

## Advances in artificial design of light-driven carbon dioxide reductase

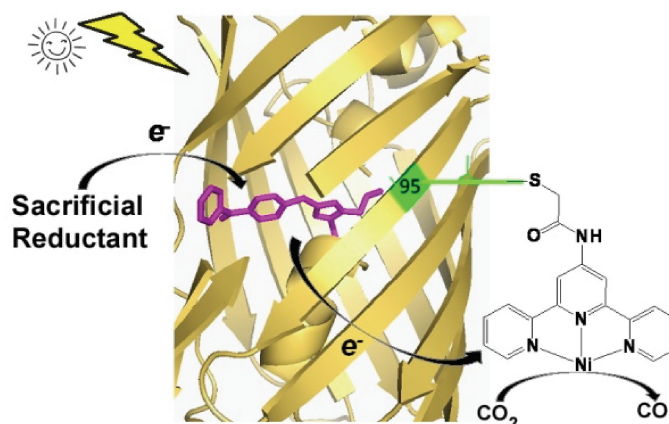
With the support by the National Key R&D Program of China, the National Natural Science Foundation of China, and the Chinese Academy of Sciences, the research team led by Prof. Wang JiangYun (王江云) at the Institute of Biophysics, CAS, rationally designed a genetically encoded photosensitizer protein (PSP) that facilitates photocatalytic CO<sub>2</sub> reduction, which was published in *Nature Chemistry* (2018, DOI:10.1038/s41557-018-0150-4).

In recent years, searching methods to convert solar energy into chemical energy and to control the increasing atmosphere CO<sub>2</sub> concentration has become a key issue in the field of chemistry and biology. The natural photosynthesis system (PS) has attracted lots of attention, because of its advantages including environmental friendliness, sustainability, self-assemble ability and highly efficient photo-induced charge separation efficiency. However, it is difficult to genetically engineer the photosynthetic machinery consisting of a large number of membrane proteins and cofactors, which remains a significant technological challenge. Moreover, compared with small molecule CO<sub>2</sub> reduction catalysts, the natural PS has a relatively low CO<sub>2</sub> reduction activity. After years of efforts on metalloenzymes designing, Wang's team developed an artificial light-driven carbon dioxide reductase, which combines the advantages of the natural photosystem and small molecule catalysts.

Previous studies have proved that fluorescent proteins (FPs) could be transformed into photocatalysts. Meanwhile, the chromophore could be rationally designed by replacing its natural tyrosine residue with a genetic encoded UAA. Thus, the photochemistry features of the chromophore, including absorption spectrum, life time and radical reductive potential, could be rationally attuned with high accuracy (*ANIE*, 2012, 51: 10261; 2013, 52: 4805; *JACS*, 2014, 136: 13094; 2015, 137: 7270–3).

Based on the previous work, with the genetic encode technology, a PSP by incorporating Bpa that contains a benzophenone moiety into chromophore of FP was developed. The PSP protein can be photo-converted to a long-lived photo-excited state. If a reductant is present, the PSP protein in the excited state then facilitates an electron transfer reaction, resulting in the formation of a PSP radical. Electrochemistry analysis suggested the redox potential of radical state is close to  $-1.46$  V (vs NHE), which is much lower than CO<sub>2</sub> reduction potential and many biological relevant reductants. More excitingly, the X-ray chromatography results show that the radical's conformation forms in an extended conjugated  $\pi$ -electron system, corresponding to a significantly red-shifted UV-Vis spectrum. To the best of their knowledge, this is the first report of a protonated, neutral benzophenone radical structure.

When ligated with a CO<sub>2</sub> reduction catalyst nickel-terpyridine (PSP2T), the PSP2T can photocatalyze CO<sub>2</sub> to CO, with more than 100 TONs and a 2.6% quantum yield. Compared with small photoredox molecules, the photoredox protein has the following additional merits: 1. heavy-metal free; 2. capable of being easily introduced into various organisms; 3. having dramatically expanded abilities through rational design or directed evolution.



**Figure** Schematic diagram of proposed catalytic mechanism of PSP2T.