



Visible-Light-Driven CO₂ Reduction with Carbon Nitride: Enhancing the Activity of Ruthenium Catalysts**

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Abstract: A heterogeneous photocatalyst system that consists of a ruthenium complex and carbon nitride (C₃N₄), which act as the catalytic and light-harvesting units, respectively, was developed for the reduction of CO₂ into formic acid. Promoting the injection of electrons from C₃N₄ into the ruthenium unit as well as strengthening the electronic interactions between the two units enhanced its activity. The use of a suitable solvent further improved the performance, resulting in a turnover number of greater than 1000 and an apparent quantum yield of 5.7% at 400 nm. These are the best values that have been reported for heterogeneous photocatalysts for CO₂ reduction under visible-light irradiation to date.

The production of transportable fuels through artificial photosynthesis on a large scale is of interest owing to the increasing demand for renewable energy as an alternative to fossil fuels and nuclear energy.^[1] The photocatalytic reduction of CO₂ into energy-rich chemicals has the potential to produce renewable energy while also reducing the amount of the greenhouse gas CO₂.^[2–16] One of the two-electron reduction products of CO₂, formic acid, is a useful liquid fuel that can be readily decomposed into H₂ and CO₂ in the presence of a suitable catalyst.^[17] Finally, the combustion of H₂ produces a high energy density ($\Delta G^\circ = 238 \text{ kJ mol}^{-1}$), giving water as the sole product. The reduction/re-oxidation thus completes a carbon-neutral cycle without the release of harmful byproducts.

The seminal work by Lehn et al. in 1983^[2] was followed by the preparation of several types of homogeneous (photo)-catalysts that are based on metal complexes that contain Re or Ru, which enabled the selective formation of CO or

HCOOH.^[3–6] In particular, supramolecular complexes with a light-harvesting and a catalytic unit with two or more metal centers possessed improved properties.^[6] The number of reports on CO₂ reduction using a heterogeneous photocatalyst under visible-light irradiation has been increasing.^[11–16] However, none of these have yielded a satisfactory result; state-of-the-art catalysts enable reactions with turnover numbers (TONs) of approximately 200 and apparent quantum yields (AQYs) of approximately 2%.^[11,13a] The present study describes the synthesis of a high-performance heterogeneous photocatalyst for the reduction of CO₂ into formic acid under visible-light irradiation using carbon nitride (C₃N₄) and a Ru complex. By careful design of the catalytically active site and the reaction environment to maximize the efficiency of the CO₂ reduction process, a substantial improvement in photocatalytic performance was achieved, leading to the highest TON (> 1000) and AQY (5.7% at 400 nm) reported for such catalysts to date.

Carbon nitride (C₃N₄) is a widely studied functional material for various applications, including heterogeneous (photo)catalysis.^[18] C₃N₄ has been used for photocatalytic reactions, including water reduction/oxidation,^[19] the decomposition of harmful pollutants,^[20] organic transformation,^[21] and the production of hydrogen peroxide,^[22] and it has also been explored as a photocatalyst for the reduction of CO₂ into formic acid under visible-light irradiation when modified with a molecular Ru^{II} complex (RuCP in Scheme 1).^[13] Although C₃N₄ consists entirely of carbon and nitrogen atoms, the formic acid produced originates not from C₃N₄ decomposition, but from photocatalytic CO₂ reduction, as confirmed by isotope tracer experiments with ¹³CO₂. In contrast to conventional heterogeneous catalysts for CO₂ conversion, which require high temperatures and pressures,^[23] this photocatalytic system works at room temperature and under ambient pressure. This was the first example of reproducible CO₂ reduction using carbon nitride as a visible-light-responsive photocatalyst. Follow-up studies on this hybrid material elucidated the effect of the pore-wall structure of carbon nitride on the photocatalytic CO₂ reduction.^[13b] However, no principles for improving the activity of this system were discovered that enable the optimization of the structure of the immobilized metal complex despite its vital role in CO₂ reduction. As a result, the current performance of this system is not satisfactory.

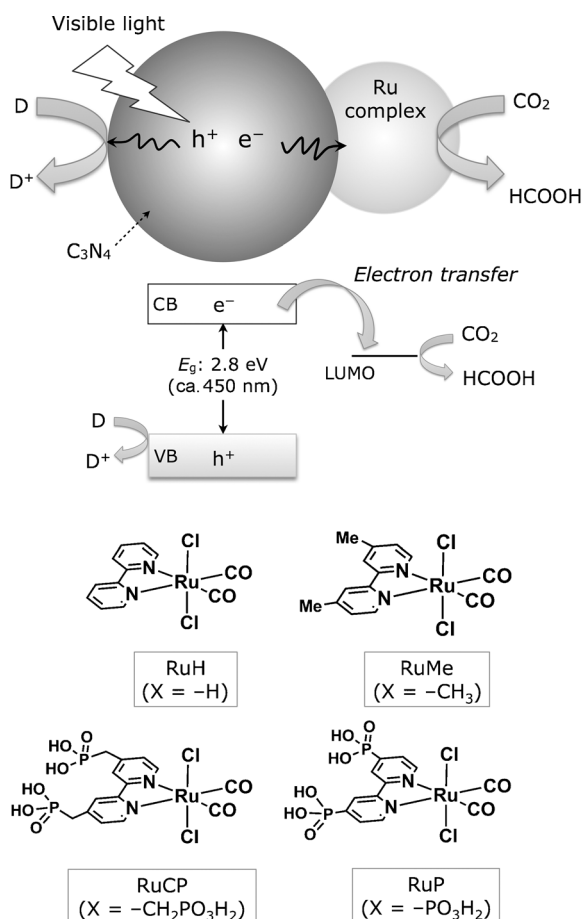
As illustrated in Scheme 1, the immobilized metal complex plays two important roles: It accepts electrons from the conduction band of C₃N₄ and hosts the active site for CO₂ reduction. This suggests that the photocatalytic activity for CO₂ reduction is strongly dependent on the structure of the metal complex employed. Metal complexes can be designed

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Scheme 1. CO_2 reduction using a Ru complex/ C_3N_4 hybrid photocatalyst, along with structures of the Ru complexes used. CB = conduction band, VB = valence band.

on a molecular scale, allowing for an adjustment of the catalytic functionality.^[4–6] Guidelines for the preparation of a highly efficient photocatalytic CO_2 reduction system using rhenium(I) complexes in a homogeneous environment have been established by Ishitani et al.^[5] Herein, four different Ru complexes, $trans(Cl)-[Ru(bpyX_2)(CO)_2Cl_2]$ ($bpyX_2 = 2,2'$ -bipyridine with substituents X in the 4-positions, $X = H, CH_3, PO_3H_2$, or $CH_2PO_3H_2$), were used as kinetic promoters for CO_2 reduction, along with a suitable reaction environment to increase the efficiency of the overall process. The structures of these complexes are shown in Scheme 1, along with their abbreviations.

Graphitic C_3N_4 with 12 nm mesopores (specific surface area: $180 \text{ m}^2 \text{ g}^{-1}$; pore volume: $0.7 \text{ cm}^3 \text{ g}^{-1}$) was used as the building block (represented by C_3N_4 for simplicity). A detailed method for the preparation of such C_3N_4 samples has been reported previously.^[13] Functionalization of C_3N_4 with a Ru complex was performed by dispersing the C_3N_4 powder in a methanol solution containing the appropriate amount of a Ru complex with continuous stirring at room temperature overnight. Results indicated that RuP and RuCP were adsorbed quantitatively up to approximately $40 \mu\text{mol g}^{-1}$. However, no adsorption was found to occur for RuH and RuMe, which do not have an anchoring group.

To assess the electronic interactions between C_3N_4 and immobilized Ru (RuP and RuCP), FT-IR spectra were recorded. As shown in the Supporting Information, Figure S1, two peaks that can be assigned to the vibration modes of two carbonyl groups, were observed in both cases. It should be noted that carbon nitride alone does not produce any IR bands in this region.^[13] The positions of these peaks did not change for the RuCP sample after loading onto C_3N_4 , indicating that electronic interactions between C_3N_4 and RuCP and any structural changes in the complex were negligible. This result is reasonable because the $-CH_2-$ spacers between the phosphoric acid groups and the bpy moiety prevent electronic conjugation. In contrast, the positions of the CO ligand peaks of RuP changed when the complex was grafted onto C_3N_4 , which suggests that there is an electronic interaction between the loaded RuP and C_3N_4 , presumably because of the lack of $-CH_2-$ spacers.

The catalytic activity of the Ru complexes in CO_2 reduction was investigated using an electrochemical technique. Cyclic voltammograms of the Ru complexes in a DMA (*N,N*-dimethylacetamide)/TEOA (triethanolamine) mixture containing Et_4NBF_4 (0.1 M) as a supporting electrolyte are shown in Figure S2. Onset potentials for the first irreversible wave, which was attributed to reduction of the diimine ($bpyX_2$) ligand, ranged from approximately -1.4 to -1.5 V. Under a CO_2 atmosphere, a clear catalytic current that was due to CO_2 reduction was generated at a more negative potential, indicating that all of the Ru complexes tested had the ability to reduce CO_2 . However, the onset potentials of the first reduction wave for RuP and RuH were observed at approximately -1.4 V, a potential that is 0.1 V more positive than those of RuCP and RuMe, meaning that RuP and RuH were more susceptible to reduction than RuCP and RuMe. This is reasonable considering that two $-CH_2-PO_3H_2$ (or $-CH_3$) groups lead to an increase in the energy of the π^* orbitals of these complexes because of their electron-donating nature.

Using the prepared hybrid photocatalysts, CO_2 reduction reactions were conducted under visible-light irradiation in MeCN/TEOA (4:1, v/v) saturated with atmospheric CO_2 ($\lambda > 400 \text{ nm}$). Similarly, reactions were performed using C_3N_4 in a MeCN/TEOA solution with dissolved RuH or RuMe. As shown in Figure S3, C_3N_4 has a steep absorption edge near 450 nm and a tail extending to 600 nm. In contrast, the Ru complexes show little absorption in the visible-light region. Therefore, under visible-light irradiation ($\lambda > 400 \text{ nm}$), the C_3N_4 component can be selectively activated.

Table 1 lists the activity of C_3N_4 in combination with four different Ru complexes for HCOOH generation under visible-light irradiation ($\lambda > 400 \text{ nm}$). All of the materials tested, except for RuMe+ C_3N_4 (entry 2), were active catalysts of this reaction, but their performance depended on the Ru complex used. The order of activity was: RuP > RuCP $\approx$ RuH $\gg$ RuMe. In all cases except for the RuMe-catalyzed reaction, HCOOH was produced in a catalytic cycle as the TONs were greater than one. During the reaction, not only HCOOH, but also small amounts of H_2 and CO were generated. The selectivity of HCOOH production was greater than 80 % in all cases.

Table 1: Results of the CO₂ reduction reaction ($\lambda > 400$ nm).^[a]

Entry	Photocatalyst	Solvent	Amount of HCOOH formed [μ mol]	TON ^[b]
1	RuH + C ₃ N ₄	MeCN	0.8	13
2	RuMe + C ₃ N ₄	MeCN	n.d.	–
3	RuCP/C ₃ N ₄	MeCN	1.2	20
4	RuP/C ₃ N ₄	MeCN	3.4	55
5	RuP/C ₃ N ₄	DMA	8.8	141
6	RuP/C ₃ N ₄	MeOH	1.2	20
7	RuP/C ₃ N ₄	H ₂ O	n.d.	–

[a] Reaction conditions: Ru complex (7.8 μ mol per gram of C₃N₄)/C₃N₄ (8.0 mg) in a mixture of the indicated solvent and TEOA (4:1, v/v; 4 mL). A Pyrex test tube with a septum (11 mL capacity) was used as the reaction vessel and a 400 W high-pressure Hg lamp with a NaNO₂ solution filter as the light source. Reaction time: 1 h. [b] With respect to the amount of Ru complex. Data for CO and H₂ production are shown in Table S1.

Thus, the activity of a Ru complex/C₃N₄ mixture in CO₂ reduction depended on the Ru complex (Table 1, entries 1–4). Among the Ru complexes tested, RuP was the strongest promoter of CO₂ reduction. Electrochemical analyses (Figure S2) indicated that the first reduction potentials of RuP and RuH were very similar (ca. –1.4 V vs. Ag/AgNO₃), but more positive than those of RuCP and RuMe (ca. –1.5 V). The conduction-band minimum of the C₃N₄ material used in this study was located at –1.65 V (vs. Ag/AgNO₃).^[13] Thus, the conduction-band electrons in C₃N₄ are able to move to the attached Ru complexes. The relatively poor performance of RuCP and RuMe can be explained in terms of the small potential difference between the two components of the hybrid material.

In addition to the larger potential difference between the conduction band of C₃N₄ and the reduction potential of RuP, the immobilization of a Ru complex onto the C₃N₄ surface should have a positive impact on electron transfer, as revealed by FT-IR spectroscopy (Figure S1). RuH, which does not possess any anchoring ligands, gave a relatively poor performance among the four Ru complexes tested, even though the first reduction potential of the complex lies at a relatively positive potential, and a relatively large CO₂ reduction current was observed at –1.65 V (Figure S2). RuMe, with a more negative reduction potential and no anchoring group, exhibited little activity for CO₂ reduction. Therefore, the reduction potential is crucial for efficient electron injection from C₃N₄ into the Ru complex, and the anchoring groups are essential for the direct coupling of the two units.

The results of the photocatalytic reactions with different Ru catalysts led to a rational strategy for the design of more efficient photocatalysts based on C₃N₄. This enabled a two- to three-fold improvement in the performance of the Ru complex/C₃N₄ system (Table 1 and Figure 1) compared to the system featuring RuCP as the catalytic unit.^[13a] The vital role of the Ru complex in promoting CO₂ reduction also suggests that the performance is influenced by the reaction environment because CO₂ reduction on a metal complex proceeds by a multi-step mechanism, including the substitution of ligands by solvent molecules.^[6b,24] To realize the full potential of the RuP/C₃N₄ photocatalyst, the effect of the

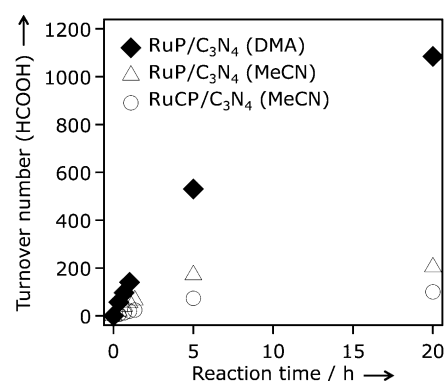


Figure 1. The turnover number of HCOOH production as a function of irradiation time using various photocatalysts. Reaction conditions: Ru complex (7.8 μ mol per gram of C₃N₄)/C₃N₄ (8.0 mg) in a mixture of the indicated solvent and TEOA (4:1, v/v; 4 mL). A Pyrex test tube with a septum (11 mL capacity) was used as the reaction vessel and a 400 W high-pressure Hg lamp with a NaNO₂ solution filter as the light source.

solvent on the photocatalytic performance was investigated because the influence of the solvent on such metal complex/semiconductor hybrid systems had not been examined before.

As expected, the photocatalytic performance of RuP/C₃N₄ in the production of formic acid depended strongly on the solvent employed. As shown in Table 1 (entries 4–7), the best result was obtained when the reaction was carried out using DMA. Ishida et al. recently reported that DMA is also a useful solvent for photochemical CO₂ reductions in homogeneous systems.^[3b] To elucidate how the solvent affects the activity in HCOOH production, photocatalytic H₂ evolution reactions were conducted with C₃N₄ modified with Pt nanoparticles (3 wt %) instead of RuP under argon atmosphere. Here, the photoexcited electrons in the conduction band moved to the loaded Pt, thereby reducing H⁺ into H₂, while the valence-band holes were consumed by the oxidation of TEOA.^[19] As listed in Table S2, a similar level of H₂ evolution activity was observed in all cases, except for the DMA/TEOA system. Even though the ability of TEOA to donate an electron decreased in the presence of H₂O,^[25] H₂ evolution in the H₂O/TEOA system was identical to that achieved using other solvents (e.g., MeCN and MeOH). For the DMA/TEOA system, which exhibited an exceptionally low H₂ evolution activity, the addition of H₂O to the system increased the activity so that it reached the same level as for the other systems. These results indicate that the low level of H₂ evolution in the DMA/TEOA system is due to proton reduction, and that oxidation of TEOA by the valence-band holes in C₃N₄ is efficient independent of the solvent used. Therefore, the solvent used for CO₂ reduction exerts an effect on the CO₂ reduction step that occurs on RuP rather than on the oxidation process.

With these refinements, a TON of greater than 1000 (20 h) was achieved using the RuP/C₃N₄ photocatalyst under visible-light irradiation with an AQY of 5.7 % at 400 nm (Figure 1). These numbers represent the greatest TON and AQY values that have been reported for visible-light-driven heterogeneous photocatalytic CO₂ reduction systems to date. The high selectivity for HCOOH production (ca. 80 %) was also

maintained even after 20 hours of reaction (HCOOH: 67.7 μmol , CO: 17.7 μmol , H_2 : 0.9 μmol). Very recently, Wang et al. also reported that carbon nitride was capable of reducing CO_2 into CO selectively with an AQY of approximately 0.9% at 420 nm when coupled to a cobalt-containing zeolitic imidazolate framework as a cocatalyst.^[16b]

In summary, a Ru catalyst with maximized electron transfer efficiency from C_3N_4 was designed. Using a suitable reaction environment for the complex, but efficient photocatalytic conversion of CO_2 into HCOOH was achieved with a Ru complex/ C_3N_4 hybrid material, which gave high TON (>1000) and AQY (5.7% at 400 nm) values. The overall performance of this hybrid material is thus superior to that of all heterogeneous photocatalysts used under visible-light irradiation to date. Thus, the present study clearly demonstrates the potential of heterogeneous photocatalysts that are based on carbon nitride for CO_2 reduction using visible light. An increasing number of reports describe new carbon nitride structures,^[26] which suggests that the performance of this CO_2 reduction process may be improved by applying a more suitable carbon nitride material. This possibility is currently under investigation.

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