

# Visible-Light CO<sub>2</sub> Reduction Using Carbon Nitride and Metal Complex Hybrid Photocatalysts

Ryo Kuriki, Osamu Ishitani, Kazuhiko Maeda  
Department of Chemistry, School of Science,  
Tokyo Institute of Technology, Tokyo, Japan  
\*E-mail: maedak@chem.titech.ac.jp

Converting CO<sub>2</sub> into energy-rich chemicals using water and sunlight as an electron donor and energy source, respectively, is of great interest as a means of addressing the depletion of fossil fuels and concomitant CO<sub>2</sub> emission. Our group has recently developed a visible-light-driven photocatalyst for CO<sub>2</sub> reduction, which consisted of an organic semiconductor, graphitic carbon nitride (abbreviation for g-C<sub>3</sub>N<sub>4</sub>) and a Ru(II) mononuclear complex [1]. In this system, g-C<sub>3</sub>N<sub>4</sub> serves as a light absorber and works as oxidation sites, while the combined Ru(II) complex acts as an active site for CO<sub>2</sub> reduction. This system is expected to be promising because of the excellent electrochemical (and/or photocatalytic) ability of metal complexes for CO<sub>2</sub> reduction and the high efficiency of semiconductors for water oxidation. In order to conduct photocatalytic CO<sub>2</sub> reduction using this hybrid system, electron transfer from g-C<sub>3</sub>N<sub>4</sub> to the loaded Ru complex is necessary. Since the efficiency of the interfacial electron transfer is influenced by the energy level of the Ru complex, we examined the structure of Ru complexes in detail. As a result, we revealed that larger potential difference between electron donor (i.e., conduction band minimum of g-C<sub>3</sub>N<sub>4</sub>) and acceptor (i.e., LUMO potential of Ru complex) is important to achieve high photocatalytic ability [2]. However, it is difficult to achieve larger potential difference using this system due to the lack of suitable structures of a Ru(II) mononuclear complex.

In this work, as another system, photocatalytic CO<sub>2</sub> reduction using g-C<sub>3</sub>N<sub>4</sub> and a Ru(II) binuclear complex hybrid is presented (Fig.1). This system is expected to photocatalyze CO<sub>2</sub> reduction through a Z-schematic electron-transfer mechanism with a two-step photoexcitation of the semiconductor and binuclear Ru(II) complex. We could get larger potential difference between electron

donor (i.e., g-C<sub>3</sub>N<sub>4</sub>) and acceptor (i.e., Ru complex) using this hybrid system, which may induce high photocatalytic ability.

Photocatalytic CO<sub>2</sub> reduction was conducted using this system. As a result, HCOOH was detected catalytically under visible light in the presence of a suitable electron donor. Control experiments indicated that no HCOOH occurred in the absence of either light, CO<sub>2</sub> or a Ru(II) binuclear complex. In addition, no HCOOH occurred using Al<sub>2</sub>O<sub>3</sub>, which is an insulator, and a Ru(II) binuclear complex hybrid. These results led to the conclusion that g-C<sub>3</sub>N<sub>4</sub> and a Ru(II) binuclear complex hybrid functioned as a CO<sub>2</sub> reduction photocatalyst.

In addition, we also found that the ability was improved dramatically, when g-C<sub>3</sub>N<sub>4</sub> was modified with Ag nanoparticles. Importantly, the amount of formed HCOOH using this Z-schematic system was higher than that achieved using Ag-loaded g-C<sub>3</sub>N<sub>4</sub> and an optimized Ru(II) mononuclear complex hybrid. These results indicated the importance of Z-schematic system to achieve high photocatalytic performance. CO<sub>2</sub> reduction with high selectivity (>95%) was achieved both in organic solvent and aqueous solution. In addition, a TON<sub>HCOOH</sub> (with respect to the amount of Ru complex) of greater than 33,000 and 2,000 were obtained in organic solvent and aqueous solution, respectively. These are the highest among visible-light-driven heterogeneous CO<sub>2</sub> reduction photocatalysts ever reported [3].

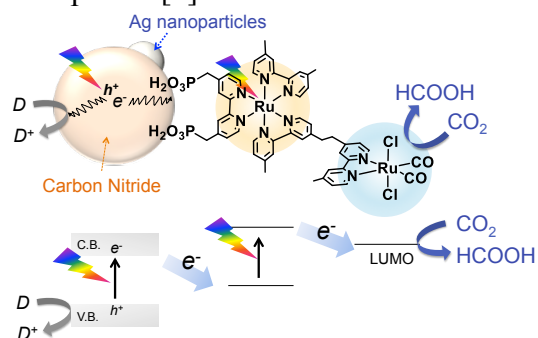


Fig.1 Carbon nitride and a Ru(II) binuclear complex hybrid photocatalyst.

- [1] K. Maeda, K. Sekizawa and O. Ishitani, Chem. Commun., 49 (2013) 10127.
- [2] R. Kuriki, K. Sekizawa, O. Ishitani and K. Maeda, Angew. Chem., Int. Ed., 54 (2015) 2406.
- [3] R. Kuriki, H. Matsunaga, T. Nakashima, K. Wada, A. Yamakata, O. Ishitani and K. Maeda, J. Am. Chem. Soc., 138 (2016) 5159.