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Supramolecular photocatalysts fixed on the inside of the polypyrrole layer in dye sensitized molecular photocathodes: application to photocatalytic CO₂ reduction coupled with water oxidation†

Fazalurahman Kuttassery,^a ‡^a Hiromu Kumagai,^b Ryutaro Kamata,^a Yusuke Ebato,^a Masanobu Higashi,^c Hajime Suzuki,^d Ryu Abe^d and Osamu Ishitani^{*a}

The development of systems for photocatalytic CO₂ reduction with water as a reductant and solar light as an energy source is one of the most important milestones on the way to artificial photosynthesis. Although such reduction can be performed using dye-sensitized molecular photocathodes comprising metal complexes as redox photosensitizers and catalyst units fixed on a p-type semiconductor electrode, the performance of the corresponding photoelectrochemical cells remains low, e.g., their highest incident photon-to-current conversion efficiency (IPCE) equals 1.2%. Herein, we report a novel dye-sensitized molecular photocathode for photocatalytic CO₂ reduction in water featuring a polypyrrole layer, [Ru(diimine)₃]²⁺ as a redox photosensitizer unit, and Ru(diimine)(CO)₂Cl₂ as the catalyst unit and reveal that the incorporation of the polypyrrole network significantly improves reactivity and durability relative to those of previously reported dye-sensitized molecular photocathodes. The irradiation of the novel photocathode with visible light under low applied bias stably induces the photocatalytic reduction of CO₂ to CO and HCOOH with high faradaic efficiency and selectivity (even in aqueous solution), and the highest IPCE is determined as 4.7%. The novel photocathode is coupled with n-type semiconductor photoanodes (CoO_x/BiVO₄ and RhO_x/TaON) to construct full cells that photocatalytically reduce CO₂ using water as the reductant upon visible light irradiation as the only energy input at zero bias. The artificial Z-scheme photoelectrochemical cell with the dye-sensitized molecular photocathode achieves the highest energy conversion efficiency of 8.3 × 10⁻²% under the irradiation of both electrodes with visible light, while a solar to chemical conversion efficiency of 4.2 × 10⁻²% is achieved for a tandem-type cell using a solar light simulator (AM 1.5, 100 mW cm⁻²).

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^aDepartment of Chemistry, Tokyo Institute of Technology, 2-12-1-NE-1, O-okayama, Meguro-ku, Tokyo 152-8550, Japan. E-mail: ishitani@chem.titech.ac.jp

^bInstitute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan

^cThe OCU Advanced Research Institute for Natural Science and Technology, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka City, Osaka 558-8585, Japan

^dDepartment of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

† Electronic supplementary information (ESI) available: Synthetic strategy and ¹H-NMR spectra of metal complexes synthesized (S1–I), additional electrochemical, characterization, photoelectrochemical CO₂ reduction and single cell artificial Z-scheme data (Fig. S1–S10). Quantitative estimation of Ru(II) by ICP-MS analysis of photocathodes (Tables S1–S4), Summary of photoelectrochemical CO₂ reduction under controlled experimental conditions (Table S5). See DOI: 10.1039/d1sc03756k

‡ Present address: Department of Chemistry, University of Calicut, Malappuram, Kerala 673635, India.

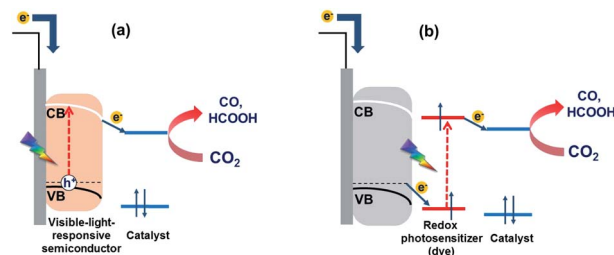
Introduction

The reduction of CO₂ to useful carbon resources using sunlight as the energy source and water as the electron donor is expected to provide a sustainable solution to the energy and environmental problems currently facing our society.^{1,2} In this regard, photocatalytic CO₂ reduction systems with transition metal complexes acting as (i) redox photosensitizers that absorb visible light to initiate electron transfer and (ii) catalysts that accept electrons from redox photosensitizers to reduce CO₂ have drawn much attention, as these complexes exhibit tunable visible light absorption and redox properties as well as high CO₂ reduction selectivity.^{3,4} For example, a mixed system comprising [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine) as the redox photosensitizer and [Ru(X₂bpy)(CO)₂Cl₂] as the catalyst efficiently and selectively catalyses the photoreduction of CO₂ in the presence of sacrificial electron donors such as 1-benzyl-1,4-dihydronicotinamide to give CO and HCOOH, the ratio of

which can be controlled by changing the reaction conditions such as solution pH and bpy substituents (X).^{5–7} Despite the abundance of photocatalytic systems that comprise only metal complexes and can efficiently promote the photoreduction of CO₂ in the presence of sacrificial electron donors, these systems cannot use water as an electron donor owing to their relatively low oxidation power and the difficulty of the four-electron oxidation of two water molecules. However, in order to be practical, photocatalytic CO₂ utilization systems should inevitably employ water as an electron donor owing to its low cost and abundance.⁸

Hybrid systems that comprise metal complexes as (photo) catalysts and semiconductor materials and feature excited states with oxidation powers sufficient to oxidize water to O₂ and/or H₂O₂ have been actively investigated to mitigate the above problem.^{9–11} Most of such hybrid systems are photoelectrochemical cells featuring a photocathode for CO₂ reduction and a photoanode for water oxidation, with the sequential excitation of these photoelectrodes endowing them with strong reduction and oxidation powers.⁸ Such photoelectrochemical cells, also known as artificial Z-scheme cells, can be broadly classified into two groups, both of which feature n-type semiconductor photoanodes (e.g., CoO_x-deposited BiVO₄ (ref. 12) and reduced SrTiO₃ (ref. 13)) for water oxidation. In the first group, the photocathode comprises a metal complex that is deposited on a visible-light-responsive semiconductor material and acts a CO₂ reduction catalyst but does not absorb light, *i.e.*, light is absorbed only by the semiconductor electrode (Scheme 1a).^{13–15} The systems of the second group feature dye-sensitized molecular photocathodes consisting of a p-type semiconductor and a supramolecular photocatalyst with redox photosensitizer and catalyst units connected to each other (Scheme 1b).^{10–12} The redox photosensitizer unit absorbs light and then transfers an electron from the valence band of the p-type semiconductor to the catalyst unit, which reduces CO₂. The hole produced in the valence band of the p-type semiconductor is filled with an electron from the n-type semiconductor photoanode, which photochemically draws up electrons from water. Therefore, in these systems, the p-type semiconductor does not absorb light, which is their largest difference from the systems of the first group. As the two systems differ in their requirements for metal complexes and semiconductor materials, one expects a broad range of suitable complexes and materials as well as construction methods. Despite the availability of photoelectrochemical cells that promote CO₂ photoreduction using water as an electron donor and visible light as an energy source, their performance metrics, especially the efficiency of light energy to chemical energy conversion, are still low.

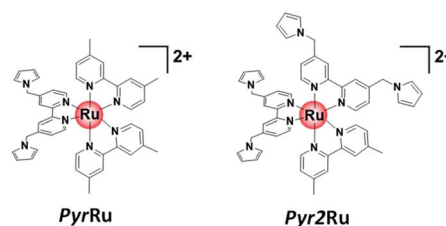
Although the photoelectrochemical systems of the second group are very rare examples of the use of molecular photocatalysts for CO₂ reduction coupled with water oxidation,^{10–12} these systems can potentially employ various redox photosensitizers with strong absorption in the visible region, which is advantageous for visible-light-driven photocathode construction. The dye-sensitized molecular photocathodes^{16,17} initially reported by Meyers *et al.*^{18,19} and our groups^{9–11} featured metal complex-based photocatalysts with anchoring groups such as



Scheme 1 Two types of photocathodes for photoelectrochemical CO₂ reduction. (a) Systems comprising a p-type semiconductor as the light absorbing unit and a metal complex as the catalyst. (b) Systems with dye-sensitized molecular photocathodes comprising a redox photosensitizer as the light absorbing unit, a metal complex as the catalyst, and a p-type semiconductor as the electron relay. VB = valence band, CB = conduction band.

–COOH and –PO₃H₂ adsorbed on the electrode surface. In these systems, the photosensitizer units are only monomolecularly adsorbed on the electrode, and the visible light absorption abilities of such dye-sensitized molecular photocathodes are therefore very low. In addition, the rapid detachment of the metal complex-based photocatalysts from the electrode due to weak immobilization *via* anchoring groups results in low photocathode durability.^{20–23} As the absorption ability of a single photosensitizer molecule is not high, the number of photosensitizer units on the p-type semiconductor electrode should be increased to elevate the corresponding light absorption ability.

The methods of overcoming these bottlenecks can be broadly classified into two main types. On the one hand, one can introduce a protective metal oxide layer by atomic layer deposition to increase the durability of the dye-sensitized molecular photocathode by suppressing the detachment of metal complexes with anchoring groups.^{24–26} However, this approach does not increase the visible light absorption of the photocathode. Methods of the second type rely on the introduction of a polymer layer, *e.g.*, Meyers¹⁹ and our^{12,27} groups employed the reductive electropolymerization of vinyl groups in the diimine ligands of metal complexes to afford a polymer layer that contained both the photosensitizer and catalyst units on the semiconductor electrode and, compared to the photoelectrode with only the anchoring groups described above, more strongly absorbed visible light owing to the accumulation of photosensitizer units.^{19,27–32} The reductive electropolymerization of molecular complexes on the dye-sensitized



Scheme 2 Molecular structures of Ru sensitizers (PyrRu and Pyr2Ru) containing the Pyrbpy ligand(s).



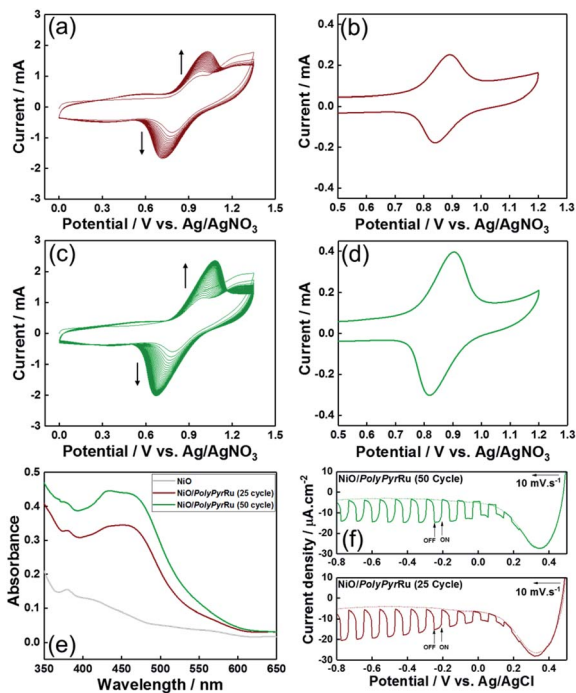


Fig. 1 Cyclic voltammograms recorded during the oxidative electropolymerization of PyrRu on NiO (electrode area = 2.5 cm²) in Ar-saturated MeCN containing PyrRu (0.5 mM) and Et₄NBF₄ (0.1 M): (a) 25 and (c) 50 cycles between 0 and +1.35 V vs. Ag/AgNO₃ at 100 mV s⁻¹. Cyclic voltammograms of NiO/PolyPyrRu as the working electrode recorded in MeCN containing 0.1 M Et₄NBF₄ as the electrolyte (counter electrode = Pt coil, reference electrode = Ag/AgNO₃) at 10 mV s⁻¹: (b) 25 and (d) 50 cycles. (e) DR spectra of NiO/PolyPyrRu and bare NiO electrodes. (f) Visible light responses of the *I*-*V* plots of NiO/PolyPyrRu working electrodes (area = 2.5 cm²) in CO₂-purged 50 mM NaHCO₃ (electrolyte) recorded using a Xe lamp with a Y-48 cutoff filter (λ = 460–650 nm), a Pt coil counter electrode and a Ag/AgCl reference electrode.

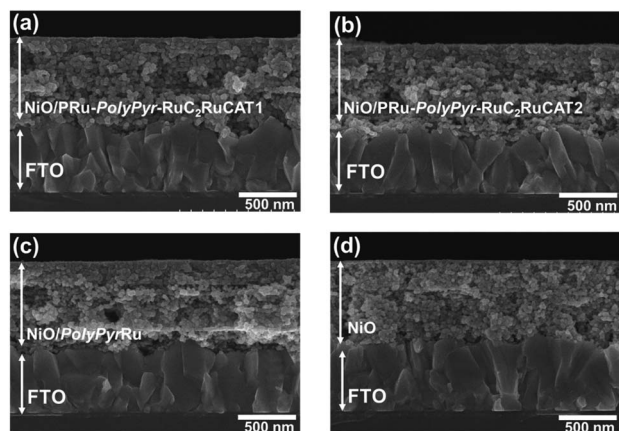
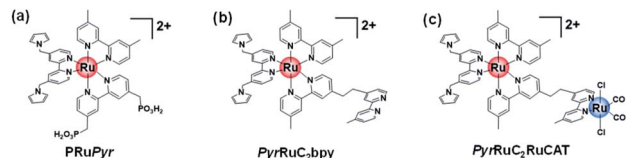
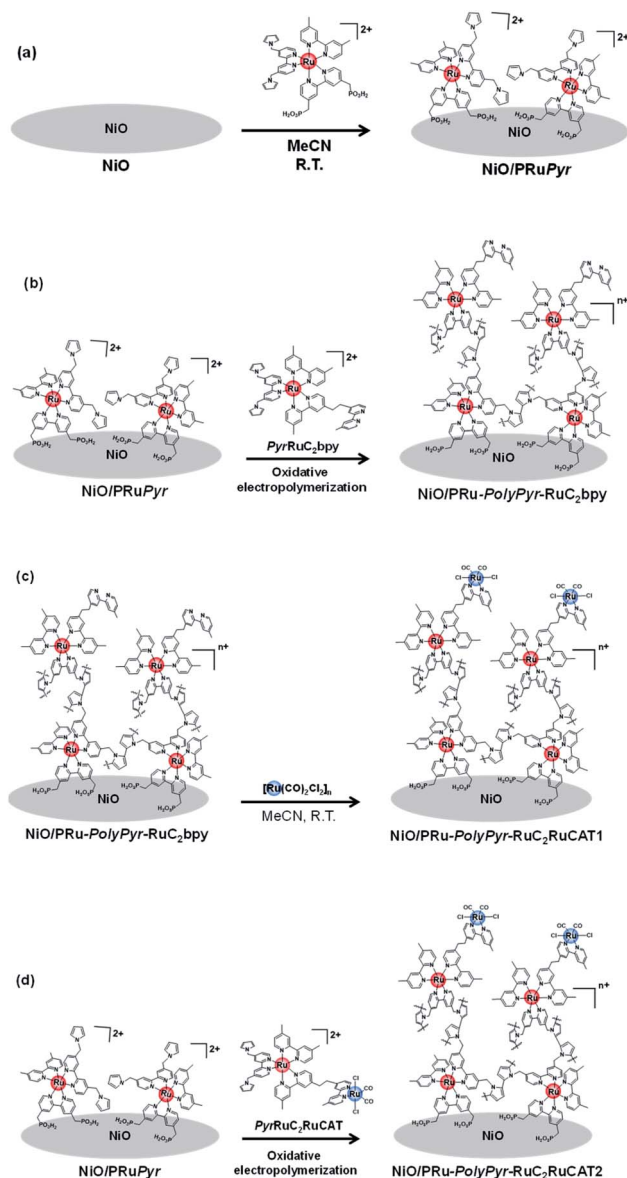


Fig. 2 SEM (side view) images of (a) NiO-PRu-PolyPyr-RuC₂RuCAT1 after 25 cycles, (b) NiO/PRu-PolyPyr-RuC₂RuCAT2, (c) NiO/PolyPyrRu, and (d) NiO on FTO.

molecular photocathode also drastically suppressed the desorption of metal complexes from the electrode and enhanced the durability of photocatalysts for CO₂ reduction.^{19,27}



Scheme 3 Molecular structures of (a) PRuPyr, (b) PyrRuC₂bpy, and (c) PyrRuC₂RuCAT.



Scheme 4 Preparation of (a) NiO/PRuPyr (step 1), (b) NiO/PRu-PolyPyr-RuC₂bpy (step 2), and (c) NiO/PRu-PolyPyr-RuC₂RuCAT1 (step 3) electrodes of a three step method of photocathode fabrication and (d) fabrication of NiO/PRu-PolyPyr-RuC₂RuCAT2 electrode by a two-step method (step 2).

However, the dye-sensitized molecular photocathodes prepared *via* the reductive polymerization of vinyl groups required a relatively negative applied potential to achieve maximal

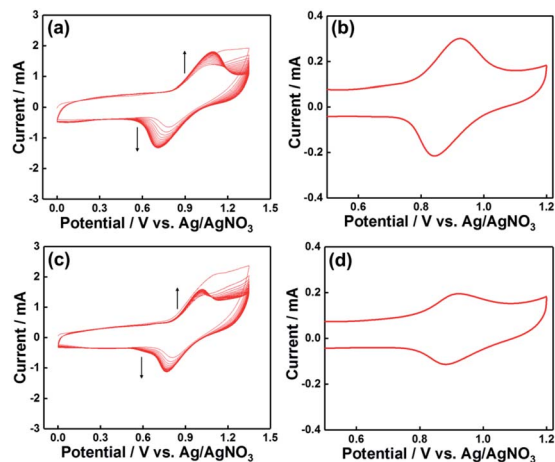


Fig. 3 Cyclic voltammograms recorded during the electro-polymerization of (a) $\text{PyrRuC}_2\text{bpy}$ and (c) $\text{PyrRuC}_2\text{RuCAT}$ on NiO/PRuPyr (area = 2.5 cm^2) in Ar-saturated MeCN containing the corresponding complex (0.5 mM) and Et_4NBF_4 (0.1 M) as an electrolyte. The applied potential was repeatedly cycled (25 times) between 0 and +1.35 V vs. Ag/AgNO_3 at 100 mV s^{-1} . Cyclic voltammograms of (b) $\text{NiO/PRu-PolyPyr-RuC}_2\text{RuCAT1}$ and (d) $\text{NiO/PRu-PolyPyr-RuC}_2\text{-RuCAT2}$ electrodes recorded in Ar-purged MeCN containing 0.1 M Et_4NBF_4 using a Ag/AgNO_3 reference electrode and a Pt counter electrode (scan rate = 10 mV s^{-1}).

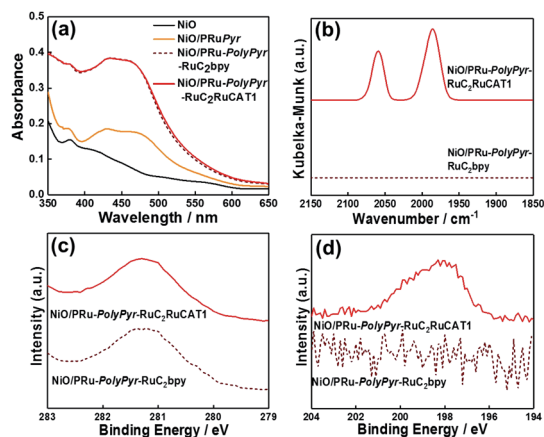


Fig. 4 (a) UV-vis (DR) absorption spectra of $\text{NiO/PRu-PolyPyr-RuC}_2\text{-RuCAT1}$ prepared by the three-step method (red), NiO (black), and samples obtained after process 1 (NiO/PRuPyr , orange) and process 2 ($\text{NiO/PRu-PolyPyr-RuC}_2\text{bpy}$, dotted brown). (b) FT-IR (DR) spectra of $\text{NiO/PRu-PolyPyr-RuC}_2\text{RuCAT1}$ (red) and $\text{NiO/PRu-PolyPyr-RuC}_2\text{bpy}$ (dotted brown) recorded at a scan rate of $2 \text{ cm}^{-1} \text{ s}^{-1}$. (c) Ru 3d and (d) Cl 2p X-ray photoelectron spectra of $\text{NiO/PRu-PolyPyr-RuC}_2\text{RuCAT1}$ (red) and $\text{NiO/PRu-PolyPyr-RuC}_2\text{bpy}$ (dotted brown).

photocurrent, and the photocurrent density remained low, probably because of the low conductivity of the saturated hydrocarbon chains formed by vinyl group polymerization. As a result, the incident photon-to-current conversion efficiencies (IPCEs) were 1.2% or less.¹² A photoelectrochemical cell comprising the dye-sensitized molecular photocathode fabricated by the reductive polymerization of vinyl groups and a $\text{CoO}_x/\text{BiVO}_4$ photoanode was reported as the most robust

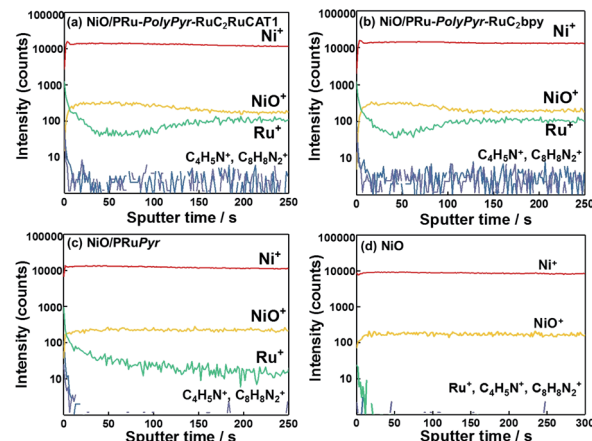


Fig. 5 TOF-SIMS spectra of (a) $\text{NiO/PRu-PolyPyr-RuC}_2\text{RuCAT1}$, (b) $\text{NiO/PRu-PolyPyr-RuC}_2\text{bpy}$, (c) NiO/PRuPyr , and (d) NiO electrodes.

photocatalytic system for CO_2 reduction with water without any external bias, with the photoenergy conversion efficiency (ECE) reaching $1.7 \times 10^{-2}\%$.¹²

The replacement of saturated hydrocarbon chains in photocathodes with conductive polymers is a promising way of reducing polymer layer resistance and increasing the efficiency of the dye-sensitized molecular photocathode. In this regard, pyrrole and its derivatives have attracted much attention owing to their high oxidative polymerization ability, relatively mild polymerization conditions, synthetic versatility, and the high conductivity of the produced polypyrrole films.^{28,29,33–35} Functional polypyrrole films containing metal complex units have been reported for various applications, *e.g.*, catalytic reactions, sensors, and drug delivery.^{28,29,33–41} Deronzier *et al.* reported that a system with a polypyrrole layer containing a $\text{Re}(\text{i})$ complex catalyst on Pt electrodes showed higher durability for electrocatalytic CO_2 reduction than the system with the corresponding mononuclear $\text{Re}(\text{i})$ complex in solution.^{33,36,42} Morikawa *et al.* deposited a polypyrrole layer containing a $\text{Ru}(\text{ii})$ complex catalyst onto a p-type semiconductor photoelectrode, *i.e.*, used a method of the first type according to the abovementioned classification.^{14,43–46} However, the construction of dye-sensitized molecular photocathodes with conducting polypyrrole for combining redox photosensitizer molecules and a p-type semiconductor electrode has not been reported so far.

Herein, we prepare new dye-sensitized molecular photocathodes *via* the formation of polypyrrole films containing both the photosensitizer and catalytic metal complexes on NiO electrodes and systematically investigate the molecular design of metal complex monomers with pyrrole groups as well as oxidative polymerization methods to develop the most efficient dye-sensitized molecular photocathode for CO_2 reduction (maximum IPCE = 4.7%). The developed photocathode is combined with two n-type semiconductor photoanodes ($\text{CoO}_x/\text{BiVO}_4$ and RhO_x/TaON) for water oxidation to develop systems for the photoelectrocatalytic reduction of CO_2 with water using visible light as the only energy input, and the maximum ECE is determined as $8.3 \times 10^{-2}\%$.

Table 1 Amounts of the adsorbed Ru(II) complexes in the electrodes and ratios between photosensitizers and catalysts

Sample	$n_{\text{Ru total}}^a$ (nmol)	n_{RuPS}^b (nmol)	n_{RuCAT}^c (nmol)	$n_{\text{RuPS}} : n_{\text{RuCAT}}$
NiO/PRuPyr	15.5	15.5	0	—
NiO/PRu-PolyPyr-RuC ₂ bpy	75.4	75.4	0	—
NiO/PRu-PolyPyr-RuC ₂ RuCAT1	100.3	75.4	24.9 ^c	3 : 1
NiO/PRu-PolyPyr-RuC ₂ RuCAT2	40.7	28.1	12.1 ^c	2.3 : 1

^a Total amount in the electrode, which was estimated by using ICP-MS analysis. ^b Amount of the photosensitizers. ^c Amount of the catalysts.

Results and discussion

Optimization of redox photosensitizer layer on electrodes

Initially, we attempted to develop suitable polymerization methods for Ru(II) complexes with pyrrole groups on the NiO electrode, for which two types of Ru(II) trisdiimine complexes containing one or two diimine ligand(s) with two pyrrole groups, that is, 4,4'-bis((1H-pyrrol-1-yl)methyl)-2,2'-bipyridine ligand (Pyrbpy), were synthesized (PyrRu and Pyr2Ru in Scheme 2). The cyclic voltammograms of these complexes recorded under Ar in acetonitrile (MeCN) containing 0.1 M Et₄NBF₄ are shown in Fig. S1a and S1c,† respectively. In the case of PyrRu, one reversible and one irreversible oxidation wave were observed at $E_{1/2}^{\text{ox}} = 0.86$ V and $E_{\text{p}}^{\text{ox}} = 1.19$ V vs. Ag/AgNO₃, respectively; the former was attributed to the one-electron oxidation of the central Ru(II) to Ru(III), as that of [Ru(dmb)₃]²⁺ (dmb = 4,4'-dimethyl-2,2'-bipyridine) is observed at $E_{1/2}^{\text{ox}} = 0.77$ V,⁴⁷ and the latter was attributed to the oxidation of pyrrole groups. On the other hand, the cyclic voltammogram of Pyr2Ru featured only one broad large oxidation wave at $E_{\text{p}}^{\text{ox}} = 1.00$ V, which was attributed to the combination of Ru(II) → Ru(III) oxidation and pyrrole group oxidation. These results suggest that the oxidative polymerization of the pyrrole groups of Pyr2Ru and PyrRu may proceed at a potential more positive than ~1 V. Both cyclic voltammograms recorded at negative potentials featured three reversible reduction waves attributable to the stepwise one-electron reduction of the diimine ligands of the Ru complexes as reported earlier (Fig. S1b and S1d†).⁴⁷

A NiO nanoparticle-modified transparent fluorine-doped tin oxide (FTO) electrode was prepared by the previously reported squeeze method^{9,10} and used as the working electrode for the oxidative electropolymerization (induced by 25 or 50 potential sweeps between $E = 0$ and +1.35 V vs. Ag/AgNO₃) of Ru(II) complexes with pyrrole groups. Fig. 1a shows the I - V curves of

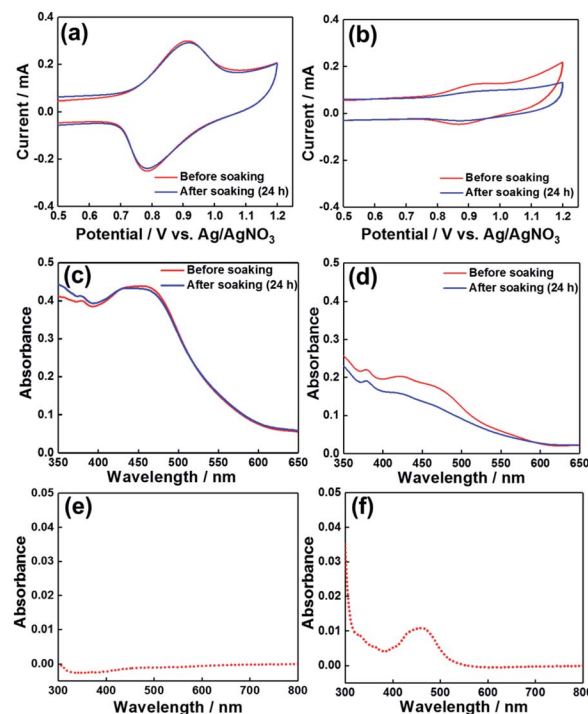


Fig. 6 Stability of photocathodes against 24 h soaking in 50 mM aqueous NaHCO₃ in the dark. Cyclic voltammograms of (a) NiO/PRu-PolyPyr-RuC₂RuCAT1 and (b) NiO/PRuPyr before and after soaking. UV-vis (DR) absorption spectra of (c) NiO/PRu-PolyPyr-RuC₂RuCAT1 and (d) NiO/PRuPyr before and after soaking. UV-vis absorption spectra of soaking solutions obtained for (e) NiO/PRu-PolyPyr-RuC₂RuCAT1 and (f) NiO/PRuPyr.

PyrRu recorded for 25 sequential potential sweeps, revealing that the current increased with increasing sweep number. The cyclic voltammogram of the electrode after 25 sweeps (Fig. 1b)

Table 2 Density of the adsorbed Ru complexes on the electrodes and estimation of percentage of electroactive Ru(II) on the NiO surface

Sample	Ru(ICP-MS) ^a (nmol cm ⁻²)	Ru(CV) ^b (nmol cm ⁻²)	Ru (CV)
			Ru(ICP-MS)
NiO/PRuPyr	6.2	2.0	0.32
NiO/PRu-PolyPyr-RuC ₂ bpy	30.2	9.6	0.32
NiO/PRu-PolyPyr-RuC ₂ RuCAT1	40.1	11.6	0.29
NiO/PRu-PolyPyr-RuC ₂ RuCAT2	16.3	4.4	0.27

^a Total amounts of Ru complexes in each electrode, that were measured by using ICP-MS analysis. ^b Amounts of electroactive Ru complexes measured by using CV analysis.



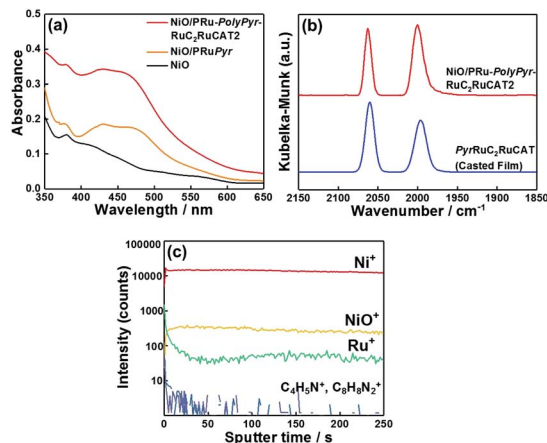


Fig. 7 (a) UV-Vis (DR) absorption spectra of NiO/PRu-PolyPyr-RuC₂-RuCAT2 (red), NiO/PRuPyr (orange), and NiO (black). (b) FT-IR (DR) spectra of NiO/PRu-PolyPyr-RuC₂RuCAT2 (red) and PyrRuC₂RuCAT cast on NiO (blue). (c) TOF-SIMS spectra of NiO/PRu-PolyPyr-RuC₂RuCAT2.

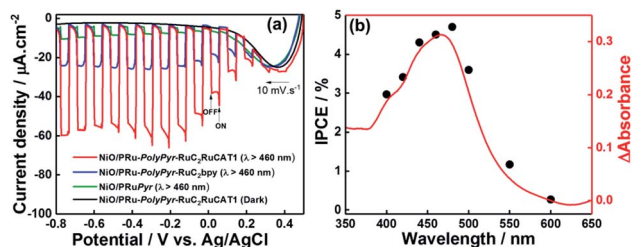


Fig. 8 (a) Responses of NiO/PRuPyr (green), NiO/PRu-PolyPyr-RuC₂bpy (blue), and NiO/PRu-PolyPyr-RuC₂RuCAT1 (red) to irradiation at $\lambda_{\text{ex}} = 460\text{--}650\text{ nm}$ (intensity = 28.2 mW cm^{-2}) in CO₂-purged 50 mM aqueous NaHCO₃ (pH 6.6, Ag/AgCl reference electrode, Pt wire counter electrode). (b) Effect of wavelength on the IPCE of NiO/PRu-PolyPyr-RuC₂RuCAT1 at -0.3 V vs. Ag/AgCl in a CO₂-purged 50 mM NaHCO₃ aqueous solution (pH 6.6, black dots). The red line shows the UV-vis absorption spectrum of NiO/PRu-PolyPyr-RuC₂-RuCAT1 with subtracted absorbance of the NiO electrode.

indicated that 8.2 nmol cm^{-2} of electrochemically active Ru complexes was immobilized on NiO, with the difference between the maxima of oxidation and reduction waves (ΔE) equaling 51 mV. The polymerization of metal complexes initiated by the oxidation of pyrrole group(s) should initiate the binding of Ru(II) complexes through C–C bond formation between the pyrrole groups, and the propagation of this process should generate a polypyrrole layer containing Ru(II)trisdiimine complex units on the electrode surface to form a Ru complex-based dye-coated NiO/PolypyrRu electrode. The singlet metal-to-ligand charge transfer (¹MLCT) absorption band of the Ru complex dye units was clearly observed in the UV-vis diffuse reflectance (DR) spectrum of NiO/PolypyrRu (Fig. 1e). Scanning electron microscopy (SEM) images of the electrodes before and after polymerization suggested that the electropolymerization of metal complex units occurred not only on the surface of the NiO electrode but also on deeper-lying NiO particles (Fig. 2c).

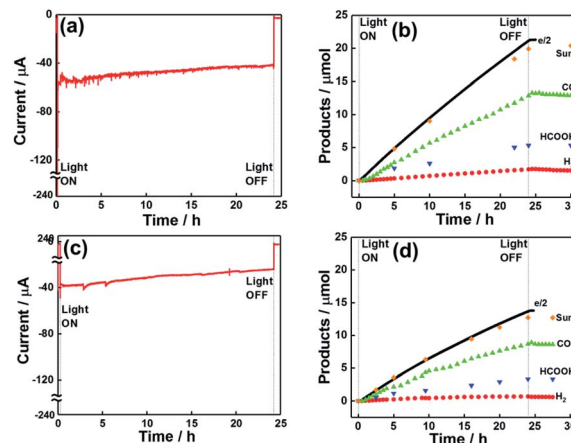


Fig. 9 Time courses of (a and c) photocurrent and (b and d) product levels expressed as half of electrons passed (black line), CO (green triangles), HCOOH (blue triangles), and H₂ (red circles). (a and b) NiO/PRu-PolyPyr-RuC₂RuCAT1, (c and d) NiO/PRu-PolyPyr-RuC₂RuCAT2 (electrode area = 2.5 cm^2 , applied bias (E) = -0.7 V vs. Ag/AgCl) were irradiated at $\lambda_{\text{ex}} = 460\text{--}650\text{ nm}$ (32 mW cm^{-2}) in CO₂-purged 50 mM aqueous NaHCO₃ (pH 6.6).

Although an increase in the sweep number to 50 (Fig. 1c) increased the amount of electrode-deposited Ru(II) complexes (14.4 nmol cm^{-2} , Fig. 1d), it also increased the difference between the peaks of the oxidation and reduction waves ($\Delta E = 83\text{ mV}$, cf. $\Delta E = 51.0\text{ mV}$ for 25 sweeps), i.e., electron mobility concomitantly decreased. The responses of the I - V curves of the polymer electrodes to visible light were investigated in CO₂-purged aqueous solutions containing 50 mM NaHCO₃ as the electrolyte (Fig. 1f), and the photocurrent density ($16.7\text{ }\mu\text{A cm}^{-2}$) of the electrode prepared by 25 sweeps exceeded that of the electrode prepared using 50 sweeps. These results clearly indicate that the sweep number of 25 is more suitable for molecular photoelectrode fabrication *via* pyrrole polymerization.

Fig. S2† shows the results obtained using Pyr2Ru as the starting complex and 25 sweeps between $E = 0$ and $+1.35\text{ V}$, revealing that the number of electrochemically active Ru complexes on the electrode exceeded that observed when PyrRu was used as the starting complex. However, upon irradiation, the former electrode afforded a lower photocurrent than the latter. The large ΔE of the electrode prepared from Pyr2Ru ($\Delta E = 133\text{ mV}$) also indicated that the electron mobility of the corresponding polymer was lower than that of the polymer prepared from PyrRu. These results provided useful guidance for the fabrication of molecular photoelectrodes from NiO and Ru(II) trisdiimine complexes connected with polypyrrole moieties, suggesting that the optimal conditions correspond to the use of Ru(II) complexes with only one Pyr₂bpy ligand and 25 sweeps between $E = 0$ and $+1.35\text{ V}$. Therefore, these polymerization conditions were chosen for subsequent experiments.

Preparation of dye-sensitized molecular photocathodes

Scheme 3 presents three Ru(II) complexes prepared to develop two kinds of polypyrrole-based dye-sensitized molecular photocathodes. PRuPyr has three different diimine ligands,



Table 3 Photoelectrochemical CO₂ reduction performances of photocathodes under various conditions

Entry	Electrode	Irradn time (h)	E_{app}^a (V)	Light intensity (mW cm ⁻²)	Products/ μmol (TON)			F_{red}^b (%)	CO ₂ red selectivity (%)
					CO	HCOOH	H ₂		
1	NiO/PRu- <i>PolyPyr</i> -RuC ₂ RuCAT1	5	-0.7	32	3.8 (152.6)	1.0 (40.2)	0.4 (16.1)	91	93
2		24	-0.7	32	14.1 (566.3)	4.6 (184.7)	1.8 (72.3)	96	92
3		24	-0.3	27	5.2 (208.8)	2.9 (116.5)	1.0 (40.2)	91	89
4		24	0.0	28	2.2 (88.4)	2.1 (84.3)	0.9 (36.1)	71	82
5		24	-0.7	8	4.9 (196.8)	3.2 (128.5)	1.1 (44.2)	87	89
6	NiO/PRu- <i>PolyPyr</i> -RuC ₂ RuCAT2	24	-0.7	36	7.8 (619)	3.4 (269.8)	1.4 (111.1)	93	89
7	NiO/PRu- <i>PolyPyr</i> -RuC ₂ RuCATbpy	5	-0.7	36	0.1	0.1	1.1	92	19
8	NiO/ <i>PolyPyr</i> -RuC ₂ RuCAT ^c	5	-0.7	32	0.2	0.6	<0.1	83	91
9	NiO/PRuPyr	5	-0.7	32	n.d. ^d	n.d. ^d	<0.1	9	n.d. ^d
10 ^e	NiO/PRuC ₂ RuCAT	5	-0.7	27	<0.1	0.2	<0.1	56	82

^a Applied potential vs. Ag/AgCl. ^b Faradaic efficiency of the total production of CO, HCOOH. ^c Without process 1. ^d Not detected. ^e Reference ¹².

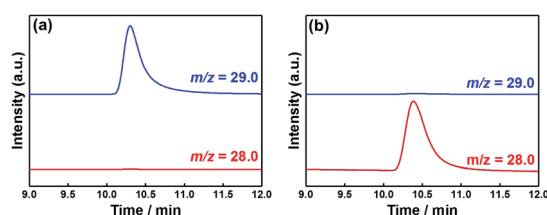


Fig. 10 GC-MS chromatograms of the gas phase formed in cells after irradiation, showing the peaks at $m/z = 28$ and 29 (¹²CO and ¹³CO, respectively). NiO/PRu-*PolyPyr*-RuC₂RuCAT1 was subjected to an applied bias of $E = -0.7$ V vs. Ag/AgCl and irradiated at $\lambda_{\text{ex}} = 460$ – 650 nm in CO₂-purged 50 mM aqueous NaHCO₃ (pH = 6.6) for 24 h using (a) ¹³CO₂ and NaH¹³CO₃ and (b) ordinary CO₂ and NaHCO₃.

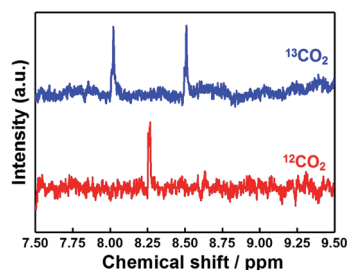


Fig. 11 ¹H NMR spectra of the solution obtained after photoelectrochemical reduction. NiO/PRu-*PolyPyr*-RuC₂RuCAT1 was subjected to a potential of $E = -0.7$ V vs. Ag/AgCl and irradiated at $\lambda_{\text{ex}} = 460$ – 650 nm in CO₂-purged 50 mM aqueous NaHCO₃ (pH = 6.6) for 24 h using ¹³CO₂ and NaH¹³CO₃ (blue) or ordinary CO₂ and NaHCO₃ (red).

namely [2,2'-bipyridine]-4,4'-diylbis(phosphonic acid) ((H₂O₃-PCH₂)₂bpy, anchor to the NiO electrode), dmb, and *Pyr*bpy. One of the other two Ru(II) complexes was dissolved in MeCN and polymerised with the PRuPyr attached to the NiO electrode to form a polypyrrole layer. *Pyr*RuC₂bpy has a free diimine moiety that can react with other metal ions after polymerization to introduce the catalyst unit, while *Pyr*RuC₂RuCAT is a supramolecular photocatalyst bearing both redox photosensitizer Ru(II) and catalytic Ru(II) units connected to each other *via* an ethylene chain.

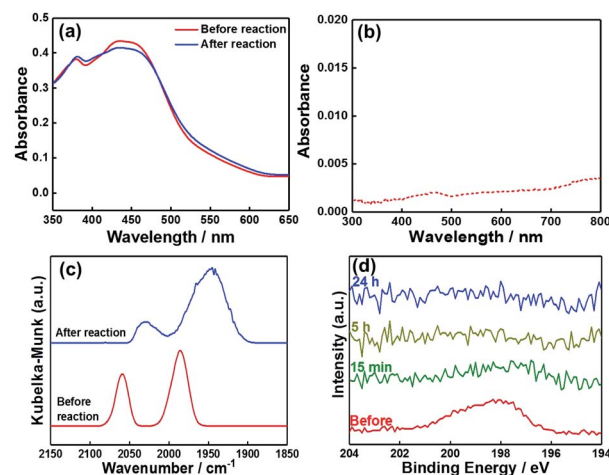


Fig. 12 (a) UV-Vis DR spectra of NiO/PRu-*PolyPyr*-RuC₂RuCAT1 before (red) and after (blue) photoelectrochemical CO₂ reduction (-0.7 V vs. Ag/AgCl, $\lambda_{\text{ex}} = 460$ – 650 nm, 24 h) in CO₂-purged 50 mM aqueous NaHCO₃. (b) UV-vis absorption spectrum of the reaction solution after the photocatalytic reaction. (c) FT-IR (DR) spectra of NiO/PRu-*PolyPyr*-RuC₂RuCAT1 before (red) and after (blue) the photocatalytic reaction. (d) Cl 2p spectra of NiO/PRu-*PolyPyr*-RuC₂-RuCAT1 before and after the photocatalytic reaction for various times.

A three-step method was used to prepare NiO/PRu-*PolyPyr*-RuC₂RuCAT1 as a dye-sensitized molecular photocathode (Scheme 4 and Fig. S3†). The NiO electrode was first modified with PRuPyr to give NiO/PRuPyr, in which the methylphosphonic acid groups of the diimine ligand work as anchors to the NiO electrode (process 1) (Scheme 4a). In the second step, NiO/PRuPyr was used as the working electrode for the oxidative electropolymerization of *Pyr*RuC₂bpy dissolved in MeCN containing Et₄NBF₄ (0.1 M) as an electrolyte (process 2) (Scheme 4b). Oxidative cyclic voltammetry cycling was carried out 25 times between $E = 0$ and $+1.35$ V vs. Ag/AgNO₃ at 100 mV s⁻¹, and the gradual increase of redox wave intensity after each scan (Fig. 3a) indicated the development of a polymer layer on the electrode to give NiO/PRu-*PolyPyr*-RuC₂bpy. Finally, NiO/PRu-*PolyPyr*-RuC₂bpy with free diimine moieties was reacted with [Ru(CO)₂Cl₂]_n in MeCN solution at room temperature to give



Table 4 Photoelectrochemical CO₂ reduction performances of NiO/PRu-PolyPyr-RuC₂RuCAT1 electrodes prepared by different number of potential sweeps for polymerization, with other electrode production and photocatalytic reaction parameters held constant

Entry	Number of sweeps	$e^-/2$ μmol	Product/μmol				CO ₂ red. selectivity (%)
			CO	HCOOH	H ₂	F_{red} (%)	
1	5	0.99	0.2	0.4	0.1	77	70
2	10	1.69	0.6	0.6	0.1	83	90
3	20	4.12	2.5	1.0	0.3	91	93
4	25	4.89	2.9	1.0	0.3	91	92
5	50	2.99	2.0	0.7	0.2	97	94
6	Fixed ^a	1.35	0.6	0.6	0.1	94	91
7	25 ^b	0.95	0.2	0.6	<0.1	83	91

^a Electrolysis for the polymerization was performed at 1.3 V vs. Ag/AgNO₃ for 30 min. ^b Without using PRuPyr to make the photocathode.

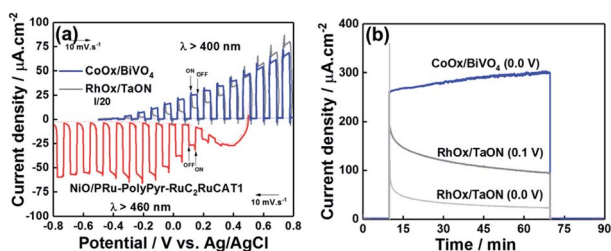
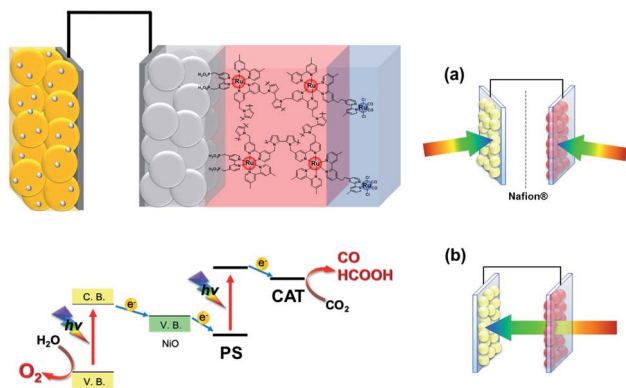


Fig. 13 (a) I - V curves of CoO_x/BiVO₄, RhO_x/TaON, and NiO/PRu-PolyPyr-RuC₂RuCAT1 as working electrodes recorded in CO₂-purged aqueous NaHCO₃ (50 mM) upon irradiation. Scan rate = 10 mV s⁻¹, λ_{ex} = 400–650 nm (41 mW cm⁻²) for CoO_x/BiVO₄ and RhO_x/TaON, and λ_{ex} = 460–650 nm (28 mW cm⁻²) for NiO/PRu-PolyPyr-RuC₂RuCAT1. (b) Time-dependent photocurrents of CoO_x/BiVO₄ at E_{app} = 0 V (blue) and RhO_x/TaON at E = 0 V (light grey) and 0.1 V (dark grey) vs. Ag/AgCl.



Scheme 5 Schematics of a full cell comprising a CoO_x/BiVO₄ or RhO_x/TaON photoanode and a NiO/PRu-PolyPyr-RuC₂RuCAT1 photocathode. (a) Irradiation of a full cell with two compartments separated by a Nafion® membrane. (b) Tandem-type full cell with a single compartment.

NiO/PRu-PolyPyr-RuC₂RuCAT1 with Ru(diimine)(CO)₂Cl₂-type complexes in the polypyrrole layer as catalytic units (process 3) (Fig. S3†) (Scheme 4c).

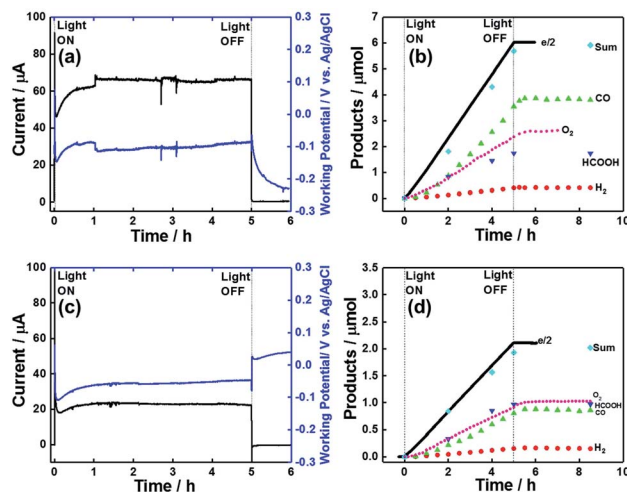


Fig. 14 (a and c) Time courses of electrode photocurrent (black) and working potential (blue), and (b and d) product amounts formed during visible light irradiation. Data recorded for photoelectrochemical cells with the NiO/PRu-PolyPyr-RuC₂RuCAT1 photocathode and (a and b) the CoO_x/BiVO₄ photoanode (photocathode: λ_{ex} = 460–650 nm, 32 mW cm⁻², photoanode: λ_{ex} = 400–650 nm, 28 mW cm⁻²) or (c and d) the RhO_x/TaON photoanode (photocathode: λ_{ex} = 460–650 nm, 34.4 mW cm⁻², photoanode: λ_{ex} = 400–650 nm, 32.2 mW cm⁻²) without any bias in aqueous CO₂-purged NaHCO₃ (50 mM, pH 6.6).

The synthesized electrodes were characterized by cyclic voltammetry (Fig. 3b and d), spectrophotometry, time-of-flight secondary ion mass spectrometry (TOF-SIMS), X-ray photoelectron spectroscopy (XPS), and SEM-based morphological analysis.

Fig. 4a shows the UV-vis DR spectra of NiO/PRu-PolyPyr-RuC₂RuCAT1, revealing an increase in the intensity of the ¹MLCT absorption band of Ru complexes after polymerization (process 2), while no such increase was observed after the formation of Ru catalyst units (process 3). This is reasonable, as Ru(diimine)(CO)₂Cl₂-type complexes have no strong absorption at wavelengths above 350 nm.¹² The Fourier transform infrared (FT-IR) DR spectrum of NiO/PRu-PolyPyr-RuC₂RuCAT1 showed two strong broad peaks at 2058 and 1986 cm⁻¹, which were attributed to the C=O stretches of CO ligands in catalyst units, whereas no such peaks were observed for NiO/PRu-PolyPyr-RuC₂bpy (Fig. 4b). The CO stretching frequencies well agreed with those of the corresponding binuclear Ru(II) complex ([*cis*-(CO)-*trans*-(Cl)-Ru(CO)₂Cl₂(bpyC₂bpy)Ru(dmb)₂](PF₆)₂ (bpyC₂bpy = 1,2-bis(4'-methyl-[2,2'-bipyridine]-4-yl)ethane)) drop-cast on the NiO electrode (2058 and 1991 cm⁻¹).¹² Fig. 4c and d show the X-ray photoelectron spectra of NiO/PRu-PolyPyr-RuC₂RuCAT1 with the Ru catalyst unit and catalyst-free NiO/PRu-PolyPyr-RuC₂bpy. Although both compounds featured a Ru 3d peak at 281.1 eV (Fig. 4c), only NiO/PRu-PolyPyr-RuC₂RuCAT1 showed a Cl 2p peak at 198.4 eV (Fig. 4d). These results suggested that the Ru(II) catalyst units on and/or in the polypyrrole polymer on the electrode existed predominantly in the form of *cis*-(CO)-*trans*-(Cl)-Ru(diimine)(CO)₂Cl₂, which has been investigated as a catalyst for CO₂ reduction in various photo- and electrocatalytic reactions.^{48–50}

Table 5 Photocatalytic performances of full-cell devices in CO₂-purged 50 mM NaHCO₃

Photo-anode	Light intensity (mW cm ⁻²)	Irradn time (h)	Products/μmol						<i>F</i> _{cathode} (%)	<i>F</i> _{anode} (%)	CO ₂ red. selectivity (%)	ECE (10 ⁻² %)
			<i>e</i> ⁻ /2	CO	HCOOH	H ₂	O ₂					
Two-component systems												
CoO _x /BiVO ₄	32.0 ^a , 28.0 ^b	5	6.0	3.9	1.7	0.4	2.6	99	87	93	8.3	
RhO _x /TaON	34.4 ^a , 32.2 ^b	5	2.1	0.9	1.0	0.2	1.0	96	97	92	2.0	
One-component systems												
CoO _x /BiVO ₄	100 ^c	1	1.6	0.6	0.9	0.1	0.6	98	74	92	4.8	
RhO _x /TaON	100 ^c	1	1.0	0.4	0.5	<0.1	0.5	95	96	95	2.7	

^a At λ_{ex} = 460–650 nm for photocathode. ^b At λ_{ex} = 400–650 nm for photoanode. ^c AM1.5.

^a At λ_{ex} = 460–650 nm for photocathode. ^b At λ_{ex} = 400–650 nm for photoanode. ^c AM1.5.

The SEM images of NiO/PRu-*PolyPyr*-RuC₂RuCAT1 and the bare NiO electrode reveals that polypyrrole-containing Ru complex units formed not only on the surface of the NiO electrode but also inside the NiO layer (Fig. 2a and d). The Ru complexes could sufficiently penetrate into the depth of electrodes owing to the porosity of the NiO electrode.

Fig. 5 shows the results of TOF-SIMS analysis, indicating the distribution of elements in the depth direction from the electrode surface, with the sputter time on the *x*-axis corresponding to the cross-sectional component in the depth direction.

Although the density of Ru⁺ species on the electrode surface was highest for NiO/PRu-*PolyPyr*-RuC₂RuCAT1, a relatively high intensity of these species was observed throughout the entire range of the NiO layer. This finding supports the conclusion that Ru complex units were fixed not only on the surface of the electrode, but also within its interior. Both the photosensitizer and catalyst moieties should be similarly dispersed on and in the NiO electrode because of the similarity of the TOF-SIMS spectra of NiO/PRu-*PolyPyr*-RuC₂RuCAT1 and NiO/PRu-*PolyPyr*-RuC₂bpy. A comparison of these spectra with that of NiO-PRuPyr indicates that polymerization increased the number of Ru complex units, especially in the NiO layer. The densities of BF₄⁻ and Et₄N⁺ in NiO/PRu-*PolyPyr*-RuC₂RuCAT1 were also measured using the TOF-SIMS analysis (Fig. S4†). BF₄⁻ was observed throughout the entire range of the NiO layer while no Et₄N⁺ was detected. This indicates that remove of reductants ions were achieved by the post handling after the polymerization (Experimental section).

We determined the total amount of the adsorbed Ru complexes on each electrode by using the ICP-MS analysis. The results are summarized in Table 1. The amount of the photosensitizers clearly increased after the oxidative polymerization: the amount of Ru(II) photosensitizer of NiO/PRu-*PolyPyr*-RuC₂bpy (step-2) was 30.2 nmol cm⁻² while that of NiO/PRuPyr (after the step-1) was 6.2 nmol cm⁻². After incorporation of the catalysts into the polymer electrode a total amount of Ru complexes increase again to 40.1 nmol cm⁻². Therefore, the adsorbed amount of the Ru catalysts was 9.9 nmol cm⁻² in the case of NiO/PRu-*PolyPyr*-RuC₂RuCAT1, which is about one third of the photosensitizers. This means about 14 nmol cm⁻² of the free bpy units remained in NiO/PRu-*PolyPyr*-RuC₂RuCAT1. Limitation of space in the polypyrrole polymer might suppress the

reaction of these bpy units with the precursor of the catalyst in the step 3.

The amounts of electrochemically active photosensitizers after each step were determined by cyclic voltammetric analysis of the film (Table 2).²⁷ The electroactive photosensitizers were also increased after each adsorption steps of the photosensitizers: 2.0 nmol cm⁻² (NiO/PRuPyr) and 9.6 nmol cm⁻² (NiO/PRu-*PolyPyr*-RuC₂bpy). After the introduction of the catalysts, the amounts of electrochemically active photosensitizers slightly increased (11.6 nmol cm⁻², NiO/PRu-*PolyPyr*-RuC₂-RuCAT1) probably because of small morphology change of the polypyrrole phase during the reaction. The proportion of the electroactive photosensitizers to the total amount of the photosensitizers was about 0.3 (Table 2). Although this result indicates that major part of the immobilized photosensitizers was silent during the electrochemical scans, the non-electroactive photosensitizers possibly worked in the photocatalytic reactions owing to slower electron hopping than the time scale of the CV measurements and/or electron transfer in the excited state.

The stability of NiO/PRu-*PolyPyr*-RuC₂RuCAT1 in an aqueous solution containing 50 mM NaHCO₃ (this solution was used for photocatalytic CO₂ reduction, as described below) was checked by spectrophotometric and electrochemical analyses using NiO/PRuPyr as a reference sample without polymerization. The voltammograms of NiO/PRu-*PolyPyr*-RuC₂RuCAT1 recorded before and after 24 h soaking in the above solution (Fig. 6a) indicated that much less than 5% of the electroactive Ru(II) complexes was detached from the electrode, whereas, in the case of NiO/PRuPyr (Fig. 6b), more than 70% of PRuPyr adsorbed on the NiO electrode through methylphosphonic acid groups was detached into the aqueous solution. A much stronger immobilization of the Ru complex units in the polypyrrole layer on the electrode was also confirmed by spectrophotometric analysis. Specifically, the ¹MLCT absorption band in the UV-vis (DR) spectrum of NiO/PRu-*PolyPyr*-RuC₂RuCAT1 remained almost unchanged after soaking (Fig. 6c), and no Ru complexes were observed in the soaking solution (Fig. 6e). On the other hand, almost no ¹MLCT absorption was observed in the UV-vis (DR) spectrum of soaked NiO/PRuPyr, and the absorption of dissolved PRuPyr was observed in the corresponding soaking solution (Fig. 6d and f). These results indicated that the fixation of Ru complexes using



the polypyrrole layer is a very powerful means of preventing their detachment from the electrode in this solution.

Another dye-sensitized molecular photocathode (NiO/PRu-*PolyPyr*-RuC₂RuCAT2) was prepared by a simple two-step method. In this case, the NiO/PRuPyr electrode was used as the working electrode for the oxidative electropolymerization of *Pyr*RuC₂RuCAT, which already has both photosensitizer and catalyst units, in MeCN containing Et₄NBF₄ (0.1 M) as an electrolyte. Oxidative cyclic voltammetry cycling was performed between 0 and +1.35 V vs. Ag/AgNO₃ at 100 mV s⁻¹ (Scheme 4a and d), *i.e.*, under the same polymerization conditions as those used for NiO/PRu-*PolyPyr*-RuC₂RuCAT1. The voltammograms recorded during electrochemical polymerization (Fig. 3c) resembled those obtained after process 2 using *Pyr*RuC₂bpy (Fig. 3a). This is reasonable, as the oxidation potential of the incorporated catalyst unit is more positive than that of the pyrrole groups (Fig. S5†). In other words, the catalyst unit incorporation did not affect the oxidative polymerization of pyrrole groups. We can use the amounts of the Ru complexes in NiO/PRuPyr and NiO/PRu-*PolyPyr*-RuC₂RuCAT2, which were obtained by using the ICP-MS analysis, to determine both amounts of the photosensitizers and catalysts in NiO/PRu-*PolyPyr*-RuC₂RuCAT2 because we can assume that the adsorbed amounts of the photosensitizer and catalyst units to NiO/PRuPyr (step 2 in the two-step method) was same to each other because the Ru(II)-Ru(II) supramolecule with the 1 : 1 ratio between the photosensitizer and catalyst units was used as the monomer for the polymerization. These results are summarized in Table 1. Both amounts of the adsorbed photosensitizers and the catalysts in NiO/PRu-*PolyPyr*-RuC₂RuCAT2 were less than half of those in NiO/PRu-*PolyPyr*-RuC₂RuCAT1. This difference was ascribed to the much higher bulkiness of the RuCAT unit of *Pyr*RuC₂RuCAT compared to that of the free diimine unit of *Pyr*RuC₂bpy, which possibly suppressed the supply of *Pyr*RuC₂RuCAT to NiO particles at the electrode depth. The number of active Ru complexes in NiO/PRu-*PolyPyr*-RuC₂-RuCAT2 estimated by cyclic voltammetry of the polymer electrode (4.4 nmol cm⁻², Fig. 3d) was smaller than that of the electrode prepared using the abovementioned three-step method (11.6 nmol cm⁻², Fig. 3b).

In the case of NiO/PRu-*PolyPyr*-RuC₂RuCAT2, similar structures and stabilities of Ru complex units in the polypyrrole layer were confirmed by UV-vis DR spectroscopy (Fig. 7a), FT-IR spectroscopy (Fig. 7b), TOF-SIMS (Fig. 7c), and SEM (Fig. 2b). Notably, the catalytic unit with the *cis*-(CO)-*trans*-(Cl)-Ru(diimine)(CO)₂Cl₂ structure did not change during oxidative polymerization. This is one of critical differences of the oxidative polymerization method of the pyrrole groups from the previously reported reductive polymerization method using a similar Ru(II)-Ru(II) supramolecular photocatalyst with vinyl groups instead of the pyrrole groups, noticeable shifts in CO stretching frequencies were observed after the reductive polymerization.¹² This finding suggested the formation of Ru-C bonds during the reductive polymerization, which induced the desorption of complexes from the electrode during photocatalytic reactions.¹² Such decomposition process of the

photoanode was not observed in the system using NiO/PRu-*PolyPyr*-RuC₂RuCAT2.

Photoresponses of dye-sensitized molecular photocathodes

Fig. 8a presents the *I*-*V* curve (linear sweep voltammogram) of NiO/PRu-*PolyPyr*-RuC₂RuCAT1 recorded during irradiation at λ_{ex} = 460–650 nm in CO₂-purged aqueous 50 mM NaHCO₃ as the electrolyte, revealing a photocathodic current response starting from *E* = +0.4 V vs. Ag/AgCl. The photocurrent steadily increased up to *E* = -0.2 V, saturating at more negative potentials. This photocurrent increase was faster than that of a previously reported NiO/PRu-*PolyVinyl*-RuC₂RuCAT photocathode¹² prepared by a similar three-step method except for the reductive polymerization of the vinyl groups of the Ru photosensitizer units instead of the oxidative polymerization of the pyrrole groups. Specifically, the maximum photocurrent (61 μA cm⁻²) was achieved even at *E* = -0.2 V in the case of NiO/PRu-*PolyPyr*-RuC₂RuCAT1, whereas *E* = -0.5 V was required to maximize the photocurrent of NiO/PRu-*PolyVinyl*-RuC₂RuCAT (28.0 μA cm⁻² at *E* = -0.2 V, 38.0 μA cm⁻² at *E* = -0.5 V). At *E* = 0 V, NiO/PRu-*PolyPyr*-RuC₂RuCAT1 maintained ~83% of the maximum photocurrent density, whereas this number equalled only 45% for NiO/PRu-*PolyVinyl*-RuC₂RuCAT. These results strongly indicated that the electric resistance of the polypyrrole layer in NiO/PRu-*PolyPyr*-RuC₂RuCAT1 was lower than that of the polyvinyl layer in NiO/PRu-*PolyVinyl*-RuC₂RuCAT.

The dependence of IPCE on the wavelength of irradiated light (Fig. 8b) well agreed with the behaviour of the ¹MLCT absorption band of Ru complex photosensitizer moieties. Therefore, the cathodic photocurrent was exclusively generated by the excitation of Ru photosensitizer moieties in the polymerized layer on the NiO electrode. The maximum IPCE (4.7% at λ_{ex} = 480 nm) was approximately four times higher than that of a previously reported system with NiO/PRu-*PolyVinyl*-RuC₂-RuCAT (IPCE = 1.2%).¹²

The responses of photocathodes obtained after each fabrication step were observed at *E* = -0.7 V and equalled 9.8 μA cm⁻² for NiO/PRuPyr prepared by process 1 and 24.5 μA cm⁻² for NiO/PRu-*PolyPyr*-RuC₂bpy prepared by process 2. Both of these values were much lower than that observed for NiO/PRu-*PolyPyr*-RuC₂RuCAT1 (57 μA cm⁻²).

Photoelectrochemical CO₂ reduction over dye-sensitized molecular photocathodes

The photocatalytic activity of dye-sensitized molecular photocathodes for CO₂ reduction under external bias was evaluated using them as working electrodes and Pt wire as a counter electrode. These electrodes were set in each compartment of an H-shaped cell, in which the compartments were separated using a Nafion® membrane, and a Ag/AgCl (Sat. KCl aq.) KCl reference electrode was set in the same compartment as the dye-sensitized molecular photocathode. Aqueous 50 mM NaHCO₃ as the electrolyte was introduced into the cell and purged with CO₂ for 30 min. The compartment with the dye-sensitized photocathode was irradiated at λ_{ex} = 460–650 nm using a 300 W Xe lamp with a cutoff filter under applied biases of *E*_{app}



= 0, -0.3, and -0.7 V. During irradiation, CO₂ flowed into the solution, and the flow gas was analysed by a micro-GC to determine the levels of the produced CO and H₂. The reaction solution was sampled using a syringe through a septum cap attached to the cathodic compartment. Fig. 9a shows the irradiation time-dependent photocurrent at $E_{\text{app}} = -0.7$ V in the system with NiO/PRu-PolyPyr-RuC₂RuCAT1 as the photocathode, revealing that a continuous photocathodic current of 57 to 43 μA was observed over 24 h. CO and HCOOH were continuously formed as major products along with small amounts of H₂ (Fig. 9b). The CO₂ reduction selectivity equalled 92%, while the faradaic efficiency (F_{red}) of this reduction equalled 96% after 24 h irradiation, even though the photocatalytic reaction proceeded in an aqueous solution with pH 6.8. The product turnover numbers after 24 h irradiation equalled 566.3 (CO), 184.7 (HCOOH), and 72.3 (H₂) (entry 2 in Table 3), and the number of Ru catalyst moieties was estimated by ICP-MS analysis as 24.9 nmol (see experimental).

Control experiments performed without irradiation, without applied potential, or under an Ar atmosphere using phosphate buffer (pH 7.4) instead of NaHCO₃ as an electrolyte gave no or less CO₂ reduction products (Table S5†), suggesting that light, applied bias, and CO₂ are required for photocatalytic CO₂ reduction. Compared to NiO/PRu-PolyPyr-RuC₂RuCAT1, the catalyst unit-free NiO/PRu-PolyPyr-RuC₂bpy showed no significant activity for CO₂ reduction but afforded some H₂ upon irradiation (entry 7 in Table 3), which indicated that the Ru catalyst unit is essential for the photocatalytic reduction of CO₂ in this photoelectrochemical system.

Fig. 10a shows a GC-MS chromatogram of the gas phase formed in the photocathode compartment after 24 h irradiation of the system containing ¹³CO₂ and NaH¹³CO₃, indicating the almost selective formation of ¹³CO ($m/z = 29$). On the other hand, a similar experiment with ordinary CO₂ and NaHCO₃ afforded a main peak at $m/z = 28$ (¹²CO; Fig. 10b). Fig. 11 shows the ¹H NMR spectra of the reaction solution formed in the cathodic compartment after irradiation. In the case of ¹³CO₂ and NaH¹³CO₃, a doublet attributable to H¹³COO⁻ was observed at 8.26 ppm ($J_{\text{CH}} = 196$ Hz) because of ¹H-¹³C coupling, while a singlet was observed at 8.26 ppm for the system with ordinary CO₂ and NaHCO₃. These isotope labelling experiments confirmed that CO₂ acted as a source of carbon in the photocatalytic reduction products (CO and HCOOH).

After the photocatalytic reaction, the photocathode was analysed by UV-vis DR spectroscopy, FT-IR (DR) spectroscopy, and XPS. Almost no changes were observed in the UV-vis DR spectra after the reaction (Fig. 12a), and no desorbed Ru(II) trisdiimine complexes were observed in the reaction solution (Fig. 12b). These results indicate that the Ru(II) photosensitizer units were stable and that the polypyrrole layer was strong enough to keep the Ru photosensitizer units in its layer during the photocatalytic reaction for at least one day. Fig. 12c shows the expanded FT-IR (DR) spectra depicting the ν_{CO} bands before and after the reaction. Although these bands were still observed after the reaction, they were shifted to lower wavenumbers ($\nu_{\text{CO}} = 1945, 2030 \text{ cm}^{-1}$), which suggest that the Cl⁻ ligands of Ru catalyst units were replaced with electron-donating ligands

such as OH⁻ or HCOO⁻. The exchange of Cl⁻ ligands during the photocatalytic reaction was further confirmed by the disappearance of the Cl 2p peaks in the X-ray photoelectron spectra (Fig. 12d), which indicate that the loss of Cl⁻ mostly proceeded within the initial 15 min of the photocatalytic reaction. As the concentration change of Ru catalyst units could not be determined, one cannot discuss the reason(s) of why the photocatalytic reaction rate decreased with time, even though it remained at 76% of the initial value after 24 h (Fig. 9a).

The formation of reduction products became slower at lower applied potentials, *i.e.*, at $E_{\text{app}} = -0.3$ and 0 V (entries 3 and 4 in Table 3), even though the photocurrents at $E_{\text{app}} \leq -0.2$ V were similar (Fig. 8). The back electron transfer from the reduced Ru complex units to the electrode might have proceeded more efficiently at $E_{\text{app}} = -0.3$ V than at $E_{\text{app}} = -0.7$ V. It should be noted, however, that photocatalytic CO₂ reduction still actively proceeded even at $E_{\text{app}} = 0$ V. Interestingly, the HCOOH : CO ratio at these lower applied potentials exceeded that obtained at $E_{\text{app}} = -0.7$ V (entry 2 in Table 3). A similar change in reduction product ratio, that is, a decrease in the fraction of CO, was observed with decreasing irradiation intensity (32 → 8 mW cm⁻²) even at $E_{\text{app}} = -0.7$ V (entries 2 and 5 in Table 3 and Fig. S6†). These results suggest that slower electron injection into the catalyst units favours the formation of HCOOH. Ishida *et al.* reported a similar phenomenon in homogeneous solutions, *i.e.*, the HCOOH : CO ratio increased with decreasing irradiation intensity in the homogeneous photocatalytic reduction of CO₂ promoted by a mixture of Ru(bpy)(CO)₂Cl₂ and [Ru(bpy)₃]²⁺ (bpy = 2,2'-bipyridine), and proposed that slower electron injection into the one-electron-reduced intermediate produced from the Ru catalyst induces the formation of a Ru catalyst dimer, with further reduction affording HCOOH.⁵¹ Kubiak *et al.* proposed that in the electrocatalytic reduction of CO₂ using Ru(6Mesbpy)(CO)₂Cl₂, the bpy ligand of which has bulky mesityl groups at 6,6'-positions to suppress dimerization, slower electron injection into a Ru(II) formate complex as an intermediate of both CO and HCOOH formation induces the loss of the formate ligand from the Ru catalyst unit.⁵² Although we cannot clarify the real reason of why faster electron injection into the Ru catalyst unit favours CO production, we note that the selectivity for CO₂ over H₂ remained high even in slower-electron-injection systems.

Subsequently, we determined the optimal number of potential sweeps in the polymerization of PyrRuC₂bpy with NiO/PRuPyr (process 2) for the photocatalytic reduction of CO₂ (Fig. S7,† Table 4). The best performance was obtained for the photoelectrode prepared by 25 sweeps (entry 4, Table 4), in good agreement with the electrochemical properties of the photoelectrodes described in the section "Optimization of redox photosensitizer layer on electrodes." Notably, the photoelectrode prepared by continuous electrolysis at a fixed potential (1.3 V vs. Ag/AgNO₃) for 30 min exhibited poor photocatalytic performance (entry 6, Table 4).

To check the necessity of the first process of NiO/PRu-PolyPyr-RuC₂RuCAT1 fabrication (process 1), we performed the direct polymerization of PyrRuC₂bpy on the NiO electrode without PRuPyr using 25 potential sweeps between 0 and



+1.35 V vs. Ag/AgNO₃ at 100 mV s⁻¹, and the electrode was then reacted with [Ru(CO)₂Cl₂]_n in MeCN solution at room temperature, as in processes 2 and 3 for the synthesis of NiO/PRu-PolyPyr-RuC₂RuCAT1 (entry 7 in Table 4).

Although this photocathode without phosphonic acid anchoring groups showed a certain photoresponse, its photocatalytic activity was much poorer than that of NiO/PRu-PolyPyr-RuC₂RuCAT1 (entry 7 in Table 4). Therefore, process 1 was concluded to be important for the synthesis of an efficient dye-sensitized molecular photocathode.

Fig. 9c and d show the photocatalytic performance of the system with NiO/PRu-PolyPyr-RuC₂RuCAT2 as a photocathode under an applied bias of -0.7, revealing the continuous production of CO and HCOOH as the main products for 24 h. The faradaic efficiency of reduction was 93% after 24 h. As the number of Ru catalyst units in this photoelectrode (12.6 nmol) was much smaller than that in NiO/PRu-PolyPyr-RuC₂RuCAT1 (24.9 nmol), the amount of reduction products was also smaller in the former system. However, the TONs obtained for NiO/PRu-PolyPyr-RuC₂RuCAT2 (entry 6 in Table 3) exceeded those obtained for NiO/PRu-PolyPyr-RuC₂RuCAT1 (entry 2 in Table 3).

In conclusion of this section, both NiO/PRu-PolyPyr-RuC₂-RuCAT1 and NiO/PRu-PolyPyr-RuC₂RuCAT2 were found to be good dye-sensitized molecular photocathodes for photocatalytic CO₂ reduction, exhibiting high selectivity, durability, and faradaic efficiency and featuring IPCEs much higher (IPCE_{max} = 4.7%) and onset potentials more positive than those of previously reported dye-sensitized molecular photocathodes (IPCE_{max} < 2%)^{11,12,19,27} such as NiO/PRu-PolyVinyl-RuC₂RuCAT with a polyvinyl polymer layer instead of the polypyrrole layer.¹² The faster electron hopping through the conjugated polypyrrole assembly should generate a higher photocurrent density at a lower bias in comparison with the polyvinyl-based electrodes. Therefore, polypyrrole systems are highly promising for the fabrication of good full-cell devices that drive photocatalytic CO₂ reduction using water as the reductant under zero bias conditions with visible light irradiation as the only energy input. Owing to the faster speed of product formation, we chose NiO/PRu-PolyPyr-RuC₂RuCAT1 as a photocathode for constructing full cells as follows.

Full cells for photocatalytic CO₂ reduction coupled with water oxidation

We chose two types of photoanodes, *i.e.*, BiVO₄ modified with CoO_x as a co-catalyst (CoO_x/BiVO₄)^{53,54} and TaON modified with RhO_x as a co-catalyst (RhO_x/TaON),⁵⁵ as they were reported as stable semiconductor photoanodes for water oxidation under visible light irradiation with sufficient stability and sufficiently negative conduction band potentials to pass electrons to the valence band of NiO.^{56,57} The photoelectrochemical properties of CoO_x/BiVO₄ and RhO_x/TaON were first checked by measuring their light responses (λ_{ex} = 400–650 nm, 41.2 mW cm⁻²) (Fig. 13a, blue and gray lines), and in both cases, we observed good overlaps with the *I*-*V* curve of the NiO/PRu-PolyPyr-RuC₂-RuCAT1 photocathode (red line) in CO₂-purged aqueous solutions containing 50 mM NaHCO₃ as the electrolyte (pH = 6.6).

Therefore, the above electrodes were then used for photocatalytic CO₂ reduction. Relatively stable photocurrents continuously flowed in both photoanodes under low applied biases (E_{app} = 0 or 0.1 V vs. Ag/AgCl) and visible light irradiation in the same solutions (Fig. 13b and S8†). We used two types of photoelectrochemical cells with the NiO/PRu-PolyPyr-RuC₂-RuCAT1 photocathode and the CoO_x/BiVO₄ or RhO_x/TaON photoanode. One type of cells featured a two-compartment system where the photocathode and the photoanode were separated from each other by a Nafion® membrane and were irradiated using different light sources (32–34 mW cm⁻² at λ_{ex} = 460–650 nm for the photocathode, 28–32 mW cm⁻² at λ_{ex} = 400–650 nm for the photoanode (Scheme 5a). In cells of the other (tandem) type, both photoelectrodes were set in the same compartment. Simulated solar light (AM1.5) first illuminated the photocathode, and then the permeated light illuminated the photoanode (Scheme 5b, Fig. S9 and S10†). No external bias was applied to the photoelectrodes in either cell type, that is, visible light was the only energy source.

Fig. 14a shows the time courses of the electrode photocurrent and working potential in the two-component system with the CoO_x/BiVO₄ photoanode, revealing that they were stable during 5 h irradiation. During this irradiation, CO and HCOOH were constantly produced in the photocathodic compartment, while O₂ was produced in the photoanodic compartment (Fig. 14b). The following results were obtained after 5 h: CO (3.90 μ mol, TON_{CO} = 156.6), HCOOH (1.82 μ mol, TON_{HCOOH} = 73.1), and O₂ (2.60 μ mol). The much lower amount of produced H₂ (0.42 μ mol) indicated high selectivity for CO₂ reduction (93%). The faradaic efficiencies of the photocathode and photoanode equaled 99 and 87%, respectively. The highest energy conversion efficiency obtained in the reported full cells with dye-sensitized molecular photocathodes equaled $8.3 \times 10^{-2}\%$ (Table 5). The full cell with the RhO_x/TaON photoanode also drove the photocatalytic reduction of CO₂ with water (Fig. 14c and d). The main products were also CO (0.88 μ mol, TON_{CO} = 35.3) and HCOOH (0.97 μ mol, TON_{HCOOH} = 39.0), and a high selectivity was observed for CO₂ reduction (92%) in the photocathodic compartment, while O₂ (1.02 μ mol) was formed in the photoanodic compartment. Although a smaller photocurrent density was observed in this system, the faradaic efficiency of O₂ evolution significantly improved to F_{anode} = 98% with F_{cathode} = 96%. The energy conversion efficiency equaled $2.0 \times 10^{-2}\%$ (Table 5). The selectivity of O₂ evolution in the system with the RhO_x/TaON photoanode was higher than that in the system with the CoO_x/BiVO₄ photoanode, which produced O₂ as well as H₂O₂, in line with previous reports.^{58–60}

The mechanism of the photocatalytic reduction of CO₂ with water as the reductant in the full-cell system is illustrated in Scheme 5. Visible light is sequentially absorbed by the Ru(II) photosensitizer unit in the photocathode and n-type semiconductor (BiVO₄ or TaON) in the photoanode, in which a two-photon process, the so-called Z-scheme, induces electron transfer from the photoanode to the photocathode, and causes both strong reduction and oxidation powers on each side. The produced active electron is finally transferred to the Ru(II)



catalyst unit, and the hole is transferred to the co-catalyst (CoO_x or RhO_x).

These Z-scheme electron transfer processes continuously proceed during irradiation, inducing the two-electron reduction of one CO_2 molecule on the photocathode and the four-electron oxidation of two water molecules to furnish CO , HCOOH , and O_2 (partial two-electron oxidation of one water molecule to afford H_2O_2 also occurs on the $\text{CoO}_x/\text{BiVO}_4$ photoanode).

Conclusions

The introduction of a polypyrrole assembly into a dye-sensitized molecular photocathode as a connector between the redox photosensitizer, catalyst, and NiO electrode increased the photocatalytic performance of this electrode for CO_2 reduction, especially IPCE, which was more than three times higher than that of a previously reported dye-sensitized molecular photocathode constructed by the polymerization of vinyl groups instead of pyrrole groups. The maximum photocurrent was obtained even at a low applied potential ($E = -0.2$ V vs. Ag/AgCl). The durability of the modified photoelectrode was reasonably good, i.e., 81% of the initial photocurrent was maintained even after 24 h irradiation. Full cells comprising this novel dye-sensitized molecular photocathode and the $\text{CoO}_x/\text{BiVO}_4$ or RhO_x/TaON photocathode could efficiently and selectively reduce CO_2 with water using visible light as the only energy source without any external bias, and the highest energy conversion efficiency was achieved in the reported full-cell systems with dye-sensitized molecular photocathodes.

Experimental

General procedures

^1H NMR (400 MHz) and ^{31}P NMR (162 MHz) spectra were recorded on a JEOL ECA400-II spectrometer. Transmission FT-IR spectra of metal complexes in MeCN were recorded using a JASCO FT/IR-6600 spectrometer at a resolution of 1 cm^{-1} . FT-IR spectra in DR mode were recorded using an FT/IR-6600 spectrometer equipped with a DR unit (DR-81, JASCO) at a resolution of 2 cm^{-1} . Electrospray ionization-mass spectrometry (ESI-MS) analyses were performed using a Shimadzu LC-MS-2010 system with MeCN as the mobile phase. Inductively coupled plasma mass spectrometry (ICP-MS) analyses were performed in $\text{H}_2\text{O} : \text{HCl} : \text{H}_2\text{SO}_4$ (1 : 1 : 1) mixed acid solutions containing Ru complexes desorbed from the electrode. SEM images were obtained using a Hitachi S4700 system. The electrochemical analysis of metal complexes in MeCN solution and oxidative polymerization were performed in a three-electrode system using a BAS760Es electrochemical analyser. TOF-SIMS analyses were performed using a 5-100-AD instrument (ION-TOF GmbH). UV-vis absorption spectra in DR mode were recorded using a JASCO V-565 spectrophotometer. X-ray photoelectron spectra were recorded using a Shimadzu ESCA-4000 instrument, and Ru 3d and Cl 2p binding energies were corrected using the C 1s peak at 285.0 eV as a reference. The light responses of I - V curves during photoelectrochemical CO_2 reduction were measured using a Hokuto Denko potentiostat

(Hokuto Denko HZ-7000) with a MAX 303 light source equipped with HOYA Y48 ($\lambda > 460\text{ nm}$) or L42 ($\lambda > 400\text{ nm}$) cutoff filters. Gas analysis was carried out using a micro-GC instrument (Agilent), and isotopic labelling studies were performed using GC-MS (Shimadzu MS-2010).

Materials

Acetonitrile (MeCN) was distilled twice after refluxing over P_2O_5 overnight and then distilled over CaH_2 immediately before use. Tetrabutylammonium tetrafluoroborate (Et_4NBF_4) was recrystallized from MeCN/ethyl acetate and then dried under reduced pressure at 373 K overnight before utilization. $^{13}\text{CO}_2$ (99% ^{13}C) was purchased from Cambridge Isotope Laboratories, Inc. $\text{NaH}^{13}\text{CO}_3$ (98% ^{13}C) was purchased from Sigma Aldrich. 4,4'-Bis(bromomethyl)-2,2'-bipyridine,⁶¹ 1,2-bis(4'-methyl-[2,2'-bipyridin]-4-yl)ethane (bpyC_2bpy),⁶² 4,4'-bis-(methylphosphonate)-2,2'-bipyridine ($(\text{Et}_2\text{O}_3\text{PCH}_2)_2\text{bpy}$),⁶¹ $[\text{Ru}(\text{dmb})_2]\text{Cl}_2$,^{63,64} and $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ ⁶⁵ as well as NiO ¹⁰ and $\text{CoO}_x/\text{BiVO}_4$ (ref. 12) photoanodes were prepared as reported elsewhere. Pyrrole (TCI, >99%) was freshly distilled under reduced pressure and immediately used for synthesis. All other reagents and solvents were commercially available and used without further purification. The synthetic scheme and ^1H NMR spectra of all other metal complexes are given in the ESI† (SI-1).

Synthesis

4,4'-Bis((1H-pyrrol-1-yl)methyl)-2,2'-bipyridine (Pyrdmb). KOH pellets (1 g, 17.9 mmol) were crushed to a fine powder and transferred to a three-neck round-bottom flask kept under Ar flow. Dry dimethylformamide (DMF) (10 mL) was then injected into the flask, and the mixture was stirred. Freshly distilled pyrrole (1 mL, 15.42 mmol) was injected, and the mixture was left for 15 min until the solution turned pale yellow. 4,4'-Bis(bromomethyl)-2,2'-bipyridine (0.5 g, 1.47 mmol) dissolved in DMF (5 mL) was dropwise added to the pale-yellow pyrrole-KOH mixture, and the solution was stirred at 25 °C overnight under Ar. The crude yellowish product was collected by precipitation in water and further extracted with dichloromethane (DCM) ($3 \times 50\text{ mL}$) and the combined organic layers were evaporated to dryness. The crude product was purified by recrystallization from DCM-hexane to yield the final product as pale-yellow crystals (315 mg, 60.8%). ^1H NMR (400 MHz, CDCl_3) δ /ppm: 8.56 (d, $J = 4\text{ Hz}$, 2H), 8.21 (s, 2H), 6.88 (d, $J = 4\text{ Hz}$, 2H), 6.71 (t, $J = 2\text{ Hz}$, 4H), 6.23 (t, $J = 2\text{ Hz}$, 4H, C-H (Pyr)), 5.15 (s, 4H, $-\text{CH}_2-$). ESI-MS (in MeCN): m/z 315.0 $[\text{M}]^+$

$[\text{Ru}(\text{Pyrdmb})_2\text{Cl}_2]$. A DMF solution of LiCl (56.73 mg, 1.34 mmol), $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (50 mg, 0.191 mmol), and Pyrdmb (60.06 mg, 0.191 mmol) was refluxed under Ar for 2.5 h and extracted using DCM ($4 \times 30\text{ mL}$). The combined organic layer was washed with water ($4 \times 15\text{ mL}$), dried over anhydrous Na_2SO_4 , and evaporated to dryness. The residue was purified by re-precipitation in DCM-diethyl ether to yield the final product as purplish black solids (76.4 mg, 81.2%). ^1H NMR (400 MHz, CDCl_3) δ /ppm: 10.05 (d, $J = 8\text{ Hz}$, 2H), 7.42 (dd, $J = 12, 4\text{ Hz}$, 8H), 6.73 (t, $J = 2\text{ Hz}$, 4H), 6.54 (t, $J = 2\text{ Hz}$, 4H), 6.45 (d, $J = 5.2\text{ Hz}$,



2H) 6.27 (t, $J = 2$ Hz, 4H), 6.18 (t, $J = 2$ Hz, 4H), 5.22 (s, 4H), 5.01 (s, 4H). ESI-MS (in MeCN): $m/z = 806.0$ $[\text{M-Cl} + \text{MeCN}]^+$.

[Ru(dmb)(Pyrdmb)Cl₂]. A solution of $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (162.0 mg, 0.296 mmol) and 4,4'-dimethyl-2,2'-bipyridine (103 mg, 0.561 mmol) in MeCN (20 mL) was refluxed for 5 h under Ar and evaporated to afford $[\text{Ru}(\text{dmb})(p\text{-cymene})\text{Cl}]\text{Cl}$. ESI-MS (in MeCN) $m/z = 455$ $[\text{M-Cl}]^+$. $[\text{Ru}(\text{dmb})(p\text{-cymene})\text{Cl}]\text{Cl}$ was then dissolved in MeCN (500 mL), and N₂ was bubbled into the solution for 30 min. The solution was then irradiated with a high-pressure Hg lamp (300 W) for 24 h, and the formation of $[\text{Ru}(\text{dmb})(\text{MeCN})_3\text{Cl}]\text{Cl}$ was confirmed by ESI-MS ($m/z = 444.0$ $[\text{M-Cl}]^+$). The black solid obtained after solvent removal was mixed with 4,4'-bis((1H-pyrrol-1-yl)methyl)-2,2'-bipyridine (Pyrdmb) (176 mg, 0.56 mmol) in 150 mL of an acetone–MeOH (5 vol%) mixture, and the solution was refluxed under Ar overnight. $[\text{Ru}(\text{dmb})(\text{Pyrdmb})\text{Cl}_2]$ was obtained by re-precipitation in DCM–diethyl ether as a purplish black solid. ESI-MS (in MeCN): $m/z = 670.0$ $[\text{M}]^+$.

[Ru(dmb)₂(Pyrdmb)](PF₆)₂ (PyrRu). A solution of $[\text{Ru}(\text{dmb})_2\text{Cl}_2]$ (35.0 mg, 0.0647 mmol) and 4,4'-bis((1H-pyrrol-1-yl)methyl)-2,2'-bipyridine (25.0 mg, 0.0795 mmol) in ethanol (20 mL) was refluxed under Ar overnight and then evaporated. The crude product was extracted using 150 mL of a DCM–water (1 : 2) mixture containing 0.1 M NH₄PF₆, and the product was isolated from the organic layer. The crude solids were recrystallized from acetone–diethyl ether to yield the final product as red crystals (50 mg, 72%). ¹H NMR (400 MHz, acetone-*d*₆) δ /ppm: 8.39 (s, 4H), 7.98 (s, 2H), 7.66 (d, $J = 5.8$ Hz, 2H), 7.55 (dd, 5.8, 2 Hz, 4H); 7.29 (m, 4H); 7.01 (m, 2H), 6.85 (t, $J = 2.4$ Hz, 4H), 6.28 (t, $J = 2.4$ Hz, 4H), 5.36 (s, 4H), 2.57 (d, $J = 6$ Hz, 12H). ESI-MS (in MeCN): $m/z = 392.0$ $[\text{M}-2\text{PF}_6]^{2+}$. Elemental analysis: C (49.22%), H (3.81%), and N (10.25%), calculated for C₄₄H₄₂N₈P₂F₁₂Ru: C (49.15%), H (3.94%), and N (10.42%).

[Ru(Pyrdmb)₂(dmb)](PF₆)₂ (Pyr2Ru). A solution of $[\text{Ru}(\text{Pyrdmb})_2\text{Cl}_2]$ (25.0 mg, 0.0313 mmol) and 4,4'-dimethyl-2,2'-bipyridine (8.0 mg, 0.0434 mmol) in ethanol (15 mL) was refluxed under Ar overnight and then evaporated. The crude product was extracted with 150 mL of a DCM–water (1 : 2) mixture containing 0.1 M NH₄PF₆. The product was isolated from the organic layer, and the obtained solids were precipitated from DCM–diethyl ether to yield the final product as red solids (19.8 mg, 51.2%). ¹H NMR (400 MHz, acetone-*d*₆) δ /ppm: 8.59 (s, 2H), 8.30 (s, 4H); 7.85 (dd, $J = 10.4$, 5.6 Hz, 4H), 7.70 (d, $J = 6$ Hz, 2H), 7.31 (d, $J = 5.6$ Hz, 2H), 7.0 (dd, 4H), 6.76 (dt, $J = 9.2$, 2 Hz, 8H), 6.11 (dt, $J = 9.2$, 2 Hz, 8H), 5.37 (d, $J = 4.4$ Hz, 8H), 2.49 (s, 6H). ESI-MS (in MeCN): $m/z = 457.0$ $[\text{M}-2\text{PF}_6]^{2+}$. Elemental analysis: C (51.86%), H (4.24%), and N (11.54%), calculated for C₅₂H₄₈N₁₀P₂F₁₂Ru: C (51.82%), H (4.02%), and N (11.61%).

[Ru(dmb)(Pyrdmb)((H₂O₃PCH₂)₂bpy)](PF₆)₂ (PRuPyr). A solution of $[\text{Ru}(\text{dmb})(\text{Pyrdmb})\text{Cl}_2]$ (30.0 mg, 0.044 mmol) and 4,4'-bis-(methylphosphonate)-2,2'-bipyridine ((Et₂O₃PCH₂)₂bpy) (51 mg, 0.112 mmol) in ethanol (20 mL) was refluxed overnight and evaporated. The residue was dissolved in water (15 mL), the solid was filtered off, and the solution was further washed with chloroform (3 \times 5 mL). Saturated aqueous NH₄PF₆ (10 mL) and DCM (75 mL) were added, and the mixture was stirred for 2 h.

The DCM layer was washed with water (3 \times 10 mL) and dried over anhydrous Na₂SO₄. The solid obtained after evaporation was recrystallized from DCM and diethyl ether to yield the final product as red crystals (45.61 mg, 77%). $[\text{Ru}(\text{dmb})(\text{Pyrdmb})((\text{Et}_2\text{O}_3\text{PCH}_2)_2\text{bpy})](\text{PF}_6)_2$ (40.0 mg, 0.037 mmol) was refluxed with bromotrimethylsilane (0.1 mL, 0.53 mmol) in MeCN (15 mL) under Ar overnight. The reaction mixture was cooled to room temperature and then evaporated. The obtained solid was dissolved in water (10 mL), and saturated aqueous NH₄PF₆ (5 mL) was added to precipitate $[\text{Ru}(\text{dmb})(\text{Pyrdmb})((\text{H}_2\text{O}_3\text{PCH}_2)_2\text{bpy})](\text{PF}_6)_2$ (PRuPyr) as a red solid, which was collected by filtration and sequentially washed with water and diethyl ether (24.0 mg, 67%). ¹H NMR (400 MHz, acetone-*d*₆) δ /ppm: 8.66 (s, 2H); 8.63 (s, 2H), 8.33 (s, 2H), 7.89 (m, 4H), 7.74 (m, 2H); 7.47 (m, 2H); 7.34 (d, $J = 6$ Hz, 2H), 6.97 (m, 2H), 6.75 (t, $J = 2$ Hz, 4H), 6.15 (t, $J = 2$ Hz, 4H), 5.39 (d, $J = 4.2$ Hz, 4H); 3.99 (m, 8H), 3.48 (d, $J = 4$ Hz, 2H), 3.43 (d, $J = 4$ Hz, 2H), 2.53 (s, 3H), 2.50 (s, 3H), 1.1 (m, 12H). ³¹P NMR (162 MHz, acetone-*d*₆) δ /ppm: 23.11 (s, 2P, -PO₃Et₂), -144 (sep., 2P, PF₆⁻). ESI-MS (in MeCN): $m/z = 528$ $[\text{M}-2\text{PF}_6]^{2+}$. Elemental analysis: C (44.98%), H (3.87%), N (9.08%), calculated for C₄₄H₄₄N₈O₆P₄F₁₂Ru: C (42.83%), H (3.59%), and N (9.08%).

[Ru(dmb)(Pyrdmb)(bpyC₂bpy)](PF₆)₂ (PyrRuC₂bpy). A solution of $[\text{Ru}(\text{dmb})(\text{Pyrdmb})\text{Cl}_2]$ (60 mg, 0.0895 mmol) and bpyC₂bpy (98.5 mg, 0.269 mmol) in ethanol (20 mL) was refluxed overnight under Ar and then evaporated. The solid was taken up in water, the filtrate was washed with chloroform (3 \times 10 mL) and supplemented with saturated aqueous NH₄PF₆ (5 mL). The product was extracted with DCM (3 \times 50 mL), and the combined organic layer was dried over anhydrous Na₂SO₄ and evaporated to give a red precipitate. PyrRuC₂bpy was separated by column chromatography on SP Sephadex C-25 (MeCN–H₂O 1 : 1, v/v) and recrystallized from acetone–ether to yield the final product as red solids (85.4 mg, 76%). ¹H NMR (400 MHz, acetone-*d*₆) δ /ppm: 8.76 (s, 2H), 8.61 (s, 4H), 8.52–8.42 (m, 2H), 8.30 (s, 2H), 7.93–7.73 (m, 6H), 7.50–7.40 (m, 2H), 7.37–7.28 (m, 2H), 7.26–7.16 (m, 2H), 7.04–6.94 (m, 2H), 6.75 (t, $J = 2.4$ Hz, 4H), 6.12 (t, $J = 2.4$ Hz, 4H); 5.38 (d, $J = 2.4$ Hz, 4H), 3.2 (m, 4H), 2.5 (m, 12H). ESI-MS (in MeCN): $m/z = 483$ $[\text{M}-2\text{PF}_6]^{2+}$. Elemental analysis: C (53.86%), H (4.09%), and N (11.39%), calculated for C₅₆H₅₂N₁₀P₂F₁₂Ru: C (53.86%), H (4.36%), and N (11.02%).

[Ru(dmb)(Pyrdmb)(bpyC₂bpy)Ru(CO)₂Cl₂](PF₆)₂ (PyrRuC₂-RuCAT). A solution of $[\text{Ru}(\text{dmb})(\text{Pyrdmb})(\text{bpyC}_2\text{bpy})](\text{PF}_6)_2$ (30 mg, 0.0239 mmol) and $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ (9 mg, 0.036 mmol) in EtOH–acetone (1 : 1, 10 mL) was refluxed for 5 h under Ar and then evaporated. The obtained red solid was recrystallized from acetone–ether to yield the final product as red solids (34 mg, 96%). ¹H NMR (400 MHz, acetone-*d*₆) δ /ppm: 8.98–8.88 (m, 2H); 8.37–8.17 (m, 6H), 7.85 (s, 2H), 7.60–7.35 (m, 8H), 7.22–7.02 (m, 4H), 6.94–6.86 (m, 2H), 6.73 (t, $J = 2.4$ Hz, 4H), 6.16 (t, $J = 2.4$ Hz, 4H), 5.24 (d, $J = 6.4$ Hz, 4H), 3.25 (d, $J = 7.8$ Hz, 4H), 2.5 (m, 12H). ESI-MS (in MeCN): $m/z = 597$ $[\text{M}-2\text{PF}_6]^{2+}$. FT-IR (cast film) $\nu_{\text{CO}}/\text{cm}^{-1}$: 1996, 2060. Elemental analysis: C (47.26%), H (3.28%), N (9.58%); calculated for C₅₈H₅₂N₁₀Cl₂O₂P₂F₁₂Ru₂: C (47.27%), H (3.70%), and N (9.34%).



Fabrication of photocathodes

NiO/PRuPyr. The NiO electrode (area = 2.5 cm²) was immersed into a MeCN–methanol (9 : 1, v/v) solution (4 mL) of PRuPyr (5 μM) in the dark overnight, washed with MeCN–methanol (9 : 1, v/v), and dried in air. The total amount of the metal complex adsorbed on the NiO electrode (n_{PRuPyr}) was determined from the difference in the absorbance of the solution before and after adsorption as well as by the ICP-MS analysis of H₂O : HCl : H₂SO₄ (1 : 1 : 1) mixed acid solutions containing the Ru complex desorbed from the NiO/PRuPyr electrode, as described later in detail.

Oxidative electropolymerization of the metal complexes on NiO and NiO/PRuPyr electrodes. A MeCN solution (8 mL) containing PyrRu, Pyr₂Ru, PyrRuC₂bpy, or PyrRuC₂RuCAT (0.5 mM) and Et₄NBF₄ (0.1 M) as the supporting electrolyte was introduced into a one-component electrochemical cell. The NiO or NiO/PRuPyr electrode, a Ag/AgNO₃ electrode (Ag wire immersed in MeCN containing 0.01 M AgNO₃ and 0.1 M Et₄NBF₄ separated by Vycor[®] glass), and a Pt wire were used as working, reference, and counter electrodes, respectively. After Ar gas was flown into the cell for 15 min, the potential was cycled between 0 and +1.35 V at 100 mV s⁻¹. The obtained electrodes were washed with MeCN and stored in air in the dark.

Introduction of Ru catalyst unit to electropolymerized electrodes. The electropolymerized electrode was soaked in a MeCN solution (4 mL) containing [Ru(CO)₂Cl₂]_n (0.5 mM) for 24 h, washed with MeCN, and air-dried in the dark.

Estimation of the Ru complexes adsorbed on the electrodes and TONs. The amounts of electrochemically active Ru centers (n_{CV}/mol) were determined by cycling the electrodes between 0.4 and +1.2 V vs. Ag/AgNO₃ in MeCN solutions containing 0.1 M Et₄NBF₄ as a supporting electrolyte at 10 mV s⁻¹,¹² and by using the following equation.

$$n_{\text{CV}} = S/F\nu \quad (1)$$

where S is the area under the Ru(II)/(III) peak (A V), F is the Faraday constant (96 485 C mol⁻¹), and ν is the scan rate (0.01 V s⁻¹). The areal density of electroactive Ru units was calculated by dividing n_{CV} by the area of the electrode (2.5 cm²).

The total number of Ru units (n_{total}), that is, Ru photosensitizer units + RuCAT units adsorbed on the electrodes, was estimated by ICP-MS analysis of H₂O : HCl : H₂SO₄ (1 : 1 : 1) mixed acid solutions containing the Ru complexes desorbed from the electrodes. Similarly the total number of the photosensitizers estimated using the electrode after the step-2 (n_{PS}). The corresponding concentration was estimated from calibration plots prepared using the standard Ru atomic absorption standard solution (Aldrich, 1000 μg mL⁻¹ Ru in 5% HCl). The amount of RuCAT units (n_{cat}) was estimated using eqn (2) and calculated as the average of four experimental trials, as shown in Tables S1–S4.†

$$n_{\text{cat}} = (n_{\text{total}} - n_{\text{PS}}) \quad (2)$$

Product TONs were calculated as

$$\text{TON} = [\text{product}]/n_{\text{cat}} \quad (3)$$

where [product] is the amount of the product, that is, CO, HCOOH, or H₂.

Fabrication of the RhO_x/TaON photoanode

Particulate TaON was prepared according to a previously reported method.⁶⁶ Ta₂O₅ (2 g) particles were heated in a flow of NH₃ (20 mL min⁻¹) at 1123 K for 15 h. Rh species (0.7 wt% metal basis) was loaded on TaON particles by impregnation with aqueous Na₃[RhCl₆]·*n*H₂O followed by heating at 673 K for 30 min in air to afford RhO_x/TaON.⁵⁵ The as-prepared RhO_x/TaON particles were deposited on a Ti substrate as follows. The particles (60 mg) were dispersed in acetone (25 mL) by 5 min sonication, and an aliquot of this dispersion (60 μL) was dropped onto the Ti substrate and dried in air at room temperature. The drop-casting/drying cycle was repeated 20 times. The representative amount of RhO_x/TaON particles on Ti was approximately 2.9 mg. The coated area was 1.5 cm × 4 cm. Post-necking was applied to provide sufficient conductivity between the particles as well as between the particles and the substrate.^{55,57,66–69} The RhO_x/TaON electrodes were coated with 50 μL of methanolic TaCl₅ (10 mM) and then dried in air at room temperature. After this process was performed five times, the electrode was heated in an NH₃ flow (10 mL min⁻¹) at 723 K for 30 min.

Photoelectrochemical measurements and photocatalytic CO₂ reduction using dye-sensitized molecular photocathodes

The IPCEs of the electrodes were measured according to previous reports.^{12,27} Photocatalytic performance was also evaluated using a previously reported method, with the vital parts briefly outlined below. Photoelectrochemical CO₂ reduction was conducted in a Pyrex H-shaped cell with two compartments containing aqueous NaHCO₃ (15–18 mL, 50 mM) and separated by a Nafion[®] film (Aldrich, Nafion 117). The working electrode (photocathode) and a Ag/AgCl reference electrode were placed in the cathode compartment, while a Pt wire counter electrode was placed in the anode compartment. The three-electrode setup was connected to a potentiostat (HZ-7000, Hokuto Denko). The reaction was conducted by flowing CO₂ into the cathode compartment for 30 min. The photoanode was irradiated using a 300 W Xe lamp (MAX-303, Asahi Spectra) equipped with a cutoff filter (HOYA Y48 for λ_{ex} = 460–650 nm) and the CO and H₂ produced in the gas phase were analyzed using a micro-GC MGC3000A (Inficon), while HCOOH in the solution was analyzed using a capillary electrophoresis apparatus (Agilent 7100 L, Otsuka Electronics).

Photocatalytic CO₂ reduction with water oxidation (two-compartment setup)

The reaction was carried out using the two-compartment cell and setup explained in the previous section, except that a CoO_x/BiVO₄ or a RhO_x/TaON photoanode was used instead of a Pt wire counter electrode. An HZ-7000 potentiostat was used in the non-resistance ammeter mode. The photocathode (2.5 cm²) was

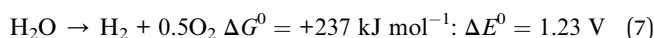
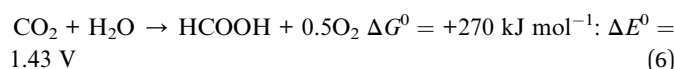
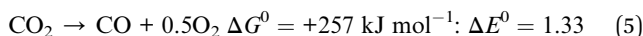


irradiated at $\lambda_{\text{ex}} = 460\text{--}650\text{ nm}$ using a 300 W Xe lamp with a cutoff filter. $\text{CoO}_x/\text{BiVO}_4$ ($1.2\text{--}2.0\text{ cm}^2$) was irradiated at $\lambda_{\text{ex}} = 400\text{--}650\text{ nm}$ using a 300 W Xe lamp (Asahi Spectra, MAX-302) with a cutoff filter (HOYA, L42) and an IR-cut filter. CO, H_2 , HCOOH, and O_2 were analyzed as described previously for half-cell experiments.

ECE (%) was calculated as

$$\text{ECE} = E_{\text{chemical}}/E_{\text{photon}} \times 100\% \quad (4)$$

where E_{photon} is the total energy of irradiated photons calculated as P_1 ($32.0\text{ mW cm}^{-2} \times 2.5\text{ cm}^2$) + P_2 ($28.0\text{ mW cm}^{-2} \times 1.55\text{ cm}^2$) \times irradiation time ($18\,000\text{ s}$) = 2.22 kJ . The total chemical energies of the generated CO, HCOOH, and H_2 (E_{chemical}) were calculated using eqn (5)–(8).



$$E_{\text{chemical}} = \Sigma[\text{product}] \times 2FV_{\text{theoretical}} \quad (8)$$

where [product] is the amount of generated CO, HCOOH, and H_2 , F is the Faraday constant, $V_{\text{theoretical}}$ is the theoretical formation voltage for each product, and E_{photon} is given by the integration of irradiated light energy.

Photocatalytic CO_2 reduction with water oxidation (one-compartment setup)

In a tandem cell with a one-compartment setup, the photocathode and photoanode were placed in a face-to-face configuration. The HAL-320 (Asahi Spectra, light intensity = 100 mW cm^{-2}) lamp containing a built-in AM 1.5G filter ($350\text{--}1100\text{ nm}$) was used as a single light source for irradiation. The photocathode was irradiated from the back side, and the photons transmitted through this electrode then reached the front side of the photoanode.

Data availability

All the data supporting this article have been included in the main text and the ESI.†

Author contributions

Fazalurahman Kuttassery: most of experiments and writing of manuscript. H. Kumagai: photoanode preparation and discussion. Ryutaro Kamata: methodology and discussion. Yusuke Ebato: setting up of gas analysis system, discussion, Masanobu Higashi: photoanode preparation, Hajime Suzuki: photoanode preparation, Ryu Abe: photoanode preparation and discussion, Osamu Ishitani: conceptualization, funding acquisition, and supervision; writing, review, and editing of manuscript.

Conflicts of interest

There are no conflicts to declare.

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