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Photocatalysis

Visible-Light-Induced Selective CO_2 Reduction Utilizing a Ruthenium Complex Electrocatalyst Linked to a p-Type Nitrogen-Doped Ta_2O_5 Semiconductor**

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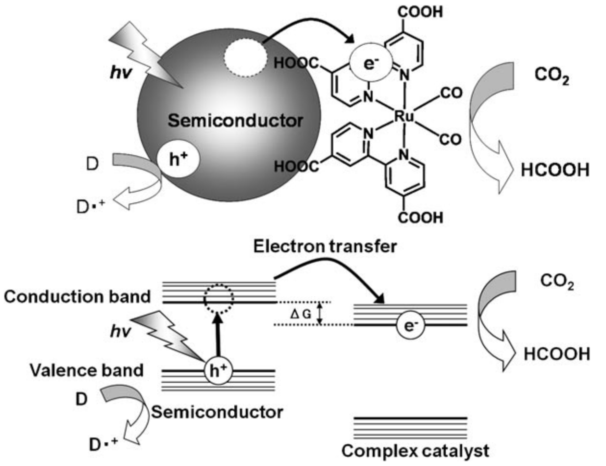
The development of photocatalysts for the reduction of CO_2 under visible light is an increasingly important research area because of the fossil fuel shortage and the global warming problem. Semiconductors are known to be able to reduce CO_2 photocatalytically.[1] However, in aqueous solutions they suffer from low quantum efficiencies owing to preferential H_2 production and low selectivity for the carbon species produced. The merit of semiconductor photocatalysis lies in the fact that such materials produce H_2 and O_2 by splitting water.[2] In other words, semiconductor photocatalysts are able to utilize H_2O as an electron donor for compensating a hole in a photoexcited state, which is the reason why photocatalytic H_2 production with semiconductor photocatalysts is considered to be feasible. In contrast, it is generally thought that photocatalytic CO_2 reduction yielding useful chemicals is more difficult than H_2 production.

Metal complexes, however, are well-known photocatalysts for CO_2 reduction.[3–6] Their quantum efficiencies and product selectivities are quite high. For example, the quantum yield of conversion of CO_2 to CO ranges up to 38% with *fac*-$[Re(bpy)(CO)_3\{P(OEt)_3\}]^+$ (bpy: 2,2′-bipyridine);[3b] only a very small amount of hydrogen and no formic acid is produced even in the presence of water. However, to ensure the success of photocatalytic CO_2 reduction with metal complexes, a suitable electron donor for the photocatalyst in the photoexicited state must be found. Currently, such photocatalysts require electron donors such as triethanolamine (TEOA), because there is no photocatalyst complex that is able to extract electrons from H_2O.

Therefore we considered that by combining photoactive semiconductors with metal complexes capable of catalytically reducing CO_2, useful organic chemicals could be obtained with high selectivity and activity in aqueous solutions. Then the so-called Z-scheme system, which makes use of heterogeneous semiconductors with different band energy potentials for producing H_2 and O_2 from H_2O, will also be applicable to a hybrid system.[7] With such combinations, electron transfer from the conduction band (CB) of a photoexcited semiconductor to a catalyst complex is crucial. If this transfer is realized, electrocatalysts (i.e. non-photoactive metal complex catalysts) developed for reducing CO_2 will provide high selectivity to photoactive semiconductors. However, there is a technical barrier to the realization of this type of photocatalytic CO_2 reduction with a hybrid system, because it is essential that photoexcited electrons be transferred from the CB of the semiconductor to the metal complex to promote selective CO_2 reduction on the complex. This type of photoinduced electron transfer has been reported for a system composed of CdSe quantum dots with adsorbed $[Re(dcbpy)(CO)_3Cl]$ (dcbpy: 4,4′-dicarboxy-2,2′-bipyridine).[8] However, there has been no report of photocatalytic reduction of CO_2 by such a mechanism.

Herein, we report the successful selective conversion of CO_2 to HCOOH under irradiation with visible light utilizing a p-type semiconductor, N-doped Ta_2O_5 (N-Ta_2O_5), linked with electrocatalysts $[Ru(dcbpy)(bpy)(CO)_2]^{2+}$ or $[Ru(dcbpy)_2(CO)_2]^{2+}$. HCOOH is a valuable liquid material with a higher density than H_2 or CO, which are important gaseous ingredients materials for producing various organic substances that can be generated through thermal treatment, a change in pH value, or catalytic reaction. This is the first report of a novel concept for photocatalytic CO_2 reduction through electron transfer from a semiconductor in the excited state to a metal complex in the ground state (Scheme 1). This work will facilitate the future development of more feasible



Scheme 1. Energy diagram of hybrid photocatalysis under visible light with a semiconductor and a metal complex.

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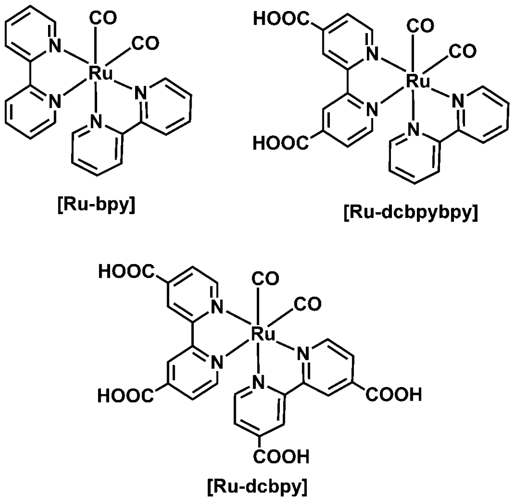
hybrid photocatalysts, because this concept is applicable to semiconductors with oxidative power strong enough to extract electrons from H_2O in aqueous solutions.



Scheme 2. Structures of the catalyst metal complexes.

We used complex catalysts $[Ru(bpy)_2(CO)_2]^{2+}(PF_6^-)_2$ ([Ru-bpy]), $[Ru(dcbpy)(bpy)(CO)_2]^{2+}(Cl^-)_2$ ([Ru-dcbpybpy]), and $[Ru(dcbpy)_2(CO)_2]^{2+}(Cl^-)_2$ ([Ru-dcbpy]), which can act as electocatalysts for CO_2 reduction (Scheme 2).[6] The reduction potential peaks of [Ru-bpy], [Ru-dcbpybpy], and [Ru-dcbpy] were confirmed to be at about −0.7 V (vs. normal hydrogen electrode, NHE) by cyclic voltammograms obtained in MeCN purged with Ar (Figure S1 in the Supporting Information). The potentials at one-electron reduction were nearly equal for the three complexes. However, the potentials of catalytic CO_2 reduction measured in an atmosphere purged with CO_2 were found to be different. The threshold potentials giving large second peaks originating from secondary electron injection into CO_2 with [Ru-bpy], [Ru-dcbpybpy], and [Ru-dcbpy] were at about −1.0, −0.9, and −0.8 V, respectively. Therefore, the CB minimum (CBM) of the semiconductor should be much more negative than the reduction potential for CO_2 of the complex.[8] For the present purpose, we developed N-Ta_2O_5 powder with the orthorhombic Ta_2O_5 crystalline structure that absorbs visible light at wavelengths smaller than 520 nm (Figure S2 in the Supporting Information).[9] Nitrogen doping not only causes a red shift at the absorption edge of Ta_2O_5 by 200 nm, as is found for N-doped TiO_2,[10] but it also provides p-type conductivity as in N-doped ZnO, as reported previously by our group.[11] Since the average crystal size estimated from full width at half maximum (FWHM) of the diffraction peak and with the Sherrer equation was around 20 nm, the band-gap widening arising from the quantum size effect was negligible. The ionization potential, or the valence-band maximum (VBM), of N-Ta_2O_5 was estimated to be about +1.1 V (vs. NHE) using photoelectron spectroscopy in air (PESA).[12] It was found that the band potential of Ta_2O_5 had shifted to a more negative position with nitrogen doping. The resulting CBM was calculated to be −1.3 V (vs. NHE), so the ΔG values (energy difference between the CBM of a semiconductor and the CO_2 reduction potential in a metal complex) between the CBM of N-Ta_2O_5 and the reduction potential of Ru complexes were −0.3, −0.4, and −0.5 V. As a reference, we also synthesized Ni(0.1 %)-doped ZnS (Ni-ZnS), which is a well-known photocatalyst for hydrogen production under visible light (below 520 nm) in a MeOH/H_2O solution.[13] The CBM of Ni-ZnS was determined to be −1.0 V (vs. NHE) by the same procedure, so the ΔG values were calculated to be −0.0, −0.1, and −0.2 V.

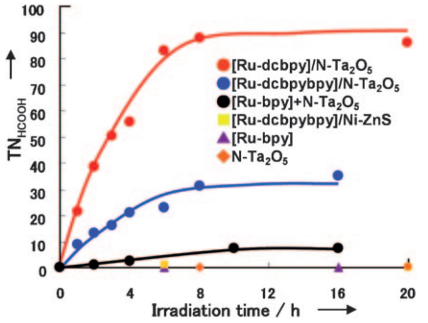


Figure 1. Turnover number (TN) for HCOOH formation from CO_2 as a function of irradiation time. Solutions were irradiated using a Xe lamp with filters producing light in the range of $410 \leq \lambda \leq 750$ nm. The concentrations of the photocatalysts were 0.05 mM and 5 mg, respectively, for Ru complexes and semiconductors in a CO_2-saturated MeCN/TEOA (5:1) solution. The catalysts used were [Ru-bpy] alone, N-Ta_2O_5 alone, a mixture of [Ru-bpy] and N-Ta_2O_5, linked [Ru-dcbpybpy]/N-Ta_2O_5, linked [Ru-dcbpy]/N-Ta_2O_5, and linked [Ru-dcbpybpy]/Ni-ZnS. Estimated errors of TN_{HCOOH} are within ±20%.

Visible light passing through UV and IR cut filters installed in the Xe lamp was used to irradiate 8 mL test tubes containing the photocatalysts (0.05 mM metal complex and/or 5 mg semiconductors) and 4 mL MeCN/TEOA (5:1 v/v) purged with CO_2. The catalysts examined were [Ru-bpy] alone, N-Ta_2O_5 alone, Ni-ZnS alone, a mixture of [Ru-bpy] and N-Ta_2O_5, a mixture of [Ru-bpy] and Ni-ZnS, linked [Ru-dcbpybpy]/N-Ta_2O_5, linked [Ru-dcbpy]/N-Ta_2O_5, and linked [Ru-dcbpybpy]/Ni-ZnS (for details, see the Supporting Information). The amounts of the main photocatalytic product (HCOOH) with increasing irradiation time under visible light are shown in Figure 1. It became clear that the mixture of [Ru-bpy] and N-Ta_2O_5 as well as Ru complexes linked with N-Ta_2O_5, such as [Ru-dcbpybpy]/N-Ta_2O_5 and [Ru-dcbpy]/N-Ta_2O_5, acted as photocatalysts for CO_2 reduction. However, [Ru-bpy] alone, N-Ta_2O_5 alone, and linked [Ru-dcbpybpy]/Ni-ZnS did not show photocatalytic activity for CO_2 reduction. Among the active catalysts, [Ru-dcbpy]/N-Ta_2O_5 exhibited the highest photocatalytic reaction rate for HCOOH generation, showing a turnover number of 89 for TN_{HCOOH} per metal complex. H_2 and CO were also detected, but the selectivity for HCOOH formation was more than 75 % before the saturation with TN_{HCOOH}. It is noteworthy that the present TN of 89 obtained using the semiconductor–complex hybrid is comparable to the highest TN of 240 for the conversion of CO_2 into CO using a rhenium complex photocatalyst.[5a] As for the amount of HCOOH produced, we confirmed that it increases linearly with the amount of [Ru-dcbpy]/N-Ta_2O_5 up to 50 mg in the same photoreactor. The photocatalytic rate of HCOOH generation using 50 mg photocatalyst was calculated to be 3.5 $\mu mol\,h^{-1}$ (Figure S3 in the Supporting Information). The photoreaction rates cannot be accurately compared because they depend on the amount of photocatalyst, the light intensity, the irradiation area, and so forth. However, this rate was found to be comparable to that of photocatalytic H_2 production using a semiconductor photocatalyst. This fact is also supported by the quantum yield of the present reaction. Figure 2 shows an action spectrum of the quantum yield of HCOOH generation on [Ru-dcbpy]/N-Ta_2O_5. The measured quantum yield of HCOOH formation (Φ_{HCOOH}) was 1.9 % at 405 nm. It was found that Φ_{HCOOH} was strongly dependent on the optical absorption of N-Ta_2O_5. Because it is well-known that [Ru-bpy] does not act as a photocatalyst (because the lifetime of the photoexcited state is very short) but does act as a electrocatalyst for CO_2 reduction, it can be concluded that photocatalytic CO_2 reduction takes place owing to electron transfer from photoexcited N-Ta_2O_5 to the Ru complex. The technical merit of this concept lies in the following: firstly, not only metal complex photocatalysts but also many electrocatalysts are available, because electrons can be supplied by photoexcited semiconductors; and secondly, no external electric bias is required, because the highly negative bias indispensable for electron transfer is determined by the position of the CBM of a photoexcited semiconductor, as is clear from the H_2 production over semiconductor photocatalysts.

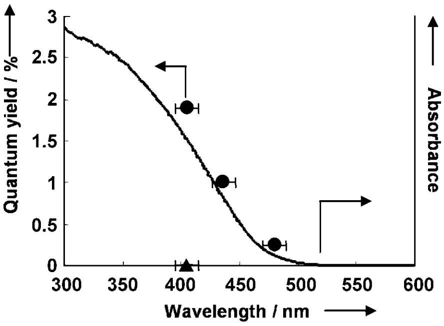


Figure 2. Quantum efficiency of HCOOH generation and optical absorption of N-Ta_2O_5 (——) as a function of wavelength of incident light. Aliquots of MeCN/TEOA (5:1 v/v, 4 mL) containing [Ru-dcbpy]/N-Ta_2O_5 (20 mg, ●) and [Ru-dcbpy] alone (0.01 mM, ▲) were irradiated under CO_2 with 405 nm (2.06×10^{-8} einstein s^{-1}), 435 nm (4.58×10^{-8} einstein s^{-1}), and 480 nm (4.89×10^{-8} einstein s^{-1}) monochromic light.

Figure 3a shows an ion chromatogram recorded after photocatalytic reaction for 20 h with [Ru-dcbpy]/N-Ta_2O_5. In Figure 3b, the main materials in the chromatogram corresponding to m/z 75, 45, 35, and 61 were identified by IC TOF-MS. The intense peak at m/z 45 ($HCOO^-$) originated from formic acid. The peak at m/z 75 was that of CH_2OHCOO^-, while the peaks at m/z 35 and 61 were assigned to Cl^- and HCO_3^-, respectively. We speculated that other small peaks were not correlated with the carbon species originating from CO_2.

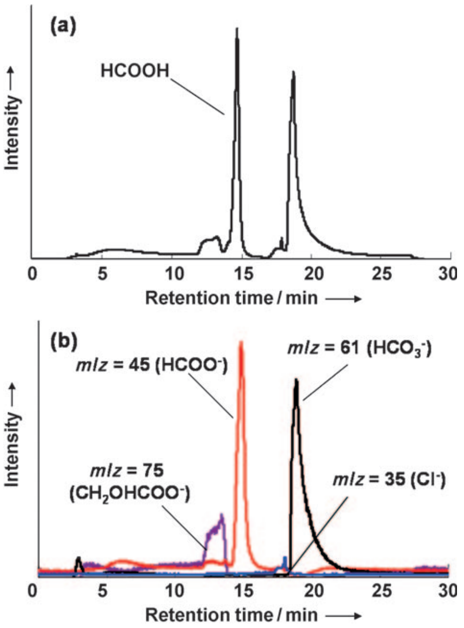


Figure 3. Ion chromatography time-of-flight mass spectrometry (IC TOF-MS) analysis of photocatalytic reaction products. The photocatalyst concentration was 5 mg for [Ru-dcbpy]/N-Ta_2O_5 in a CO_2-saturated MeCN/TEOA (5:1) solution. Solutions were irradiated using a Xe lamp with filters producing visible light in the range of $410 \leq \lambda \leq 750$ nm for 20 h. a) Ion chromatogram, b) MS chromatograms; m/z 35 (blue), 45 (red), 61 (black), and 75 (violet).

For verification of HCOOH derived through CO_2 reduction, isotope tracer analyses involving $^{13}CO_2$ were also conducted. Figure 4 shows the mass chromatograph spectra of a MeCN/TEOA (5:1 v/v) solution containing 5 mg [Ru-dcbpy]/N-Ta_2O_5 purged with $^{12}CO_2$ or $^{13}CO_2$ after irradiation for 20 h. A clear peak arising from $H^{13}COO^-$ (m/z 46) was observed with the reaction purged with $^{13}CO_2$ (Figure 4d), while no such peak was found for the reaction with $^{12}CO_2$ (Figure 4b). The peaks of other carbon species such as glycolic acid (CH_2OHCOO^-) were identified in both mass chromatograph spectra of $^{12}CO_2$ and $^{13}CO_2$, thus indicating that they were not produced from CO_2 dissolved in the solution. The formation of $H^{13}COO^-$ was also confirmed by ^{13}C NMR spectroscopy in three systems, [Ru-dcbpy]/N-Ta_2O_5, [Ru-dcbpybpy]/N-Ta_2O_5, and the mixture of [Ru-bpy] and N-Ta_2O_5 (Figure S4 in the Supporting Information). These results confirmed that the HCOOH detected in these photocatalytic reactions under visible light was produced from CO_2 dissolved in the solutions.

To form HCOOH from CO_2, two protons are also necessary. IC TOF-MS analysis using D_2O and CD_3CN was conducted to examine this aspect. As a result, we found that TEOA is necessary not only as an electron donor but also as a proton source for HCOOH formation, since negligibly small $DCOO^-$ peaks were detected for the photocatalytic reactions

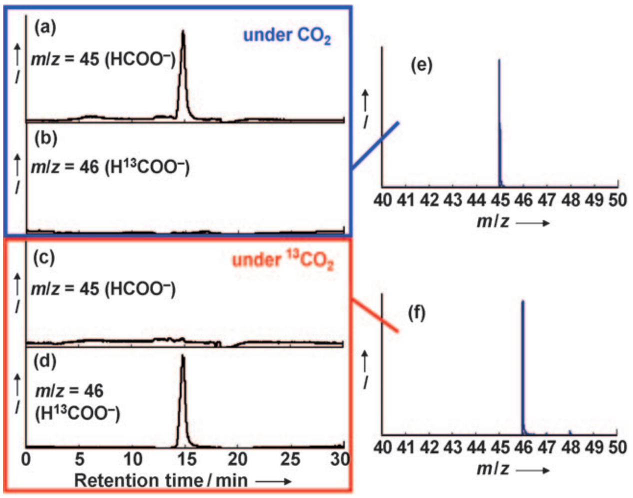


Figure 4. MS chromatograms and spectra of a MeCN/TEOA (5:1 v/v) solution containing 5 mg [Ru-dcbpy]/N-Ta_2O_5 purged with $^{13}CO_2$ or CO_2. The solution was irradiated using a merry-go-round apparatus with a Xe lamp ($410 \leq \lambda \leq 750$ nm) for 20 h. a) MS chromatogram at *m*/*z* 45 under CO_2, b) MS chromatogram at *m*/*z* 46 under CO_2, c) MS chromatogram at *m*/*z* 45 under $^{13}CO_2$, d) MS chromatogram at *m*/*z* 46 under $^{13}CO_2$, e) MS spectrum under CO_2, and f) MS spectrum under $^{13}CO_2$.

involving D_2O and/or CD_3CN (Figure S5 in the Supporting Information).

It has been reported that [Ru-bpy] cannot be quenched by TEOA,[6] and we confirmed that photocatalytic production of HCOOH is negligible in the absence of TEOA (Figure S6 in the Supporting Information). In the present reaction using linked [Ru-dcbpy]/N-Ta_2O_5, we also confirmed that the reaction rate was dependent on the TEOA concentration. These facts indicate that TEOA acted as an electron donor only for photoexcited N-Ta_2O_5. However, the amount of HCOOH produced with the bare N-Ta_2O_5 was very low compared with the amounts formed with a mixture of N-Ta_2O_5 and [Ru-bpy], linked [Ru-dcbpybpy]/N-Ta_2O_5, and linked [Ru-dcbpy]/N-Ta_2O_5, even in the presence of TEOA. Therefore, the photoexcited electrons in the CB of N-Ta_2O_5 were presumably transferred to [Ru-bpy], [Ru-dcbpybpy], and [Ru-dcbpy], thus leading to efficient reduction of CO_2 to HCOOH, for which Ru complexes acted as reaction sites for CO_2 reduction. In the present reaction, it is considered that the ΔG between the two substances is a significant factor, as discussed for semiconductor quantum dot/semiconductor[14] and semiconductor/metal complex systems[8,15] in which ΔG is regarded as the driving force for the rate of interfacial electron transfer. Though the variation in ΔG was not great in this study, the results with N-Ta_2O_5 and Ni-ZnS were quantitatively consistent. The greatly improved photocatalytic activity with the linked systems [Ru-dcbpybpy]/N-Ta_2O_5 and [Ru-dcbpy]/N-Ta_2O_5 may be attributed to a synergistic effect of ΔG and the linkage of the two substances, which could be the key factors for acceleration of the electron transfer from a semiconductor to a metal complex.

For the entire fast electron-transfer step between TEOA, N-Ta_2O_5, and Ru complexes, there are two patterns of electron transfer depending on which electron transfer occurs first: from TEOA to N-Ta_2O_5 or from N-Ta_2O_5 to Ru complexes [Eqs. (1,2)]. In [Eq. (1)], electron transfer from TEOA to photoexcited N-Ta_2O_5 takes place initially, while in [Eq. (2)], transfer from photoexcited N-Ta_2O_5 to a Ru complex has priority. Transient spectroscopy analyses of the electron transfer process are currently underway.

$$\text{N-Ta}_2\text{O}_5{}^* + \text{TEOA} \rightarrow \text{N-Ta}_2\text{O}_5{}^{\bullet-} + \text{TEOA}^{\bullet+} \tag{1a}$$

$$\begin{aligned} &\text{N-Ta}_2\text{O}_5{}^{\bullet-} + [\text{Ru(L-L)(L-L}')(\text{CO})_2]^{2+} \\ &\qquad \rightarrow \text{N-Ta}_2\text{O}_5 + [\text{Ru(L-L}^{\bullet-})(\text{L-L}')(\text{CO})_2]^{+} \end{aligned} \tag{1b}$$

$$\begin{aligned} &\text{N-Ta}_2\text{O}_5{}^* + [\text{Ru(L-L)(L-L}')(\text{CO})_2]^{2+} \\ &\qquad \rightarrow \text{N-Ta}_2\text{O}_5{}^{\bullet+} + [\text{Ru(L-L}^{\bullet-})(\text{L-L}')(\text{CO})_2]^{+} \end{aligned} \tag{2a}$$

$$\text{N-Ta}_2\text{O}_5{}^{\bullet+} + \text{TEOA} \rightarrow \text{N-Ta}_2\text{O}_5 + \text{TEOA}^{\bullet+} \tag{2b}$$

As for the reduction process on Ru complexes, injection of the second electron into Ru complexes needs more negative potential energy than does the first (one-electron reduction) into a diimine complex such as $[Ru(bpy)_3]^{2+}$. However, in the present hybrid system, the potential of electrons being transferred to Ru complexes is fixed at −1.3 V vs. NHE by the energy level of the CBM of N-Ta_2O_5 (a hot-carrier or multiple-exciton-generation effect is considered to be negligible), which is sufficiently negative to reduce CO_2 with two electrons on the Ru complexes, as described above (Figure S1 in the Supporting information). At this stage, it is speculated that some structural change in the one-electron-reduced Ru complex took place before acceptance of the second electron, because the first reduction (one-electron reduction) peaks were irreversible. This structural change is probably accompanied by dissociation of CO (monodentate ligand), as recently clarified for the CO_2 photoreduction process on Re complexes.[16]

Finally, in the process of production of HCOOH with the present Ru complex/N-Ta_2O_5 system, TEOA acted as both an electron donor and a proton source for N-Ta_2O_5 and the Ru complex. Since the valence band maximum (VBM) of N-Ta_2O_5 (+1.1 V vs. NHE) is more negative than the potential of oxidation of H_2O to O_2 (+1.23 V vs. NHE), N-Ta_2O_5 is not able to utilize H_2O as an electron donor. However, this fact indicates that this hybrid system could replace TEOA with H_2O if N-Ta_2O_5 is replaced with another semiconductor capable of oxidizing H_2O. Therefore, the present concept should lead to the development of novel photocatalysts that recycle CO_2 in aqueous solutions under solar irradiation in the near future.

In conclusion, we have successfully achieved selective, visible-light-induced reduction of CO_2 to HCOOH for the first time by utilizing the combination of a p-type semiconductor photosensitizer, N-Ta_2O_5, and a reducing catalyst, a Ru complex such as [Ru-bpy], [Ru-dcbpybpy], or [Ru-dcbpy], in an acetonitrile/triethanolamine solution. The selectivity for HCOOH was more than 75 % and the quantum efficiency was 1.9 % at 405 nm with the linked [Ru-dcbpy]/N-Ta_2O_5 catalyst. The ΔG between the CBM of the semiconductor and the CO_2 reduction potential of the complex is an indispensable factor for realizing such photocatalytic CO_2 reduction. Furthermore, we found that the linkage between the complex and the semiconductor is essential for greatly enhancing the reaction rate. This concept of connecting semiconductors and complex catalysts taking the energy potentials of materials into account would be applicable to systems for producing HCOOH and other useful organic chemicals from CO_2 utilizing semiconductor photocatalysts active under visible light. By changing the kind of metal complex catalyst, the photoactivity, selectivity, and long-term stability could be enhanced. Because some semiconductor photocatalysts possess strong ability to photooxidize H_2O by extracting electrons, this concept would also be applicable to semiconductor-based tandem or Z-scheme systems for solar fuel production in aqueous solutions.

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