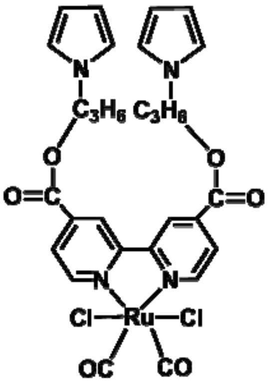
Supporting information

Reference 6

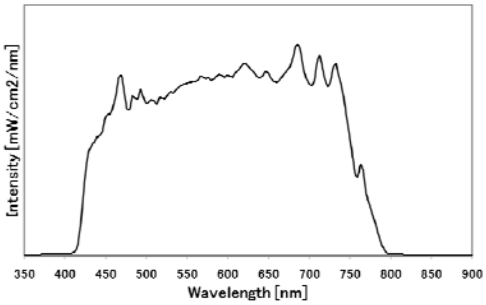


The structure of $[Ru^{II}(L\text{-}L)(CO)_2Cl_2]$

Detail of polymerization process of RCP/p-InP-Zn

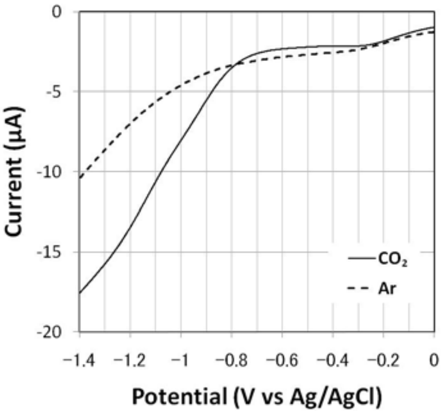
0.1 M Bu_4NClO_4 (TBAP) in acetonitrile media was used as an electrolyte.. 5 ml of the electrolyte was introduced in Pyrex glass cell and 1 mg of $[Ru(L\text{-}L)(CO)_2Cl_2]$ was dissolved in the electrolyte. p-InP-Zn photoelectrode was used as working electrode. Glassy carbon and I^-/I_3^- are used as counter and reference electrode, respectively. The cell was capped with Teflon and purged with Ar gas to remove oxygen in the cell. Cathodic electropolymerization was conducted at -1.4 V (vs. I^-/I_3^-) for 30 minutes under light irradiation. Xenon light source equipped with an optical filter and a cold mirror was used to irradiate the photoelectrode. The spectrum of light source was shown in Ref. 7. The photoelectrode modified with ruthenium complex polymer was rinsed with acetonitrile after electopolymeriztion process.

Reference 7



The spectrum of the Xenon light source equipped with an optical filter and a cold mirror.

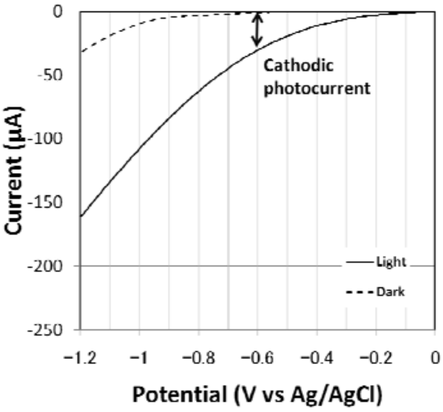
Reference 8



Linear-sweep voltammetry of RCP/carbon under Ar bubbling and CO_2 bubbling.

A current difference between Ar bubbling and CO_2 bubbling was observed around -0.8 V (vs. Ag/AgCl).

Reference 9



Linear-sweep voltammetry of an unmodified p-InP-Zn electrode under dark and visible-light irradiation, with CO_2 bubbling.

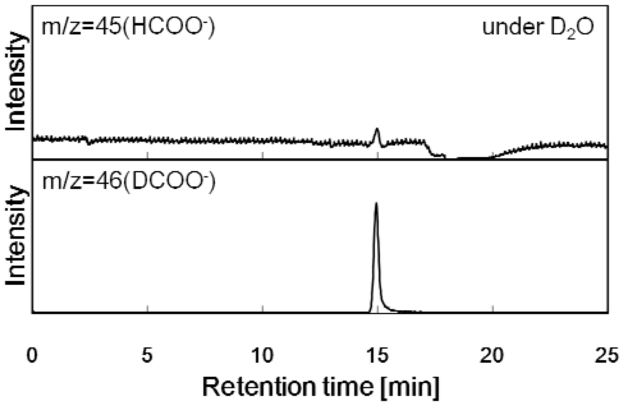
The open circuit potential of the unmodified p-InP-Zn electrode was about 0 V.

Reference 11

Detail of polymerization process of RCP/p-InP-Zn (C,A)

0.1 M Bu_4NClO_4 (TBAP) in acetonitrile media was used as an electrolyte.. 5 ml of the electrolyte was introduced in Pyrex glass cell and 1 mg of $[Ru(L\text{-}L)(CO)_2Cl_2]$ was dissolved in the electrolyte. p-InP-Zn photoelectrode was used as working electrode. Glassy carbon and I^-/I_3^- are used as counter and reference electrode, respectively. The cell was capped with Teflon and purged with Ar gas to remove oxygen in the cell. Cathodic electropolymerization was conducted at -1.4 V (vs. I^-/I_3^-) for 30 minutes under light irradiation. Xenon light source equipped with an optical filter and a cold mirror was used to irradiate the photoelectrode. The spectrum of light source was shown in Ref. 7. After cathodic electropolymerization, anodic electropolymerization was conducted at 1.6 V (vs. I^-/I_3^-) for 30 minutes under dark condition. The photoelectrode modified with ruthenium complex polymer was rinsed with acetonitrile after electopolymeriztion process.

Reference 13



IC-TOFMS spectra of a tracer experiment utilizing D_2O.

The photoelectrochemical reaction utilizing an RCP/p-InP-Zn electrode was conducted under $^{12}CO_2$ bubbling. D_2O was used as the electrolyte. The cell was irradiated with visible light ($400 < \lambda < 800$ nm) for 3 hours.

Experimental information

Determination of products

The amount of $HCOO^-$ was determined using an ion chromatograph (ICS-2000, Dionex Corporation) with IonPacAS15 and IonPacAG15 columns. The column temperature was maintained at 308 K. A 3 mM KOH solution was used as the first eluent for 10 minutes, and then the eluent was gradually changed to a 10 mM KOH solution for the next 5 minutes, after which the eluent was gradually changed to a 30 mM KOH solution for the next 5 minutes.

Isotope analysis

To detect the formation of $H^{13}COO^-$ and $DCOO^-$, an ion chromatograph, interfaced with a time-of-flight mass spectroscopy system (IC-TOFMS, JEOL JMS-T100LP), was used with MeOH added as the mobile phase.