

Mechanistic study of photocatalytic CO₂ reduction by a Ru(II)-Re(I) supramolecular photocatalyst

(¹*School of Science, Tokyo Institute of Technology*, ²*Graduate School of Science, Nagoya University*, ³*Graduate School of Science, Kyushu University*, ⁴*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○ Kei Kamogawa¹, Yuki Kato², Yuushi Shimoda³, Kiyoshi Miyata³, Ken Onda³, Takumi Noguchi², Yusuke Tamaki¹, Osamu Ishitani^{1,4}

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Photocatalytic CO₂ reduction using visible light as an energy source potentially gives a solution to the energy shortage and global warming problems. Although many researchers have intensively been working on developing CO₂ reduction photocatalysts, one of the significant problems in this field is the insufficiency of mechanistic insights into photocatalysis.

A Ru(II)-Re(I) supramolecular photocatalyst (**RuC2Re**, Fig. 1) consisting of [Ru(diimine)₃]²⁺ redox photosensitizer and *fac*-[Re(diimine)(CO)₃(OC(O)OC₂H₄NR₂)] catalyst can efficiently capture CO₂ and reduce CO₂ to CO with high durability and selectivity.¹ Recently, our group has reported the formation processes of one-electron reduced species (OERS) of the Re unit of **RuC2Re** (**RuC2(Re)⁻**), which is a crucial intermediate in the initial stage of photocatalytic CO₂ reduction, in detail.² However, the mechanism of the subsequent processes after the formation of **RuC2(Re)⁻** was still unclear.

In this work, we investigated the unknown mechanism of the subsequent processes of **RuC2(Re)⁻**, utilizing various methods such as FT-IR spectroscopy and liquid chromatography analysis of photocatalytic reaction solution. The carboxylate complex **RuC2Re(COOH)** with a *fac*-Re(diimine)(CO)₃(COOH) unit was successfully detected as a subsequent intermediate of **RuC2(Re)⁻** by using time-resolved infrared spectroscopy combining laser flash photolysis and rapid-scan FT-IR method. This important intermediate was also detected by FT-IR measurements of photocatalytic reaction solution during steady-state light irradiation. Furthermore, it has been clarified that **RuC2Re(COOH)** eventually releases CO and OH⁻ and turns into the starting complex **RuC2Re**. In the presentation, the mechanism of these reactions, including the source of the second electron and the kinetics of each process, will be discussed in detail.

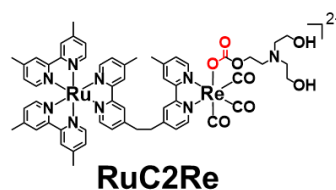


Fig. 1 Structure of **RuC2Re**

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