CONSPECTUS: Photocatalytic CO₂ reduction is a critical objective in the field of artificial photosynthesis because it can potentially make a total solution for global warming and shortage of energy and carbon resources. We have successfully developed various highly efficient, stable, and selective photocatalytic systems for CO₂ reduction using transition metal complexes as both photosensitizers and catalysts. The molecular architectures for constructing selective and efficient photocatalytic systems for CO₂ reduction are discussed herein. As a typical example, a mixed system of a ring-shaped Re(I) trinuclear complex as a photosensitizer and fac-[Re(bpy)(CO)₃{OC₂H₄N(C₂H₄OH)₂}] as a catalyst selectively photocatalyzed CO₂ reduction to CO with the highest quantum yield of 82% and a turnover number (TON) of over 600. Not only rare and noble metals but also earth abundant ones, such as Mn(I), Cu(I), and Fe(II) can be used as central metal cations. In the case using a Cu(I) dinuclear complex as a photosensitizer and fac-Mn(bpy)(CO)₃Br as a catalyst, the total formation quantum yield of CO and HCOOH from CO₂ was 57% and TON_{CO+HCOOH} exceeded 1300. Efficient supramolecular photocatalysts for CO₂ reduction, in which photosensitizer and catalyst units are connected through a bridging ligand, were developed for removing a diffusion control on collisions between a photosensitizer and a catalyst. Supramolecular photocatalysts, in which [Ru(N≡N)₃]⁺⁺-type photosensitizer and Re(I) or Ru(II) catalyst units are connected to each other with an alkyl chain, efficiently and selectively photocatalyzed CO₂ reduction in solutions. Mechanistic studies using time-resolved IR and electrochemical measurements provided molecular architecture for constructing efficient supramolecular photocatalysts. A Ru(II)–Re(I) supramolecular photocatalyst constructed according to this molecular architecture efficiently photocatalyzed CO₂ reduction even when it was fixed on solid materials. Harnessing this property of the supramolecular photocatalysts, two types of hybrid photocatalytic systems were developed, namely, photocatalysts with light-harvesting capabilities and photoelectrochemical systems for CO₂ reduction.

Introduction of light-harvesting capabilities into molecular photocatalytic systems should be important because the intensity of solar light shone on the earth’s surface is relatively low. Periodic mesoporous organosilica, in which methyl acridone groups are embedded in the silica framework as light harvesters, was combined with a Ru(II)–Re(I) supramolecular photocatalyst with phosphonic acid anchoring groups. In this hybrid, the photons absorbed by approximately 40 methyl acridone groups were transferred to one Ru(II) photosensitizer unit, and then, the photocatalytic CO₂ reduction commenced.

To use water as an abundant electron donor, we developed hybrid photocatalytic systems combining metal-complex photocatalysts with semiconductor photocatalysts that display high photooxidation powers, in which two photons are sequentially absorbed by the metal-complex photosensitizer and the semiconductor, resulting in both high oxidation and reduction power. Various types of dye-
sensitized molecular photocathodes comprising the p-type semiconductor electrodes and the supramolecular photocatalysts were developed. Full photoelectrochemical cells combining these dye-sensitized molecular photocathodes and n-type semiconductor photoanodes achieved CO₂ reduction using only visible light as the energy source and water as the reductant. Drastic improvement of dye-sensitized molecular photocathodes is reported.

The results presented in this Account clearly indicate that we can construct very efficient, selective, and durable photocatalytic systems constructed with the metal-complex photosensitizers and catalysts. The supramolecular-photocatalyst architecture in which the photosensitizer and the catalyst are connected to each other is useful especially on the surface of solid owing to rapid electron transfer from the photosensitizer to the catalyst. On basis of these findings, we successfully constructed hybrid systems of the supramolecular photocatalysts with photoactive solid materials. These hybridizations can add new functions to the metal-complex photocatalytic systems, such as water oxidation and light harvesting.

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### INTRODUCTION

Photoelectron transfer has been extensively studied in various research fields. For example, the Marcus theory provides concrete kinetic and thermodynamic information, and in redox photosensitized reactions (also known as photoredox catalytic reactions), photoelectron transfer is initiated by an excited photosensitizer. In these photochemical reactions, in principle, one-time excitation of a molecule causes a single one-electron transfer.

In CO₂ reduction, however, multielectron reduction, typically two-electron, is required because one-electron CO₂ reduction is a highly endothermic reaction (eq 1) and two-electron reduction coupled with chemical reactions with protons (eqs 2 and 3 at pH 7) or another CO₂ molecule (eq 4) can drastically reduce the endothermicity of CO₂ reduction. For this reason, two-component systems are generally used, comprising a redox photosensitizer that initiates photochemical one-electron transfer from an electron donor to a catalyst, and the catalyst that obtains multiple electrons, reacts with CO₂, and releases reduction products. Transition metal complexes have various advantages, both as redox photosensitizers and catalysts for CO₂ reduction. For example, visible-colored and emissive metal complexes, such as [Ru(N'N)₂]²⁺, [Os(N'N)₂]³⁺, [Re(N'N)(CO)₂(PR₃)₂]⁺, and [Ir(ppy)₂(N’N)]⁺ (N’N = dimine ligand; ppy = 2-phenylpyridinato-C₂N ligand) have been reported as photosensitizers, and their colors can be systematically changed by changing the ligands. Their excited states have sufficiently long lifetimes for photoelectron transfer with the electron donor owing to rapid intersystem crossing to the lowest triplet excited state. In terms of the catalyst, ligands, such as N’N, can function as a stable electron pool in the reduced metal complex, and the metal ion can fix CO₂ onto itself, which results in low overpotential and high selectivity for CO₂ reduction against hydrogen evolution. In typical photocatalytic CO₂ reduction systems, Tanaka and Ishida et al. employed [Ru(bpy)₂]³⁺ (bpy = 2,2’-bipyridine), which is the frequently used photosensitizer, and [Ru(bpy)₂(CO)₂]¹⁺ or Ru(bpy)₂(CO)₂Cl₂ as the catalyst. Visible light irradiation of a mixed system of [Ru(bpy)₂]³⁺ and one of these catalysts in the presence of an electron donor resulted in CO₂ reduction to HCOOH or CO. Lehr and Ziesseg et al. reported that fac-Re(bpy)(CO)ₓ X (X = Cl, Br) functions as a “single-handed” photocatalyst for CO₂ reduction selectively to CO when triethanolamine (TEOA) was used as an electron donor. Recently, however, we established that the fac-Re(bpy)(CO)ₓBr complex is largely transformed to a carbonic-acid-ester complex in the initial stage of the photocatalytic reaction (eq 5). Therefore, a mixed system comprising the carbonic-acid–ester complex functioning as a catalyst and the

\[
\begin{align*}
\text{CO}_2 + e^- & \rightarrow \text{CO}_2^+ \quad (1) \\
\text{CO}_2 + 2\text{H}^+ + 2e^- & \rightarrow \text{HCOOH} \quad (2) \\
\text{CO}_2 + 2\text{H}^+ + 2e^- & \rightarrow \text{CO} + \text{H}_2\text{O} \quad (3) \\
2\text{CO}_2 + 2e^- & \rightarrow \text{CO} + \text{CO}_2^+ \quad (4) \\
\end{align*}
\]

E'/V vs. NHE

- 1.9
- 0.61
- 0.53
- 0.64
remaining \( \text{fac-Re(bpy)}(\text{CO})_3\text{Br} \) operating as a photosensitizer is largely responsible for CO formation. In fact, a mixed system of \([\text{Ru(bpy)}_3]^2+\) and \(\text{fac-Re(bpy)}(\text{CO})_3\text{Cl} \) exhibited superior photocatalytic activity than \(\text{fac-Re(bpy)}(\text{CO})_3\text{Cl} \) alone.

Although photocatalytic systems based solely on metal complexes can attain high selectivities and low overpotentials for \(\text{CO}_2 \) reduction as described above, they lack several functionalities important for practical use, such as water oxidation capabilities for supplying electrons, and light-harvesting capacities. In this Account, we discuss our results on four interconnected research topics for photocatalytic \(\text{CO}_2 \) reduction: (1) efficient photocatalysis using mixed systems comprising photosensitizer and catalyst complexes; (2) constructing efficient supramolecular photocatalysts consisting of both the photosensitizer and catalyst complexes in one molecule; (3) imparting the photocatalyst with light-harvesting properties; and (4) photocatalytic reduction of \(\text{CO}_2 \) using water as a reductant and visible light as energy. Transition metal complexes play the central role in all of the above topics.

### PHOTOSENSITIZER/CATALYST MIXED SYSTEMS

To improve \(\text{CO}_2 \)-reduction photocatalysis by metal-complex systems in homogeneous solutions, three important objectives should be fulfilled: (1) the development of a photosensitizer that absorbs a wide range of visible light well, is highly oxidative in the excited state, highly reductive in the reduced state, and stable in both the excited and reduced states; (2) the development of a catalyst capable of rapid \(\text{CO}_2 \) reduction with a low overpotential, weak absorption of visible light, and is stable during the photocatalytic reaction; and (3) rapid electron transfer from the reduced photosensitizer to the catalyst. We have successfully developed highly efficient mixed photocatalytic systems by improving the photosensitizer and catalyst properties as described below.

Some ring-shaped \(\text{Re(I)} \) multinuclear complexes (\text{Re-rings}) display fascinating photosensitizing properties.\textsuperscript{15–17} For example, \textbf{Re-ring-1} can absorb visible light to give a triplet metal-to-ligand charge-transfer (3MLCT) excited state having a long lifetime (\( \tau = 5.4 \mu \text{s} \)) and high oxidation capacity (Figure 1).\textsuperscript{18}

\textbf{Re-ring-1} can accept three electrons in one molecule, and the reduced state is highly stable in solution, even at room temperature (eq 6). The one-electron reduced state (OERS) of \textbf{Re-ring-1} is highly reductive (\( E_{1/2} = -1.87 \text{ V vs Ag/AgNO}_3 \)).\textsuperscript{18}

We found that \(\text{fac-}[\text{Re(bpy)}(\text{CO})_3(\text{OC}_2\text{H}_4\text{N}(\text{C}_2\text{H}_4\text{OH})_2)] \) can capture \(\text{CO}_2 \) to be converted into a carbonic-acid-ester complex (\textbf{Re-CO}_2\text{-TEOA} in eq 7).\textsuperscript{14,19} Although this \(\text{CO}_2 \) insertion into the Re–O bond is an equilibrium reaction, the equilibrium constant is very large (\( K = 1.7 \times 10^3 \text{ M}^{-1} \)); in other words, this reaction supplies \(\text{CO}_2 \) to the metal-complex catalyst before the photocatalytic reaction commences. This \(\text{CO}_2 \) capturing reaction enables direct reduction of low concentrations of \(\text{CO}_2 \), such as 1%, in electrocatalytic\textsuperscript{19} and photocatalytic reactions.\textsuperscript{20}

A mixed photocatalytic system of \textbf{Re-ring-1} and \textbf{Re-CO}_2\text{-TEOA} selectively reduced \(\text{CO}_2 \) to \(\text{CO} \) with the highest quantum yield (\( \Phi_{\text{CO}} = 82\% \)) among the reported systems (eq 8).\textsuperscript{15}

Herein, we used the formal definition of the quantum yield, that is, the product amount divided by the number of absorbed photons (eq 9). The turnover number (the product amount divided by the number of the photosensitizer or catalyst, TON) of produced CO was 526.

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\( \Phi_{\text{CO}} = 82\% \)

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**Figure 1.** UV–vis absorption, emission, and structure of \textbf{Re-ring-1}.
Photocatalytic systems using only earth-abundant elements have recently been increasingly investigated for photocatalytic CO₂ reduction.²¹ Because the lack of efficient rare-or noble-metal-free photosensitizers was a significant concern, we developed new binuclear Cu(I) complexes with excellent photosensitizing capabilities, in which two quadridentate ligands are complexed with two Cu(I) ions (Cu₂Xph in Chart 1).²²

Although mononuclear Cu(I) complexes having both diimine and bisphosphine ligands have been reported as photosensitizers,²³ they are unstable in polar solvents even at room temperature owing to ligand detachment. However, Cu₂Xph is highly stable under the same conditions, and the excited state and OERS of Cu₂Xph are also stable with long lifetimes (several microseconds in acetonitrile at 25 °C). A mixed system comprising Cu₂Hph with fac-Mn(MeO-bpy)(CO)₃Br¹ or Fe(phen)₂(SCN)₂ as catalysts efficiently photocatalyzed CO₂ reduction, as shown in Figure 2. The analogues bearing CF₃ or Ph groups as X in Cu₂Xph (Chart 1) were more efficient photosensitizers than Cu₂Hph because of stronger oxidation power in the excited state or stronger absorption in visible region.²⁴

The heavy metal effect of Os increases the probability of direct excitation to the triplet excited state (S-T absorption), which is ordinarily a forbidden transition. We applied this phenomenon to create a panchromatic photosensitizer, Os(L)(L’) capable of utilizing the entire visible light range (Figure 3).²⁶ Irradiation of a N,N-dimethylacetamide (DMA) solution containing Os(L)-(L’), Ru(bpy)(CO)₂Cl₂ as a catalyst, and 1,3-dimethyl-2-(o-hydroxyphenyl)-2,3-dihydro-1H-benzo[d]imidazole (BI(OH)-H) as a sacrificial electron donor, induced photocatalytic CO₂ reduction to HCOOH, even at λₑₓ > 770 nm.

### SUPRAMOLECULAR PHOTOCATALYSTS

In the mixed systems of a photosensitizer and catalyst, the electron transfer from the OERS of the photosensitizer to the catalyst is limited by diffusion collisions between them. To accelerate electron transfer and improve photocatalytic activity, multinuclear metal complexes consisting of photosensitizer and catalyst have been developed;²⁷ these are referred to as “supramolecular photocatalysts.”²⁸ In 2005, we reported the successful supramolecular photocatalysts for CO₂ reduction for the first time.²⁹ The supramolecular photocatalysts comprising [Ru(N’N)₃]₂⁺-type photosensitizer and fac-Re(N’N)(CO)₃CI-type catalyst units achieved both TONs ≫ 1 and better photocatalytic activities than a mixed system of the corresponding mononuclear complexes.

Chart 2 shows the structures and abbreviations of the Ru(II)−Re(I) multinuclear complexes, and Table 1 summarizes their photocatalytic performances.

### Table 1. Photocatalytic Performances of Ru(II)−Re(I) Complexes

| entry | photocatalyst | ΦCO | TONCO |
|-------|---------------|-----|-------|
| 1     | Ru−Re1       | 0.12| 170   |
| 2     | [Ru(dmb)₃]²⁺ + fac-Re(dmb)(CO)Cl | 0.062| 101   |
| 3     | Ru−Re2       | 0.062|       |
| 4     | Ru−Re3       | 3   |       |
| 5     | Ru−Re4       | 28  |       |

³⁵CO₂-saturated DMF−TEOA (5:1 v/v) solutions containing the complex and BNAH (0.1 M) were irradiated at λₑₓ > 500 nm. dmb = 4,4’-dimethyl-2,2’-bipyridine.
photocatalytic activities. Ru–Re1, in which the [Ru(N(N)N)]2+ photosensitizer unit and the fac-Re(N(N)N)(CO)3Cl catalyst unit are bridged by an alkyl chain between two N=N moieties, photocatalytically reduced CO2 selectively to CO in the presence of a sacrificial electron donor, 1-benzyl-1,4-dihydronicotinamide (BNAH), under visible-light irradiation ($\lambda_{\text{ex}} > 500$ nm). CO produced with a high quantum yield ($\Phi$) and the system was highly durable (entry 1 in Table 1: $\Phi_{\text{CO}} = 0.12$, TON$_{\text{CO}} = 170$), being superior to the mixed system of [Ru(dmb)]$_2^{2+}$ and fac-Re(dmb)(CO)$_3$Cl (entry 2: $\Phi_{\text{CO}} = 0.062$, TON$_{\text{CO}} = 101$). The reaction mechanism of photocatalytic CO$_2$ reduction using Ru–Re1 was partially clarified as follows. [Process 1] Selective photon absorption by the Ru(II) photosensitizer unit forms the 3MLCT excited state, which then follows. [Process 2] The 3MLCT excited Ru unit is reduced by BNAH, producing the OERS. [Process 3] The unpaired electron on the Ru unit transfers intramolecularly to the Re(I) unit. [Process 4] CO$_2$ is reduced to CO on the Re unit via a second one-electron reduction (Figure 4).

The peripheral ligands of the Ru(II) unit and the bridging ligand strongly affected the photocatalytic activity. Ru–Re2 (entry 3: TON$_{\text{CO}} = 50$) and Ru–Re3 (entry 4: TON$_{\text{CO}} = 3$) with 2,2′-bipyridine or 4,4′-bis(trifluoromethyl)-2,2′-bipyridine as peripheral ligands exhibited significantly lower photocatalytic activities than Ru–Re1. This was because of slow intramolecular electron transfer [process 3] in the cases of the OERS of Ru–Re2 and Ru–Re3, whereby the unpaired electron localizes predominantly on the peripheral ligands of the Ru unit rather than the bridging ligands, and the intramolecular electron transfer becomes endergonic: in the case of Ru–Re3, for example, $E_{1/2}^{\text{red}}(\text{Ru}^{II}) = -1.23 \text{ V}$ while $E_{1/2}^{\text{red}}(\text{Re}^{0/1}) = -1.76 \text{ V}$ vs Ag/AgNO$_3$. On the other hand, both the Ru and Re units of Ru–Re1 are reduced by one electron at an almost equal potential ($E_{1/2}^{\text{red}} = -1.77 \text{ V}$), and intramolecular electron transfer proceeds readily. This intramolecular electron transfer process will be discussed in detail later.

Ru–Re4 exhibited a low photocatalytic activity (entry 5: TON$_{\text{CO}} = 28$), even though the intramolecular electron transfer from the one-electron reduced Ru unit to the Re unit should proceed rapidly as it is highly exothermic. The reason is that the conjugation of the bridging ligand lowers the reducing power of the OERS of the Re catalyst unit ($E_{1/2}^{\text{red}} = -1.10 \text{ V}$), which inhibits CO$_2$ activation on the Re unit. We noted a strong relationship between the photocatalytic performances of mononuclear Re(I) complexes, namely, fac-[Re(4,4′-X$_2$-bpy)- (CO)$_3$(PR$_3$)]$^+$, and their first reduction potentials (Table 2): overall, the Re(I) complexes should have a more negative reduction potential than $E_{1/2}^{\text{red}} = -1.4 \text{ V}$ to function as effective catalysts for the reduction of CO$_2$.

### Table 2. Photocatalytic Performances of fac-[Re(4,4′-X$_2$-bpy)(CO)$_3$(PR$_3$)]$^+$ Complexes and Their First Reduction Potentials

| X   | R      | $\Phi_{\text{CO}}$ | TON$_{\text{CO}}$ | $E_{1/2}^{\text{red}}/\text{V}$ |
|-----|--------|---------------------|-------------------|----------------------------------|
| Me  | OEt    | 0.18                | 4.1               | -1.55                            |
| H   | OPr    | 0.20                | 6.2               | -1.44                            |
| H   | OEt    | 0.16                | 5.9               | -1.43                            |
| H   | OMe    | 0.17                | 5.5               | -1.41                            |
| H   | Et     | 0.024               | 0.83              | -1.39                            |
| H   | Bu     | 0.013               | 0.65              | -1.39                            |
| CF$_3$ | OEt | 0.005               | 0.10              | -1.03                            |

A DMF-TEOA (5:1 v/v, 4 mL) solution of the complex (2.6 mM) was irradiated at 365 nm under CO$_2$ atmosphere. Redox potentials measured in MeCN containing 0.1 M Bu$_4$NClO$_4$ using Ag/AgNO$_3$ (10 mM) as a reference electrode. Although there should be a ground state (Ru–Re in Figure 5) and two intermediates ($^{7}$Ru$^{0/1}$–Re and Ru$^{*}$–Re$^{0/1}$) in solution after irradiation in the presence of an electron donor before the intramolecular electron transfer proceeds, they should have similar $\nu_{\text{CO}}$ values owing to the alkyl chain separating the excited or reduced Ru unit from the Re unit. Only the product of intramolecular electron transfer (Ru–Re$^{*}$) shows lower-energy shifts of its $\nu_{\text{CO}}$ bands owing to reinforcement by $\pi$-back-donation from the Re center. Figure 5 shows the FT-IR spectrum of Ru–C2–Re, which has an ethylene chain connecting the Ru and Re units, and the TR-IR
spectra obtained after selective excitation of the Ru photosensitizer unit in the presence of BIH as a sacrificial electron donor. We can calculate the rate constant of the intramolecular electron transfer at $k_e = 7.1 \times 10^8 \text{s}^{-1}$ using increments in the $\nu_{\text{CO}}$ bands at 1872 and 1934 cm$^{-1}$. It is noteworthy that this electron transfer is sufficiently rapid not to be the rate-limiting process in the photocatalytic reaction.

When a longer alkyl chain was used in the bridging ligand (Ru−C$n$−Re, $n = 2, 4, 6$ in Figure 6), the electron transfer rate $k_e$ was lower, as shown in Figure 6, and a linear relationship was observed between the logarithm of $k_e$ and the distance between Ru and Re with an apparent decay coefficient factor ($\beta$) of 0.74 Å$^{-1}$. In addition, Ru−C2−Re, in which two ethylene chains connect the Ru and Re units, induced significantly faster intramolecular electron transfer than Ru−C2−Re bearing one ethylene chain. These results indicate that the intramolecular electron transfer from the OERS of the Ru unit to the Re unit proceeds via the through-bond mechanism.

From the results described above, the molecular architecture necessary to construct effective supramolecular photocatalysts can be obtained: [Rule 1] The photosensitizer unit must have equal to or more negative reduction potential than the catalyst unit to promote intramolecular electron transfer from the reduced photosensitizer unit to the catalyst unit. [Rule 2] The bridging ligand should not be conjugated to maintain the reducing power of the Ru(II) unit.

The advantage of supramolecular photocatalysts over the mixed systems consisting of mononuclear complexes is more pronounced when the metal complexes are fixed on a solid surface. When the mononuclear complexes of a photosensitizer and catalyst are fixed on a solid surface, the electron transfer from the photosensitizer to the catalyst should become more rapid compared to the free solution state. To fix the supramolecular photocatalysts on the solid, phosphonic acid anchoring groups were introduced at the peripheral ligands of the Ru(II) photosensitizing unit and a bridging ligand with a $-\text{CH}_{2}-$ chain, the supramolecular photocatalysts involving the Ru(II) carbonyl complexes as a catalyst unit instead of the Re(I) catalyst were developed (Chart 3).33,34

**Figure 6.** Relationship between the intramolecular electron transfer rate constant ($k_e$) and the distance between Ru and Re.

**Chart 3.** Ru(II)−Ru(II) and Os(II)−Re(I) Complexes

$cis$-[Ru($N^\infty$N)$_2$(CO)$_2$]$^{2+}$35,36 and $cis, trans$-Ru($N^\infty$N)-(CO)$_2$Cl$_2$36 are well-known electrochemical catalysts for the reduction of CO$_2$ to HCOOH with high selectivity under basic conditions. $\text{Ru−Ru1}$ with a [$\text{Ru}(N^\infty N)(\text{dmb})(\text{CO})_2]^2^+\text{unit}$ photocatalyzed CO$_2$ reduction to HCOOH with high selectivity and durability in the presence of BNAH under visible-light irradiation ($\Phi_{\text{HCOOH}} = 0.038$, TON$_{\text{HCOOH}} = 315$, selectivity = 90%).33,37 $\text{Ru−Ru2}$ with a $cis, trans$-$\text{Ru}(N^\infty N)(\text{CO})_2\text{Cl}_2$ unit also functioned as a similarly active photocatalyst to reduce CO$_2$ to HCOOH.34

The photosensitizer unit was changed from the Ru complex to the corresponding $[\text{Os}(N^\infty N)_{2}(\text{BL})]^{3+}$-type complex. This complex (Os−Re, Chart 3) photocatalyzed CO$_2$ reduction under irradiation even at $\lambda_{\text{ex}} > 620$ nm, whereas the supramolecular photocatalysts containing the Ru photosensitizer unit do not absorb light at this wavelength and therefore did not induce CO$_2$ reduction under the same conditions.38

To impart additional functions to photocatalytic systems consisting of metal complexes, hybrid systems comprising photocatalysts and photofunctional solid materials such as semiconductor photocatalysts are good candidates. To fix the supramolecular photocatalysts on the solid surface, phosphonic acid anchoring groups were introduced at the peripheral ligands of the Ru(II) photosensitizing unit and a bridging ligand with a $-\text{CH}_{2}-$ chain, the supramolecular photocatalysts involving the Ru(II) carbonyl complexes as a catalyst unit instead of the Re(I) catalyst were developed (Chart 3).33,34

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extremely slow or not occur at all depending on the distance between these complexes (Figure 7b). In the case of a supramolecular photocatalyst, on the other hand, this electron transfer occurs intramolecularly and should therefore be faster (Figure 7a).

In fact, PRu-Re and the corresponding mononuclear complexes bearing anchoring groups were fixed on insulator Al₂O₃ particles, and their photocatalytic performances were compared using BNAH as a sacrificial electron donor. The Al₂O₃/PRu-Re composite photocatalyzed CO₂ reduction to CO effectively even when the average distance between the supramolecular photocatalysts was considerably longer (6.3 nm) than the size of PRu-Re (maximum length = 2.4 nm). In contrast, in the case of Ru(II) and Re(I) mononuclear complexes, significantly less CO was produced at a comparable absorption density on Al₂O₃. Therefore, we decided to use a supramolecular photocatalyst for fabricating hybrid photocatalytic systems, as described below.

**HYBRID PHOTOCATALYSTS WITH LIGHT-HARVESTING FUNCTIONALITY**

Because the intensity of solar light is low and the absorption cross sections of molecular photosensitizers are small, introduction of light-harvesting capabilities is important for molecular photocatalytic systems.

We successfully combined a supramolecular photocatalyst with periodic mesoporous organosilica (PMO), in which abundant organic molecules (R) are embedded in the silica framework as light harvesters (Figure 8a). Methyl acridone groups (ACR), which are capable of absorbing visible light, were used as the organic molecules in the PMO framework. The silica moiety interacts strongly with the phosphonic acid groups of PRu-Re (Chart 4, left) and confines PRu-Re mainly inside the mesopores, generating a hybrid (Figure 8b). The photons absorbed by approximately 40 ACR groups were transferred to a Ru(II) photosensitizer unit of one PRu-Re molecule in this hybrid, and then the photocatalytic reduction of CO₂ commenced. This light-harvesting function of the PMO hybrid enhanced the photocatalytic formation rate of CO by a factor of 10 compared to that of PRu-Re-adsorbed mesoporous silica without a light harvester. In the photocatalytic reaction using BIH as the electron donor, the TONCO was >600.

**HYBRID PHOTOCATALYTIC SYSTEMS USING WATER AS A REDUCTANT**

In terms of practical photocatalytic CO₂ reduction, water is an ideal electron donor because of its abundance, low cost, and harmlessness. However, the low photooxidation power of metal-complex photosensitizers and the requirement of four-electron oxidation of two molecules of water lead difficulty in use of water in photocatalytic systems consisting of only metal complexes. To address these problems, we developed hybrid photocatalytic systems combining metal-complex photocatalysts with semiconductor photocatalysts that display high photooxidation powers, in which two photons are sequentially absorbed by the metal-complex photosensitizer and the semiconductor to obtain both high reduction and oxidation power. The photocatalytic units for the CO₂ reduction and water oxidation were designed as photocathode and photoanode, respectively (Figure 9). The desired direction of photoelectron transfer from the semiconductor to the metal complex can be achieved by the appropriate coupling of these two photoelectrodes. In addition, the cell allows for separate product generation while avoiding reverse reactions.

**Figure 7.** Conceptual images of a (a) supramolecular photocatalyst and (b) mixed system of mononuclear complexes on the surface of heterogeneous materials. PS and Cat represent photosensitizer and catalyst, respectively.

**Figure 8.** (a) Conceptual structure of PMO. (b) PRu-Re confined inside the mesopores of PMO with ACR, and photocatalytic CO₂ reduction by this hybrid capable of light harvesting.
We developed a dye-sensitized molecular photocathode comprising PRu-Re (Chart 4, left) coupled with the p-type semiconductor NiO electrode.40,41 The MLCT excited state of the Ru photosensitizer unit of PRu-Re adsorbed on the electrode can obtain an electron from the valence band of NiO, instead of the ordinal sacrificial electron donor, to drive CO2 reduction. The electron flow through this NiO/PRu-Re photocathode corresponds to the cathodic photocurrent, and PRu-Re produces CO as the photocatalytic reduction product of CO2 under irradiation at λ > 460 nm and with appropriate external bias both in an organic solvent (DMF–TEOA (5:1, v/v)),40 as well as in aqueous solution41 with high selectivity (∼100% and 91%, respectively). Here, the downward band bending at the solid–liquid interface of the p-type semiconductor is beneficial for the reductive quenching of the excited photosensitizer unit and subsequent charge separation. These results revealed that the PRu-Re photocatalyst can function as the CO2 reduction side of the hybrid photoelectrochemical system.

We next combined the NiO/PRu-Re photocathode and an n-type semiconductor TaON photoanode for water oxidation to construct a full photoelectrochemical cell. TaON absorbs visible light (λ < 500 nm) and CoOx cocatalyst was loaded onto it to improve the activity and stability for water oxidation.42 Under irradiation at λ > 400 nm for both electrodes in an aqueous solution, the photoelectrochemical cell produced CO and O2 from the photocathode and photoanode, respectively. The TONCO based on the PRu-Re adsorbed on the electrode was 17. In this system, electrical and chemical biases (totally 0.4 V) were required to progress the photocatalytic reaction. The light-to-energy conversion efficiency of the reaction was 1.6 × 10−3%.

The applicability of the hybrid cell was demonstrated by replacing the photoanode material with a Ta/N-codoped TiO2.43 This cell also required an external bias of 0.5 V between the two photoelectrodes and provided a conversion efficiency of 1.1 × 10−3% with considering the bias applied.

These hybrid photoelectrochemical cells suffer several drawbacks. First, an external applied bias is necessary to drive the photocatalytic reaction, owing to the energy loss during electron transfer, even though potential of photoexcited electrons in the semiconductor photoanode is sufficiently negative to transfer an electron to the excited Ru photosensitizer unit in PRu-Re. Therefore, we replaced NiO with another p-type semiconductor, CuGaO2 of which flat band potential is 0.16 V more positive than that of NiO.44 The onset potential of the cathodic photocurrent of the photocathode comprising CuGaO2 (CuGaO2/PRu-Re) shifted 0.4 V more positive from that of NiO/PRu-Re (Figure 10). This large positive shift arises from reduced energy loss in the electron transfer process from the valence band of the p-type semiconductor electrode to the excited Ru photosensitizer unit. Owing to the improved photocathode, the hybrid photoelectrochemical cell consisting of the CuGaO2/PRu-Re photocathode and the CoOx/TaON photoanode achieved photocatalytic reduction of CO2 and water oxidation without the application of an external bias (Figure 10c). The products were CO (232 nmol, TONCO = 22) and H2 (311 nmol) at the photocathode site and O2 (232 nmol) at the photoanode site. This is the first self-driven photoelectrochemical cell constructed using a metal complex photocatalyst that achieves CO2 reduction using only visible light as the energy source and water as the reductant.

Another problem with the dye-sensitized molecular photocathodes with metal complex photocatalyst described above is their low efficiency and stability. The external quantum efficiency (termed the incident-photon-to-current efficiency, IPCE) was very low. In addition, the photocurrent decayed rapidly within several hours of irradiation. One of the main reasons for this is inadequate adsorption of the metal complex photocatalyst onto the electrode surface; the PRu-Re molecules are adsorbed only via hydrogen bonding involving the phosphonic acid groups to form a unimolecular layer on the surface of the p-type semiconductors. Therefore, the amount of adsorbed PRu-Re was only ∼4 nmol cm−2, which limits light absorption and in turn the activity of the photocathodes. In addition, the phosphonate-acid anchor groups were weakly adsorbed, thus, PRu-Re gradually detached and the photocathode activity decayed. We adopted electrochemical polymerization to reinforce the attachment of a larger amount of the...
supramolecular photocatalyst onto the electrode surface. We used two types of metal complexes bearing vinyl groups on the bipyridine ligands of the Ru(II) photosensitizer unit, that is, a mononuclear Ru(II) diimine-type photosensitizer (PRuV) and a Ru(II)−Re(I) supramolecular photocatalyst (RuReV, middle in Scheme 1a). PRuV has another bipyridine ligand bearing methyl phosphonic acid groups for its first attachment to the NiO electrode to form NiO/PRuV (the left side of Scheme 1a). NiO/PRuV was soaked in electrolyte containing RuReV, and then a negative potential was applied to the electrode to give the polyethylene-modified photocathode (NiO/PRu−polyEt−Ru−Re), which contained a larger amount of Ru photosensitizer units (∼10 nmol cm$^{-2}$) than PRu−Re adsorbed only via the methyl phosphonic acid anchor groups, and was more stable against detachment in the aqueous electrolyte. This molecular photocathode NiO/PRu−polyEt−Ru−Re produced approximately 2.5-fold more CO, and its total Faradaic efficiency of the reduction products also enhanced from 57% (NiO/PRu−Re) to 85%. The maximum IPCE was also improved to 0.93% at −0.7 V vs Ag/AgCl under 480 nm irradiation. However, the stability of the NiO/PRu−polyEt−Ru−Re was still unsatisfactory: the Re−C bonds were formed via the side reaction of the vinyl group with the Re center during reductive polymerization and cleaved during the photocatalytic reaction.

To address this issue, a three-step method for constructing dye-sensitized molecular photocathodes was developed (Scheme 1b). In the first step, the NiO/PRuV electrode was synthesized as described above. In the second step, electrochemical polymerization was performed between the adsorbed PRuV and another Ru(II) mononuclear complex bearing diimine ligands with a vinyl group and a noncoordinated diimine moiety (VRu-N=N) to form NiO/PRu-polyEt-Ru−N=N. In the last step, a catalyst complex unit Ru(N=NC)2Cl2 was formed via the reaction of the noncoordinated diimine moiety of NiO/PRu-polyEt-Ru−N=N with [Ru(CO)2Cl2]n. The produced photocathode (NiO/PRu-polyEt-Ru-RuCAT) was highly stable: photoelectrochemical CO$_2$ reduction proceeded for over 100 h under visible light, affording CO and HCOOH without noticeable degradation (Figure 11, reproduced from ref 46 with permission. Copyright 2021 Royal Society of Chemistry).
Although the reductive polymerization approach using vinyl groups is highly effective for improving both the efficiency and stability of the dye-sensitized molecular photocathode, the saturated hydrocarbon chain formed by the vinyl polymerization possibly causes low conductivity in the polymer layer, which limits the improvement of its photocatalysis. Therefore, we...

**Scheme 2. Preparation of NiO/PRu-polyPyr-Ru-RuCAT**

**Figure 12.** (a) Current–potential curves of NiO/PRu-PolyPyr-Ru-RuCAT under irradiation at $\lambda_{\text{ex}} = 460–650$ nm (28.2 mW cm$^{-2}$) in CO$_2$-purged 50 mM aqueous NaHCO$_3$. (b) Dependence of the IPCE of NiO/PRu-PolyPyr-Ru-RuCAT by the irradiated wavelength at $-0.3$ V vs Ag/AgCl with absorption spectrum of NiO/PRu-PolyPyr-Ru-RuCAT subtracted with the absorbance of the NiO electrode (red line).

**Figure 13.** (a) Photoelectrochemical cell comprising the NiO/PRu-polyPyr-Ru-RuCAT photocathode and the CoO$_x$/BiVO$_4$ photoanode. (b) Tandem-type configuration in a single compartment cell irradiated by simulated sunlight (AM1.5G, 100 mW cm$^{-2}$).

Although the reductive polymerization approach using vinyl groups is highly effective for improving both the efficiency and stability of the dye-sensitized molecular photocathode, the
developed another dye-sensitized molecular photocathode produced by oxidative polymerization of pyrrole groups to afford a polypyrrole phase containing the metal complexes. The synthesis method of this photoelectrode (NiO/PRu-polypyr-Ru-RuCAT) is similar to that of NiO/PRu-polypolymer-Pyr-Ru-RuCAT, except for the use of Ru(II) complexes containing pyrrole groups (PRuPyr and PyrRu-N`N` in Scheme 2) instead of PRuV and VRu-N`N`, and the application of the potential scan in the positive instead of the negative direction. The produced NiO/PRu-polypyr-Ru-RuCAT contained both the photosensitizer and catalyst units in a ratio of ~3:1, and the photocurrent reached a maximum at $E_{app} = -0.1$ V vs Ag/AgCl (Figure 12a), whereas in the case of NiO/PRu-polypolymer-Ru-RuCAT, an $E_{app}$ of $-0.5$ V was required. This suggests an improvement in the conductivity of the polymer phase in the NiO/PRu-polypolymer-Ru-RuCAT photoelectrode. The maximum IPCE was 4.7% (Figure 12b), which is the highest value reported for dye-sensitized molecular photocathodes. Visible light irradiation of NiO/PRu-polypolymer-Ru-RuCAT at $E_{app} = -0.7$ V induced continuous photocatalytic CO2 reduction for 24 h to produce CO and HCOOH with a small amount of H2 (selectivity for CO2 reduction was 92%) in CO2-purged 50 mM aqueous NaHCO3 solution. The TONs for CO and HCOOH were 566 and 185, respectively, after 24 h of irradiation. A full photoelectrochemical cell comprising this photocathode and the CoO2/BiVO4 photoanode induced simultaneous photocatalytic CO2 reduction and water oxidation in the respective photoelectrodes (Figure 13a). For the same setup described in Figure 10c, the light energy conversion efficiency was 0.083% with Faraday efficiencies of 99% (photocathode) and 87% (photoanode). Another full cell in tandem configuration, wherein the photocathode was illuminated first and the photoanode absorbed the permeated light in the same compartment cell (Figure 13b), exhibited a solar-to-chemical conversion efficiency of 0.048% under simulated sunlight (AM1.5G). This state-of-the-art achievement suggests the possibility of solar energy conversion to useful chemicals with the use of a supramolecular photocatalyst as the photocatalytic center for CO2 reduction. There are still many opportunities for improving the photocatalytic efficiency of full cells comprising dye-sensitized molecular photocathodes, such as strengthening the absorption of the photosensitizer units, especially at longer wavelengths, and enhancing the conductivities in p-type semiconductors and polymers, as well as between them.

CONCLUSIONS AND PERSPECTIVES

The results presented in this account clearly indicate that we can construct very efficient, selective, and durable photocatalytic systems consisting of metal-complex photosensitizers and catalysts according to the “rules”. The supramolecular-photocatalyst architecture in which the photosensitizer and the catalyst are connected to each other is useful especially on the solid surface owing to rapid electron transfer between the photosensitizer and the catalyst. Based on these findings, we successfully constructed hybrid systems of the supramolecular photocatalysts with photoactive solid materials such as the mesoporous organosilica and the semiconductors. These hybridizations can add new functions, that is, light harvesting and water oxidation to the metal-complex photocatalytic systems. For developing practical systems of photocatalytic CO2 reduction, we have to add many functions to the systems as summarized in Figure 14. Although our approaches achieved to combine some of these functions, we have to add all of them in one system. Many additional efforts and new ideas should be directed to building “artificial photosynthesis” for CO2 utilization.

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