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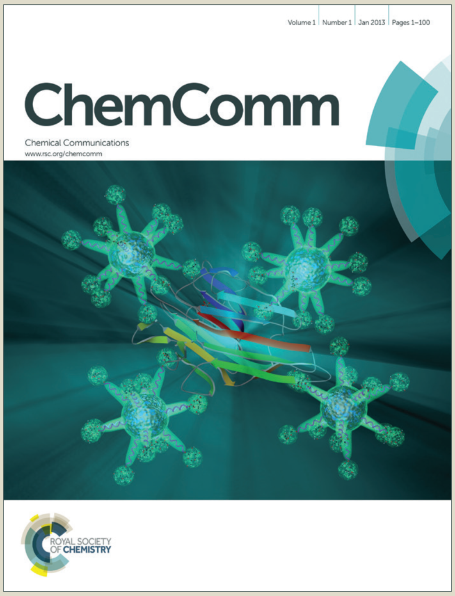

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ARTICLE TYPE

Photoelectrochemical CO_2 reduction using a Ru(II)–Re(I) multinuclear metal complex on a p-type semiconducting NiO electrode

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A photocathode for CO_2 reduction was successfully developed using a hybrid electrode comprising a Ru(II)–Re(I) supramolecular photocatalyst and a NiO electrode. Selective photoexcitation of the Ru photosensitizer unit of the photocatalyst at −1.2 V vs. Ag/$AgNO_3$ selectively afforded CO with high faradaic efficiency.

Conversion of CO_2 to high-energy compounds using solar energy is an ideal solution to global warming and the depletion of fossil fuels. Multinuclear metal complexes constructed with both photosensitizer and catalyst units, known as supramolecular photocatalysts, have been developed as visible-light-driven photocatalysts for CO_2 reduction with very high selectivity, durability, and efficiency.[1] However, their oxidizing power is too low to oxidize water; for practical use, it is desirable to use water as a reductant for CO_2 reduction. In nature, photosynthesis efficiently uses visible light to drive both CO_2 fixation and water oxidation using a "Z-scheme," where two photons are absorbed stepwise to produce both an electron with strong reducing power and a hole with strong oxidizing power. Artificial Z-scheme systems containing an InP photocathode with a Ru(II) complex for CO_2 reduction and a $SrTiO_3$ photoanode have been previously reported.[2] In this system, both semiconductor electrodes absorbed light, while the metal complex worked only as a catalyst for CO_2 reduction. However, there is a need for a photocathode system comprising a supramolecular photocatalyst that absorbs a wide range of visible light and a semiconductor electrode that need not absorb light. Only one fully artificial system has been reported: a dyad with a Zn(II) porphyrin as a photosensitizer and a Re(I) complex as a catalyst for CO_2 reduction immobilized on a p-type NiO electrode. This system was able to reduce CO_2 to CO;[3] however, the turnover number and faradaic efficiency were both low ($TON_{CO} = 10$, faradaic efficiency = 6.2%).

Herein, we report a new hybrid photocathode, Ru(II)–Re(I) metal complex (**RuRe**)[4] immobilized on NiO, and its high photocatalytic ability for CO_2 reduction.

Chart 1 shows the structures of the complexes used in this study, which possess methyl phosphonate groups as anchors to metal oxide.[5] In the case of **RuRe**, the Ru and Re units are connected through an ethylene chain, which causes weak electronic interaction between the two units, increasing the oxidizing power of the excited Ru unit. This interaction also caused slightly positive shift of the reduction potential of the Re unit, which was observed at 0.06 V more positive compared with that of Re(4,4'-Me_2bpy)$(CO)_3$Br (Table S3). This induces efficient electron transfer from the reduced Ru unit to the Re catalyst.[6]

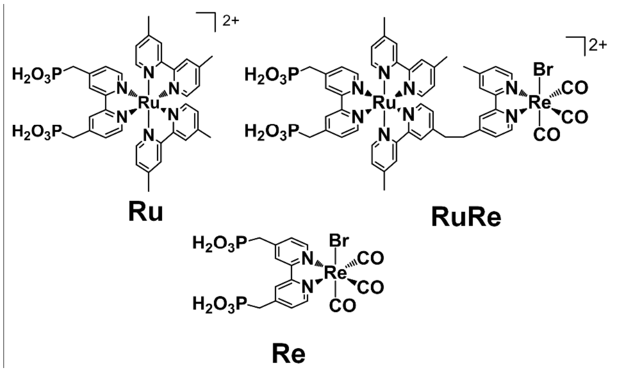

Chart 1. Structures of the metal complexes.

The NiO electrode, which is fluorine doped tin oxide (FTO) glass coated with a NiO film (active area: ca. 2.5 cm^2), was prepared using a modified version of the method reported by Suzuki and coworkers.[7] Details of this preparation are described in the Supporting Information. X-ray diffraction (XRD) patterns indicated that only the NiO phase was formed (Figure S3). The absorption spectrum of NiO on a glass slide, which was prepared similarly to the NiO electrode, was measured. From the Tauc plot (Figure S5) of the NiO electrode, the indirect band gap of the NiO film was estimated to be 3.46 eV, which is consistent with a previous report.[8]

The metal complexes were adsorbed on the NiO electrode through immersion of the electrode in an acetonitrile solution containing the metal complex (5 μM, 4 mL) overnight, giving colour change of the electrode of which diffuse reflection absorption spectrum showed a new peak at around 460 nm attributable to the MLCT absorption band of **RuRe** (Figure S6). The adsorption amounts, which were estimated by measuring the absorbance of the solution at 461 nm between before and after the immersion, were 5–8 nmol for **RuRe**, 16 nmol for **Ru**, and 4 nmol for **Re**.

The photoresponse of the electrode modified with **Ru** (**NiO–Ru**) was investigated by selectively exciting **Ru** on the electrode in an acetonitrile solution containing Et_4NBF_4 (0.1 M). Obvious cathodic response was observed during irradiation, as shown in

Figure 1. Conversely, the NiO electrode without **Ru** showed almost no photoresponse through irradiation, as it could not absorb the light (the band gap of NiO was 3.46 eV, as described above). Figure 2 shows the action spectrum of the initial photocurrent at −1.0 V vs. Ag/AgNO$_3$ obtained with various excitation wavelengths, where the photocurrent was normalized by the irradiated photon flux. This was similar to the absorption spectrum of **Ru**, which clearly indicates that the cathodic photocurrent was induced by photoexcitation of **Ru**. Since the photocurrent was cathodic and the valence band maximum (−0.2 V vs. Ag/AgNO$_3$ [9]) was more negative than the redox potential of the excited state of **Ru** ((**Ru***/**Ru**$^-$) = 0.15 V), an electron transfer from the valence band of NiO to the excited state of **Ru** should occur.[10]

Table 1 Photoelectrochemical CO$_2$ reduction[a]

Entry	Sample	Metal complex	Potential	$h\nu$	CO$_2$	Products		Faradaic efficiency / %
		nmol	V vs. Ag/AgNO$_3$			CO / nmol (TON$_{CO}$)	H$_2$ / nmol	
1	**NiO-RuRe**	7.9	−1.2	○	○	255(32)	n.d.	62 (0 ~ 3 h) 98 (3 ~ 5 h)
2	**NiO-RuRe**	7.1	−1.0	○	○	115(16)	n.d.	41
3	**NiO-RuRe**	5.9	−0.8	○	○	n.d	n.d.	0
4	**NiO-RuRe**	4.8	−1.2	×[b]	○	n.d.	n.d.	0
5	**NiO-RuRe**	6.5	−1.2	○	×[c]	n.d.	n.d.	0
6	NiO	–	−1.0	○	○	n.d.[d]	n.d.[d]	0
7	**NiO-Ru**	16.3	−1.0	○	○	n.d.[d]	n.d.[d]	0
8	**NiO-Re**	3.8	−1.0	○	○	n.d.[d]	n.d.[d]	0

[a]Irradiated at $\lambda > 460$ nm with a 300-W Xe lamp for 5 h, [b]in the dark, [c]under Ar atmosphere, [d]22 h irradiation.

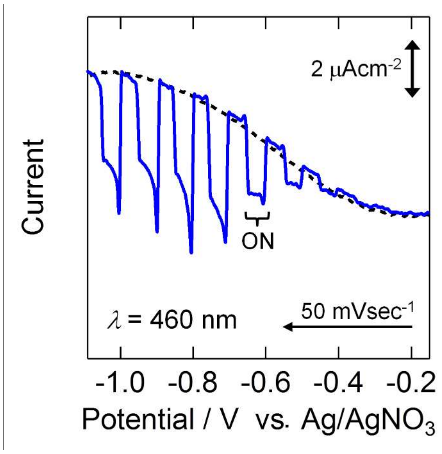

Figure 1. I–V curve of **NiO–Ru** under visible light irradiation in an acetonitrile solution containing Et$_4$NBF$_4$ (0.1 M) under Ar. Solid blue line: under frequent irradiation. Dashed black line: under dark conditions.

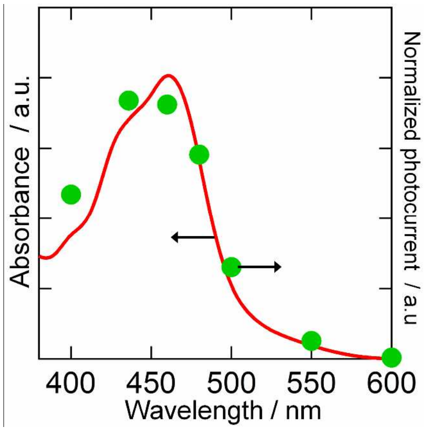

Figure 2. Action spectrum of **NiO–Ru**. Green dots: photocurrent at −1.0 V vs. Ag/AgNO$_3$ of each irradiation wavelength normalized by photon flux. Red line: absorption spectrum of **Ru** in acetonitrile.

We examined photoelectrochemical CO$_2$ reduction using supramolecular **RuRe** adsorbed on the NiO electrode. This was because not only did the electron transfer proceed from the NiO electrode to the excited **Ru** but also the oxidizing power of the excited Ru unit of **RuRe** was slightly stronger than that of **Ru**. In a typical run, the electrode modified with **RuRe** (**NiO–RuRe**) was irradiated using $\lambda > 460$ nm (300-W Xe lamp with a cutoff filter) light at −1.2 V vs. Ag/AgNO$_3$ in a DMF-triethanolamine (5:1, v/v) mixed solution containing Et$_4$NBF$_4$ (0.1 M) as a supporting electrolyte under a CO$_2$ atmosphere. The main product was CO, without formation of H$_2$ or CH$_4$. These results are shown in Figure 3. The amounts of products and a half amount of electrons passing through the outer circuit (e$^-$/2) because formation of CO from CO$_2$ requires two electrons. The turnover number for CO formation (TON$_{CO}$) was 32 (based on **RuRe**) and the average faradaic efficiency was 71% for 5 h irradiation. Although the faradaic efficiency of CO was 62% in the initial stage (up to 3 h irradiation), further irradiation increased the faradaic efficiency to up to 98%. After the photocatalytic reaction, the visible absorption of **NiO-RuRe**, of which original colour was pale black, decreased in whole wavelength range. Nickel trivalent ions (Ni^{3+}), which originally existed in NiO, might be reduced during the reaction because Ni^{3+} is the origin of the black to blown colour of NiO.[11]

The photocatalytic ability of **NiO–RuRe** was investigated with more positive applied potentials (Figure 4, Table 1 entries 2 and 3). At −1.0 V, the photocurrent, CO formation, and faradaic efficiency (41% after 5 h irradiation) decreased compared with those at −1.2 V. At a lower applied potential, such as −0.8 V, much lower photocurrent and no CO formation were observed. This strongly suggests that the electrons used for the photocatalytic CO$_2$ reduction came from the NiO film of **NiO–RuRe**.

Either without irradiation or under an Ar atmosphere, **NiO–**

RuRe could not produce CO (Table 1 entries 4 and 5). The carbon source of CO formation was investigated through labeling experiments using $^{13}CO_2$. In the case of the photoelectrochemical reaction under a $^{13}CO_2$ atmosphere, GC-MS analysis revealed that only ^{13}CO was produced (Figure S9). It has been reported that the "O_2^{-}" acceptor is CO_2 giving carbonate anion in both photochemical CO_2 reduction using Ru-Re type photocatalysts and electrochemical CO_2 reduction using $Re(bpy)(CO)_3Cl$ and its derivatives as catalysts.[1,12,13] Therefore, the following reaction might proceed in this photoelectrochemical reduction of CO_2 on the **NiO-RuRe**.

$$2CO_2 + 2e^- \rightarrow CO \text{ and } CO_3^{2-} \qquad (1)$$

These results clearly indicated that the evolved CO was the photochemical reduction product of CO_2. When using a NiO electrode without **RuRe**, instead of **NiO–RuRe**, photocatalytic reduction of CO_2 was not observed (entry 6). Irradiation of a NiO electrode with either **Ru** or **Re** did not cause any CO formation (entries 7 and 8). Therefore, both the NiO electrode and supramolecular photocatalysts are required for photoelectrochemical CO_2 reduction.

The reduction potential of the excited Ru unit should be similar to or more positive than that of excited **Ru** (0.15 V), as well as more positive than the valence band edge of NiO (−0.2 V), allowing for electron transfer from NiO to the excited Ru unit of **RuRe** (Table S3). This then allows for the intramolecular electron transfer from the reduced Ru unit to the Re unit, as the reduction potential of the Ru unit was more negative than that of the Re unit (= −1.76 V, Figure S2),[6] allowing for reduction of CO_2 on the reduced Re unit.

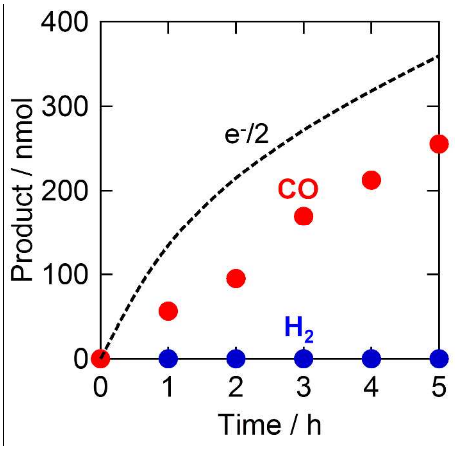

Figure 3. Time course of the photoelectrochemical CO_2 reduction products and a half amount of electrons passing using **NiO–RuRe**. The **NiO–RuRe** was irradiated with $\lambda > 460$ nm at −1.2 V vs. $Ag/AgNO_3$ under CO_2 atmosphere.

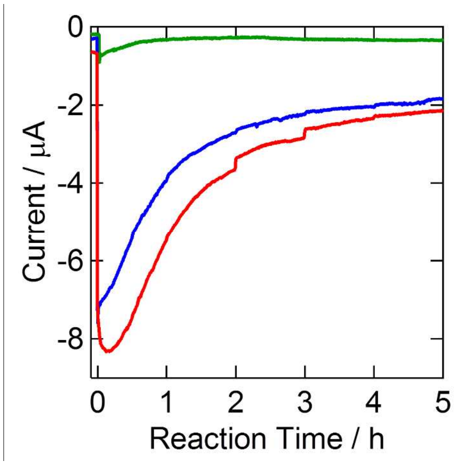

Figure 4. Time course of photocurrent during photoelectrochemical CO_2 reduction at each applied potential. Red: −1.2 V vs. $Ag/AgNO_3$. Blue: −1.0 V vs. $Ag/AgNO_3$. Green: −0.8 V vs. $Ag/AgNO_3$.

In conclusion, we successfully developed a hybrid photocathode composed of a Ru(II)–Re(I) supramolecular metal complex immobilized on a NiO electrode. This system allowed for catalytic CO_2 reduction with high faradaic efficiency, high selectivity of the product, and relatively high durability. Development of artificial Z-scheme systems using this photocathode is now in progress.

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Notes and references

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† Electronic Supplementary Information (ESI) available: experimental details, photophysical and electrochemical properties of the complexes, and results of the labeling experiment are shown. See DOI: 10.1039/b000000x/

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