Supplementary Information (SI) for Sustainable Energy & Fuels.

Supporting Information

Unassisted visible-light driven NADH regeneration based on the dual photoelectrodes system

Koya Kano [a], Masanobu Higashi [b]* and Yutaka Amao [a,c]*

[a] Graduate School of Science, Osaka Metropolitan University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

[b] Institutional Advancement and Communications, Kyoto University, Yoshida-Honcho, Sakyo-ku, Kyoto 606-8501, Japan

[c] Research Centre for Artificial Photosynthesis (ReCAP), Osaka Metropolitan University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

a) Fabrication of $CuInS_2$ photocathode

The $CuInS_2$ photocathode was fabricated by sequential electrodeposition of Cu and In on a Mo substrate (Nilaco, 99.95 %) and subsequent sulfurization treatment, according to a report on the preparation of $CuInS_2$ films.[1] An electrochemical cell consisting of a Mo substrate working electrode, a Pt counter electrode, and an Ag/AgCl reference electrode. The applied potential of the working electrode was controlled by using a potentiostat (VersaSTAT 4, Princeton Applied Research Co., Ltd.). For Cu deposition, an aqueous solution (50 mL) containing both 110 mM of $CuSO_4•5H_2O$ (99.5%, Wako Pure Chemical Co., Ltd.) and 10 mM of citric acid (98.0%, Wako Pure Chemical Co., Ltd.) was used (pH = ~2.4). Cu deposition on the Mo working electrode was then conducted with a constant applied potential of –0.4 V vs. Ag/AgCl until the charge density that passed through the outer circuit exceeded 1042 mC cm^{-2}. For In deposition, an aqueous solution (50 mL) containing 30 mM of $InCl_3•4H_2O$ (97.0%, Wako Pure Chemical Co., Ltd.), 36 mM of trisodium citrate dihydrate (99.0%, Wako Pure Chemical Co., Ltd.) and 10 mM of citric acid was used (pH = ~2.8). The applied potential was fixed to –0.78 V vs. Ag/AgCl until the charge density that passed through the outer circuit exceeded 1200 mC cm^{-2}.

The deposited In/Cu/Mo samples were sulfurized by heating in a stream of H_2S gas. The sample was placed on the inside of a quartz tube (i.d.: 26 mm), and then the gas inside was thoroughly purged with a stream of N_2 gas (99.999%, 100 mL min^{-1}) at room temperature. The temperature of the sample was increased to 383 K at 20 K min^{-1} and then maintained for 60 min. The temperature was then increased to 793 K at 40 K min^{-1}. The N_2 gas stream was replaced with diluted H_2S (5 vol% in Ar, 10 mL min^{-1}) immediately upon reaching 793 K to avoid the unfavorable formation of a solid solution of

In and Cu at high temperatures. After maintaining this sample temperature for 30 min, the stream of H_2S/Ar was changed to 99.999% N_2 gas (100 mL min^{-1}). Finally, the sample was cooled naturally. The obtained sample was rinsed in water, immersed in 10% aqueous KCN for 2 min (to remove the surface Cu_xS layers that were generated during sulfurization), thoroughly washed with water, and finally dried at room temperature. Electrode areas of $CuInS_2$ were 1.5 × 4.0 cm for photoelectrochemical lactate production using water as an electron source and 1.5 × 1.5 cm for the other measurements, respectively.

b) Surface modification of $CuInS_2$ photocathode

The $CuInS_2$/Mo samples were modified with CdS, by which charge separation in $CuInS_2$ is generally enhanced, by a chemical bath deposition (CBD) method according to a report.[2] $CuInS_2$/Mo sample was immersed in 100 mL of an aqueous solution containing both 2.51 mmol of $Cd(CH_3COO)_2$ (98.0%, Wako Pure Chemical Co., Ltd.) and 0.67 mol of NH_4OH (98.0%, Wako Pure Chemical Co., Ltd.) at 75 °C for 1 min in order to adsorb Cd^{2+} onto the $CuInS_2$. Then, 38.09 mmol of $SC(NH_2)_2$ (98.0%, Wako Pure Chemical Co., Ltd.) was added to the solution, and the $CuInS_2$/Mo sample was immersed for 180 s. After the CdS deposition, the sample was rinsed in water. The resulting electrode was calcined at 673 K under N_2 gas flow. The back and sides of the electrodes were covered with epoxy resin.

c) Preparation of CoO_x/TaON, RhO_x/TaON and IrO_x/TaON electrodes

A particulate sample of TaON was prepared according to a previously reported method. The TaON particles were prepared by heating Ta_2O_5 (2 g, 99.99%, Kojundo Chemical Co., Ltd.) particles under NH_3 flow (20 mL min^{-1}) at 1123 K for 15 h. Co, Rh or Ir species 5 wt% CoO_x, 0.7 wt% RhO_x and 1 wt% IrO_x, calculated as metal; optimal loadings for CoO_x[3] and RhO_x[4]) were loaded onto TaON particles by impregnation from an aqueous $Co(NO_3)_2 \cdot 6H_2O$ (98.0%, Wako Pure Chemical Industries, Ltd.), $Na_3[RhCl_6] \cdot nH_2O$ (80%, Kanto Chemical Co., Inc.) or $Na_2[IrCl_6] \cdot 6H_2O$ (97%, Kanto Chemical Co., Inc.) solution, followed by heating at 673 K for 30 min in air (samples are hereafter referred to as CoO_x/TaON, RhO_x/TaON or IrO_x/TaON), respectively. The as-prepared particles were deposited on a Ti substrate as follows: The particles (60 mg) were dispersed in acetone (25 mL) by sonication for 5 min. The dispersed solution (60 μL) was dropped onto the Ti substrate and then dried in air at room temperature. This set of drop-casting and drying was repeated twenty times. The representative amount of particles on Ti was approximately 2.9 mg. The coated area was 1.5 × 4.0 cm. Post-necking was applied to provide sufficient conductivity among the particles, as well as between the particles and the substrate. The electrodes were dropped with 50 μL of a $TaCl_5$ methanol solution (10 mM) and then dried in air at room temperature. After performing this process five times, the electrode was heated in NH_3 flow (10 mL min^{-1}) at 723 K for 30 min.

d) Preparation of [Cp*Rh(bpy)(H_2O)]$^{2+}$

[Cp*Rh(bpy)(H_2O)]$^{2+}$ was prepared according to a previous report.[5, 6] [Cp*RhCl_2]$_2$ (0.1 mmol, Tokyo Chemical Industry Co., Ltd) was added to methanol (4.0 mL) and then 2,2′-bipyridine (0.2 mmol) was introduced into the above mixture. An orange homogeneous solution was immediately formed. Diethyl ether was added to the above solution at 277 K until orange [Cp*Rh(bpy)Cl]Cl precipitated and then the precipitate was collected by filtration. The obtained precipitate was dried in a vacuum oven for 3 h. [Cp*Rh(bpy)Cl]Cl was added to the phosphate buffer solution and readily hydrolysed to [Cp*Rh(bpy)(H_2O)]$^{2+}$.

e) Photoelectrochemical measurements of CdS/CuInS_2 and TaON electrodes

The electrochemical cell used for the photocurrent measurements consisted of a prepared electrode, a counter electrode (Pt wire), a Ag/AgCl reference electrode, and a phosphate buffer solution (pH 7.0). The phosphate buffer solution was prepared by mixing 0.1 M Na_2HPO_4 aq. and 0.1 M NaH_2PO_4 aq. In some cases, [Cp*Rh(bpy)(H_2O)]$^{2+}$ (1.0 mM) was added to the solution. The potential of the working electrode was controlled using a potentiostat (VersaSTAT 4, Princeton Applied Research Co., Ltd.). The solution was purged with Ar for more than 20 min prior to the measurement. The electrodes were irradiated by a 300 W Xe lamp (LX-300F, Cermax) fitted with a cut-off filter (L-42, Hoya) to block light in the ultraviolet (UV) region.

f) Photoelectrochemical reduction of NAD$^+$ and pyruvate to L-lactate

A two-compartment cell divided by a Nafion membrane (Nafion 117, Sigma-Aldrich) was used (each solution volume = 15 mL, each gaseous phase volume = 10 mL). Phosphate buffer solution (pH = 7.0) was used as an electrolyte. [Cp*Rh(bpy)(H_2O)]$^{2+}$ (1.0 mM) and β-NAD$^+$ (2.0 mM, Oriental Yeast Co., Ltd) were added to the solution of cathode side. The electrolyte solution was purged with Ar for over 20 min prior to the measurement. The applied potential of CdS/CuInS_2 photocathode was fixed to –0.2 V vs. Ag/AgCl. The electrode (area: 2.25 cm^2) was irradiated by the 300 W Xe lamp fitted with L-42 cut-off filter. The electrochemical cell was immersed in a water bath to maintain the solution temperature at 288 K during photoirradiation. The produced NADH was analyzed by the high-performance liquid chromatography (HPLC; Shimadzu LC-20AD SP pump, Shimadzu SPD-20A UV-Vis detector (detection wavelength: 260 nm), Shodex ORpak CRX-853 column) and UV-Vis absorption spectroscopy (MultiSpec-1500, Shimadzu) with the molar coefficient at 340 nm ($\varepsilon = 6.22 \times 10^3$ cm^{-1} M^{-1}).

For L-lactate production, lactate dehydrogenase (LDH; Oriental Yeast Co., Ltd) was used as a catalyst. LDH (27 nM) was added to the solution of cathode side of the above system. The produced L-lactate was analyzed using ionic chromatograph system (Metrohm Eco IC; electrical conductivity detector) with an ion exclusion column (Metrohm Metrosep Organic Acid - 250/7.8; column length: 250 × 7.8 mm; composed of a polystyrene/divinylbenzene copolymer with sulfonic acid groups; Temperature: 308 K). The aqueous solution of 1.0 mM perchloric acid and 50 mM lithium chloride were used as an eluent and a regenerant for an ionic chromatograph system, respectively.

2.4. Photoelectrochemical NADH regeneration and L-lactate production using water as an electron source

For this reaction, another tightly sealed two-compartment electrochemical cell (each solution volume = 130 mL, each gaseous phase volume = 50 mL) divided by the Nafion membrane was used. The prepared TaON photoanode and CdS/$CuInS_2$ photocathode (6 cm^2) were set in each cell including phosphate buffer solution (pH 7.0). LDH (27 nM) and sodium pyruvate (10 mM) were added to the solution of the cathode side, together with $[Cp^*Rh(bpy)(H_2O)]^{2+}$ (1.0 mM) and NAD^+ (2.0 mM). Ar gas was bubbled into the solution to remove air and then the flow rate was set to 5.0 mL min^{-1} during the reaction. The applied bias between the electrodes was set to 0 V. The photoanode and photocathode were irradiated by using two 300 W Xe lamp (LX-300F, Cermax) fitted with a cut-off filter (L-42, Hoya). The electrochemical cell was immersed in a water bath to maintain the solution temperature at 288 K during photoirradiation. The evolved H_2 and O_2 gases were detected by an online gas chromatograph (Shimadzu, GC-8A with a thermal conductivity detector (TCD) and an MS-5A column; carrier gas: Ar].

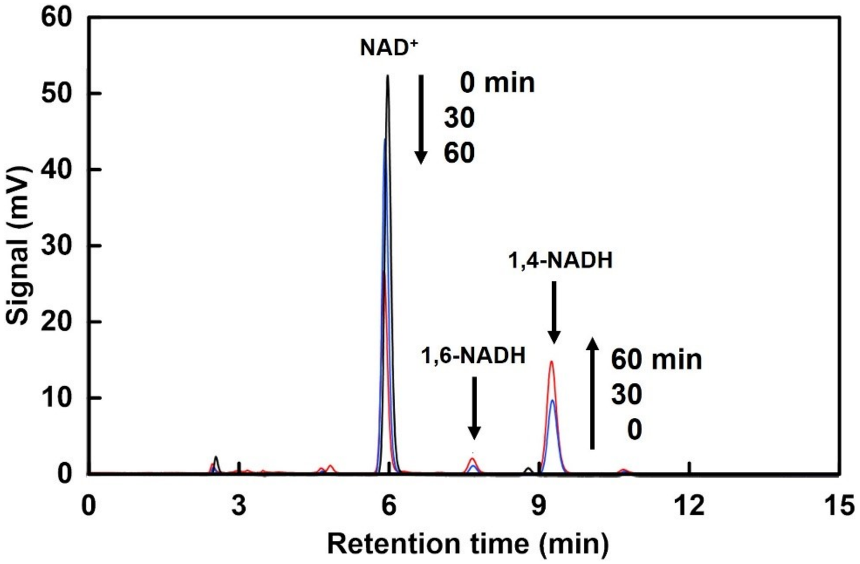

Figure S1. HPLC chromatograms of NAD$^+$ reduction over CdS/CuInS$_2$ photocathode in two-compartment cell containing phosphate buffer solution (pH 7.0) at –0.2 V vs. Ag/AgCl under visible light irradiation. Cathode side: [Cp*Rh(bpy)(H$_2$O)]$^{2+}$ (1.0 mM), and NAD$^+$ (2.0 mM).

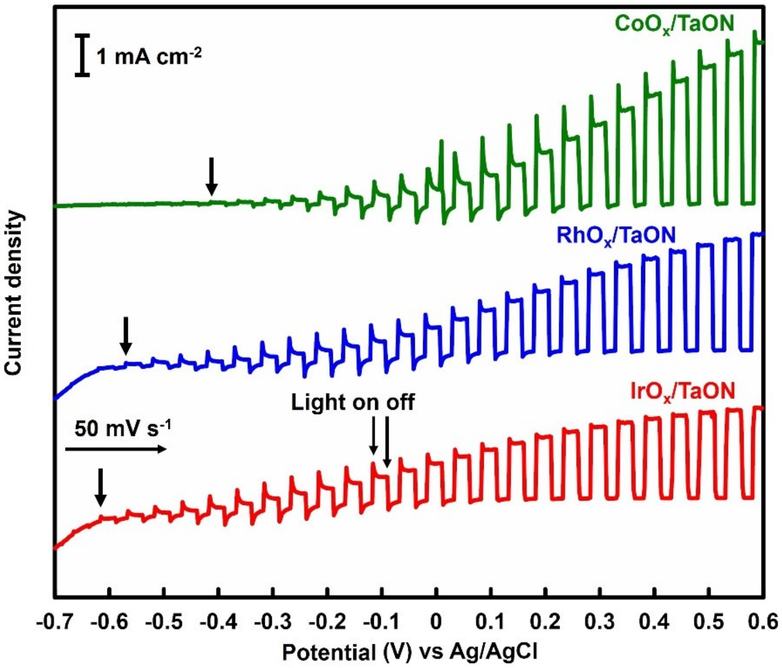

Figure S2. Photocurrent-potential curves for CoO$_x$/TaON, RhO$_x$/TaON and IrO$_x$/TaON photoanodes in phosphate buffer solution (pH 7.0) under chopped visible light irradiation. Bold arrows indicate the onset potentials of the photocurrents.

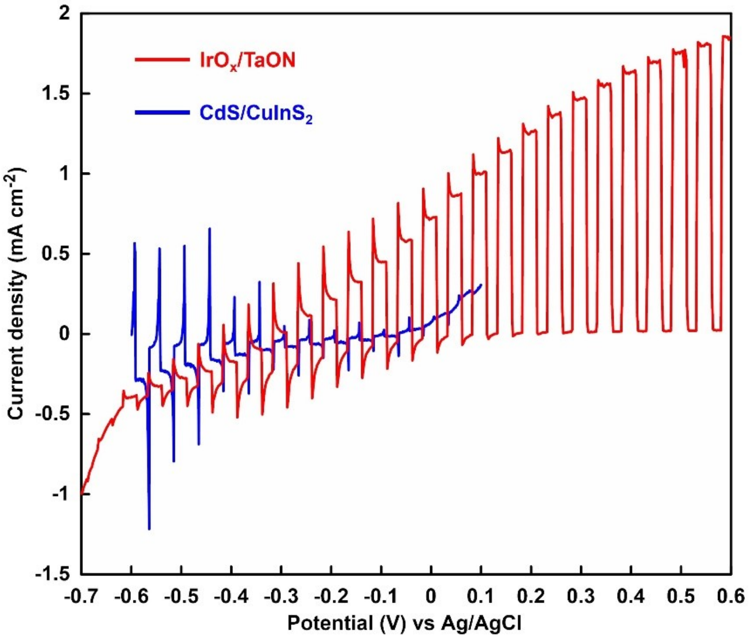

Figure S3. The overlay of photocurrent-potential curves for IrO_x/TaON photoanodes and $CdS/CuInS_2$ photocathode in the presence of $[Cp^*Rh(bpy)(H_2O)]^{2+}$ under chopped visible light irradiation.

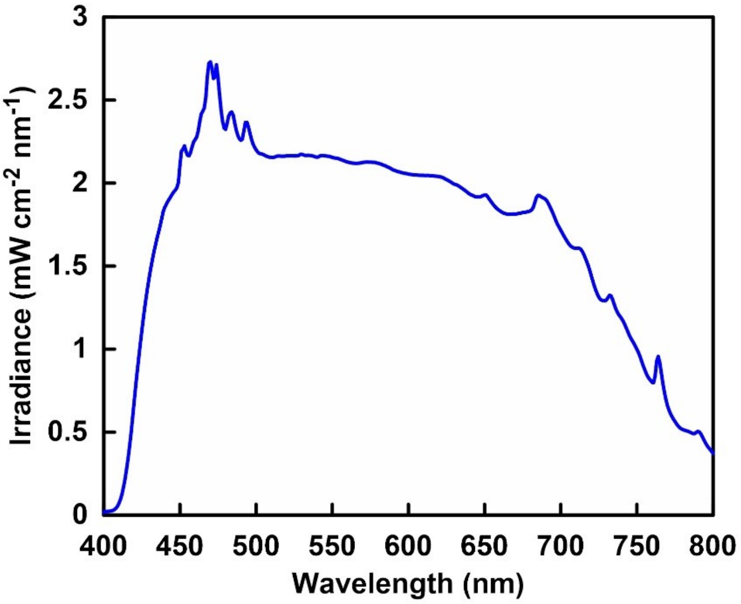

Figure S4. Emission intensity distribution of the 300 W Xe lamp fitted with L-42 cut-off filter.

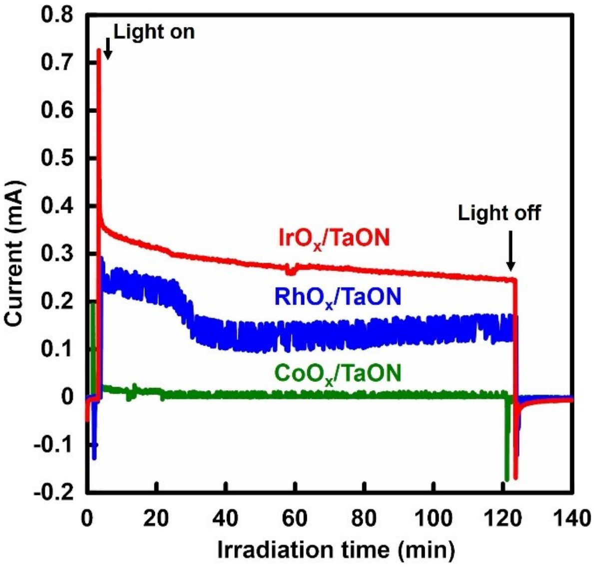

Figure S5. Time courses of photocurrent over the combination of $CuInS_2$ photocathode (electrode area: 6.0 cm^2) and IrO$_x$/TaON, RhO$_x$/TaON or CoO$_x$/TaON photoanode (electrode area: 6.0 cm^2) in two-compartment cell containing phosphate buffer solution (pH 7.0) without an external bias under visible light irradiation. Cathode side: $[Cp^*Rh(bpy)(H_2O)]^{2+}$ (1.0 mM), NAD$^+$ (2.0 mM), LDH (27 nM) and pyruvate (10 mM).

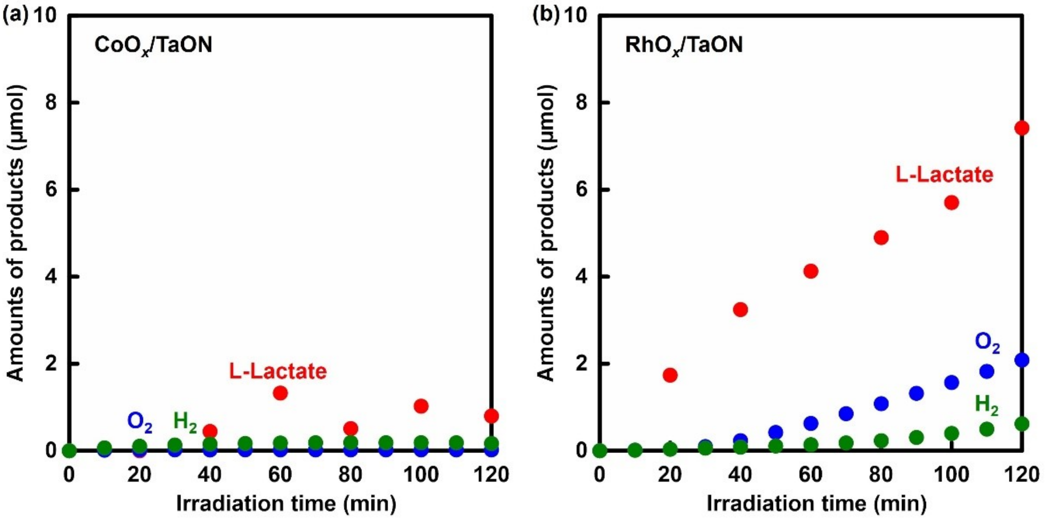

Figure S6. Time courses of produced L-lactate, O_2 and H_2 over the combination of $CuInS_2$ photocathode (electrode area: 6.0 cm^2) and (a) CoO$_x$/TaON or (b) RhO$_x$/TaON photoanode (electrode area: 6.0 cm^2) in two-compartment cell containing phosphate buffer solution (pH 7.0) without an external bias under visible light irradiation. Cathode side: $[Cp^*Rh(bpy)(H_2O)]^{2+}$ (1.0 mM), NAD$^+$ (2.0

mM), LDH (27 nM) and pyruvate (10 mM).

References

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