A Visible-Light Harvesting System for CO₂ Reduction Using a Ru-II–Re-I Photocatalyst Adsorbed in Mesoporous Organosilica

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A photocatalytic system for CO₂ reduction exhibiting visible-light harvesting was developed by preparing a hybrid consisting of a supramolecular metal complex as photocatalyst and periodic mesoporous organosilica (PMO) as light harvester. A Ru-II–Re I binuclear complex (Ru–Re) with methylphosphonic acid anchor groups was adsorbed on acridone or methylacridone embedded in the walls of PMO mesochannels to yield the hybrid structure. The embedded organic groups absorbed visible light, and the excitation energy was funneled to the Ru units. The energy accumulation was followed by electron transfer and catalytic reduction of CO₂ to CO on the Re unit. The light harvesting of these hybrids enhanced the photocatalytic CO evolution rate by a factor of up to ten compared with that of Ru–Re adsorbed on mesoporous silica without a light harvester.

The conversion of CO₂ to energy-rich compounds using solar light has recently attracted considerable attention owing to global warming and energy shortage problems. In particular, significant efforts are focused on the development of supramolecular photocatalysts constructed of redox photosensitizer and catalyst units for CO₂ reduction because of their high efficiency, durability, speed, and selectivity to products.[1] However, these photocatalysts require certain additional functionalities.

Specifically, light harvesting (LH) is needed in molecular photocatalysts with a small cross section for absorption because the photon flux of solar light is too low.[2] In natural photosynthesis, typical LH systems consisting of regularly arranged chlorophylls collect sunlight and efficiently transfer the excitation energy to a reaction center that initiates redox reactions. Many artificial LH systems have been developed from porphyrin assemblies,[3d] dendrimers comprising organic chromophores or transition metal complexes,[3b] metal–organic frameworks,[3c] assemblies,[3a] dendrimers comprising organic chromophores or transition metal complexes,[3b] metal–organic frameworks,[3c] and dye/clay hybrids.[3e] However, despite efficient energy accumulation, utilization of harvested photon energy in catalytic reactions has been very rare, especially for CO₂ reduction.

In this study, periodic mesoporous organosilica (PMO)[6] acted as LH material in which numerous acridone groups are embedded in the silica framework as visible-light absorbers[5] and was combined with a supramolecular photocatalyst comprising a Ru-II photosensitizer and Re-I catalyst for CO₂ reduction[1c] (Scheme 1). Various PMO materials have been proven to

![Scheme 1. Schematic representation of PMO and metal complex structures](image)

be effective artificial LH systems.[5,6] However, only one hybrid material incorporating a Re-I complex in biphenyl-embedded PMO mesochannels has served as a CO₂ reduction photocatalyst.[6a] But this material did not harvest visible light because the biphenyl groups absorbed only UV light and the turnover number (TON) of CO₂ reduction to CO was unfortunately very low (TON_CO = 2). In contrast, the new hybrid LH photocatalyst described herein utilizes visible light and accelerates the photocatalytic reduction of CO₂ up to ten times compared with the corresponding molecular photocatalyst. Its TON_CO reached 635, and CO formation was highly selective (> 98%).

LH materials with acridone (Acd–PMO) or methylacridone (MeAcd–PMO) embedded in PMO mesochannels were synthesized using two types of acridone-bridged organosilane precursors...
sors (Scheme 1). The X-ray diffraction (XRD) patterns (Figure S1 in the Supporting Information) and N2 adsorption/desorption isotherms (Figure S2) of the synthesized PMOs showed well-defined mesoporous structures. The mesochannels exhibited pore diameters of 4.6 and 3.7 nm for Acd–PMO and MeAcd–PMO, respectively, exceeding the longest molecular length in the RuRe complex estimated from the van der Waals radii (ca. 2.4 nm) and, thus, providing enough space for encapsulation of metal complexes. Only the hybridization and photophysical properties of Acd–PMO are described in detail below because both materials exhibited similar characteristics (Figure S3).

To facilitate the hybridization of Acd–PMO with the supramolecular photocatalyst, a RuRe complex with a 2,2’-bipyridine ligand bearing methylphosphonic acids as anchor groups (Ru–Re, Scheme 1) was synthesized. The hybrid material (Ru–Re/Acd–PMO) was easily obtained by adding Acd–PMO powder to a Ru–Re solution in MeCN and stirring the dispersion overnight at an ambient temperature. Next, the dispersed powder was collected by filtration and washed with MeCN several times. All dissolved Ru–Re was adsorbed in Acd–PMO when the amount of Ru–Re in the solution was below 70 μmol per gram of Acd–PMO (μmol g-1 is used as the unit for the hybrid materials in the remainder of the manuscript). When the amount of dissolved Ru–Re exceeded this concentration, the adsorbed Ru–Re gradually reached saturation at 95 ± 2 μmol g-1 (Figure S4). No elution of the complex or decomposition of Ru–Re was observed even when the hybrid was dispersed and stirred overnight in the 5:1 N,N-dimethylformamide–triethanolamine (DMF–TEOA, v/v) mixture, which was used as a solvent for CO2 reduction. The XRD pattern of Ru–Re/Acd–PMO (63 μmol g-1) was similar to that of Acd–PMO (Figure S5), suggesting that Acd–PMO retained its original structure upon Ru–Re adsorption. Table 1 summarizes the textural properties of Acd–PMO and Ru–Re/Acd–PMO (63 μmol g-1). Ru–Re/Acd–PMO exhibited slightly 15% smaller pore volume than Acd–PMO. This decrease in pore volume upon Ru–Re adsorption closely agrees with the total volume of adsorbed Ru–Re, which was estimated from molecular volumes of the mononuclear model complexes [Ru(dbm)2(L1)](PF6)2 (11.5 nm3) and [Re(dbm)(CO)3]Br (4.2 nm3) (dbm = 4,4’-dimethyl-2,2’-bipyridine, L1 = 4,4’-bis(methyl-phosphonate)-2,2’-bipyridine), indicating that Ru–Re mostly adsorbed in the mesochannels of Acd–PMO.

The UV/Vis diffuse reflectance spectra of Acd–PMO and Ru–Re/Acd–PMO showed a strong absorption band at around 380 nm, which corresponds to the π–π* transition of the Acd units in Acd–PMO (Figure S6). Ru–Re/Acd–PMO showed an additional absorption band at around 460 nm attributable to the metal-to-ligand charge transfer (MLCT) absorption band of Ru–Re because of its similarity to that of Ru–Re adsorbed in mesoporous silica MCM-41(I) (7), which has mesochannels identical to Acd–PMO (Table 1, Figure S7) without absorbing light above 350 nm. The FTIR spectrum of a KBr pellet of Ru–Re/Acd–PMO showed similar peaks to those of Ru–Re (Figure S8).

Figure 1A shows emission spectra of Acd–PMO and Ru–Re/Acd–PMO dispersions in MeCN for different amounts of adsorbed Ru–Re at an excitation wavelength of 405 nm. Approximately 88% of these excitation photons were absorbed by Acd units, even for the highest amount of adsorbed Ru–Re (93 μmol g-1) (see the Supporting Information). In the absence of Ru–Re, Acd groups showed a maximum emission at 520 nm (Figure S5), which resembled that of Ru–Re/MCM-41(I) upon excitation at 456 nm (Figure S9).

The hybrid materials Ru/MCM-41(I) and Re/MCM-41(I), consisting of Ru or Re mononuclear complexes adsorbed in MCM-41(I) (Scheme 1), were used to determine emission quantum yields for each component (Acd–PMO, Ru, and Re units). Ru/MCM-41(I) displayed an emission band at around 640 nm with a quantum yield of 0.029. An increase in the adsorbed Ru–Re amount quenched the emission of the Acd units and enhanced a new emission band at around 640 nm, which resembled that of Ru–Re/MCM-41(I) upon excitation at 456 nm (Figure S9).

Table 1. Textural Properties of PMO, MCM-41 and their Ru–Re Hybrid Materials.

| Material          | S BET (m2 g-1) | V micropore (cm3 g-1) | d4(002) (nm) | Particle size (µm) |
|-------------------|----------------|-----------------------|--------------|--------------------|
| Acd–PMO           | 947            | 0.80                  | 4.6          | 1.5                |
| Ru–Re/Acd–PMO     | 805            | 0.68                  | 3.5          | –                  |
| MCM-41(I)         | 1028           | 0.89                  | 4.6          | 0.1               |
| Ru–Re/MCM-41(I)   | 755            | 0.62                  | 3.7          | –                  |
| MeAcd–PMO         | 760            | 0.40                  | 3.7          | 0.2                |
| MCM-41(I)         | 897            | 0.64                  | 3.7          | 0.1                |

(a) Brunauer–Emmett–Teller specific surface area. [b] Pore volume calculated from the I plot. [c] Porosity calculated by density functional theory. [d] Adsorbed Ru–Re amounts were 64 and 63 μmol g-1 in Acd–PMO and MCM-41(I), respectively.

Figure 1. (A) Emission spectra of Acd–PMO and Ru–Re/Acd–PMO dispersions in MeCN at various adsorbed Ru–Re amounts. (B) Photocatalytic CO formation using Ru–Re/Acd–PMO (black solid line), Ru–Re/MCM-41(I) (black dotted line), Ru–Re/MeAcd–PMO (red solid line), and Ru–Re/MCM-41(I) (red dotted line).

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and Re/MCM-41(I)). This analysis indicated that the emission maximum detected at 620 nm only resulted from the 3MLCT excited state of the Ru unit and almost no emission originated from the Re unit. Interestingly, the emission from Acd–PMO was largely quenched in Ru/Acd–PMO (80 μmol g⁻¹), but not efficiently quenched in Re/Acd–PMO (80 μmol g⁻¹; Figure S11). These results clearly indicate that the Förster-type energy transfer from Acd–PMO to the Ru unit proceeds with high efficiency but less effectively from Acd–PMO to the Re unit because the spectral overlap is relatively larger between the absorption of the Ru unit and emission of Acd–PMO than between the absorption of the Re unit and emission of Acd–PMO (Figure S12). [8]

Emission lifetimes measured at 500 nm for Acd units in Acd–PMO and Re/Ru–Acd–PMO (Figure S13 and Table S2) also showed that the Ru–Re complex efficiently quenched the excited state of Acd–PMO. A new emissive species was observed at 700 nm, which was attributed to the emission from the Ru unit by comparison with the lifetime of Ru/MCM-41(I) (Table S2).

The quantum yield of emission from the excited Ru unit produced via energy transfer from the Acd unit to the Ru unit (Φ_{hybrid}(Ru)) was calculated using Equation (1).

\[ \Phi_{hybrid}(Ru) = \frac{n_{em}(Ru)}{n_{abs}(Acd)} \]  

(1)

where \( n_{abs}(Acd) \) is the number of photons absorbed by Acd–PMO and \( n_{em}(Ru) \) is the number of photons emitted by the Ru unit through energy transfer from the Acd unit (see the Supporting Information). On the other hand, the direct excitation of the Ru unit in Ru–Re/Acd–PMO at 460 nm resulted in an emission quantum yield (Φ_{Ru,Ru}) of 0.109, as described above. Energy transfer efficiencies (η_{ET}) were obtained for various Ru–Re/Acd–PMO materials at different adsorbed Ru–Re amounts (Figure S14) using Equation (2).

\[ \eta_{ET} = \frac{\Phi_{hybrid}(Ru)}{\Phi_{Ru,Ru}} \]  

(2)

When the ratio between Ru–Re and Acd units increased but remained relatively low (below 2 mol%), η_{ET} increased linearly. For ratios exceeding 2 mol%, η_{ET} reached a saturation point of (80 ± 1)%. At a ratio of 2 mol%, only 10% of the light emitted by the Acd units remained. Two possible mechanisms explain the “missing” excited state of the Acd units (ca. 10%): a trivial energy transfer mechanism and/or another deactivation process induced by Ru–Re adsorption. The trivial mechanism involves a radiation (from the Acd units) + re-absorption (by Ru–Re) process (the emission quantum yield of the Acd units only equalled 0.029).

The number of excited Acd units that potentially transfer excitation energy to one Ru unit (N) was calculated using Equation (3) (Table S1). [6b]

\[ N = \eta_{ET} \times \frac{[Acd]}{[Ru–Re]} \]  

(3)

For example, for \( N = 42 \), photons absorbed by 42 Acd units could be accumulated into one Ru unit at a ratio of 1.9 mol% (64 μmol g⁻¹), which was used for CO₂ reduction.

The photocatalytic performance of Ru–Re/Acd–PMO (63 μmol g⁻¹) for CO₂ reduction was evaluated in 5:1 DMF–TEOA (ν/v) using 1,3-dimethyl-2-phenylbenzimidazoline (BIH, 0.1 m) [8] as a sacrificial reductant by irradiation at 405 nm employing a high-pressure mercury lamp with solution filters comprising 1 % NaNO₂ in H₂O (w/v) and 0.75 % I₂ in CCl₄ (w/v) [Eq. (4)].

\[
\text{CO}_2 + \text{BIH} \rightarrow \text{CO}_2 + \text{H}_2 \quad (4)
\]

The irradiation of a Ru–Re/Acd–PMO dispersion at 405 nm under CO₂ atmosphere caused a catalytic and selective CO formation with a very small amount of H₂ and without HCOOH formation (entry 1 in Table 2). For the initial 3 h irradiation, CO was continuously evolved with a turnover frequency (TOF$_{CO}$) of 109 h⁻¹ and TON$_{CO}$ reached 635 depending on the amount of Ru–Re used after 24 h irradiation. On the other hand, in control experiments using hybrids without Ru–Re (i.e., with Ru or Re instead of Ru–Re), in the dark, or under an Ar atmosphere instead of CO₂, no CO or only small amounts of CO were observed (Table S3). Ru–Re/MeAcd–PMO (54 μmol g⁻¹) also showed a catalytic and selective CO formation with TOF$_{CO}$ and TON$_{CO}$ values of 81 and 294, respectively (entry 3).

To evaluate the effect of LH on the photocatalytic reaction, control experiments were conducted using hybrids combining Ru–Re with mesoporous silica MCM-41(I) and (II), which have mesochannel diameters similar to Acd–PMO and MeAcd–PMO, respectively. MCM-41(I) and (II) did not present any light-harvesting ability as they did not contain any organic light absorber. The Ru–Re/MCM-41(I) (63 μmol g⁻¹) and Ru–Re/MCM-41(II) (57 μmol g⁻¹) dispersions photocatalyzed the CO₂ reduction under the same reaction conditions as the PMO hybrids because the adsorbed Ru–Re in the MCM-41 samples was directly excited by irradiation at 405 nm. However, their activities were much lower than those of the corresponding PMO hybrids (Figure 18), clearly indicating that the LH ability of PMOs enhanced the photocatalytic activity of Ru–Re for CO₂ reduction.

The Ru–Re/Acd–PMO photocatalyst exhibited a threefold larger TOF$_{CO}$ than Ru–Re/MCM-41(I). The TOF$_{CO}$ was tenfold
larger for Ru–Re/MeAcd–PMO than for Ru–Re/MCM-41(II). Considering the ratio between the numbers of photons absorbed by each unit in the hybrids and the energy transfer efficiency from PMO to Ru units, the number of excited Ru units in PMO hybrids is expected to be about tenfold larger than in MCM-41 hybrids (see the Supporting Information). The difference in the photocatalytic activity enhancement between Acd–PMO and MeAcd–PMO should be attributed to the difference in their light scattering at 405 nm. The particle sizes of Acd–PMO were on the microscale, which were larger than those of MeAcd–PMO, MCM-41(I), and MCM-41(II) (Table 1, Figure S15). Under photocatalytic conditions, visible-light scattering resulted in the devitrification of the Ru–Re/Acd–PMO suspension and limited its light absorption (405 nm). On the other hand, Ru–Re/MeAcd–PMO, Ru–Re/MCM-41(I), or Ru–Re/MCM-41(II) suspensions looked almost transparent because their sizes were equal to or less than 0.2 μm (Figure S16). This suggests that both Acd–PMO and MeAcd–PMO exhibited effective LH in photocatalytic reactions and that most photons accumulated by the Acd or MeAcd groups were used for CO₂ reduction.

Another hybrid [(Ru+ Re)/Acd–PMO] combining Acd–PMO with mononuclear Ru and Re complexes (62 μmol g⁻¹ each) was also synthesized, and its photocatalytic activity was investigated under the same reaction conditions. However, its TON₃₅ and selectivity (entry 5) were much lower than for Ru–Re/Acd–PMO (64 μmol g⁻¹, entry 1). This result indicates that the covalent bonding between the Ru and Re units in the supramolecular photocatalyst played a crucial role in the photocatalytic activity of the hybrid material for CO₂ reduction. This bonding may enhance the electron transfer efficiency from the one-electron-reduced Ru unit to the Re unit in the supramolecular system compared with the case where Ru and Re adsorb separately in the Acd–PMO mesochannels.

Although Ru–Re/MeAcd–PMO and Ru–Re/Acd–PMO display exceptionally high activities relative to other photocatalytic systems with LH ability, the potential ability of the supramolecular photocatalyst Ru–Re may not be fully developed in these hybrid systems, as suggested by a previous homogeneous solution system that has achieved higher photocatalytic systems with LH ability, the potential ability of the supramolecular photocatalyst Ru–Re may not be fully developed in these hybrid systems, as suggested by a previous homogeneous solution system that has achieved higher photocatalytic activities relative to other photocatalytic systems with LH ability.

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