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Selective CO_2 Conversion to Formate Conjugated with H_2O Oxidation Utilizing Semiconductor/Complex Hybrid Photocatalysts

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Supporting Information

ABSTRACT: Photoelectrochemical reduction of CO_2 to $HCOO^-$ (formate) over p-type InP/Ru complex polymer hybrid photocatalyst was highly enhanced by introducing an anchoring complex into the polymer. By functionally combining the hybrid photocatalyst with TiO_2 for water oxidation, selective photoreduction of CO_2 to $HCOO^-$ was achieved in aqueous media, in which H_2O was used as both an electron donor and a proton source. The so-called Z-scheme (or two-step photoexcitation) system operated with no external electrical bias. The selectivity for $HCOO^-$ production was >70%, and the conversion efficiency of solar energy to chemical energy was 0.03−0.04%.

Solar-based production of organic chemicals by the reduction of carbon dioxide is an increasingly important area that addresses global warming and fossil fuel shortages. If CO_2 can be reduced using water as both an electron donor and a proton source, such a reaction could lead to artificial photosynthesis for the conversion of H_2O and CO_2 into carbohydrates and oxygen using sunlight. Metal complexes are well-known photocatalysts or electrocatalysts for CO_2 reduction.[1,2] Their quantum efficiencies or current efficiencies and product selectivity are quite high. However, looking at the future prospect of photocatalytic CO_2 reduction with metal complexes, a possible issue would be the choice of an electron donor for photocatalyst in the photoexcited state. Currently, a sacrificial reagent such as triethanolamine is required as an electron donor because there is no metal complex photocatalyst that is able to extract electrons from H_2O with CO_2 reduction.

On the other hand, semiconductors (SCs) are known to have photocatalytic ability for the reduction of CO_2 using H_2O.[3] However, regarding CO_2 reduction in aqueous solutions, they suffer from low quantum efficiencies due to preferential H_2 production and low selectivity for the carbon species produced. The merit of SC photoelectrochemical systems and photocatalysts lies in the fact that they produce H_2 and O_2 by splitting H_2O;[3,4] in other words, SC photocatalysts use H_2O as an electron donor for compensating a hole in a photoexcited state. This is why photocatalytic H_2 production with SC 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. Recently, without splitting H_2O, systems for photoelectrocatalytic CO_2 reduction using combinations of GaP/pyridine and Si/Re complex have been reported to overcome the low selectivity.[5,6]

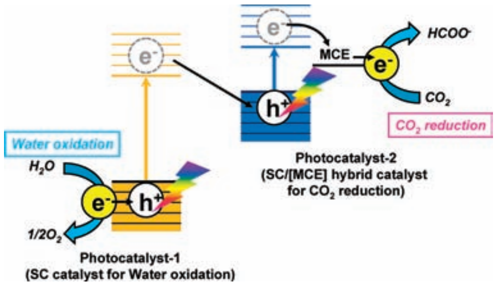

Figure 1. Total reaction of the Z-scheme system for CO_2 reduction.

We considered that by combining photoactive SCs with metal-complex catalysts capable of reducing CO_2, useful organic chemicals could be obtained with high selectivity and activity in aqueous solutions. With such a concept, electron transfer (ET) from the conduction band of a SC in a photoexcited state to a metal-complex catalyst is crucial. Recently, we have developed a hybrid photocatalyst for selective CO_2 reduction to $HCOO^-$ (formate) in H_2O with an electrical bias by modifying a SC surface with a metal-complex electrocatalyst (MCE) such as SC/[MCE] hybrid photocatalyst,[7] which was a combination of a zinc-doped indium phosphide (InP), p-type SC, and a ruthenium complex polymer electrocatalyst, $[Ru\{4,4'\text{-di}(1H\text{-pyrrolyl-3-propyl carbonate})\text{-}2,2'\text{-bipyridine}\}(CO)_2]_n$,[1c] as the MCE. We have already appreciated that a driving force ΔG, the energy difference between the conduction band minimum (E_{CBM}) of the SC and the CO_2 reduction potential of the MCE (E_{red}), is an indispensable factor for facilitating ET from the SC to the MCE.[8] The resulting photocatalytic CO_2 reduction kinetics was also discussed.[8] The SC/[MCE] can reduce CO_2 in H_2O; therefore, it can be expected that this will facilitate the development of a photorecycling system of CO_2 that utilizes H_2O as both an electron donor and a proton source by combining the SC/[MCE] with a photocatalyst capable of H_2O oxidation in aqueous media such as a Z-scheme (or two-step photoexcitation) system (Figure 1), because it is reported that heterogeneous SCs with different band-energy potentials for producing H_2 and O_2 from H_2O are applied to the systems for photocatalytic H_2O splitting.[9] However, we did not detect products of CO_2 reduction when we combined the SC/[MCE] with the H_2O oxidation photocatalysts because the reactivity of SC/[MCE] was not enough to construct the system.

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Table 1. Results of Photoelectrochemical CO_2 Reduction over SC Alone and SC/[MCE]

hybrid photocatalyst			
SC	MCE	$HCOO^-/\mu mol\ cm^{-2}$	EFF/%
N-Ta_2O_5	–	0	0
N-Ta_2O_5	MCE4	0.48	48
N-Ta_2O_5	MCE3-A+MCE4	0.72	63
GaP	–	0	0
GaP	MCE4	0.02	45
GaP	MCE2-A+MCE4	2.48	57
InP	–	0	0
InP	MCE1	1.09	62
InP	MCE2-A	0.81	24
InP	MCE4	2.18	81
InP	MCE2-A+MCE4	4.71	78

In this report, we introduce another Ru complex containing an anchor ligand into MCE with the aim of improving the ET from SC to MCE. As a result, the rate of two-electron reduction of CO_2 over SC/[MCE] is significantly improved by the effective functionalization of the MCE with an anchor ligand. A highly active hybrid SC/[MCE] photocatalyst was obtained, and by conjugating the SC/[MCE] with a SC capable of H_2O oxidation, we achieved the photorecycling of CO_2 in the Z-scheme system, which reduces CO_2 to $HCOO^-$ in an aqueous medium under simulated sunlight with no external electrical bias. The sources of carbon, protons, and electrons for $HCOO^-$ were identified to be CO_2 and H_2O from isotope tracer experiments. These rigorous experiments eliminated any doubt that hydrocarbons detected might originate from contaminations, which raised an alert over the recent cursory research on CO_2 reduction over TiO_2.[10] An electrical-bias-free reaction is essential for future practical applications of solar fuel production. The concept established in this work will facilitate the future development of a more feasible system, because the photocatalytic ability can be further improved by the use and structural control of different combinations of metal-complex catalysts and SCs.

The following Ru complex polymer electrocatalysts were synthesized: [Ru{4,4′-di(1*H*-pyrrolyl-3-propyl carbonate)-2,2′-bipyridine}$(CO)_2Cl_2$] (MCE1), [Ru(4,4′-diphosphate ethyl-2,2′-bipyridine)$(CO)_2Cl_2$] (MCE2-A), [Ru(4,4′-dicarboxylic acid-2,2′-bipyridine)$(CO)_2Cl_2$] (MCE3-A), and [Ru{4,4′-di(1*H*-pyrrolyl-3-propyl carbonate)-2,2′-bipyridine}(CO)(MeCN)Cl_2] (MCE4) (see Scheme S1 in the Supporting Information (SI) for structures of catalysts). MCE2-A and MCE3-A have 4,4′-diphosphate ethyl-2,2′-bipyridine and 4,4′-dicarboxylic acid-2,2′-bipyridine (dcbpy) anchor ligands, respectively, and ET between the SC and MCE-A is expected to be accelerated by these anchor ligands. To demonstrate the versatility of the SC/[MCE] hybrid photocatalysts, several p-type SCs were selected, such as gallium phosphide (GaP), indium phosphide (InP), and nitrogen-doped tantalum pentoxide (N-Ta_2O_5),[11] all of which have a more negative E_{CBM} than E_{red} over the MCEs. MCEs formed on surfaces of SCs by electro or chemical polymerization (see SI for sample preparation details). All of the SC/[MCE] samples examined, InP/[MCE]s, GaP/[MCE]s, and N-Ta_2O_5/[MCE]s, exhibited catalytic activity for the photoelectrochemical reduction of CO_2 to $HCOO^-$ in pure H_2O at −0.4 V vs Ag/AgCl, which demonstrates the versatility of the SC/[MCE] system[7] under visible light irradiation for 1 h (shown in Table 1, detail of experimental method in SI). The current efficiency for formate formation (EFF) was calculated by dividing the total number of electrons stored in formate by the amount of consumed charge. Among the SCs, InP/[MCE]s had the highest rates for $HCOO^-$ formation. Because the E_{CBM} values of N-Ta_2O_5, GaP, and InP were evaluated to be −1.6, −2.2, and −1.35 V (vs Ag/AgCl),[3a,7,8] the driving force of ET, ΔG, was calculated to be 0.8, 1.4, and 0.55 V, respectively. However, the photocatalytic $HCOO^-$ formation rate did not correlate with the quantity of ΔG, though ΔG is indispensable for determining ET from SC to MCE. This result indicates that other important factors, such as total photons absorbed and electronic state at the SC/MCE interface, must be taken into account to discuss the difference in the CO_2 reduction rates in more detail. Because the ET from SC to MCE is a very important factor for this CO_2 reduction, analyses of the ET process by spectroscopic techniques are now underway.

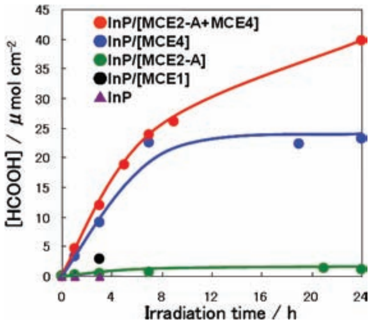

Figure 2. Photoelectrocatalytic HCOOH formation from CO_2 as a function of irradiation time over InP/[MCE]s. Photoelectrochemical CO_2 reduction was performed in pure H_2O using a three-electrode configuration (see SI, Figure S1a). The photocathode (hybrid InP/[MCE]s photocatalyst), glassy carbon, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively. A Pyrex glass cell was used as a reactor, and a xenon light source equipped with an optical filter (λ > 400 nm) and a cold mirror was used to irradiate visible light (~70 sun). The applied potential was −0.4 V (vs Ag/AgCl). The InP/[MCE] hybrid photocatalysts used were InP only, electro-polymerized InP/[MCE1], chemical-polymerized InP/[MCE2-A], chemical-polymerized InP/[MCE4], and chemical-polymerized InP/[MCE2-A+MCE4].

Figure 2 shows successive $HCOO^-$ generation from CO_2 over the InP/[MCE]s performed using a three-electrode configuration in pure H_2O under visible light irradiation (see Figure S1a). The applied potential (−0.4 V vs Ag/AgCl) was set more positive than E_{red} (−0.8 V vs Ag/AgCl) and was approximately equal to the E_{CBM} of anatase TiO_2 (described later). All of the InP/[MCE]s could reduce CO_2 to $HCOO^-$, which was confirmed as the main product and identified as $m/z = 45$ using ion chromatography time-of-flight mass spectroscopy (IC-TOFMS). The applied potential was more positive than E_{red}, and almost no cathodic current was observed in darkness, which suggests that photoexcited electrons in the CB of the InP are transferred to the MCE and reduce CO_2.[7,8] However, the InP alone showed almost no activity toward $HCOO^-$ formation, which suggests preferential H_2 production, as also reported in the literature.[12,13] The InP/[MCE4] (chemical-polymerized) exhibited higher photocatalytic activity than InP/[MCE1] (electro-polymerized) used in our previous study.[7] Furthermore, InP/[MCE2-A+MCE4] exhibited the highest photocatalytic reaction rate for $HCOO^-$ generation. MCE2-A possesses the 4,4′-diphosphate ethyl-2,2′-bipyridine anchor ligand, so that

MCE2-A can link tightly with the surface of InP.[15] Therefore, one possible reason for the enhanced reaction rate for the mixture of MCE2-A and MCE4 is accelerated ET from the photoexcited InP to [MCE2-A+MCE4], as was elucidated for the CdSe/[Re(dcbpy)(CO)$_3$Cl] fast photoexcited ET system[14] and the N-Ta_2O_5/[Ru(dcbpy)$_2$(CO)$_2$]$^{2+}$ photocatalyst[8b] that contain complexes with anchor ligands linked to the SCs. Diffuse reflectance transient spectroscopic analyses of this type of fast ET process in the present system are now underway. Scanning electron microscopy observations revealed that the MCE4 polymer catalyst exfoliated from the surface of InP after photocatalytic reaction, which suggests the generation of bubbles at the interface between InP and MCE4 (Figure S2). The bubbles are considered to be mainly H_2, because InP is known to photocatalytically produce H_2 in aqueous solution.[16] Therefore, ET between InP and the MCE4 polymer catalyst was not efficient in the absence of an anchor ligand. However, detachment of a polymer catalyst consisting of a mixture of MCE2-A and MCE4 was not observed after the photocatalytic reaction (Figure S3), which is considered to be one of the reasons for the higher durability of InP/[MCE2-A+MCE4], as shown in Figure 2. The porous structure induced by mixing with MCE2-A may also be a reason for the higher durability, due to the effective ejection of gaseous species produced at the SC surface. Furthermore, ET from MCE2-A to MCE4 is presumed to occur in the mixture, for the following reasons. (i) InP/[MCE2-A] exhibited a lower $HCOO^-$ generation rate, a lower EFF, and a resulting higher photocurrent (photocatalytic ability) than InP/[MCE4], which indicates that InP/[MCE2-A] has less selectivity for $HCOO^-$ generation (Figure 2 and Table 1). (ii) InP/[MCE2-A+MCE4] had a higher rate for $HCOO^-$ generation than InP/[MCE4], although their EFF values were almost identical (~80%), which indicates that a larger reaction photocurrent (photocatalytic ability) was generated in InP/[MCE2-A+MCE4] than in InP/[MCE4] (Table 1). These results indicate that MCE2-A could play a more important role as an ET facilitator to improve CO_2 reduction over MCE4 in InP/[MCE2-A+MCE4] rather than as a catalyst for $HCOO^-$ generation.

The activity of InP/[MCE2-A+MCE4] was also determined in the presence of electrolyte solutes, such as $NaHCO_3$, Na_3PO_4, and Na_2SO_4 (Table S1). The electrical conductivity of an electrolyte solution is higher than that of pure H_2O; therefore, the cathodic photocurrent could be increased. The value of EFF over InP/[MCE2-A+MCE4] in a Na_3PO_4 or Na_2SO_4 solution decreased from 78 to 58%, which suggests preferential H_2 generation. In contrast, the charge observed over InP/[MCE2-A+MCE4] in $NaHCO_3$ solution was 1.75 times that in pure H_2O while the EFF decreased slightly to 70%. As a result, the highest $HCOO^-$ generation rate over InP/[MCE2-A+MCE4] was in an aqueous solution of $NaHCO_3$ and was about 7 times that over InP/[MCE1] reported previously.[7] Consequently, InP/[MCE2-A+MCE4] was selected as the photocatalyst for CO_2 reduction.

Next, in order to realize the system to reduce CO_2 in H_2O with no external electrical bias, the photocatalyst for CO_2 reduction was functionally combined with a photocatalyst for H_2O oxidation. The valence band maximum (E_{VBM}) of the photocatalyst for H_2O oxidation must be more positive than the potential for H_2O oxidation (theoretically 1.23 V vs NHE). Furthermore, the E_{CBM} of the photocatalyst for H_2O oxidation should be more negative than the E_{VBM} of the photocatalyst for CO_2 reduction to ensure ET from the photoanode to the photocathode with no external electrical bias. In the present work, platinum-loaded anatase titanium dioxide on conducting glass (TiO_2/Pt) was selected as the photocatalyst for H_2O oxidation (see SI for sample preparation details), taking into account the E_{CBM} of TiO_2/Pt, the E_{VBM} of InP/[MCE2-A+MCE4], and the O_2 generation ability for oxidizing H_2O.[17] The potential difference of E_{CBM} of TiO_2 toward E_{VBM} of InP was estimated to be −0.5 V. Hence, successful ET between two photocatalysts with no external electrical bias can be facilitated due to this potential difference.[18] Here, the Pt cocatalyst facilitates O_2 production from H_2O_2 originated from H_2O.[19]

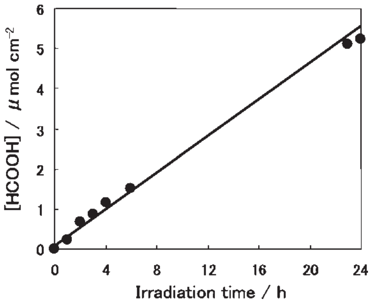

Figure 3. Photocatalytic HCOOH formation from CO_2 as a function of irradiation time using InP/[MCE2-A+MCE4] conjugated with TiO_2/Pt. CO_2 reduction was performed using a two-electrode configuration with no external electrical bias in 10 mM $NaHCO_3$ solution (see Figure S1b). InP/[MCE2-A+MCE4] and TiO_2/Pt were used as photocatalysts for CO_2 reduction and H_2O oxidation, respectively. A two-compartment Pyrex cell separated by a proton exchange membrane (Nafion117, DuPont) was used as the reactor. A solar simulator, in which the intensity was adjusted to 1 sun (AM1.5), was used as the light source. Light was irradiated from the TiO_2/Pt side, and InP/[MCE2-A+MCE4] was irradiated with light transmitted through the translucent TiO_2/Pt and proton exchange membrane. The irradiation area was 10 × 10 mm^2.

The reduction of CO_2 in conjunction with H_2O oxidation was performed using a two-electrode configuration (see Figure S1b for experimental details). CO_2 reduction photocatalyst InP/[MCE2-A+MCE4] (20 × 15 mm^2, black) and H_2O oxidation photocatalyst TiO_2/Pt (20 × 15 mm^2, translucent) were used. A two-compartment Pyrex cell separated with a proton exchange membrane was used as the reactor to prevent reoxidation of the $HCOO^-$ over TiO_2/Pt. A 10 mM $NaHCO_3$ solution was a suitable electrolyte for InP/[MCE2-A+MCE4]; it also accelerates catalytic O_2 generation over the TiO_2 photoanode.[20] A solar simulator equipped with an air mass 1.5 (AM1.5) filter was used as the light source with the intensity adjusted to 1 sun. The irradiation area was 10 × 10 mm^2. Light was irradiated from the TiO_2/Pt side, and InP/[MCE2-A+MCE4] was irradiated with light transmitted through the TiO_2/Pt photocatalyst electrode (translucent) and proton exchange membrane. No external electrical bias was applied between the two photocatalysts.

Photocatalytic CO_2 reduction was conducted using the reactor, and stable and reproducible reactivity was observed for 24 h under irradiation (1 sun) with CO_2 bubbling, as shown in Figure 3. $HCOO^-$ was produced in this case; however, no $HCOO^-$ was generated with Ar bubbling. The turnover number for HCOOH was >17 at 24 h, and a larger value is expected with further irradiation. Even though H_2 and CO were also detected, the value of EFF reached 70%, similar to that observed over InP/[MCE2-A+MCE4] in the three-electrode configuration. We also confirmed that negligibly small amounts of H_2, CO, and $HCOO^-$ were produced in the TiO_2/Pt compartment, suggesting that electrons extracted from H_2O were transferred to InP/[MCE2-A+MCE4] through the external circuit. The photosynthesis process in plants also consists of this kind of Z-scheme reaction, which utilizes two photosystems called PSI and PSII. Thus, the InP/[MCE2-A+MCE4]-TiO_2/Pt system mimics photosynthesis in plants. The conversion efficiency from solar energy to chemical energy was reproducible and the value was 0.03%, calculated by dividing the combustion heat of formic acid generated by the integrated energy of the irradiated solar-simulating light (AM1.5).[21] We also confirmed that our system proceeded without the Pt cocatalyst. The value of solar conversion was 0.04% using the InP/[MCE2-A+MCE4]-TiO_2 system. This value is one-fifth of 0.2%, the solar conversion efficiency of switchgrass, a promising crop for biomass fuel.[22]

The carbon and proton sources of formate were identified to be CO_2 and H_2O by isotope tracer analysis, respectively. The oxygen generated by oxidizing water was also detected in isotope tracer analysis (details in SI). These results verified that CO_2 was reduced to formate by electrons extracted from H_2O during the oxidation process to O_2, and that protons were also originated from H_2O.

In conclusion, photoelectrochemical reduction of CO_2 to $HCOO^-$ over SC/[MCE] was drastically enhanced by introducing an anchoring complex into the MCE. The photoreduction of CO_2 to $HCOO^-$ using H_2O as an electron donor and proton source can be achieved as a Z-scheme system by functionally conjugating the InP/[MCE2-A+MCE4] photocatalyst for CO_2 reduction with a TiO_2 photocatalyst for H_2O oxidation. The conversion efficiency from solar energy to chemical energy was 0.03−0.04% which approaches that for photosynthesis in a plant. This system can be applied to many others inorganic SCs and MCEs; the efficiency and reaction selectivity can be enhanced by optimization of the ET process including the energy-band configurations, conjugation conformation, and the catalyst structure. Optimization of the reaction cell, such as the configuration and enhanced transparency of the photoanode and proton exchange membrane, would also prove effective to enhance the photocatalysis. This electrical-bias-free reaction is necessary for future practical application of artificial photosynthesis under solar irradiation to produce organic species such as alcohols, hydrocarbons, and syngas, which are useful as alternative fuels or carbon resources.

■ ASSOCIATED CONTENT

Supporting Information. Materials, general procedures, and methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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