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# Supramolecular photocatalysts fixed on the inside of the polypyrrole layer in dye sensitized molecular photocathodes: application to photocatalytic CO<sub>2</sub> reduction coupled with water oxidation†

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The development of systems for photocatalytic CO<sub>2</sub> 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 CO<sub>2</sub> reduction in water featuring a polypyrrole layer, [Ru(diimine)<sub>3</sub>]<sup>2+</sup> as a redox photosensitizer unit, and Ru(diimine)(CO)<sub>2</sub>Cl<sub>2</sub> 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 CO<sub>2</sub> 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<sub>x</sub>/BiVO<sub>4</sub> and RhO<sub>x</sub>/TaON) to construct full cells that photocatalytically reduce CO<sub>2</sub> 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<sup>-2</sup>% under the irradiation of both electrodes with visible light, while a solar to chemical conversion efficiency of 4.2 × 10<sup>-2</sup>% is achieved for a tandem-type cell using a solar light simulator (AM 1.5, 100 mW cm<sup>-2</sup>).

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† Electronic supplementary information (ESI) available: Synthetic strategy and <sup>1</sup>H-NMR spectra of metal complexes synthesized (S1–I), additional electrochemical, characterization, photoelectrochemical CO<sub>2</sub> 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 CO<sub>2</sub> reduction under controlled experimental conditions (Table S5). See DOI: 10.1039/d1sc03756k

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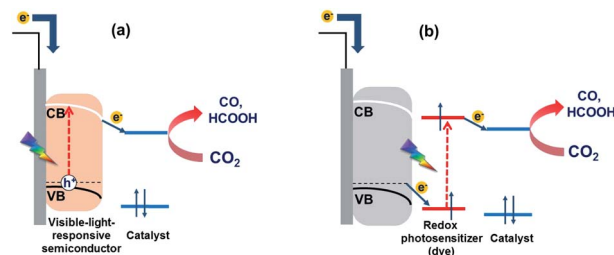
## Introduction

The reduction of CO<sub>2</sub> 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.<sup>1,2</sup> In this regard, photocatalytic CO<sub>2</sub> 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 CO<sub>2</sub> have drawn much attention, as these complexes exhibit tunable visible light absorption and redox properties as well as high CO<sub>2</sub> reduction selectivity.<sup>3,4</sup> For example, a mixed system comprising [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (bpy = 2,2'-bipyridine) as the redox photosensitizer and [Ru(X<sub>2</sub>bpy)(CO)<sub>2</sub>Cl<sub>2</sub>] as the catalyst efficiently and selectively catalyses the photoreduction of CO<sub>2</sub> 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).<sup>5–7</sup> Despite the abundance of photocatalytic systems that comprise only metal complexes and can efficiently promote the photoreduction of CO<sub>2</sub> 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 CO<sub>2</sub> utilization systems should inevitably employ water as an electron donor owing to its low cost and abundance.<sup>8</sup>

Hybrid systems that comprise metal complexes as (photo) catalysts and semiconductor materials and feature excited states with oxidation powers sufficient to oxidize water to O<sub>2</sub> and/or H<sub>2</sub>O<sub>2</sub> have been actively investigated to mitigate the above problem.<sup>9–11</sup> Most of such hybrid systems are photoelectrochemical cells featuring a photocathode for CO<sub>2</sub> reduction and a photoanode for water oxidation, with the sequential excitation of these photoelectrodes endowing them with strong reduction and oxidation powers.<sup>8</sup> 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<sub>x</sub>-deposited BiVO<sub>4</sub> (ref. 12) and reduced SrTiO<sub>3</sub> (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 CO<sub>2</sub> reduction catalyst but does not absorb light, *i.e.*, light is absorbed only by the semiconductor electrode (Scheme 1a).<sup>13–15</sup> 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).<sup>10–12</sup> 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 CO<sub>2</sub>. 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 CO<sub>2</sub> 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.

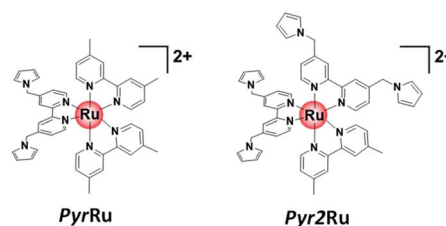
Although the photoelectrochemical systems of the second group are very rare examples of the use of molecular photocatalysts for CO<sub>2</sub> reduction coupled with water oxidation,<sup>10–12</sup> these systems can potentially employ various redox photosensitizers with strong absorption in the visible region, which is advantageous for visible-light-driven photocathode construction. The dye-sensitized molecular photocathodes<sup>16,17</sup> initially reported by Meyers *et al.*<sup>18,19</sup> and our groups<sup>9–11</sup> featured metal complex-based photocatalysts with anchoring groups such as



**Scheme 1** Two types of photocathodes for photoelectrochemical CO<sub>2</sub> 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 –PO<sub>3</sub>H<sub>2</sub> 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.<sup>20–23</sup> 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.<sup>24–26</sup> 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.*, Meyers<sup>19</sup> and our<sup>12,27</sup> 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.<sup>19,27–32</sup> 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).



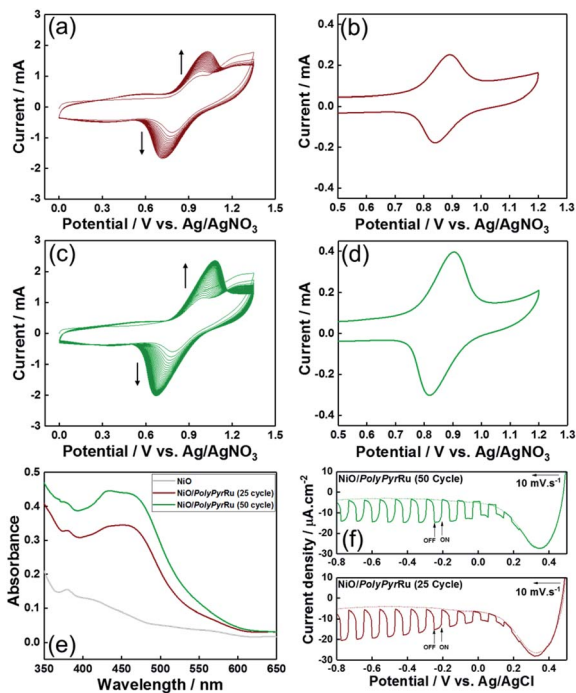


Fig. 1 Cyclic voltammograms recorded during the oxidative electropolymerization of PyrRu on NiO (electrode area = 2.5 cm<sup>2</sup>) in Ar-saturated MeCN containing PyrRu (0.5 mM) and Et<sub>4</sub>NBF<sub>4</sub> (0.1 M): (a) 25 and (c) 50 cycles between 0 and +1.35 V vs. Ag/AgNO<sub>3</sub> at 100 mV s<sup>-1</sup>. Cyclic voltammograms of NiO/PolyPyrRu as the working electrode recorded in MeCN containing 0.1 M Et<sub>4</sub>NBF<sub>4</sub> as the electrolyte (counter electrode = Pt coil, reference electrode = Ag/AgNO<sub>3</sub>) at 10 mV s<sup>-1</sup>: (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 cm<sup>2</sup>) in CO<sub>2</sub>-purged 50 mM NaHCO<sub>3</sub> (electrolyte) recorded using a Xe lamp with a Y-48 cutoff filter ( $\lambda$  = 460–650 nm), a Pt coil counter electrode and a Ag/AgCl reference electrode.

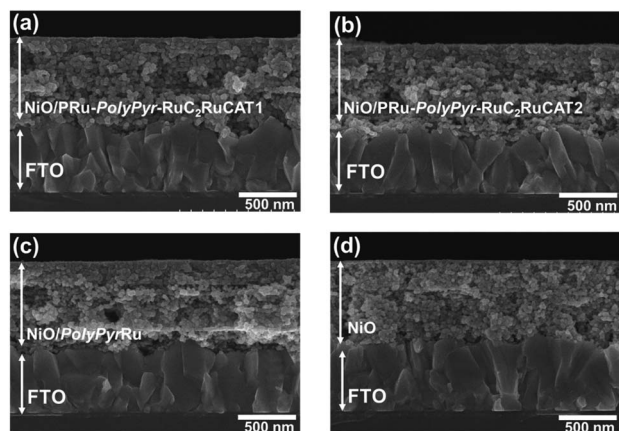
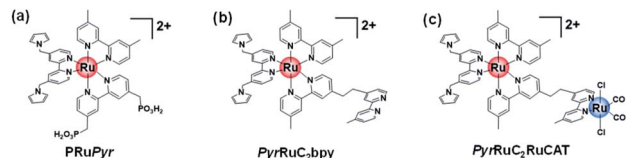
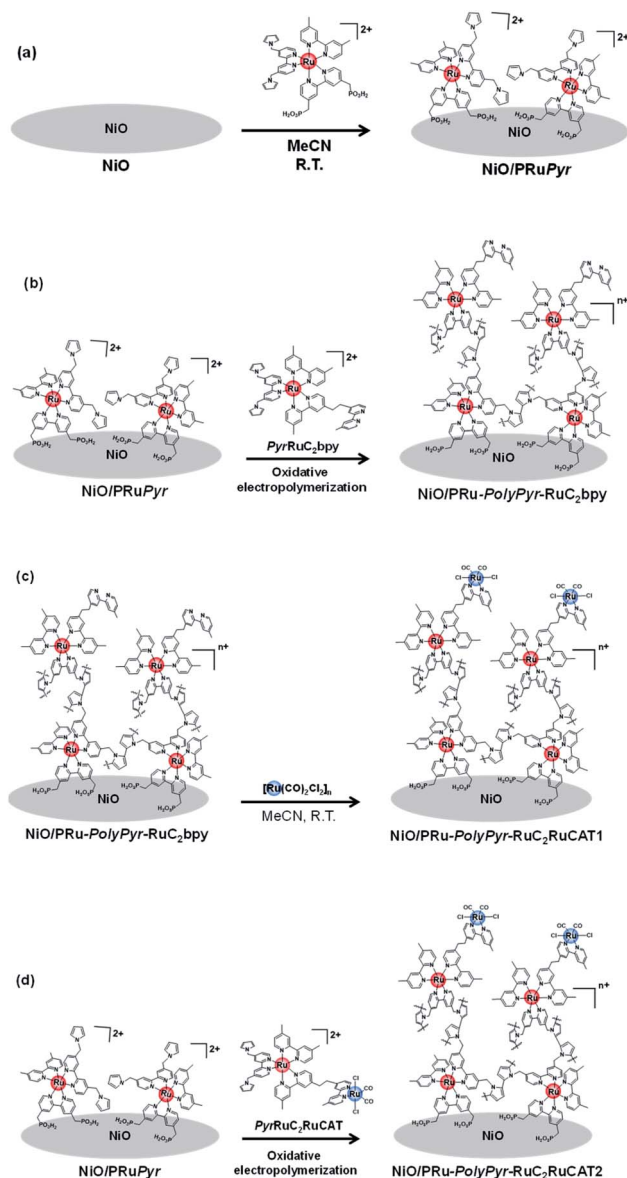


Fig. 2 SEM (side view) images of (a) NiO-PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 after 25 cycles, (b) NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT2, (c) NiO/PolyPyrRu, and (d) NiO on FTO.

molecular photocathode also drastically suppressed the desorption of metal complexes from the electrode and enhanced the durability of photocatalysts for CO<sub>2</sub> reduction.<sup>19,27</sup>



Scheme 3 Molecular structures of (a) PRuPyr, (b) PyrRuC<sub>2</sub>bpy, and (c) PyrRuC<sub>2</sub>RuCAT.



Scheme 4 Preparation of (a) NiO/PRuPyr (step 1), (b) NiO/PRu-PolyPyr-RuC<sub>2</sub>bpy (step 2), and (c) NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 (step 3) electrodes of a three step method of photocathode fabrication and (d) fabrication of NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT2 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



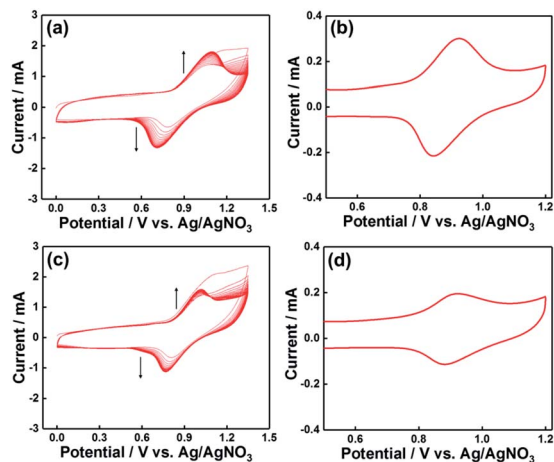


Fig. 3 Cyclic voltammograms recorded during the electro-polymerization of (a)  $\text{PyrRuC}_2\text{bpy}$  and (c)  $\text{PyrRuC}_2\text{RuCAT}$  on  $\text{NiO/PRuPyr}$  (area =  $2.5 \text{ cm}^2$ ) in Ar-saturated MeCN containing the corresponding complex (0.5 mM) and  $\text{Et}_4\text{NBF}_4$  (0.1 M) as an electrolyte. The applied potential was repeatedly cycled (25 times) between 0 and +1.35 V vs.  $\text{Ag/AgNO}_3$  at  $100 \text{ mV s}^{-1}$ . 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  $\text{Et}_4\text{NBF}_4$  using a  $\text{Ag/AgNO}_3$  reference electrode and a Pt counter electrode (scan rate =  $10 \text{ mV s}^{-1}$ ).

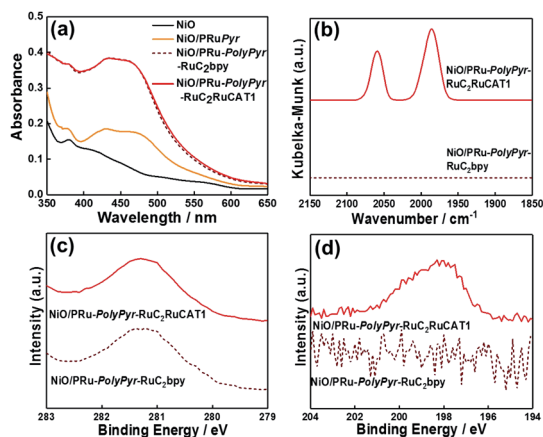


Fig. 4 (a) UV-vis (DR) absorption spectra of  $\text{NiO/PRu-PolyPyr-RuC}_2\text{-RuCAT1}$  prepared by the three-step method (red),  $\text{NiO}$  (black), and samples obtained after process 1 ( $\text{NiO/PRuPyr}$ , orange) and process 2 ( $\text{NiO/PRu-PolyPyr-RuC}_2\text{bpy}$ , dotted brown). (b) 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.<sup>12</sup> 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

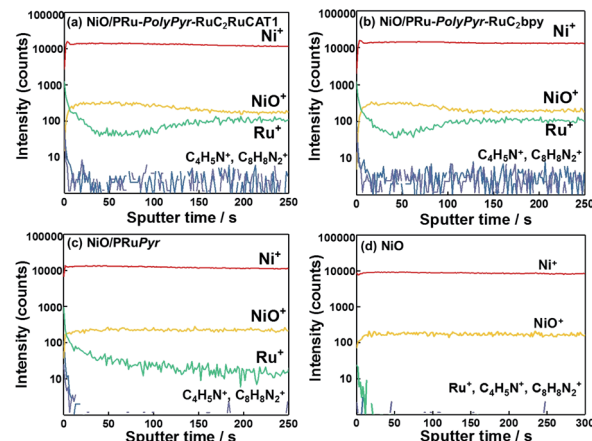


Fig. 5 TOF-SIMS spectra of (a)  $\text{NiO/PRu-PolyPyr-RuC}_2\text{RuCAT1}$ , (b)  $\text{NiO/PRu-PolyPyr-RuC}_2\text{bpy}$ , (c)  $\text{NiO/PRuPyr}$ , and (d)  $\text{NiO}$  electrodes.

photocatalytic system for  $\text{CO}_2$  reduction with water without any external bias, with the photoenergy conversion efficiency (ECE) reaching  $1.7 \times 10^{-2}\%$ .<sup>12</sup>

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.<sup>28,29,33–35</sup> Functional polypyrrole films containing metal complex units have been reported for various applications, *e.g.*, catalytic reactions, sensors, and drug delivery.<sup>28,29,33–41</sup> 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  $\text{CO}_2$  reduction than the system with the corresponding mononuclear  $\text{Re}(\text{i})$  complex in solution.<sup>33,36,42</sup> 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.<sup>14,43–46</sup> 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  $\text{NiO}$  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  $\text{CO}_2$  reduction (maximum IPCE = 4.7%). The developed photocathode is combined with two n-type semiconductor photoanodes ( $\text{CoO}_x/\text{BiVO}_4$  and  $\text{RhO}_x/\text{TaON}$ ) for water oxidation to develop systems for the photoelectrocatalytic reduction of  $\text{CO}_2$  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)	$n_{\text{RuPS}}^b$ (nmol)	$n_{\text{RuCAT}}^c$ (nmol)	$n_{\text{RuPS}} : n_{\text{RuCAT}}$
NiO/PRuPyr	15.5	15.5	0	—
NiO/PRu-PolyPyr-RuC <sub>2</sub> bpy	75.4	75.4	0	—
NiO/PRu-PolyPyr-RuC <sub>2</sub> RuCAT1	100.3	75.4	24.9 <sup>c</sup>	3 : 1
NiO/PRu-PolyPyr-RuC <sub>2</sub> RuCAT2	40.7	28.1	12.1 <sup>c</sup>	2.3 : 1

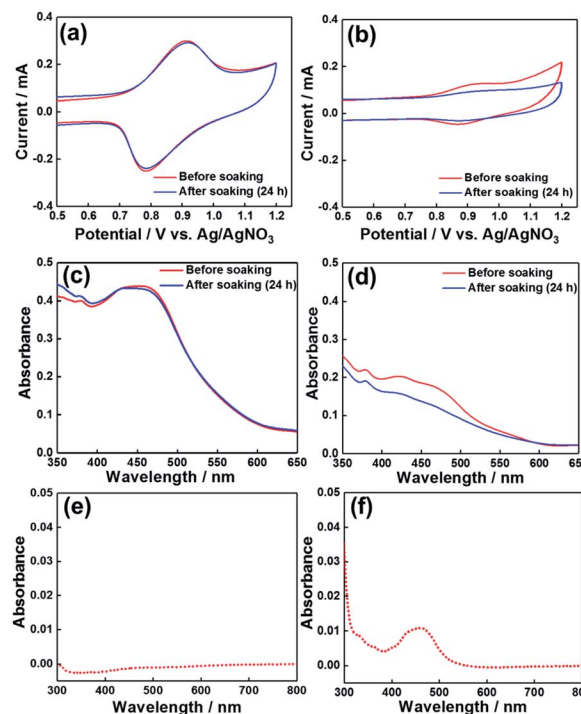
<sup>a</sup> Total amount in the electrode, which was estimated by using ICP-MS analysis. <sup>b</sup> Amount of the photosensitizers. <sup>c</sup> Amount of the catalysts.

## 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 Et<sub>4</sub>NBF<sub>4</sub> 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/AgNO<sub>3</sub>, respectively; the former was attributed to the one-electron oxidation of the central Ru(II) to Ru(III), as that of [Ru(dmb)<sub>3</sub>]<sup>2+</sup> (dmb = 4,4'-dimethyl-2,2'-bipyridine) is observed at  $E_{1/2}^{\text{ox}} = 0.77$  V,<sup>47</sup> 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†).<sup>47</sup>

A NiO nanoparticle-modified transparent fluorine-doped tin oxide (FTO) electrode was prepared by the previously reported squeeze method<sup>9,10</sup> 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/AgNO<sub>3</sub>) 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 NaHCO<sub>3</sub> in the dark. Cyclic voltammograms of (a) NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 and (b) NiO/PRuPyr before and after soaking. UV-vis (DR) absorption spectra of (c) NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 and (d) NiO/PRuPyr before and after soaking. UV-vis absorption spectra of soaking solutions obtained for (e) NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 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) <sup>a</sup> (nmol cm <sup>-2</sup> )	Ru(CV) <sup>b</sup> (nmol cm <sup>-2</sup> )	Ru (CV)
			Ru(ICP-MS)
NiO/PRuPyr	6.2	2.0	0.32
NiO/PRu-PolyPyr-RuC <sub>2</sub> bpy	30.2	9.6	0.32
NiO/PRu-PolyPyr-RuC <sub>2</sub> RuCAT1	40.1	11.6	0.29
NiO/PRu-PolyPyr-RuC <sub>2</sub> RuCAT2	16.3	4.4	0.27

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



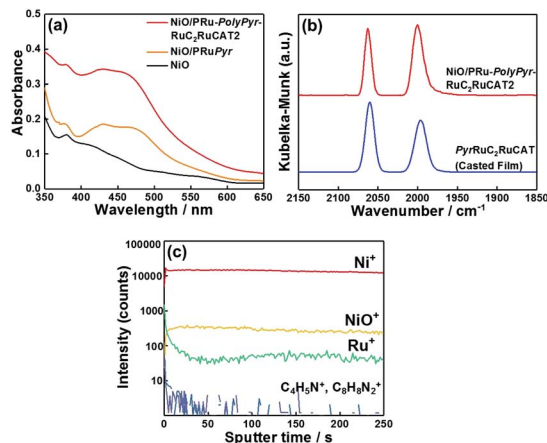


Fig. 7 (a) UV-Vis (DR) absorption spectra of NiO/PRu-PolyPyr-RuC<sub>2</sub>-RuCAT2 (red), NiO/PRuPyr (orange), and NiO (black). (b) FT-IR (DR) spectra of NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT2 (red) and PyrRuC<sub>2</sub>RuCAT cast on NiO (blue). (c) TOF-SIMS spectra of NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT2.

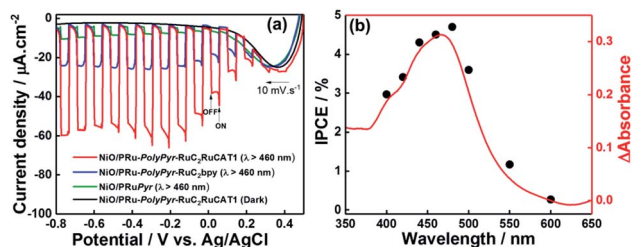


Fig. 8 (a) Responses of NiO/PRuPyr (green), NiO/PRu-PolyPyr-RuC<sub>2</sub>bpy (blue), and NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 (red) to irradiation at  $\lambda_{\text{ex}} = 460\text{--}650\text{ nm}$  (intensity =  $28.2\text{ mW cm}^{-2}$ ) in CO<sub>2</sub>-purged 50 mM aqueous NaHCO<sub>3</sub> (pH 6.6, Ag/AgCl reference electrode, Pt wire counter electrode). (b) Effect of wavelength on the IPCE of NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 at  $-0.3\text{ V}$  vs. Ag/AgCl in a CO<sub>2</sub>-purged 50 mM NaHCO<sub>3</sub> aqueous solution (pH 6.6, black dots). The red line shows the UV-vis absorption spectrum of NiO/PRu-PolyPyr-RuC<sub>2</sub>-RuCAT1 with subtracted absorbance of the NiO electrode.

indicated that  $8.2\text{ nmol cm}^{-2}$  of electrochemically active Ru complexes was immobilized on NiO, with the difference between the maxima of oxidation and reduction waves ( $\Delta E$ ) 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 (<sup>1</sup>MLCT) 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).

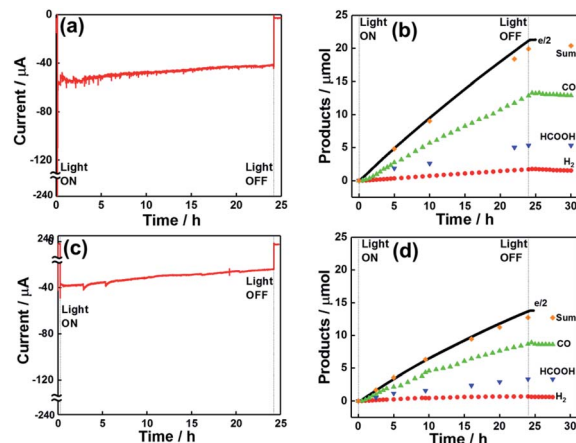


Fig. 9 Time courses of (a and c) photocurrent and (b and d) product levels expressed as half of electrons passed (black line), CO (green triangles), HCOOH (blue triangles), and H<sub>2</sub> (red circles). (a and b) NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1, (c and d) NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT2 (electrode area =  $2.5\text{ cm}^2$ , applied bias ( $E$ ) =  $-0.7\text{ V}$  vs. Ag/AgCl) were irradiated at  $\lambda_{\text{ex}} = 460\text{--}650\text{ nm}$  ( $32\text{ mW cm}^{-2}$ ) in CO<sub>2</sub>-purged 50 mM aqueous NaHCO<sub>3</sub> (pH 6.6).

Although an increase in the sweep number to 50 (Fig. 1c) increased the amount of electrode-deposited Ru(II) complexes ( $14.4\text{ nmol cm}^{-2}$ , 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 CO<sub>2</sub>-purged aqueous solutions containing 50 mM NaHCO<sub>3</sub> 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  $\Delta E$  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 Pyrbpy 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 CO<sub>2</sub> reduction performances of photocathodes under various conditions

Entry	Electrode	Irradn time (h)	$E_{\text{app}}^a$ (V)	Light intensity (mW cm <sup>-2</sup> )	Products/ $\mu\text{mol}$ (TON)			$F_{\text{red}}^b$ (%)	CO <sub>2</sub> red selectivity (%)
					CO	HCOOH	H <sub>2</sub>		
1	NiO/PRu- <i>PolyPyr</i> -RuC <sub>2</sub> 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 <sub>2</sub> 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 <sub>2</sub> RuCATbpy	5	-0.7	36	0.1	0.1	1.1	92	19
8	NiO/ <i>PolyPyr</i> -RuC <sub>2</sub> RuCAT <sup>c</sup>	5	-0.7	32	0.2	0.6	<0.1	83	91
9	NiO/PRuPyr	5	-0.7	32	n.d. <sup>d</sup>	n.d. <sup>d</sup>	<0.1	9	n.d. <sup>d</sup>
10 <sup>e</sup>	NiO/PRuC <sub>2</sub> RuCAT	5	-0.7	27	<0.1	0.2	<0.1	56	82

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

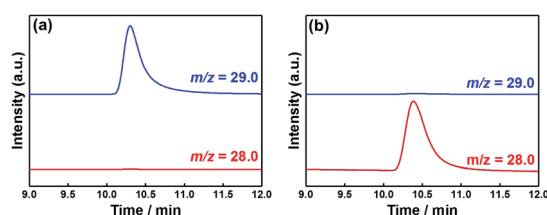


Fig. 10 GC-MS chromatograms of the gas phase formed in cells after irradiation, showing the peaks at  $m/z = 28$  and  $29$  (<sup>12</sup>CO and <sup>13</sup>CO, respectively). NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1 was subjected to an applied bias of  $E = -0.7$  V vs. Ag/AgCl and irradiated at  $\lambda_{\text{ex}} = 460$ – $650$  nm in CO<sub>2</sub>-purged 50 mM aqueous NaHCO<sub>3</sub> (pH = 6.6) for 24 h using (a) <sup>13</sup>CO<sub>2</sub> and NaH<sup>13</sup>CO<sub>3</sub> and (b) ordinary CO<sub>2</sub> and NaHCO<sub>3</sub>.

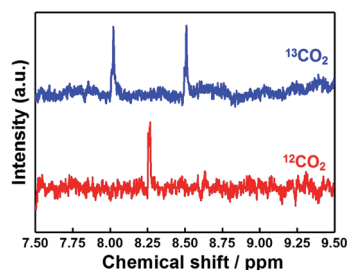


Fig. 11 <sup>1</sup>H NMR spectra of the solution obtained after photoelectrochemical reduction. NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1 was subjected to a potential of  $E = -0.7$  V vs. Ag/AgCl and irradiated at  $\lambda_{\text{ex}} = 460$ – $650$  nm in CO<sub>2</sub>-purged 50 mM aqueous NaHCO<sub>3</sub> (pH = 6.6) for 24 h using <sup>13</sup>CO<sub>2</sub> and NaH<sup>13</sup>CO<sub>3</sub> (blue) or ordinary CO<sub>2</sub> and NaHCO<sub>3</sub> (red).

namely [2,2'-bipyridine]-4,4'-diylbis(phosphonic acid) ((H<sub>2</sub>O<sub>3</sub>-PCH<sub>2</sub>)<sub>2</sub>bpy, 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*RuC<sub>2</sub>bpy has a free diimine moiety that can react with other metal ions after polymerization to introduce the catalyst unit, while *Pyr*RuC<sub>2</sub>RuCAT is a supramolecular photocatalyst bearing both redox photosensitizer Ru(II) and catalytic Ru(II) units connected to each other *via* an ethylene chain.

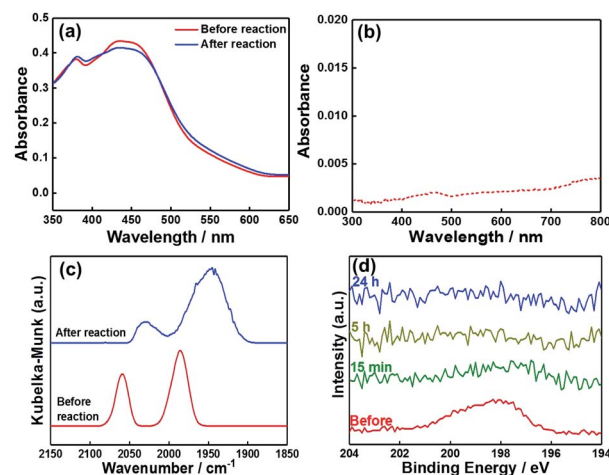


Fig. 12 (a) UV-Vis DR spectra of NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1 before (red) and after (blue) photoelectrochemical CO<sub>2</sub> reduction ( $-0.7$  V vs. Ag/AgCl,  $\lambda_{\text{ex}} = 460$ – $650$  nm, 24 h) in CO<sub>2</sub>-purged 50 mM aqueous NaHCO<sub>3</sub>. (b) UV-vis absorption spectrum of the reaction solution after the photocatalytic reaction. (c) FT-IR (DR) spectra of NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1 before (red) and after (blue) the photocatalytic reaction. (d) Cl 2p spectra of NiO/PRu-*PolyPyr*-RuC<sub>2</sub>-RuCAT1 before and after the photocatalytic reaction for various times.

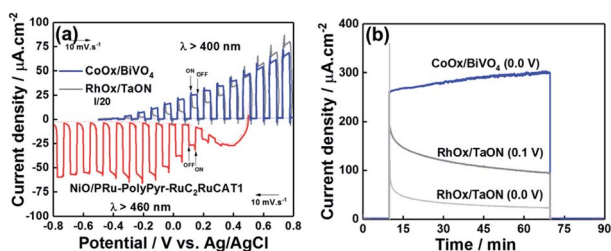
A three-step method was used to prepare NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1 as a dye-sensitized molecular photocathode (Scheme 4 and Fig. S3†). The NiO electrode was first modified with PRuPyr to give NiO/PRuPyr, in which the methylphosphonic acid groups of the diimine ligand work as anchors to the NiO electrode (process 1) (Scheme 4a). In the second step, NiO/PRuPyr was used as the working electrode for the oxidative electropolymerization of *Pyr*RuC<sub>2</sub>bpy dissolved in MeCN containing Et<sub>4</sub>NBF<sub>4</sub> (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/AgNO<sub>3</sub> at  $100$  mV s<sup>-1</sup>, 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*-RuC<sub>2</sub>bpy. Finally, NiO/PRu-*PolyPyr*-RuC<sub>2</sub>bpy with free diimine moieties was reacted with [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub> in MeCN solution at room temperature to give



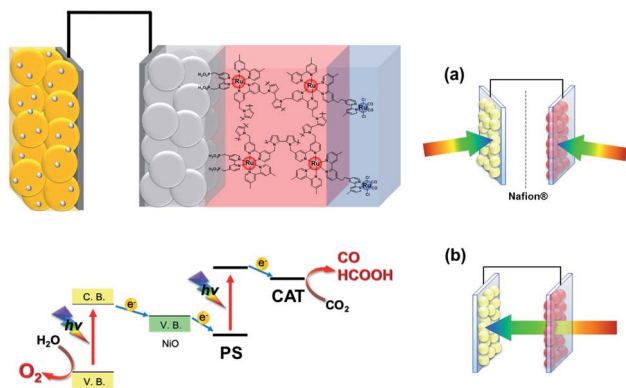
**Table 4** Photoelectrochemical CO<sub>2</sub> reduction performances of NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 electrodes prepared by different number of potential sweeps for polymerization, with other electrode production and photocatalytic reaction parameters held constant

Entry	Number of sweeps	$e^-/2$ μmol	Product/μmol				CO <sub>2</sub> red. selectivity (%)
			CO	HCOOH	H <sub>2</sub>	$F_{\text{red}}$ (%)	
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 <sup>a</sup>	1.35	0.6	0.6	0.1	94	91
7	25 <sup>b</sup>	0.95	0.2	0.6	<0.1	83	91

<sup>a</sup> Electrolysis for the polymerization was performed at 1.3 V vs. Ag/AgNO<sub>3</sub> for 30 min. <sup>b</sup> Without using PRuPyr to make the photocathode.

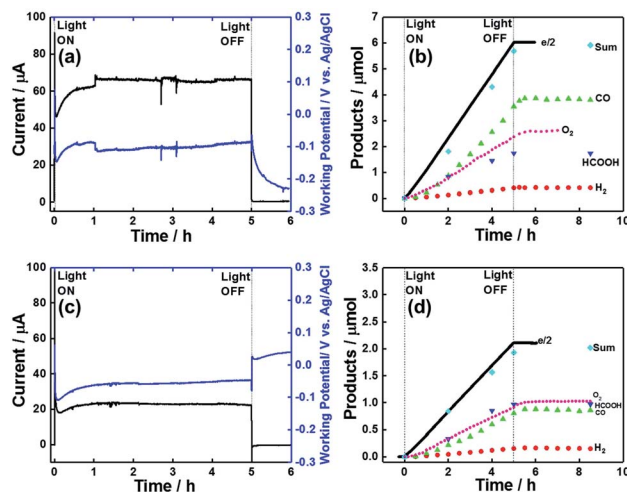


**Fig. 13** (a)  $I$ - $V$  curves of CoO<sub>x</sub>/BiVO<sub>4</sub>, RhO<sub>x</sub>/TaON, and NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 as working electrodes recorded in CO<sub>2</sub>-purged aqueous NaHCO<sub>3</sub> (50 mM) upon irradiation. Scan rate = 10 mV s<sup>-1</sup>,  $\lambda_{\text{ex}}$  = 400–650 nm (41 mW cm<sup>-2</sup>) for CoO<sub>x</sub>/BiVO<sub>4</sub> and RhO<sub>x</sub>/TaON, and  $\lambda_{\text{ex}}$  = 460–650 nm (28 mW cm<sup>-2</sup>) for NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1. (b) Time-dependent photocurrents of CoO<sub>x</sub>/BiVO<sub>4</sub> at  $E_{\text{app}}$  = 0 V (blue) and RhO<sub>x</sub>/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<sub>x</sub>/BiVO<sub>4</sub> or RhO<sub>x</sub>/TaON photoanode and a NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 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-RuC<sub>2</sub>RuCAT1 with Ru(diimine)(CO)<sub>2</sub>Cl<sub>2</sub>-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-RuC<sub>2</sub>RuCAT1 photocathode and (a and b) the CoO<sub>x</sub>/BiVO<sub>4</sub> photoanode (photocathode:  $\lambda_{\text{ex}}$  = 460–650 nm, 32 mW cm<sup>-2</sup>, photoanode:  $\lambda_{\text{ex}}$  = 400–650 nm, 28 mW cm<sup>-2</sup>) or (c and d) the RhO<sub>x</sub>/TaON photoanode (photocathode:  $\lambda_{\text{ex}}$  = 460–650 nm, 34.4 mW cm<sup>-2</sup>, photoanode:  $\lambda_{\text{ex}}$  = 400–650 nm, 32.2 mW cm<sup>-2</sup>) without any bias in aqueous CO<sub>2</sub>-purged NaHCO<sub>3</sub> (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-RuC<sub>2</sub>RuCAT1, revealing an increase in the intensity of the <sup>1</sup>MLCT 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)<sub>2</sub>Cl<sub>2</sub>-type complexes have no strong absorption at wavelengths above 350 nm.<sup>12</sup> The Fourier transform infrared (FT-IR) DR spectrum of NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 showed two strong broad peaks at 2058 and 1986 cm<sup>-1</sup>, which were attributed to the C=O stretches of CO ligands in catalyst units, whereas no such peaks were observed for NiO/PRu-PolyPyr-RuC<sub>2</sub>bpy (Fig. 4b). The CO stretching frequencies well agreed with those of the corresponding binuclear Ru(II) complex ([*cis*-(CO)-*trans*-(Cl)-Ru(CO)<sub>2</sub>Cl<sub>2</sub>(bpyC<sub>2</sub>bpy)Ru(dmb)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (bpyC<sub>2</sub>-bpy = 1,2-bis(4'-methyl-[2,2'-bipyridine]-4-yl)ethane)) drop-cast on the NiO electrode (2058 and 1991 cm<sup>-1</sup>).<sup>12</sup> Fig. 4c and d show the X-ray photoelectron spectra of NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 with the Ru catalyst unit and catalyst-free NiO/PRu-PolyPyr-RuC<sub>2</sub>bpy. Although both compounds featured a Ru 3d peak at 281.1 eV (Fig. 4c), only NiO/PRu-PolyPyr-RuC<sub>2</sub>-RuCAT1 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)<sub>2</sub>Cl<sub>2</sub>, which has been investigated as a catalyst for CO<sub>2</sub> reduction in various photo- and electrocatalytic reactions.<sup>48–50</sup>



Table 5 Photocatalytic performances of full-cell devices in CO<sub>2</sub>-purged 50 mM NaHCO<sub>3</sub>

Photo-anode	Light intensity (mW cm <sup>-2</sup> )	Irradn time (h)	Products/μmol					<i>F</i> <sub>cathode</sub> (%)	<i>F</i> <sub>anode</sub> (%)	CO <sub>2</sub> red. selectivity (%)	ECE (10 <sup>-2</sup> %)
			<i>e</i> <sup>-</sup> /2	CO	HCOOH	H <sub>2</sub>	O <sub>2</sub>				
Two-component systems											
CoO <sub>x</sub> /BiVO <sub>4</sub>	32.0 <sup>a</sup> , 28.0 <sup>b</sup>	5	6.0	3.9	1.7	0.4	2.6	99	87	93	8.3
RhO <sub>x</sub> /TaON	34.4 <sup>a</sup> , 32.2 <sup>b</sup>	5	2.1	0.9	1.0	0.2	1.0	96	97	92	2.0
One-component systems											
CoO <sub>x</sub> /BiVO <sub>4</sub>	100 <sup>c</sup>	1	1.6	0.6	0.9	0.1	0.6	98	74	92	4.8
RhO <sub>x</sub> /TaON	100 <sup>c</sup>	1	1.0	0.4	0.5	<0.1	0.5	95	96	95	2.7
<sup>a</sup> At λ <sub>ex</sub> = 460–650 nm for photocathode. <sup>b</sup> At λ <sub>ex</sub> = 400–650 nm for photoanode. <sup>c</sup> AM1.5.											

<sup>a</sup> At λ<sub>ex</sub> = 460–650 nm for photocathode. <sup>b</sup> At λ<sub>ex</sub> = 400–650 nm for photoanode. <sup>c</sup> AM1.5.

The SEM images of NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1 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<sup>+</sup> species on the electrode surface was highest for NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1, 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*-RuC<sub>2</sub>RuCAT1 and NiO/PRu-*PolyPyr*-RuC<sub>2</sub>bpy. 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 BF<sub>4</sub><sup>-</sup> and Et<sub>4</sub>N<sup>+</sup> in NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1 were also measured using the TOF-SIMS analysis (Fig. S4†). BF<sub>4</sub><sup>-</sup> was observed throughout the entire range of the NiO layer while no Et<sub>4</sub>N<sup>+</sup> 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*-RuC<sub>2</sub>bpy (step-2) was 30.2 nmol cm<sup>-2</sup> while that of NiO/PRuPyr (after the step-1) was 6.2 nmol cm<sup>-2</sup>. After incorporation of the catalysts into the polymer electrode a total amount of Ru complexes increase again to 40.1 nmol cm<sup>-2</sup>. Therefore, the adsorbed amount of the Ru catalysts was 9.9 nmol cm<sup>-2</sup> in the case of NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1, which is about one third of the photosensitizers. This means about 14 nmol cm<sup>-2</sup> of the free bpy units remained in NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1. 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).<sup>27</sup> The electroactive photosensitizers were also increased after each adsorption steps of the photosensitizers: 2.0 nmol cm<sup>-2</sup> (NiO/PRuPyr) and 9.6 nmol cm<sup>-2</sup> (NiO/PRu-*PolyPyr*-RuC<sub>2</sub>bpy). After the introduction of the catalysts, the amounts of electrochemically active photosensitizers slightly increased (11.6 nmol cm<sup>-2</sup>, NiO/PRu-*PolyPyr*-RuC<sub>2</sub>-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*-RuC<sub>2</sub>RuCAT1 in an aqueous solution containing 50 mM NaHCO<sub>3</sub> (this solution was used for photocatalytic CO<sub>2</sub> 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*-RuC<sub>2</sub>RuCAT1 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/PRu-*Pyr* (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 <sup>1</sup>MLCT absorption band in the UV-vis (DR) spectrum of NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1 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 <sup>1</sup>MLCT 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*-RuC<sub>2</sub>RuCAT2) 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*RuC<sub>2</sub>RuCAT, which already has both photosensitizer and catalyst units, in MeCN containing Et<sub>4</sub>NBF<sub>4</sub> (0.1 M) as an electrolyte. Oxidative cyclic voltammetry cycling was performed between 0 and +1.35 V vs. Ag/AgNO<sub>3</sub> at 100 mV s<sup>-1</sup> (Scheme 4a and d), i.e., under the same polymerization conditions as those used for NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1. The voltammograms recorded during electrochemical polymerization (Fig. 3c) resembled those obtained after process 2 using *Pyr*RuC<sub>2</sub>bpy (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*-RuC<sub>2</sub>RuCAT2, which were obtained by using the ICP-MS analysis, to determine both amounts of the photosensitizers and catalysts in NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT2 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*-RuC<sub>2</sub>RuCAT2 were less than half of those in NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1. This difference was ascribed to the much higher bulkiness of the RuCAT unit of *Pyr*RuC<sub>2</sub>RuCAT compared to that of the free diimine unit of *Pyr*RuC<sub>2</sub>bpy, which possibly suppressed the supply of *Pyr*RuC<sub>2</sub>RuCAT to NiO particles at the electrode depth. The number of active Ru complexes in NiO/PRu-*PolyPyr*-RuC<sub>2</sub>-RuCAT2 estimated by cyclic voltammetry of the polymer electrode (4.4 nmol cm<sup>-2</sup>, Fig. 3d) was smaller than that of the electrode prepared using the abovementioned three-step method (11.6 nmol cm<sup>-2</sup>, Fig. 3b).

In the case of NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT2, 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)<sub>2</sub>Cl<sub>2</sub> 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.<sup>12</sup> 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.<sup>12</sup> Such decomposition process of the

photoanode was not observed in the system using NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT2.

### Photoresponses of dye-sensitized molecular photocathodes

Fig. 8a presents the *I*-*V* curve (linear sweep voltammogram) of NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1 recorded during irradiation at λ<sub>ex</sub> = 460–650 nm in CO<sub>2</sub>-purged aqueous 50 mM NaHCO<sub>3</sub> 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*-RuC<sub>2</sub>RuCAT photocathode<sup>12</sup> 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<sup>-2</sup>) was achieved even at *E* = -0.2 V in the case of NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1, whereas *E* = -0.5 V was required to maximize the photocurrent of NiO/PRu-*PolyVinyl*-RuC<sub>2</sub>RuCAT (28.0 μA cm<sup>-2</sup> at *E* = -0.2 V, 38.0 μA cm<sup>-2</sup> at *E* = -0.5 V). At *E* = 0 V, NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1 maintained ~83% of the maximum photocurrent density, whereas this number equalled only 45% for NiO/PRu-*PolyVinyl*-RuC<sub>2</sub>RuCAT. These results strongly indicated that the electric resistance of the polypyrrole layer in NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1 was lower than that of the polyvinyl layer in NiO/PRu-*PolyVinyl*-RuC<sub>2</sub>RuCAT.

The dependence of IPCE on the wavelength of irradiated light (Fig. 8b) well agreed with the behaviour of the <sup>1</sup>MLCT 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<sub>ex</sub> = 480 nm) was approximately four times higher than that of a previously reported system with NiO/PRu-*PolyVinyl*-RuC<sub>2</sub>-RuCAT (IPCE = 1.2%).<sup>12</sup>

The responses of photocathodes obtained after each fabrication step were observed at *E* = -0.7 V and equalled 9.8 μA cm<sup>-2</sup> for NiO/PRuPyr prepared by process 1 and 24.5 μA cm<sup>-2</sup> for NiO/PRu-*PolyPyr*-RuC<sub>2</sub>bpy prepared by process 2. Both of these values were much lower than that observed for NiO/PRu-*PolyPyr*-RuC<sub>2</sub>RuCAT1 (57 μA cm<sup>-2</sup>).

### Photoelectrochemical CO<sub>2</sub> reduction over dye-sensitized molecular photocathodes

The photocatalytic activity of dye-sensitized molecular photocathodes for CO<sub>2</sub> 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 NaHCO<sub>3</sub> as the electrolyte was introduced into the cell and purged with CO<sub>2</sub> for 30 min. The compartment with the dye-sensitized photocathode was irradiated at λ<sub>ex</sub> = 460–650 nm using a 300 W Xe lamp with a cutoff filter under applied biases of *E*<sub>app</sub>



= 0, -0.3, and -0.7 V. During irradiation, CO<sub>2</sub> flowed into the solution, and the flow gas was analysed by a micro-GC to determine the levels of the produced CO and H<sub>2</sub>. 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-RuC<sub>2</sub>RuCAT1 as the photocathode, revealing that a continuous photocathodic current of 57 to 43  $\mu\text{A}$  was observed over 24 h. CO and HCOOH were continuously formed as major products along with small amounts of H<sub>2</sub> (Fig. 9b). The CO<sub>2</sub> reduction selectivity equalled 92%, while the faradaic efficiency ( $F_{\text{red}}$ ) 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 (H<sub>2</sub>) (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 NaHCO<sub>3</sub> as an electrolyte gave no or less CO<sub>2</sub> reduction products (Table S5†), suggesting that light, applied bias, and CO<sub>2</sub> are required for photocatalytic CO<sub>2</sub> reduction. Compared to NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1, the catalyst unit-free NiO/PRu-PolyPyr-RuC<sub>2</sub>bpy showed no significant activity for CO<sub>2</sub> reduction but afforded some H<sub>2</sub> upon irradiation (entry 7 in Table 3), which indicated that the Ru catalyst unit is essential for the photocatalytic reduction of CO<sub>2</sub> 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 <sup>13</sup>CO<sub>2</sub> and NaH<sup>13</sup>CO<sub>3</sub>, indicating the almost selective formation of <sup>13</sup>CO ( $m/z = 29$ ). On the other hand, a similar experiment with ordinary CO<sub>2</sub> and NaHCO<sub>3</sub> afforded a main peak at  $m/z = 28$  (<sup>12</sup>CO; Fig. 10b). Fig. 11 shows the <sup>1</sup>H NMR spectra of the reaction solution formed in the cathodic compartment after irradiation. In the case of <sup>13</sup>CO<sub>2</sub> and NaH<sup>13</sup>CO<sub>3</sub>, a doublet attributable to H<sup>13</sup>COO<sup>-</sup> was observed at 8.26 ppm ( $J_{\text{CH}} = 196$  Hz) because of <sup>1</sup>H-<sup>13</sup>C coupling, while a singlet was observed at 8.26 ppm for the system with ordinary CO<sub>2</sub> and NaHCO<sub>3</sub>. These isotope labelling experiments confirmed that CO<sub>2</sub> 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  $\nu_{\text{CO}}$  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<sup>-</sup> ligands of Ru catalyst units were replaced with electron-donating ligands

such as OH<sup>-</sup> or HCOO<sup>-</sup>. The exchange of Cl<sup>-</sup> 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<sup>-</sup> 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 CO<sub>2</sub> 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<sup>-2</sup>) 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 CO<sub>2</sub> promoted by a mixture of Ru(bpy)(CO)<sub>2</sub>Cl<sub>2</sub> and [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (bpy = 2,2'-bipyridine), and proposed that slower 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.<sup>51</sup> Kubiak *et al.* proposed that in the electrocatalytic reduction of CO<sub>2</sub> using Ru(6Mesbpy)(CO)<sub>2</sub>Cl<sub>2</sub>, 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.<sup>52</sup> 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 CO<sub>2</sub> over H<sub>2</sub> remained high even in slower-electron-injection systems.

Subsequently, we determined the optimal number of potential sweeps in the polymerization of PyrRuC<sub>2</sub>bpy with NiO/PRuPyr (process 2) for the photocatalytic reduction of CO<sub>2</sub> (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/AgNO<sub>3</sub>) for 30 min exhibited poor photocatalytic performance (entry 6, Table 4).

To check the necessity of the first process of NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 fabrication (process 1), we performed the direct polymerization of PyrRuC<sub>2</sub>bpy on the NiO electrode without PRuPyr using 25 potential sweeps between 0 and





+1.35 V vs. Ag/AgNO<sub>3</sub> at 100 mV s<sup>-1</sup>, and the electrode was then reacted with [Ru(CO)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub> in MeCN solution at room temperature, as in processes 2 and 3 for the synthesis of NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 (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-RuC<sub>2</sub>RuCAT1 (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-RuC<sub>2</sub>RuCAT2 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-RuC<sub>2</sub>RuCAT1 (24.9 nmol), the amount of reduction products was also smaller in the former system. However, the TONs obtained for NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT2 (entry 6 in Table 3) exceeded those obtained for NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 (entry 2 in Table 3).

In conclusion of this section, both NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 and NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT2 were found to be good dye-sensitized molecular photocathodes for photocatalytic CO<sub>2</sub> reduction, exhibiting high selectivity, durability, and faradaic efficiency and featuring IPCEs much higher (IPCE<sub>max</sub> = 4.7%) and onset potentials more positive than those of previously reported dye-sensitized molecular photocathodes (IPCE<sub>max</sub> < 2%)<sup>11,12,19,27</sup> such as NiO/PRu-PolyVinyl-RuC<sub>2</sub>RuCAT with a polyvinyl polymer layer instead of the polypyrrole layer.<sup>12</sup> 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 CO<sub>2</sub> 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-RuC<sub>2</sub>RuCAT1 as a photocathode for constructing full cells as follows.

### Full cells for photocatalytic CO<sub>2</sub> reduction coupled with water oxidation

We chose two types of photoanodes, *i.e.*, BiVO<sub>4</sub> modified with CoO<sub>x</sub> as a co-catalyst (CoO<sub>x</sub>/BiVO<sub>4</sub>)<sup>53,54</sup> and TaON modified with RhO<sub>x</sub> as a co-catalyst (RhO<sub>x</sub>/TaON),<sup>55</sup> 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.<sup>56,57</sup> The photoelectrochemical properties of CoO<sub>x</sub>/BiVO<sub>4</sub> and RhO<sub>x</sub>/TaON were first checked by measuring their light responses ( $\lambda_{\text{ex}}$  = 400–650 nm, 41.2 mW cm<sup>-2</sup>) (Fig. 13a, blue and gray lines), and in both cases, we observed good overlaps with the *I*-*V* curve of the NiO/PRu-PolyPyr-RuC<sub>2</sub>RuCAT1 photocathode (red line) in CO<sub>2</sub>-purged aqueous solutions containing 50 mM NaHCO<sub>3</sub> as the electrolyte (pH = 6.6).

Therefore, the above electrodes were then used for photocatalytic CO<sub>2</sub> reduction. Relatively stable photocurrents continuously flowed in both photoanodes under low applied biases ( $E_{\text{app}}$  = 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-RuC<sub>2</sub>RuCAT1 photocathode and the CoO<sub>x</sub>/BiVO<sub>4</sub> or RhO<sub>x</sub>/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<sup>-2</sup> at  $\lambda_{\text{ex}}$  = 460–650 nm for the photocathode, 28–32 mW cm<sup>-2</sup> at  $\lambda_{\text{ex}}$  = 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<sub>x</sub>/BiVO<sub>4</sub> photoanode, revealing that they were stable during 5 h irradiation. During this irradiation, CO and HCOOH were constantly produced in the photocathodic compartment, while O<sub>2</sub> was produced in the photoanodic compartment (Fig. 14b). The following results were obtained after 5 h: CO (3.90  $\mu$ mol, TON<sub>CO</sub> = 156.6), HCOOH (1.82  $\mu$ mol, TON<sub>HCOOH</sub> = 73.1), and O<sub>2</sub> (2.60  $\mu$ mol). The much lower amount of produced H<sub>2</sub> (0.42  $\mu$ mol) indicated high selectivity for CO<sub>2</sub> 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<sub>x</sub>/TaON photoanode also drove the photocatalytic reduction of CO<sub>2</sub> with water (Fig. 14c and d). The main products were also CO (0.88  $\mu$ mol, TON<sub>CO</sub> = 35.3) and HCOOH (0.97  $\mu$ mol, TON<sub>HCOOH</sub> = 39.0), and a high selectivity was observed for CO<sub>2</sub> reduction (92%) in the photocathodic compartment, while O<sub>2</sub> (1.02  $\mu$ mol) was formed in the photoanodic compartment. Although a smaller photocurrent density was observed in this system, the faradaic efficiency of O<sub>2</sub> evolution significantly improved to  $F_{\text{anode}} = 98\%$  with  $F_{\text{cathode}} = 96\%$ . The energy conversion efficiency equaled  $2.0 \times 10^{-2}\%$  (Table 5). The selectivity of O<sub>2</sub> evolution in the system with the RhO<sub>x</sub>/TaON photoanode was higher than that in the system with the CoO<sub>x</sub>/BiVO<sub>4</sub> photoanode, which produced O<sub>2</sub> as well as H<sub>2</sub>O<sub>2</sub>, in line with previous reports.<sup>58–60</sup>

The mechanism of the photocatalytic reduction of CO<sub>2</sub> 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 (BiVO<sub>4</sub> 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 ( $\text{CoO}_x$  or  $\text{RhO}_x$ ).

These Z-scheme electron transfer processes continuously proceed during irradiation, inducing the two-electron reduction of one  $\text{CO}_2$  molecule on the photocathode and the four-electron oxidation of two water molecules to furnish  $\text{CO}$ ,  $\text{HCOOH}$ , and  $\text{O}_2$  (partial two-electron oxidation of one water molecule to afford  $\text{H}_2\text{O}_2$  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  $\text{NiO}$  electrode increased the photocatalytic performance of this electrode for  $\text{CO}_2$  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.  $\text{Ag}/\text{AgCl}$ ). 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  $\text{RhO}_x/\text{TaON}$  photocathode could efficiently and selectively reduce  $\text{CO}_2$  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

$^1\text{H}$  NMR (400 MHz) and  $^{31}\text{P}$  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  $1\text{ cm}^{-1}$ . 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  $2\text{ cm}^{-1}$ . 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  $\text{CO}_2$  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  $\text{P}_2\text{O}_5$  overnight and then distilled over  $\text{CaH}_2$  immediately before use. Tetrabutylammonium tetrafluoroborate ( $\text{Et}_4\text{NBF}_4$ ) was recrystallized from MeCN/ethyl acetate and then dried under reduced pressure at 373 K overnight before utilization.  $^{13}\text{CO}_2$  (99%  $^{13}\text{C}$ ) was purchased from Cambridge Isotope Laboratories, Inc.  $\text{NaH}^{13}\text{CO}_3$  (98%  $^{13}\text{C}$ ) was purchased from Sigma Aldrich. 4,4'-Bis(bromomethyl)-2,2'-bipyridine,<sup>61</sup> 1,2-bis(4'-methyl-[2,2'-bipyridin]-4-yl)ethane ( $\text{bpyC}_2\text{bpy}$ ),<sup>62</sup> 4,4'-bis-(methylphosphonate)-2,2'-bipyridine ( $(\text{Et}_2\text{O}_3\text{PCH}_2)_2\text{bpy}$ ),<sup>61</sup>  $[\text{Ru}(\text{dmb})_2]\text{Cl}_2$ ,<sup>63,64</sup> and  $[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$ <sup>65</sup> as well as  $\text{NiO}$ <sup>10</sup> 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  $^1\text{H}$  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%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ /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  $\text{Na}_2\text{SO}_4$ , 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%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ /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):  $m/z = 806.0$   $[\text{M}-\text{Cl} + \text{MeCN}]^+$ .

**[Ru(dmb)(Pyrdmb)Cl<sub>2</sub>].** 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)  $m/z = 455$   $[\text{M}-\text{Cl}]^+$ .  $[\text{Ru}(\text{dmb})(p\text{-cymene})\text{Cl}]\text{Cl}$  was then dissolved in MeCN (500 mL), and N<sub>2</sub> 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 ( $m/z = 444.0$   $[\text{M}-\text{Cl}]^+$ ). 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)<sub>2</sub>(Pyrdmb)](PF<sub>6</sub>)<sub>2</sub> (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 NH<sub>4</sub>PF<sub>6</sub>, 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%). <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>)  $\delta$ /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 C<sub>44</sub>H<sub>42</sub>N<sub>8</sub>P<sub>2</sub>F<sub>12</sub>Ru: C (49.15%), H (3.94%), and N (10.42%).

**[Ru(Pyrdmb)<sub>2</sub>(dmb)](PF<sub>6</sub>)<sub>2</sub> (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 NH<sub>4</sub>PF<sub>6</sub>. 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%). <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>)  $\delta$ /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 C<sub>52</sub>H<sub>48</sub>N<sub>10</sub>P<sub>2</sub>F<sub>12</sub>Ru: C (51.82%), H (4.02%), and N (11.61%).

**[Ru(dmb)(Pyrdmb)((H<sub>2</sub>O<sub>3</sub>PCH<sub>2</sub>)<sub>2</sub>bpy)](PF<sub>6</sub>)<sub>2</sub> (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 ((Et<sub>2</sub>O<sub>3</sub>PCH<sub>2</sub>)<sub>2</sub>bpy) (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 NH<sub>4</sub>PF<sub>6</sub> (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 Na<sub>2</sub>SO<sub>4</sub>. 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 NH<sub>4</sub>PF<sub>6</sub> (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%). <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>)  $\delta$ /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). <sup>31</sup>P NMR (162 MHz, acetone-*d*<sub>6</sub>)  $\delta$ /ppm: 23.11 (s, 2P, -PO<sub>3</sub>Et<sub>2</sub>), -144 (sep., 2P, PF<sub>6</sub><sup>-</sup>). 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 C<sub>44</sub>H<sub>44</sub>N<sub>8</sub>O<sub>6</sub>P<sub>4</sub>F<sub>12</sub>Ru: C (42.83%), H (3.59%), and N (9.08%).

**[Ru(dmb)(Pyrdmb)(bpyC<sub>2</sub>bpy)](PF<sub>6</sub>)<sub>2</sub> (PyrRuC<sub>2</sub>bpy).** A solution of  $[\text{Ru}(\text{dmb})(\text{Pyrdmb})\text{Cl}_2]$  (60 mg, 0.0895 mmol) and bpyC<sub>2</sub>bpy (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 NH<sub>4</sub>PF<sub>6</sub> (5 mL). The product was extracted with DCM (3  $\times$  50 mL), and the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to give a red precipitate. PyrRuC<sub>2</sub>bpy was separated by column chromatography on SP Sephadex C-25 (MeCN–H<sub>2</sub>O 1 : 1, v/v) and recrystallized from acetone–ether to yield the final product as red solids (85.4 mg, 76%). <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>)  $\delta$ /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 C<sub>56</sub>H<sub>52</sub>N<sub>10</sub>P<sub>2</sub>F<sub>12</sub>Ru: C (53.86%), H (4.36%), and N (11.02%).

**[Ru(dmb)(Pyrdmb)(bpyC<sub>2</sub>bpy)Ru(CO)<sub>2</sub>Cl<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (PyrRuC<sub>2</sub>-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%). <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>)  $\delta$ /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 C<sub>58</sub>H<sub>52</sub>N<sub>10</sub>Cl<sub>2</sub>O<sub>2</sub>P<sub>2</sub>F<sub>12</sub>Ru<sub>2</sub>: C (47.27%), H (3.70%), and N (9.34%).





## Fabrication of photocathodes

**NiO/PRuPyr.** The NiO electrode (area = 2.5 cm<sup>2</sup>) 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 ( $n_{\text{PRuPyr}}$ ) was determined from the difference in the absorbance of the solution before and after adsorption as well as by the ICP-MS analysis of H<sub>2</sub>O : HCl : H<sub>2</sub>SO<sub>4</sub> (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, Pyr<sub>2</sub>Ru, PyrRuC<sub>2</sub>bpy, or PyrRuC<sub>2</sub>RuCAT (0.5 mM) and Et<sub>4</sub>NBF<sub>4</sub> (0.1 M) as the supporting electrolyte was introduced into a one-component electrochemical cell. The NiO or NiO/PRuPyr electrode, a Ag/AgNO<sub>3</sub> electrode (Ag wire immersed in MeCN containing 0.01 M AgNO<sub>3</sub> and 0.1 M Et<sub>4</sub>NBF<sub>4</sub> separated by Vycor<sup>®</sup> 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<sup>-1</sup>. 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)<sub>2</sub>Cl<sub>2</sub>]<sub>n</sub> (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 ( $n_{\text{CV}}/\text{mol}$ ) were determined by cycling the electrodes between 0.4 and +1.2 V vs. Ag/AgNO<sub>3</sub> in MeCN solutions containing 0.1 M Et<sub>4</sub>NBF<sub>4</sub> as a supporting electrolyte at 10 mV s<sup>-1</sup>,<sup>12</sup> 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<sup>-1</sup>), and  $\nu$  is the scan rate (0.01 V s<sup>-1</sup>). The areal density of electroactive Ru units was calculated by dividing  $n_{\text{CV}}$  by the area of the electrode (2.5 cm<sup>2</sup>).

The total number of Ru units ( $n_{\text{total}}$ ), that is, Ru photosensitizer units + RuCAT units adsorbed on the electrodes, was estimated by ICP-MS analysis of H<sub>2</sub>O : HCl : H<sub>2</sub>SO<sub>4</sub> (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 ( $n_{\text{PS}}$ ). The corresponding concentration was estimated from calibration plots prepared using the standard Ru atomic absorption standard solution (Aldrich, 1000 μg mL<sup>-1</sup> Ru in 5% HCl). The amount of RuCAT units ( $n_{\text{cat}}$ ) 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 H<sub>2</sub>.

## Fabrication of the RhO<sub>x</sub>/TaON photoanode

Particulate TaON was prepared according to a previously reported method.<sup>66</sup> Ta<sub>2</sub>O<sub>5</sub> (2 g) particles were heated in a flow of NH<sub>3</sub> (20 mL min<sup>-1</sup>) at 1123 K for 15 h. Rh species (0.7 wt% metal basis) was loaded on TaON particles by impregnation with aqueous Na<sub>3</sub>[RhCl<sub>6</sub>]·*n*H<sub>2</sub>O followed by heating at 673 K for 30 min in air to afford RhO<sub>x</sub>/TaON.<sup>55</sup> The as-prepared RhO<sub>x</sub>/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<sub>x</sub>/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.<sup>55,57,66–69</sup> The RhO<sub>x</sub>/TaON electrodes were coated with 50 μL of methanolic TaCl<sub>5</sub> (10 mM) and then dried in air at room temperature. After this process was performed five times, the electrode was heated in an NH<sub>3</sub> flow (10 mL min<sup>-1</sup>) at 723 K for 30 min.

## Photoelectrochemical measurements and photocatalytic CO<sub>2</sub> reduction using dye-sensitized molecular photocathodes

The IPCEs of the electrodes were measured according to previous reports.<sup>12,27</sup> Photocatalytic performance was also evaluated using a previously reported method, with the vital parts briefly outlined below. Photoelectrochemical CO<sub>2</sub> reduction was conducted in a Pyrex H-shaped cell with two compartments containing aqueous NaHCO<sub>3</sub> (15–18 mL, 50 mM) and separated by a Nafion<sup>®</sup> 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 CO<sub>2</sub> 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<sub>ex</sub> = 460–650 nm) and the CO and H<sub>2</sub> 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 CO<sub>2</sub> 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<sub>x</sub>/BiVO<sub>4</sub> or a RhO<sub>x</sub>/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 cm<sup>2</sup>) was

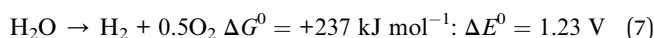
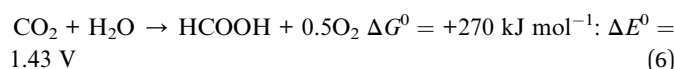
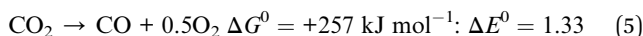


irradiated at  $\lambda_{\text{ex}} = 460\text{--}650\text{ nm}$  using a 300 W Xe lamp with a cutoff filter.  $\text{CoO}_x/\text{BiVO}_4$  ( $1.2\text{--}2.0\text{ cm}^2$ ) was irradiated at  $\lambda_{\text{ex}} = 400\text{--}650\text{ nm}$  using a 300 W Xe lamp (Asahi Spectra, MAX-302) with a cutoff filter (HOYA, L42) and an IR-cut filter.  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{HCOOH}$ , and  $\text{O}_2$  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  $E_{\text{photon}}$  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 ( $18\,000\text{ s}$ ) =  $2.22\text{ kJ}$ . The total chemical energies of the generated  $\text{CO}$ ,  $\text{HCOOH}$ , and  $\text{H}_2$  ( $E_{\text{chemical}}$ ) 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  $\text{CO}$ ,  $\text{HCOOH}$ , and  $\text{H}_2$ ,  $F$  is the Faraday constant,  $V_{\text{theoretical}}$  is the theoretical formation voltage for each product, and  $E_{\text{photon}}$  is given by the integration of irradiated light energy.

### Photocatalytic $\text{CO}_2$ 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 =  $100\text{ mW cm}^{-2}$ ) 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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