Photocatalytic CO_2 reduction under visible light using carbon nitride and a binuclear Ru(II) complex

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Abstract: Ag nanoparticles loaded metal-free organic semiconductor, graphitic carbon nitride, coupled with a Ru(II) binuclear complex containing photosensitizer and catalytic units reduced CO_2 into formate under visible light in the presence of a suitable electron donor with high durability and selectivity, both in organic solvent and even in aqueous solution. In this system, photocatalytic CO_2 reduction was mainly progressed via step-by-step photoexcitation and through Z-schematic electron transfer mechanism, which is similar to nature photosynthesis in green plants. Under optimized conditions, turnover numbers (TON) with respect to loaded Ru complexes reached 33000 and 2000 in organic solvent and in aqueous solution, respectively. These values are highest among the hybrid systems to date.

Keywords: Artificial photosynthesis, Hybrid system of semiconductors and metal complexes, Carbon nitride

1. Introduction

Converting CO_2 into energy-rich chemicals using sunlight as an energy source is of great interest as a means of addressing the depletion of fossil fuels and concomitant CO_2 emission. As promising systems, hybrid systems using semiconductors and metal complexes have been researched because of the excellent electrochemical ability of metal complexes for CO_2 reduction and the high efficiency of semiconductors for various oxidation reactions, respectively.[1]

Our group has recently developed a visible-light-driven photocatalyst for CO_2 reduction, which consisted of an organic semiconductor, graphitic carbon nitride (abbreviated as C_3N_4), and a Ru(II) mononuclear complex and revealed that this system is quite suitable for CO_2 reduction.[2] Unfortunately, however, this system could work only in organic solvents such as *N*,*N*-dimethylacetamide (DMA) and acetonitrile. For practical application, photocatalytic reaction should be performed in aqueous solution, because water is the most abundant solvent on the earth. In order to achieve photocatalytic CO_2 reduction in aqueous solution, here we show another hybrid system, Z-schematic system, using C_3N_4 and a Ru(II) binuclear complex, as shown in Figure 1. Interestingly, durable and selective CO_2 reduction was progressed under visible light by introducing Ag nanoparticles on the surface of C_3N_4.[3,4]

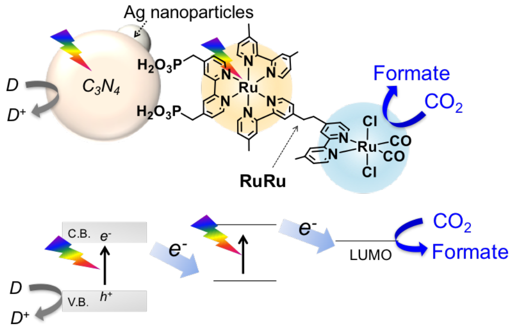

Figure 1. Attempted Z-schematic system using C_3N_4 and a Ru(II) binuclear complex (abbreviated as **RuRu**)

2. Experimental

A binuclear Ru(II) complex (abbreviated as **RuRu**, see Figure 1), C_3N_4 and their hybrids were synthesized according to our previous reports.[3] Photocatalytic CO_2 reduction reactions were performed at room temperature using an 8 mL test tube that contained 4.0 mL of solution and 4.0 mg of photocatalyst powder. Prior to irradiation, the suspension was purged with pure CO_2 for 20–30 min. A high-pressure Hg lamp was employed as a light source equipped with an aqueous $NaNO_2$ solution to allow for visible light irradiation ($\lambda > 400$ nm). The gaseous reaction products and formate generated were analyzed using a gas chromatograph and a capitally electrophoresis system, respectively.

3. Results and discussion

As a result of photocatalytic CO_2 reduction using a hybrid of **RuRu** and C_3N_4, formate was detected catalytically under visible light in the presence of triethanolamine (TEOA) as an electron donor (see Table 1, Entry 1). Control experiments indicated that no formate was produced in the absence of either light, CO_2, **RuRu** or C_3N_4, indicating that C_3N_4 and a **RuRu** hybrid progresses CO_2 reduction reaction under visible light (Entries 2–5). In addition, the activity was dramatically improved, when C_3N_4 was modified with Ag nanoparticles (Entry 6). Importantly, the amount of formed formate in this condition was higher than that achieved using C_3N_4 and an optimized Ru(II) mononuclear complex (abbreviated as **RuP**, see Table 1) hybrid even with the use of Ag nanoparticles (Entries 6 and 7). These results showed the importance of two-step photoexcitation system and Ag nanoparticles to achieve high CO_2 reduction activities.

In order to investigate the detail roles of Ag nanoparticles in this system, time resolved IR measurements, that can access the photogenerated charge careers in semiconductor materials, were conducted. The decay of the signals assigned to shallowly trapped and/or free electrons in C_3N_4, generated after photoexcitation, was more pronounced upon introduction of Ag nanoparticles on the surface of C_3N_4. This result strongly suggested that electron transfer from C_3N_4 to Ag nanoparticles occurred. Thus, we concluded that Ag nanoparticles work as an electron sink in C_3N_4, inducing the high photocatalytic performance. TON for formate generation (with respect to the amount of Ru complex) of greater than 33000 and 2000 were obtained in organic solvent and in aqueous solution with high selectivity (> 90%), respectively, under optimized conditions. These values are the highest among visible-light-driven heterogeneous CO_2 reduction photocatalysts to date.[3,4]

Table 1. Results of photocatalytic CO_2 reduction [a]

Entry	Photocatalyst	Formate / μmol	TON (Formate)	Selectivity (Formate) / %
1	**RuRu**/C_3N_4	0.6	43	52
2 [b]	**RuRu**/C_3N_4	N.D.	-	-
3 [c]	**RuRu**/C_3N_4	<0.1	-	-
4	C_3N_4	N.D.	-	-
5	**RuRu**/Al_2O_3	N.D.	-	-
6 [d]	**RuRu**/Ag/C_3N_4	42.3	3110	99
7 [d, e]	**RuP**/Ag/C_3N_4	19.2	1428	98

[a] Condition: Photocatalyst, 4.0 mg; Solution, DMA-TEOA mixed solution (4 : 1 v/v) 4.0 mL; *hν* 5 h, > 400 nm; Amounts of loaded Ru(II) complexes, 3.4 μmol g^{-1}. [b] In the dark. [c] Under Ar. [d] Ag, 5 wt %. [e] **RuP** = $[Ru\{bpy(PO_3H_2)_2\}(CO)_2Cl_2]$.

4. Conclusions

An artificial Z-scheme system was constructed using a metal-free semiconductor (C_3N_4) and a Ru(II) binuclear complex hybrid that exhibited high selectivity toward formate production via CO_2 reduction reaction under visible light. This hybrid produced a TON of ~33000 under optimized conditions with high selectivity (~90%), indicating that it was 30 times greater than analogues modified with a mononuclear Ru(II) complex.[2,3] This hybrid could progress even in aqueous solution with high CO_2 reduction selectivity (> 95%) and TON (~ 2100). TON achieved in this system (~33000 in organic solvent and ~2100 in aqueous solution, respectively) are highest among the hybrid systems to date.

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