

# Hybrid Photocatalyst Constructed with an Yttrium-Tantalum Oxynitride and a Binuclear Ru(II) Complex for Visible Light CO<sub>2</sub> Reduction

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Recently, CO<sub>2</sub> conversion into useful compounds such as transportable formic acid is an important subject, because the rise of concentration of carbon dioxide and the lack of energy resources are serious problems. Among many reactions or schemes that have been suggested so far, heterogeneous photocatalysis could be one of the most promising candidates to solve these problems. We have developed such heterogeneous photocatalysts consisting of a semiconductor (e.g. TaON, CaTaO<sub>2</sub>N, and C<sub>3</sub>N<sub>4</sub>) and a Ru(II) complex (Fig. 1).<sup>[1-3]</sup>

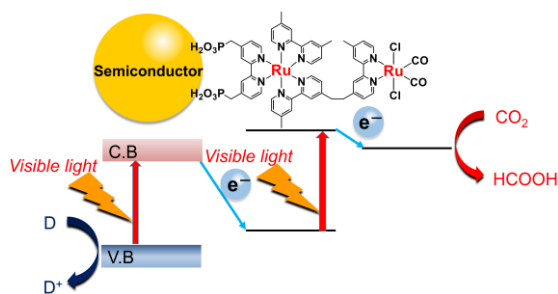


Fig. 1. Visible-light CO<sub>2</sub> reduction by a hybrid of a semiconductor and a binuclear Ru(II) complex (**RuRu'**).

However these reported semiconductors can harvest visible light only at a wavelength shorter than 500 nm. From the viewpoint of solar energy conversion, a semiconductor that can harvest >500 nm photons is highly desirable. Here we report a hybrid photocatalyst consisting of an yttrium-tantalum oxynitride (YTON) having a band gap of 2.1 eV and **RuRu'**.<sup>[4]</sup>

In photocatalytic CO<sub>2</sub> reduction, combining YTON with **RuRu'** resulted in HCOOH production with very high selectivity (>99%) and a catalytic turnover number (TON) of 4 based on the amount of loaded **RuRu'**. We also conducted control experiments using model complexes of **RuRu'** and various modification. From these experiments, it was concluded that both the YTON and the **RuRu'** are essential to realizing HCOOH production. The TON over the **RuRu'**/Ag/YTON was improved with increases in the amount of Ag loaded, up to 1.5 wt%.

To understand the effect of Ag loading, we observed reductive electron transfer by investigating the lifetime of the excited state of photosensitizer unit of **RuRu'** (noted as **Ru(PS)**) immobilized on the Ag/YTON surface. Fig. 2 shows that increasing the loading amount of Ag accelerated the emission decay of the excited state of **Ru(PS)**. It is noted that oxidative quenching of the excited state of the **Ru(PS)** did not occur, because **Ru(PS)** ( $E_{ox}^* = -1.30$  V) to the conduction band of the YTON (-1.40 V) is energetically unfavorable. Therefore, the more pronounced emission quenching is attributed to the acceleration of the reductive quenching of the excited state of the **Ru(PS)** by YTON as well as facilitation of the interfacial electron transfer between the YTON and **Ru(PS)** by the added Ag.

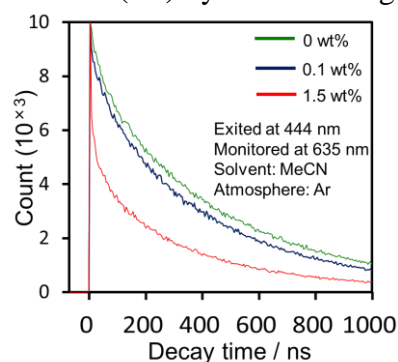


Fig. 2. Emission decay profiles of **Ru(PS)**/Ag/YTON with different Ag loadings.

## REFERENCES

- [1] Sekizawa, K. et al., *J. Am. Chem. Soc.* 135 (2013) 4596.
- [2] Yoshitomi, F. et al., *ACS Appl. Mater. Interfaces* 7 (2015) 13092.
- [3] Kuriki, R. et al., *J. Am. Chem. Soc.* 138 (2016) 5159.
- [4] Muraoka, K. et al., *Chem. Commun.* 52 (2016) 7886.