Supporting information

Reference 6

The structure of [Ru^{II}(L-L)(CO)_{2}Cl_{2}]

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

0.1 M Bu_{4}NClO_{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-L)(CO)_{2}Cl_{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 electopolymerization 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$_4$NClO$_4$ (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-L)(CO)$_2$Cl$_2$] was dissolved in the electrolyte. p-InP-Zn photode electrode was used as working electrode. Glassy carbon and 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-/I₃⁻) 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-/I₃⁻) for 30 minutes under dark condition. The photoelectrode modified with ruthenium complex polymer was rinsed with acetonitrile after electopolymerization process.

Reference 13

IC-TOFMS spectra of a tracer experiment utilizing D₂O.
The photoelectrochemical reaction utilizing an RCP/p-InP-Zn electrode was conducted under ¹²CO₂ bubbling. D₂O was used as the electrolyte. The cell was irradiated with visible light (400 < λ < 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⁺¹³COO⁻ 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.