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Artificial Z-Scheme Constructed with a Supramolecular Metal Complex and Semiconductor for the Photocatalytic Reduction of CO_2

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Ⓢ *Supporting Information*

ABSTRACT: A hybrid for the visible-light-driven photocatalytic reduction of CO_2 using methanol as a reducing agent was developed by combining two different types of photocatalysts: a Ru(II) dinuclear complex (**RuBLRu′**) used for CO_2 reduction is adsorbed onto Ag-loaded TaON (Ag/TaON) for methanol oxidation. Isotope experiments clearly showed that this hybrid photocatalyst mainly produced HCOOH (TN = 41 for 9 h irradiation) from CO_2 and HCHO from methanol. Therefore, it converted light energy into chemical energy ($\Delta G^\circ = +83.0$ kJ/mol). Photocatalytic reaction proceeds by the stepwise excitation of Ag/TaON and the Ru dinuclear complex on Ag/TaON, similar to the photosynthesis Z-scheme.

Humans are facing serious problems, including shortage of energy and carbon resources and increasing CO_2 concentrations in the atmosphere, because of excessive dependence on fossil resources. One of the best solutions for these problems could be conversion of CO_2 into energy-rich chemicals using solar light as an energy source. Photosynthesis uses an exquisite up-conversion system of light energy—the so-called Z-scheme—which uses two photons, each with a relatively low energy, one after the other to drive the reactions involved in water oxidation and reduction of the coenzyme NADP, which require higher energy than either photon alone can provide. Therefore, photosynthesis can use a wide range of visible light.

Several artificial Z-scheme systems have been reported. Mixed systems, utilizing two types of semiconductor particles, have been successfully applied to split water using visible light, even though neither semiconductor could achieve that alone.[1−4] The efficiencies of these photocatalytic reactions are still very low because the flow of electrons from the water-oxidation photocatalyst to the water-reduction photocatalyst cannot be controlled sufficiently. Moreover, photoelectrochemical cells that can photocatalyze water splitting[5] or CO_2 reduction[6] using two or more semiconductors as light absorbers have been developed.

Recently, we reported highly effective CO_2 reduction using supramolecular metal complexes as photocatalysts, which are constructed with photosensitizer and catalyst units.[7−12] These photocatalysts can use visible light and have better reaction rates and durability than other reported photocatalysts.[10,11] However, a sacrificial electron donor is needed because of their weak oxidation powers.

Some types of semiconductor particles such as TaON can photocatalyze the oxidation of methanol and even water in the presence of a sacrificial electron acceptor using visible light with very high efficiency.[13−15] However, they cannot reduce CO_2 because of their low reduction power and reduction-product selectivity. Here we report the first artificial Z-scheme system for reducing CO_2 that is driven by visible light and uses a hybrid of a supramolecular metal complex (the CO_2-reduction photocatalyst) and semiconductor particles (the oxidation photocatalyst for methanol).

Scheme 1 shows the structure of the synthesized hybrid. The supramolecule with $[Ru(dmb)_2(BL)]^{2+}$ as a photosensitizer unit and $[Ru(BL)(CO)_2Cl_2]$ as a catalyst unit for CO_2 reduction (**RuBLRu′**) was adsorbed using methylphosphonic acid groups

Scheme 1. Artificial Z-Scheme for Photocatalytic CO_2 Reduction

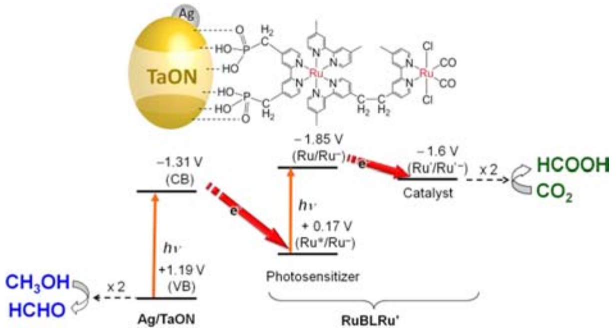

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Table 1. Photocatalytic Reaction Products from 15 h Irradiation under Various Conditions[a]

entry	photocatalyst	metal complex/ nmol	$h\nu$	MeOH	CO_2	HCOOH/nmol ($\mathrm{TN_{HCOOH}}$)[b]	H_2/ nmol	CO/nmol ($\mathrm{TN_{CO}}$)[b]
1[c]	Ag/TaON−**RuBLRu′**	24	○	○	○	969 (41)	678	68 (2.8)
2	Ag/TaON−**RuBLRu′**	25	×	○	○	n.d.	10	n.d.
3	Ag/TaON−**RuBLRu′**	24	○	×[d]	○	n.d.	12	n.d.
4	**RuBLRu′**[e]	24	○	○	○	35 (1.5)	90	40 (1.8)
5	Ag/TaON−**RuBLRu′**	28	○	○	×	n.d.	631	5 (0.2)
6	Ag/TaON	0	○	○	○	n.d.	480	n.d.
7	TaON	0	○	○	○	n.d.	135	n.d.
8	TaON−**RuBLRu′**	22	○	○	○	69 (3.1)	170	15 (0.7)
9	Pt/TaON−**RuBLRu′**	25	○	○	○	36 (1.4)	10959	n.d.
10	Ag/TaON−**Ru**[f]	29	○	○	○	n.d.	263	n.d.
11	Ag/TaON−**Ru′**[g]	25	○	○	○	19 (0.8)	437	23 (0.9)

[a] 8 mg of photocatalyst was dispersed in 4 mL of methanol. Photochemical reaction conditions: CO_2 or Ar bubbling for 20 min before irradiation using a 500-W Hg lamp with a cutoff filter (λ < 400 nm). [b] Turnover numbers (TN) were calculated on the basis of the metal complex used. [c] Reproducibility of the photocatalytic reaction is shown in Table S1. [d] Solvent was acetonitrile. [e] 6 μM **RuBLRu′** in a methanol solution. [f] **Ru** = $[Ru(dmb)_2\{bpy(CH_2PO_3H_2)_2\}]^{2+}$. [g] **Ru′** = $[Ru\{bpy(CH_2PO_3H_2)_2\}(CO)_2Cl_2]$.

at the 4,4′-positions of the 2,2′-bipyridine ligand on the TaON particles loaded with 1 wt% metallic silver (Ag/TaON).

The hybrid photocatalst was easily synthesized by mixing Ag/TaON particles in an acetonitrile solution containing **RuBLRu′** at room temperature for 6 h, followed by washing with acetonitrile. The adsorption of **RuBLRu′** onto Ag/TaON was confirmed from the FT-IR spectrum of the hybrid (Figure S3) and quantitatively analyzed by comparing the absorbance of the filtrate to the absorbance of the initial solution. No elution of **RuBLRu′** from the hybrid by methanol was observed, even after dispersing hybrid particles in methanol overnight. The detailed synthetic methods for **RuBLRu′** and Ag/TaON are described in the Supporting Information.

As a typical photocatalytic reaction run, a Ag/TaON−**RuBLRu′** dispersion (24 nmol of the complex on 8 mg of semiconductor particles) in methanol was irradiated with visible light (using a 500-W high-pressure Hg lamp with a λ < 400 nm cutoff filter; the spectrum of the incident light is shown in Figure S4) under a CO_2 atmosphere for 15 h to give HCOOH (969 nmol) and H_2 (678 nmol) with a small amount of CO (68 nmol) (entry 1, Table 1). The HCOOH formation turnover number ($\mathrm{TN_{HCOOH}}$: moles of HCOOH produced per mole of adsorbed **RuBLRu′**) reached 41. Formaldehyde (1520 nmol) was also produced during the photochemical reaction. The total amount of reduction products, i.e., HCOOH, H_2, and CO (1710 nmol), was similar to the amount of HCHO produced.

Control experiments without light or methanol did not give the photocatalytic-reduction products (entries 2 and 3, Table 1), and without Ag/TaON (i.e., only **RuBLRu′** was used) gave only very small amounts of the products (entry 4). In the absence of CO_2, i.e., irradiation under an Ar atmosphere or without **RuBLRu′** (only Ag/TaON or TaON was used), only H_2 was produced with no HCOOH or CO (entries 5−7). Without Ag on TaON (i.e., TaON−**RuBLRu′** was used, entry 8), HCOOH, H_2, and CO were produced, but the yields of all reduction products were much lower than those obtained with Ag (Ag/TaON−**RuBLRu′**, entry 1). Using Pt- instead of Ag-loaded TaON (Pt/TaON−**RuBLRu′**) caused a considerable increase in H_2 evolution but a drastic decrease in the CO_2-reduction products (entry 9).

Experiments were performed to obtain more information on the reaction mechanism. Under a $^{13}CO_2$ atmosphere (710 Torr), a methanol-d_4 suspension of Ag/TaON−**RuBLRu′** was irradiated, giving HCOOH. The ^{13}C NMR spectrum of the reaction solution clearly showed the formation of $H^{13}COOH$ (δ 160 ppm) from the photochemical reaction (Figure S1a). However, when an unlabeled CO_2-saturated methanol-d_4 solution was used, the $H^{13}COOH$ peak was not detected (Figure S1b). In the ^1H NMR of the CH_3OH solution irradiated under $^{13}CO_2$ (670 Torr), only a doublet ($J_{^{13}CH}$ = 209 Hz) was observed between 7.9 and 8.4 ppm, which was attributed to the proton coupled to the ^{13}C in $H^{13}COOH$. Only a singlet was observed at 8.18 ppm in the CH_3OH solution irradiated under unlabeled CO_2 atmosphere (Figure 1a,b). These results clearly indicate that CO_2 was almost the entire carbon source for the photochemically produced HCOOH. Although CO was a minor product, it was also analyzed by GC/MS (Figure S2). This indicated that the evolved CO mainly originated from the catalyst unit CO ligand (77%), but that it was partly produced by the photocatalytic reduction of CO_2 (23%). The detachment of CO ligands was a very slow reaction, but it was possibly a deactivation process for the photocatalyst. The irradiated solutions were also analyzed by

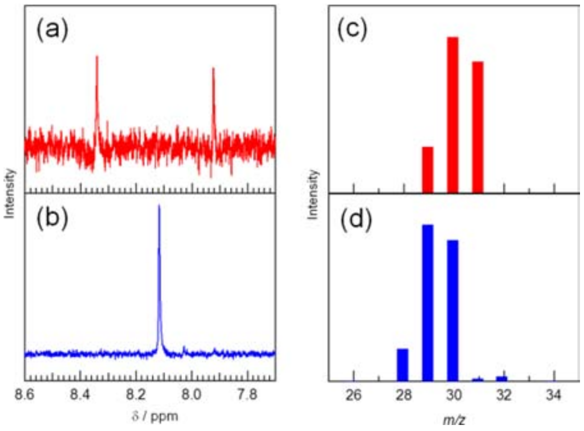

Figure 1. (a,b) ^1H NMR spectra of the photocatalytic reaction solutions (4 mL): Ag/TaON−**RuBLRu′** (8 mg) was irradiated (>400 nm light) for 15 h in (a) CH_3OH under $^{13}CO_2$ (670 Torr) and (b) CH_3OH saturated with unlabeled CO_2. (c,d) Mass spectra of formaldehyde peaks in GC/MS analysis of the photocatalytic reaction solution: Ag/TaON−**RuBLRu′** (1 mg) was irradiated (>400 nm light) for 24 h in (c) unlabeled CO_2-saturated $^{13}CH_3OH$ (0.2 mL) and (d) unlabeled CH_3OH (0.2 mL).

GC/MS. The mass spectrum of the peak attributed to formaldehyde in the $^{13}CH_3OH$ solution (Figure 1c) was different from that in the standard CH_3OH solution (Figure 1d), i.e., *m/z* values were larger in the $^{13}CH_3OH$ solution by 1 unit. This clearly indicates that formaldehyde was produced from methanol acting as a reducing agent during the photocatalytic reaction, and methanol totally worked as a two-electron donor,

$$CH_3OH \rightarrow HCHO + 2H^+ + 2e^- \qquad (1)$$

Figure 2 shows the yields of all reduction and oxidation products at various irradiation times. Formation of HCOOH, CO, and H_2 requires the two-electron reduction of CO_2 or two protons and the oxidation of methanol to HCHO to give two electrons, and the total amount of reduction products was always similar to that of HCHO during irradiation. The photocatalytic reactions are shown below:

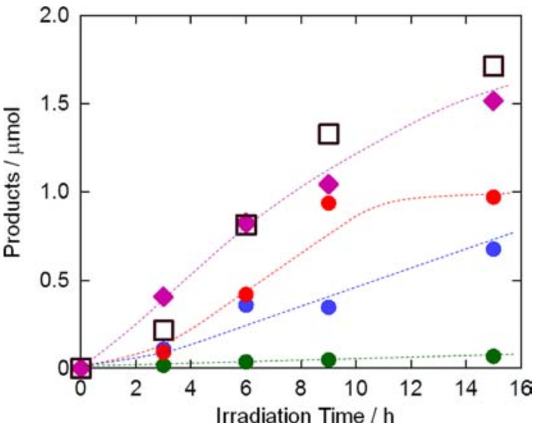

Figure 2. Time conversion curves of HCOOH (red circles), CO (green circles), H_2 (blue circles), and HCHO (purple diamonds) produced by the photocatalytic reaction. A CO_2-saturated CH_3OH (4 mL) solution containing Ag/TaON−**RuBLRu′** (8 mg, with 23 nmol adsorbed **RuBLRu′**) was irradiated using >400 nm light. The total amounts of the reduction products, i.e., HCOOH + CO + H_2, are also shown (squares).

$$CO_2 + CH_3OH \rightarrow HCOOH + HCHO \qquad \Delta G^\circ = +83.0 \text{ kJ/mol} \qquad (2)$$

$$CO_2 + CH_3OH \rightarrow CO + H_2O + HCHO \qquad \Delta G^\circ = +67.6 \text{ kJ/mol} \qquad (3)$$

$$CH_3OH \rightarrow H_2 + HCHO \qquad \Delta G^\circ = +44.4 \text{ kJ/mol} \qquad (4)$$

Because the Gibbs free-energy changes (ΔG°) of all of the reactions are positive, the photocatalytic reactions using Ag/TaON−**RuBLRu′** convert light energy to chemical energy.

The UV/vis diffuse reflectance spectrum of TaON showed an absorption band edge near 500 nm (Figure S4). However, the Ag/TaON spectrum also showed strong and broad surface plasmonic absorption by the metallic Ag in the visible region. Although the Ag/TaON−**RuBLRu′** spectrum was similar to the Ag/TaON spectrum because of the much stronger absorption of the Ag plasmon than that of **RuBLRu′**, the Ru complex MLCT absorption band was observed for TaON−**RuBLRu′** when similar amounts of **RuBLRu′** on Ag/TaON−**RuBLRu′** were adsorbed on to the TaON surface (Figure S4). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of Ag/TaON−**RuBLRu′** (Figure S6) indicated that Ag particles ranging between several tens and 100 nm were deposited on the TaON surface.

Because **RuBLRu′** was newly synthesized in this study, UV/vis absorption and emission properties and a cyclic voltammogram of **RuBLRu′**, along with those of the corresponding mononuclear model complexes, $[Ru(dmb)_2\{bpy(CH_2PO_3H_2)_2\}]^{2+}$ and $[Ru(dmb)(CO)_2Cl_2]$, are summarized in the Supporting Information. The **RuBLRu′** absorption spectrum (Figure S8) was very similar to the combined spectra of the two model complexes. Photocatalysis of this complex with a strong reductant in a homogeneous solution is also shown in Figure S7. This is reasonable because the two Ru complexes were connected by an ethylene chain, and there should be only weak through-bond electronic interaction between Ru units in the ground state. Similar phenomena were observed for the Ru(II)−Re(I)[9,10] and Ru(II)−Ru(II)[11] supramolecules, in which two metal complexes are also connected by the same bridge ligand. On the basis of this observation and the results of the diffuse reflectance spectra described above, we concluded that 405, 436, and 546 nm irradiated light was absorbed by the photosensitizer units of **RuBLRu′**, TaON, and Ag, respectively, but not by the **RuBLRu′** catalyst unit. The excitation of both TaON and **RuBLRu′** must be required for the photocatalytic reduction of CO_2 with methanol, because almost no formic acid was obtained in the absence of either TaON or the photosensitizer unit of the complex (for Ag/TaON−**Ru′**) (entries 4 and 11, Table 1).

The **RuBLRu′** emission quantum yield was approximately 20% lower than that of **Ru**. This indicates that intramolecular electron transfer from the excited photosensitizer unit to the catalyst unit partly proceeds in methanol, which might produce the one-electron-reduced (OER) catalyst unit followed by electron transfer from TaON to the oxidized photosensitizer unit. Comparing the cyclic voltammogram of **RuBLRu′** in an Ar-saturated DMF solution with those of **Ru** and **Ru′** (Figure S10) led us to conclude that the catalyst unit of **RuBLRu′** is first reduced at $E_p^{red} = -1.68$ V vs Ag/AgNO$_3$, which was observed as an irreversible broad wave at 200 mV/s scan rate. The next two reversible waves, observed at −1.85 and −2.10 V, were attributed to the stepwise reduction of the different diimine ligands of the **RuBLRu′** photosensitizer unit, respectively. This clearly indicates that electron transfer to the catalyst unit can proceed if the photosensitizer unit is first reduced via photochemical electron transfer from Ag/TaON because this process is thermodynamically favorable. A catalytic wave for CO_2 reduction was observed near −1.6 V, corresponding to the reduction of the catalyst unit in the cyclic voltammogram of **RuBLRu′** measured in a CO_2-saturated DMF solution. Therefore, we concluded that CO_2 reduction is initiated by one-electron reduction of the catalyst unit via either photochemical intramolecular electron transfer from the excited photosensitizer unit to the catalyst unit or photoinduced reduction of the photosensitizer unit.

The TaON valence and conduction band edges have been reported as +1.19 and −1.31 V, respectively, vs Ag/AgNO$_3$.[16] These values can be compared with the **RuBLRu′** redox potentials, described above, to investigate the possibility of electron flow between TaON and the **RuBLRu′** photosensitizer unit. The excitation energy of the photosensitized unit was found to be $E_{00} = 2.02$ eV by using Franck−Condon analysis[18] of the emission spectrum (Figure S9, eqs S2 and S3), so the reduction and the oxidation potentials of the excited photosensitizer unit were calculated to be +0.17 and −1.30 V vs Ag/AgNO$_3$, respectively. A comparison of these electrochemical data clearly shows that electron transfer from the valence band of TaON to the excited **RuBLRu′** photosensitizer unit ($\Delta G = +1.02$ eV), and that from the conduction band to the photosensitizer unit in the ground state (ΔG = +0.54 eV), are thermodynamically unfavorable. However, electron transfer should proceed effectively from the conduction band to the excited photosensitizer unit (ΔG = −1.48 eV) and/or the one-electron oxidation state of the photosensitizer unit (ΔG = −2.03 eV). This also strongly indicates that the photocatalytic reduction of CO_2 requires the excitation of both TaON and the **RuBLRu′** photosensitizer.

On the basis of the mechanistic aspects described above, we concluded that the mechanism is as follows (and as shown in Scheme 1): Irradiated light is absorbed mainly by TaON and the Ag particles on TaON, and partly by the **RuBLRu′** photosensitizer unit (because of the absorbance differences). The photogenerated hole in the TaON valence band can oxidize methanol ($E^{\circ}{}^{\bullet}{}_{CH_2OH,H^+/CH_3OH}$ = +0.47 V vs Ag/$AgNO_3$),[18] and the electrons accumulated in the conduction band can be transferred to the excited or oxidized photosensitizer unit, but cannot be transferred to the ground state. Therefore, another photon absorbed by the photosensitizer is required for Ag/TaON−**RuBLRu′** interfacial electron transfer that produces an OER species in the photosensitizer or catalyst unit. In the former case, the subsequent intramolecular electron transfer proceeds from the OER in the photosensitizer unit to the catalyst unit as a thermodynamically favorable process. CO_2 is reduced on the catalyst unit to give HCOOH. Because producing formic acid from CO_2 requires a two-electron reduction, the stepwise two-photon absorption and subsequent electron-transfer processes probably occur twice during the reduction of CO_2 to give one HCOOH molecule. An induction period of formation of HCOOH was observed in the photocatalytic reaction while the amount of HCHO increased in proportion to the irradiation time in the first stage, as shown in Figure 2. This is understandable because the formation of HCOOH probably requires accumulation of electrons in TaON and/or Ag before the excitation of **RuBLRu′**.

The Ag nanoparticles loaded on TaON enhanced the photocatalytic activity of the hybrid (entries 1 and 6, Table 1). Although metallic Ag nanoparticles would act as electron donors, this is implausible in the photocatalytic reaction because if the loaded Ag acts as the main electron donor, the amount of HCHO produced from methanol would be much smaller than the sum of reduced products (Figure 2). Some groups reported that the efficiency of electron−hole separation in the excitation of TiO_2 was accelerated by loading Ag nanoparticles onto TiO_2 because Ag acts as an electron pool.[19] Because a similar phenomenon occurs for Ag/TaON, we believe that Ag loading probably improves the efficiency of methanol oxidation and the accumulation of electrons by Ag/TaON. Therefore, the subsequent photochemical reduction of **RuBLRu′** should be accelerated. Electron transfer from Ag to the excited and oxidized photosensitized unit might proceed because approximately 60% of the TaON surface was covered by **RuBLRu′** (Figure S5). Another advantage of using Ag is that the greater potential of Ag for proton reduction, compared to other noble metals (such as Pt), suppresses the evolution of H_2. In fact, Pt/TaON−**RuBLRu′** mainly produced H_2 under irradiation, even under a CO_2 atmosphere, and a very small amount of HCOOH (entry 9, Table 1). We do not have clear experimental evidence for participation of plasmon of Ag in the photocatalytic reaction.

In conclusion, we successfully synthesized the first visible-light-driven Z-scheme for the photocatalytic reduction of CO_2. The photocatalyst Ag/TaON−**RuBLRu′** mainly produces formic acid as a reduction product and formaldehyde as the oxidized product of methanol. This process converts light energy to chemical energy, with ΔG° = +83.0 kJ/mol.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General procedures and results, spectra, microscopy images of the hybrid, and photophysical and electrochemical properties of the metal complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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