



News & Views

Polyhedral metal cage for photocatalytic CO₂ reduction

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Solar-driven conversion of carbon dioxide (CO₂) into useful fuels or chemical feedstocks is one of promising approaches to alleviate the ever-increasing CO₂ emission and environmental concerns. Compared to the reduction of water into H₂, the efficient reduction of CO₂ with high selectivity is more complicated, because CO₂ reduction involves multiple electron transfer process and can simultaneously produce multiple products, such as CO, formic acid, methane, methanol, oxalate, etc. (Fig. 1) [1]. Current research mainly focuses on two categories of materials for photocatalytic CO₂ reduction: homogeneous metal complexes and heterogeneous solid catalysts. Molecular catalysts such as Fe, Co, Ni, and Mn complexes exhibit high activity and/or selectivity. Furthermore, well-defined and tunable structure is helpful for revealing the photocatalytic reaction mechanism, but their poor stability severely impedes their practical industrial applications. In contrast, heterogeneous catalysts feature good stability, but their indistinct active sites limit mechanism understanding. Consequently, the construction of molecular heterogeneous photocatalysts, which merges the merits of both homogeneous and heterogeneous catalysts, would be a better choice. Now, writing in *Angewandte Chemie International Edition*, Zhou and colleagues [2] report a copper-based nanocage which converts CO₂ into CO driven by solar energy with high efficiency and selectivity. With outstanding structural designability, metal nanocage with open metal sites is emerging as promising catalysts.

In nature, CO dehydrogenase (CODH) enzymes catalyze the reduction CO₂ to CO which occurs in protein cages [3]. Owing to their unique properties such as self-assemble of large numbers of subunit, container-like shape, well-defined external and internal surface as well as highly exposed monodispersed active site, artificial protein cages have recently gained tremendous attention for application in materials synthesis, drug encapsulation and delivery, catalysis as well as energy conversion and storage. These cages act as a diversity of nanoreactor for not only CO₂ reduction, but also water oxidation, hydrogen production, and oxygen reduction [3]. Slight modulation of the building blocks can tailor the structures and properties of the coordination cages to create designed functionality [3]. Zhou and colleagues demonstrate that copper boron imidazolate nanocage copper can act as a robust photocatalyst for photocatalytic conversion of CO₂ to CO (Fig. 2) with high selectivity of 82.6%.

Metal nanocage with open metal sites provides abundant accessible surface-active sites, which contribute to trapping photoexcited electrons and promoting the transfer of photoinduced

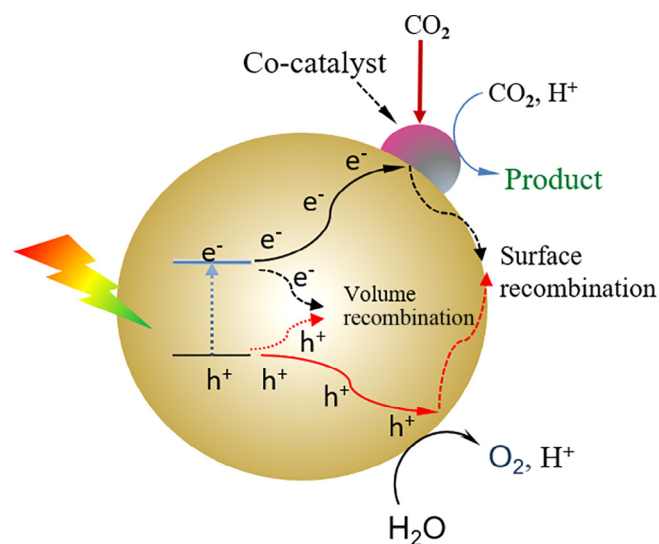


Fig. 1. (Color online) Illustration of photocatalytic CO₂ reduction [1].

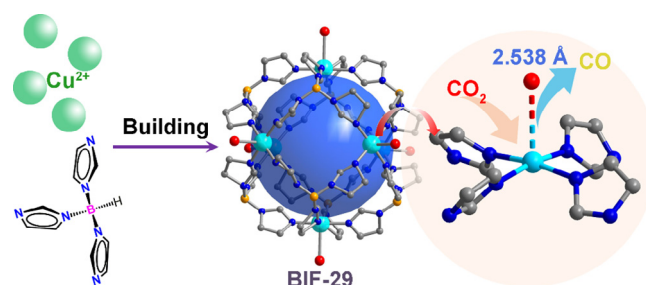


Fig. 2. (Color online) Scheme of BIF-29 (Right) synthesis and the process of unsaturated coordinated Cu site (Left) adsorb and active CO₂ molecules. Reproduced with permission from Ref. [3], Copyright 2019 Wiley.

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electrons to CO₂. As a result, compared with iodine-coordinated Cu sites in nanocage, the unsaturated coordinated Cu sites effectively promote the CO₂ activation and *CO desorption, and improving CO₂ reduction efficiency. Besides reduction efficiency, the unsaturated coordinated Cu sites also enhance the product selectivity for CO₂ reduction. In general, the selectivity is mainly affected by the coordination geometry, the structure and kind of metal centers. Taking the intensively studied Cu-based catalysts as an example, the multiple neighboring sites limit the product selectivity for CO₂ reductions. The atomic arrangement at the catalyst surface affects the CO₂ adsorption and the bond formation of the product, thus determining the selectivity of reduction reaction. An effective method to enhance product selectivity is to adjust the number of Cu atoms surrounded with each other. Interestingly, the polyhedral cage with isolated Cu active site could act as a model compound to study solar-driven conversion of CO₂ to fuels.

In summary, as a molecular heterogeneous catalyst, isolated metal active site on the cage is one of the most attractive candidates for the sustainable production of chemicals and fuels owing to the atomically dispersed catalytic sites and versatile coordination geometry. The unique structure provides a platform to tailor the reaction pathway and understand the mechanism. Nevertheless, the utilization of noble metal-based photosensitizer and organic sacrificial reagent limit their potential application. It is also important to construct bifunctional cage which serves as not only a photosensitizer but also a co-catalyst. Overall, the current work provides new insights to the development of single atom photocatalysts for CO₂ reduction, but the practical applications will require considerable further advances in catalyst design and reaction optimization.

Conflict of interest

The authors declare that they have no conflict of interest.

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