Science Bulletin 64 (2019) 1729–1730

Contents lists available at ScienceDirect

Science Bulletin

journal homepage: www.elsevier.com/locate/scib

Science Bulletin
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News & Views

Polyhedral metal cage for photocatalytic CO_2 reduction

Weijuan Wang, Tianhua Zhou *

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China

Solar-driven conversion of carbon dioxide (CO_2) into useful fuels or chemical feedstocks is one of promising approaches to alleviate the ever-increasing CO_2 emission and environmental concerns. Compared to the reduction of water into H_2, the efficient reduction of CO_2 with high selectivity is more complicated, because CO_2 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 CO_2 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 CO_2 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 (COHD) enzymes catalyze the reduction CO_2 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 CO_2 reduction, but also water oxidation, hydrogen production, and oxygen reduction [3]. Slight modulation of the building blocks can tailor the structures ad 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 CO_2 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

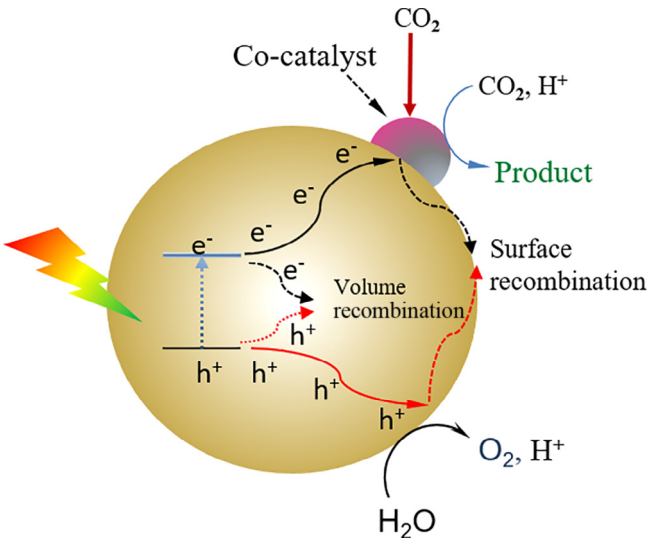

Fig. 1. (Color online) Illustration of photocatalytic CO_2 reduction [1].

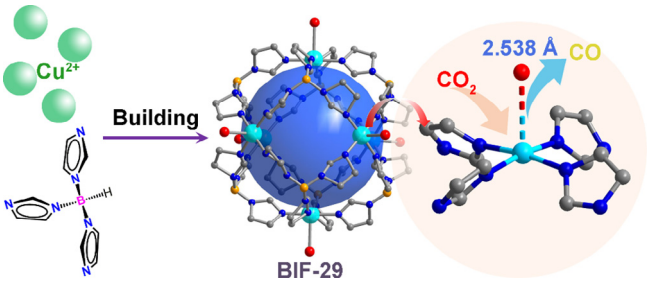

Fig. 2. (Color online) Scheme of BIF-29 (Right) synthesis and the process of unsaturated coordinated Cu site (Left) adsorb and active CO_2 molecules. Reproduced with permission form Ref. [3], Copyright 2019 Wiley.

* Corresponding author.
E-mail address: thzhou@fjirsm.ac.cn (T. Zhou).

https://doi.org/10.1016/j.scib.2019.10.008

electrons to CO_2. As a result, compared with iodine-coordinated Cu sites in nanocage, the unsaturated coordinated Cu sites effectively promote the CO_2 activation and *CO desorption, and improving CO_2 reduction efficiency. Besides reduction efficiency, the unsaturated coordinated Cu sites also enhance the product selectivity for CO_2 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 CO_2 reductions. The atomic arrangement at the catalyst surface affects the CO_2 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 CO_2 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 CO_2 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.

References

[1] Li X, Wen J, Low J, et al. Design and fabrication of semiconductor photocatalyst for photocatalytic reduction of CO_2 to solar fuel. Sci China Mater 2014;57:70–100.
[2] Zhang HX, Hong QL, Li J, et al. Isolated square planar copper in boron imidazolate nanocages for photocatalytic reduction of CO_2 to CO. Angew Chem Int Ed 2019;131:11878–82.
[3] Appel AM, Bercaw JE, Bocarsly AB, et al. Frontiers, opportunities, and challenges in biochemical and chemical catalysis of CO_2 fixation. Chem Rev 2013;113:6621–58.

Weijuan Wang received her bachelor's degree from Nanjing Normal University in 2014. Now she is a master candidate co-cultivated by Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences and Fuzhou University under the supervision of Prof. Tianhua Zhou. Her research interests focus on the design and synthesis of MOF-based catalysts for photocatalytic and electrocatalytic CO_2 reduction.

Tianhua Zhou obtained his Ph.D. degree at Fuzhou University under the supervision of Prof. Jianxi Zhao in 2008. Then he joined the faculty of Fujian Institute of Research on the Structure of Matter Chinese (FJIRSM), Chinese Academy of Sciences (CAS) (2008–2012). In 2012, Dr. Zhou moved to Singapore as a Research Fellow working with Prof. Rong Xu at the School of Chemical and Biomedical Engineering of the Nanyang Technological University (NTU). During April–October 2016, he worked as a Visiting Scholar in Emory University with Prof. Tianquan Lian to study ultrafast laser spectroscopy. In February 2017, he moved back to FJIRSM-CAS as a Full Research Professor. His current research interests focus mainly on functional metal-organic frameworks for photocatalytic and electrocatalytic applications.