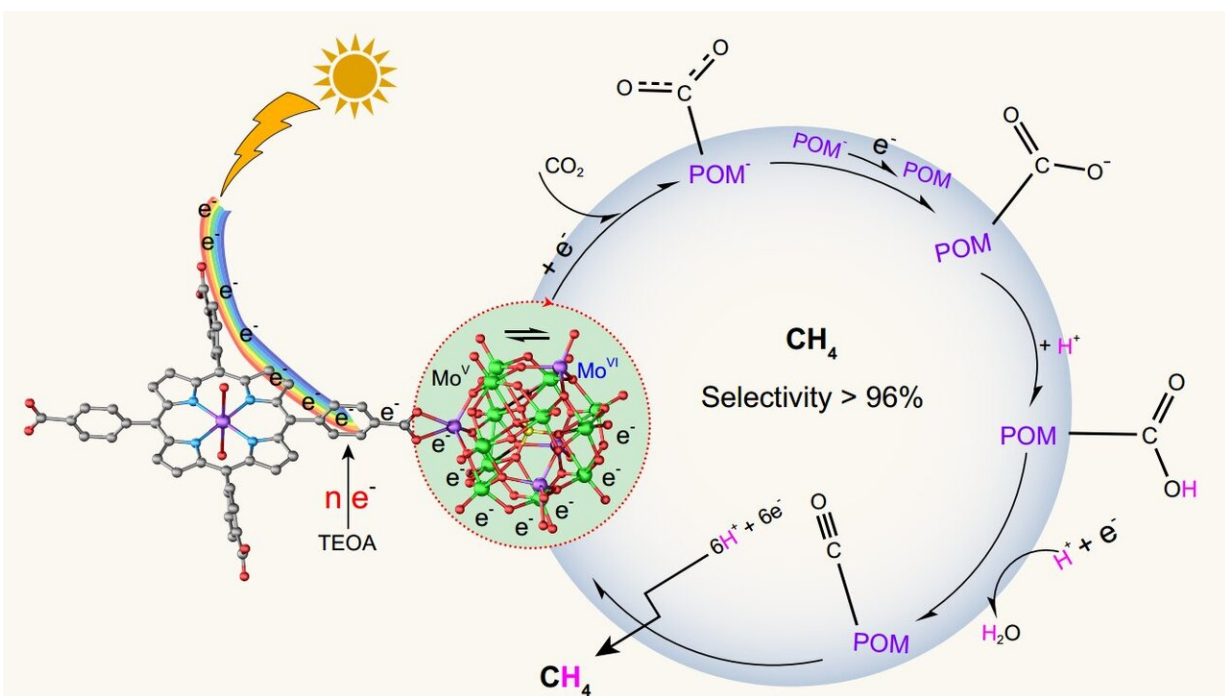


Polyoxometalate-based coordination frameworks for methane generation in photoreduction of carbon dioxide

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POMCF for converting CO₂ into CH₄ in photoreduction system Credit: ©Science China Press

Excessive CO₂ discharge derived from the continuous burning of fossil fuels has caused global warming and environmental issues. Artificial conversion of excess CO₂ into serviceable energy products is an

important pathway to achieve sustainable development. Solar-driven photocatalytic reduction of CO_2 to carbon-neutral fuels (CO , CH_4) and/or value-added chemicals (HCOOH , CH_3OH) affords a feasible strategy for the aforesaid conversion. The implementation of this reaction can mitigate the greenhouse effect and energy crisis simultaneously. However, the structural activation process of CO_2 molecule is particularly difficult because of its intrinsically chemical inertness and high $\text{C}=\text{O}$ bond cleavage enthalpy.

In order to circumvent the highly negative equilibrium potential (versus NHE) for thermodynamically unfavourable CO_2 —intermediate, proton-assisted multiple electron reductive products including chemicals and/or hydrocarbon are commonly obtained so as to lower the activation energy of photocatalytic CO_2 conversion. Even so, the formation of high-order proton and electron transferring products still needs to surmount considerable kinetic barriers, and competitive H_2 evolution further increases the difficulty for getting the product selectively. For instance, the photosynthesis of CH_4 , one of the most desirable and valuable hydrocarbon fuel in photoreaction system, has been a [grand challenge](#), since the accomplishment of eight-electron transport process requires the photocatalyst to offer both strong reducing capability and sufficient electrons theoretically.

Researchers conceived that polyoxometalate (POM)-based coordination frameworks (POMCFs), with well-known [structural stability](#) and favorable catalytic performance, are probably more beneficial to execute photocatalytic reduction of CO_2 due to the synergistic effect originated from the integration of POM and MCF. In particular, the Zn- ϵ -Keggin cluster of PMo12 "electron sponges" family, including eight MoV atoms, can behave as a strong reductive component and contribute eight electrons theoretically. In addition, the Zn- ϵ -Keggin, a tetrahedral node, is formed by four-trapped Zn(II) locating in ϵ -Keggin (PMo12). Compared with most anionic POMs, the ϵ -Keggin modified with metal

Zn becomes a cationic cluster, which is favorable for coordination with organic ligands. Consequently, if the reductive POM cluster and porphyrin derivative can be employed to fabricate POMCF, having both the visible-light harvesting and photo-excited electron migration, that would be a good strategy towards selectively photoreducing CO₂ to multielectron reductive products.

Therefore, we developed two POMCFs, NNU-13 and NNU-14, fabricated with reductive Zn- ϵ -Keggin cluster and visible-light responsive TCPP linker. These POMCFs exhibit high photocatalytic CH₄ selectivity (> 96%) and activity that have far surpassed many MCF-based photocatalysts. Theoretical calculations revealed that the photo-generated carriers of VB and CB are mostly distributed on TCPP group and Zn- ϵ -Keggin cluster, respectively. The photo-excited electrons more easily flow to POM port by efficient intercoupling between reductive Zn- ϵ -Keggin unit and TCPP linker. Noted that the introduction of POM building blocks with potent reducing ability not only endows NNU-13 and NNU-14 with favorable structural rigidity, but also it indeed facilitates the photocatalytic selectivity of CH₄ by theoretically delivering adequate electrons to accomplish the eight-electron reduction of the CO₂ molecule. We expect such a feasible approach, assembling strong reducing component into visible-light sensitized photocatalyst architecture, can ignite research enthusiasm towards the construction of efficient POMCFs photocatalysts for highly selective reduction of CO₂ to CH₄ or other high-valued hydrocarbons.

More information: Qing Huang et al, Multielectron transportation of polyoxometalate-grafted metalloporphyrin coordination frameworks for selective CO₂-to-CH₄ photoconversion, *National Science Review* (2019). [DOI: 10.1093/nsr/nwz096](https://doi.org/10.1093/nsr/nwz096)

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