

Supplementary Information

Materials

All chemicals were purchased from Fujifilm Wako Pure Chemical Corp., Kanto Chemical Co. Inc., Tokyo Chemical Industry Co., Ltd., and Merck KGaA (Sigma-Aldrich), and used without further purification. FeCl₃·6H₂O (99%), NiCl₂·8H₂O (99.9%), ethylenediamine, and 1M KOH aqueous solution were purchased from Fujifilm Wako Pure Chemical Corp. Carbon paper (TGP-H-060) was purchased from Toray Industries, Inc. Multi-walled carbon nanotube (MWCNT; MW-IE, 5 wt% MWCNTs in EtOH,) and single-walled carbon nanotube (SWCNT; eDIPS INK, 0.05 wt% SWCNTs in EtOH) dispersions were purchased from Meijo Nano Carbon Co, Ltd. Polycrystalline silicon photovoltaic cells (poly-Si cells; OPL15A25101) and triple-junction amorphous silicon on stainless steel substrate cells (3jn-a-Si cell) were purchased from OptoSupply Limited and Xunlight Corp., respectively.

Synthesis of [Mn-MeCN] catalyst

The [Mn(bpy)(CO)₃Br] ([Mn(bpy)]) complex was synthesized according to a previously reported method.¹ The desired complex was prepared using a sequential procedure with ligand replacement. [Mn(CO)₅Br] (500 mg, 1.82 mmol) and 4,4'-di(1H-pyrrolyl-3-propyl carbonate)-2,2'-bipyridine (792.5 mg, 1.82 mmol) were mixed in 1,2-dichloroethane (50 mL) and the suspension refluxed for 3 h in an Ar atmosphere. After cooling the solution to room temperature, the solvent was evaporated under reduced pressure, which yielded a [Mn{4,4'-di(1H-pyrrolyl-3-propyl carbonate)-2,2'-bipyridine}(CO)₃Br] ([Mn-Br]) product that was then purified by recrystallization from dichloromethane/hexane. All syntheses were conducted in a darkroom.

[Mn{4,4'-di(1H-pyrrolyl-3-propyl carbonate)-2,2'-bipyridine}(CO)₃Br] ([Mn-Br]): Yield: 94%. ¹H NMR (δ, 400 MHz, (CD₃)₂CO): 9.51 (dd, 2H), 9.00 (s, 2H), 8.21 (dd, 2H), 6.77 (t, 4H), 6.01 (t, 4H), 4.43 (t, 4H), 4.21 (t, 4H), 2.31 (q, 4H). m/z (ESI-MS): 629.1 [M-Br+MeOH]⁺ FT-IR (MeCN) νCO / cm⁻¹ = 2029, 1938. HRMS (ESI) calcd for C₃₀H₃₀N₄O₈Mn ([M-Br]⁺): m/z 629.1441. Found: m/z 629.1459.

[Mn-Br] (500 mg, 0.85 mmol) and AgPF₆ (228 mg, 0.90 mmol) were mixed in MeCN (30 mL), and the suspension was stirred for 15 h in an Ar atmosphere. After removal of precipitated AgBr from the mixture by filtration, the solvent was evaporated under reduced pressure to yield a red oil. The complex was purified by silica column chromatography (using a very short column) with MeCN as the eluent. The eluent was evaporated under reduced pressure to give a yellow solid. Final purification was achieved by recrystallization from dichloromethane/ether. All syntheses were conducted in a darkroom.

[[Mn{4,4'-di(1H-pyrrolyl-3-propyl carbonate)-2,2'-bipyridine}(CO)₃MeCN]⁺(PF₆)⁻] ([Mn-MeCN]): Yield: 89%. ¹H NMR (δ, 400 MHz, CD₃CN): 9.30 (dd, 2H), 8.83 (s, 2H), 8.13 (dd, 2H), 6.73 (t, 4H), 6.03 (t, 4H), 4.37 (t, 4H), 4.11 (t, 4H), 2.28 (q, 4H). m/z (ESI-MS): 638.1 [M-PF₆]⁺. FT-IR (MeCN) νCO / cm⁻¹ = 2052, 1963. HRMS (ESI) calcd for C₃₁H₂₉N₅O₇Mn ([M]⁺): m/z 638.1447. Found: m/z 638.1430.

Fabrication of carbon paper modified with multi-walled carbon nanotubes (MWCNTs)

Carbon paper (CP) was annealed at 623 K for 2 h in an Ar atmosphere. The CP was immersed into a 5 wt% dispersion of MWCNTs in ethanol and then dried. The immersion procedure was repeated 3 times and the resultant MWCNTs/CP was annealed at 623 K for 2 h in an Ar atmosphere.

Fabrication of [Mn-MeCN] electrode on MWCNTs/CP

[Mn-MeCN] was polymerized on MWCNTs/CP using a chemical method. [Mn-MeCN] (7 mg) was dissolved in MeCN (1.9 mL). A 0.2 M FeCl₃ in ethanol solution (375 μL) and 0.05 vol% pyrrole in MeCN solution (200 μL) were used as chemical polymerization initiators. The polymer solution (0.1 mL) was dropped onto the MWCNTs/CP and dried at 333 K for 5 min. The area of MWCNTs/CP was approximately 4.5 cm² (1.8×2.5 cm). The coating procedure was repeated 10 times and the resultant [Mn-MeCN]/MWCNTs/CP was placed in the dark at room temperature overnight, followed by rinsing with deionized water. SEM images of [Mn-MeCN]/MWCNTs/CP are shown in Fig. S1. CP is totally covered with MWCNTs and [Mn-MeCN] was also modified on them but it is difficult to identify. The [Mn-MeCN]/MWCNTs/CP was connected to stainless steel (SUS) foil with silver paste. Copper wire was connected to the SUS of the [Mn-MeCN]/MWCNTs/CP electrode using indium solder. The back face of the SUS foil was covered with a glass plate. Finally, the edges of the [Mn-MeCN]/MWCNTs/CP electrode and the connection point were covered with silicone rubber.

Preparation of Ni-modified β-FeOOH colloidal solution.

Ni-modified β-FeOOH (β-FeOOH:Ni) colloidal solution was prepared according to our previously reported method.² 500 mL of an aqueous solution containing FeCl₃·6H₂O (100 mmol as Fe³⁺) and NiCl₂·8H₂O (50 mmol as Ni²⁺) was mixed with ethylenediamine, followed by pH adjustment to the range of 2.0-2.4 and agitation with a magnetic stirrer at room temperature. After 30 min of continuous stirring, the solution was kept at room temperature.

Preparation of CP modified with single-walled carbon nanotubes (SWCNTs)

CP was annealed at 623 K for 2 h in an Ar atmosphere. The CP was immersed into a 0.05 wt% dispersion of SWCNTs in ethanol and then dried. The immersion procedure was repeated 2 times. The resultant SWCNTs/CP was annealed at 623 K for 2 h in an air atmosphere. The annealing procedure was repeated 2 times for both the front and back sides.

Fabrication of β-FeOOH:Ni/a-Ni(OH)₂ electrode modified on CP or SWCNTs/CP

β-FeOOH:Ni particles were coated on CP or SWCNTs/CP by immersion of the CP into β-FeOOH:Ni colloidal solution diluted with the same volume of deionized water, following by drying at room temperature. The immersion procedure was repeated 3 times. The samples were subsequently washed

with 1 M NaOH aqueous solution and deionized water, and then dried again. SEM images of β -FeOOH:Ni/a-Ni(OH)₂ electrode modified on CP or SWCNTs/CP were shown in Fig. S2. It can be recognized that CP was covered with β -FeOOH:Ni/a-Ni(OH)₂ from the comparison between bare surface of CP (Fig. S2(b)) and the surface modified with β -FeOOH:Ni/a-Ni(OH)₂ (Fig. S2(d)). The top edge of the CP or SWCNTs/CP was connected to Cu wire with silver paste and the connection point was covered with silicone rubber.

Electrodeposition of Ni(OH)₂ on β -FeOOH:Ni/a-Ni(OH)₂ electrode

Ni(OH)₂ was additionally deposited electrochemically on the β -FeOOH:Ni/a-Ni(OH)₂ electrode. The β -FeOOH:Ni/a-Ni(OH)₂ electrode, Ag/AgCl and Pt wire were used as working, reference and counter electrodes, respectively. 0.1 M NiSO₄ aqueous solution was used as an electrolyte. A potential of -0.5 V (vs. Ag/AgCl) was applied until 20 mC of total charge was observed.

Measurements

Electrochemical/photoelectrochemical measurements

A potentiostat/galvanostat (SP-150, Bio-Logic Science Instruments) or a bi-potentiostat (2325, ALS Co., Ltd.) were used for electrochemical or photoelectrochemical measurements. For the electrochemical measurement, the sample electrode, platinum wire, and a silver/silver chloride electrode (Ag/AgCl: RE-17, EC Frontier Co., Ltd.) were used as the working, counter, and reference electrodes, respectively. A Pyrex glass cell was used as the reactor, and aqueous solutions of 1 M KOH, 0.1 M KOH and 0.1 M K₂B₄O₇ + 0.2 M K₂SO₄ (KBB) saturated with CO₂ were used as electrolytes. The photoelectrochemical measurement was conducted with a two electrode configuration. Two different photoelectrochemical measurements were conducted utilizing poly-Si cells or a 3jn-a-Si cell as the light absorber. One measurement was with a combination of the [Mn-MeCN] cathode and β -FeOOH:Ni/a-Ni(OH)₂ anode in a one-compartment reactor connected with poly-Si cells (Fig. S1). The other measurement was a combination of the β -FeOOH:Ni/a-Ni(OH)₂ anode and the photocathode consisting of [Mn-MeCN] and the 3jn-a-Si cell in a one-compartment reactor (Fig. S2). A solar simulator (HAL-320, Asahi Spectra Co., Ltd.) was used as a light source. The intensity was adjusted to 1SUN [Air Mass 1.5 (AM1.5)] using a light intensity checker (CS-20, Asahi Spectra Co., Ltd.).

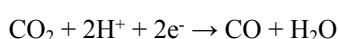
Determination of products

The amounts of CO, H₂ and O₂ in the gas phase were determined by *in situ* measurements using a flow reactor combined with a gas chromatograph. The flow reactor (Makuhari Rikagaku Garasu Inc.) was equipped with an auto sampler for *in situ* measurements and was directly connected to a gas chromatograph system (GC-2014, Shimadzu Corporation) equipped with Porapak-N and MS-13X columns. The calibration was conducted using CO₂-based standard gas containing ca. 100 ppm of H₂, N₂,

O₂, CO, and hydrocarbons. At the start of the experiment, the CO₂ gas flow was 20 mL min⁻¹ for 2 h to remove air in the reactor. CO₂ photoreduction was then conducted with a continuous CO₂ flow of 20 or 40 mL min⁻¹. The amounts of gaseous products were estimated by multiplication of the concentration of products determined by gas chromatography, the flow rate and the interval of measurement (20 min). In addition, there was a time lag for the detection of products due to the large dead volume of the flow cell; therefore, the calculated amount of products has a margin of error. The coefficient of variation (CV) for H₂, CO and O₂ those measured by our gas chromatograph using a standard gas for calibration were 0.6%, 3% and 3%, respectively. On the other hand, the CV for H₂, CO and O₂ during the static state reaction from 60 to 240 minutes in the flow reactor were 6%, 4% and 10%, respectively, while the CV of charge observed during the same time was only 0.9%. This result indicates that the CV observed during the flow reaction is large compared with the CV observed in the standard gas measurement. This reaction generates a potentially explosive mixture of H₂, CO and O₂. The concentration of H₂, CO and O₂ should be lowered than explosion limit during the flow reaction. A suitable exhaust hood is also required to prevent the exposure by CO with high concentration.

Calculation of current efficiency for CO production

The photoreduction of CO₂ to CO is described as:



The current efficiency for the production of formate was obtained using the following equation.

$$\eta_{\text{CO}} = Q_{\text{CO}} \times 2 / (C/F) \times 100$$

η_{CO} : Current efficiency for CO production

Q_{CO} : Quantity of CO (mol)

C: Charge (C)

F: Faraday constant = 96485.3365 (C mol⁻¹)

Calculation of solar-to-chemical conversion efficiency for CO production

The efficiency for CO production was calculated using the following equation:

$$\text{SCE} = (Q_{\text{CO}} \times \Delta G) / (I \times A \times T) \times 100$$

SCE: Solar-to-chemical conversion efficiency (%)

Q_{CO} : Amount of CO produced during the reaction (μmol)

ΔG : Change in Gibbs free energy per mole of CO produced from CO₂ ($\Delta G = 257.21 \text{ kJ mol}^{-1}$ at 298 K)

I: Light intensity (100 mW cm⁻²)

A: Irradiation area (cm²)

T: Irradiation time (s)

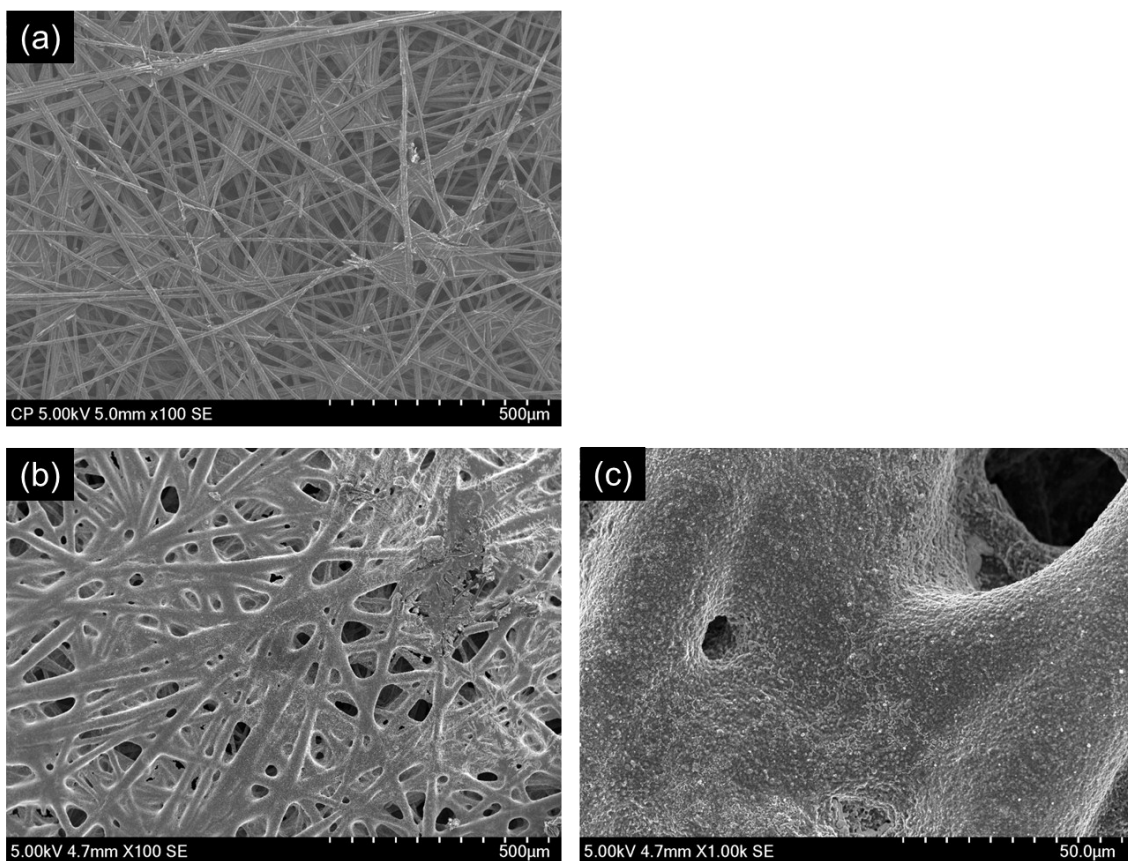


Figure S1. SEM images of [Mn-MeCN]/MWCNTs/CP

(a) bare carbon paper ($\times 100$), (b) [Mn-MeCN]/MWCNTs/CP ($\times 100$) and (c) its large magnification ($\times 1k$)

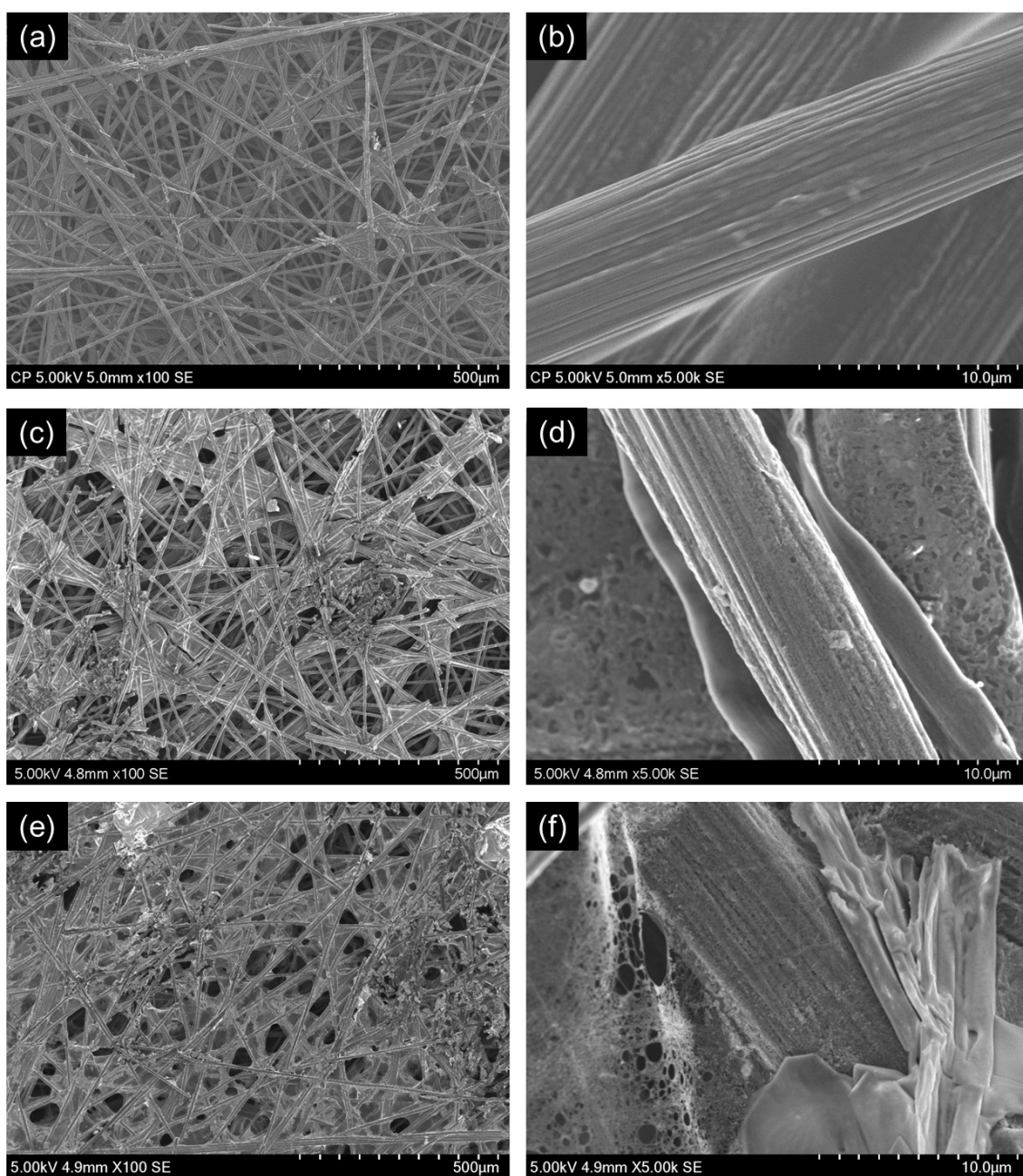


Figure S2. SEM images of β -FeOOH:Ni/a-Ni(OH)₂ electrode modified on CP or SWCNTs/CP (a) bare carbon paper (×100), (c) β -FeOOH:Ni/a-Ni(OH)₂/CP (×100), (e) β -FeOOH:Ni/a-Ni(OH)₂/SWCNTs/CP (×100) and (b), (d), (f) their large magnification images (×5k)

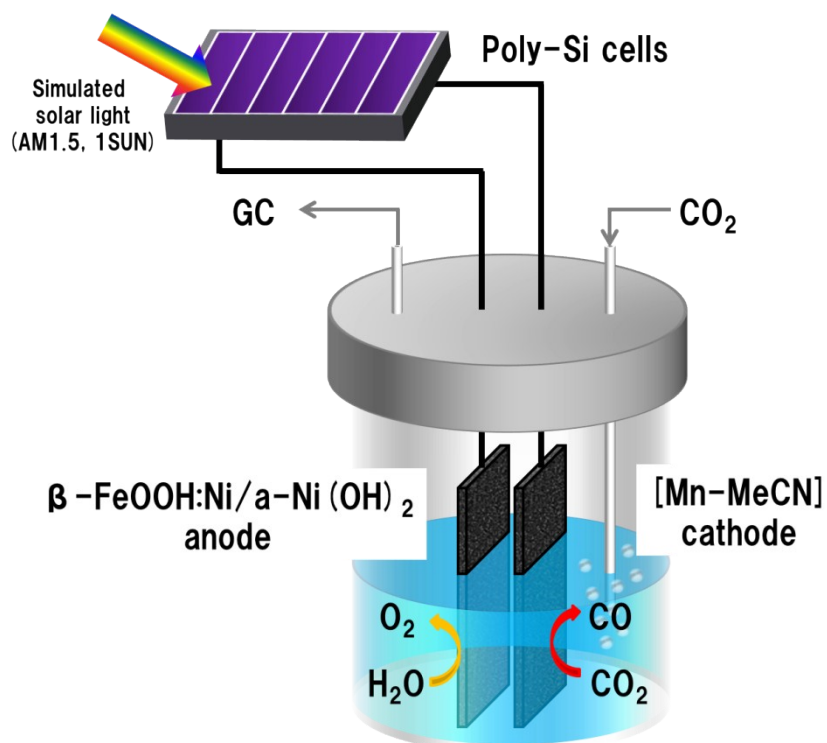


Figure S3. Schematic illustration of one-compartment CO₂ electrolyzer connected with light absorber.

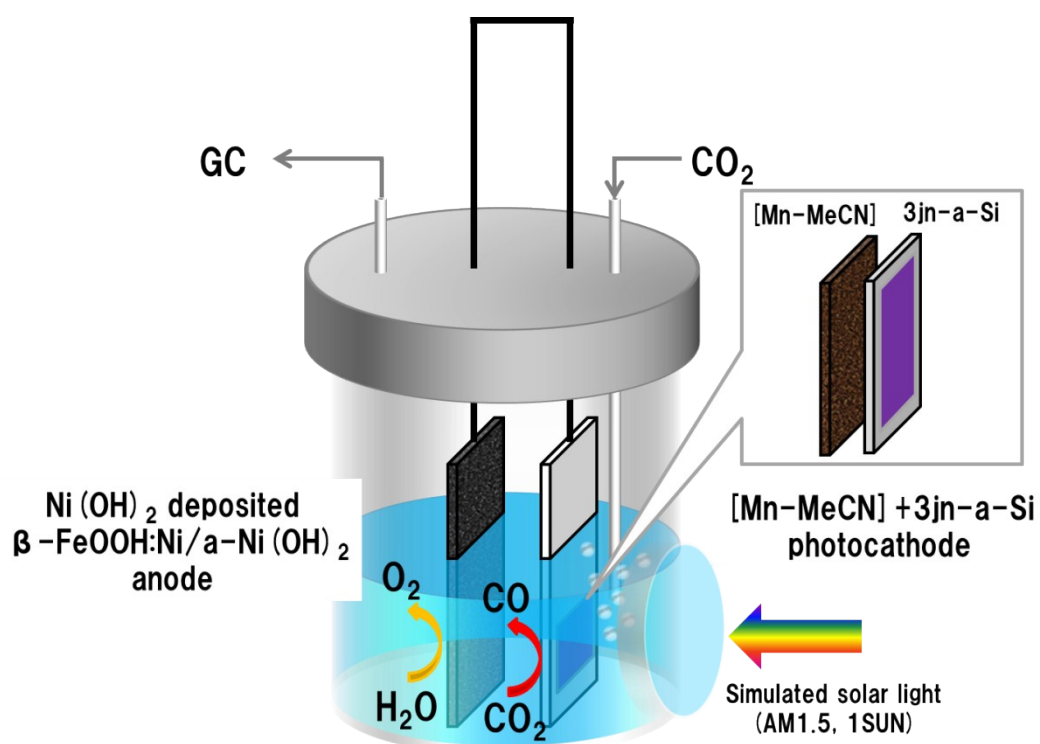


Figure S4. Schematic illustration of one-compartment reactor consisting of [Mn-MeCN]/3jn-a-Si photocathode and Ni(OH)₂ deposited β-FeOOH:Ni/a-Ni(OH)₂ anode.

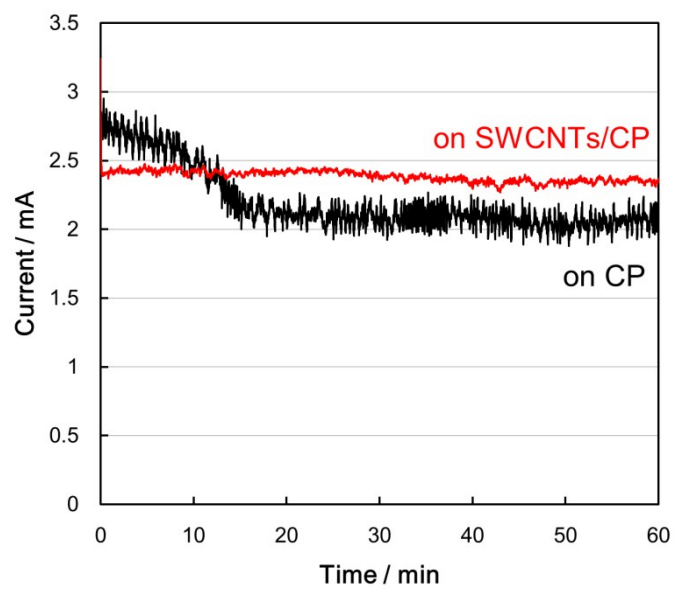


Figure S5. Time course for the current of β -FeOOH:Ni/a-Ni(OH)₂ electrode under potentiostatic conditions (applied bias +1.1 V vs. Ag/AgCl). β -FeOOH:Ni/a-Ni(OH)₂, Ag/AgCl and Pt wire are used as working, reference and counter electrodes, respectively. The electrolyte was CO₂ saturated 0.1 M KBB solution.

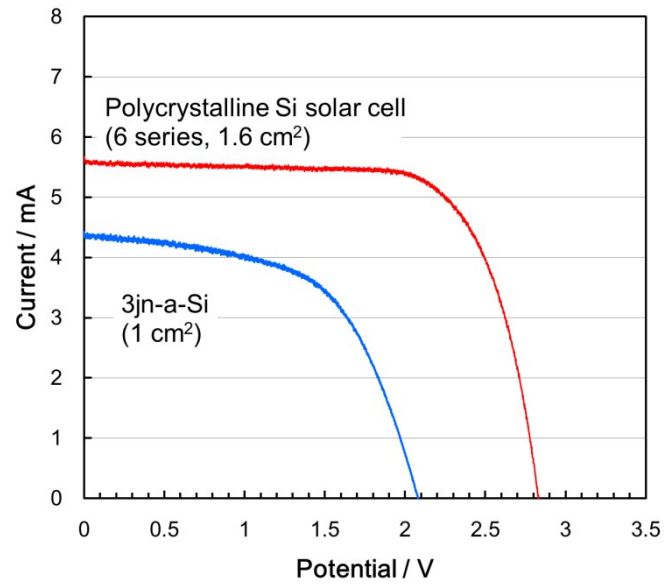


Figure S6. Current-potential characteristics of polycrystalline Si solar cell (6 series, 1.6 cm²) and 3jn-a-Si (1 cm²).

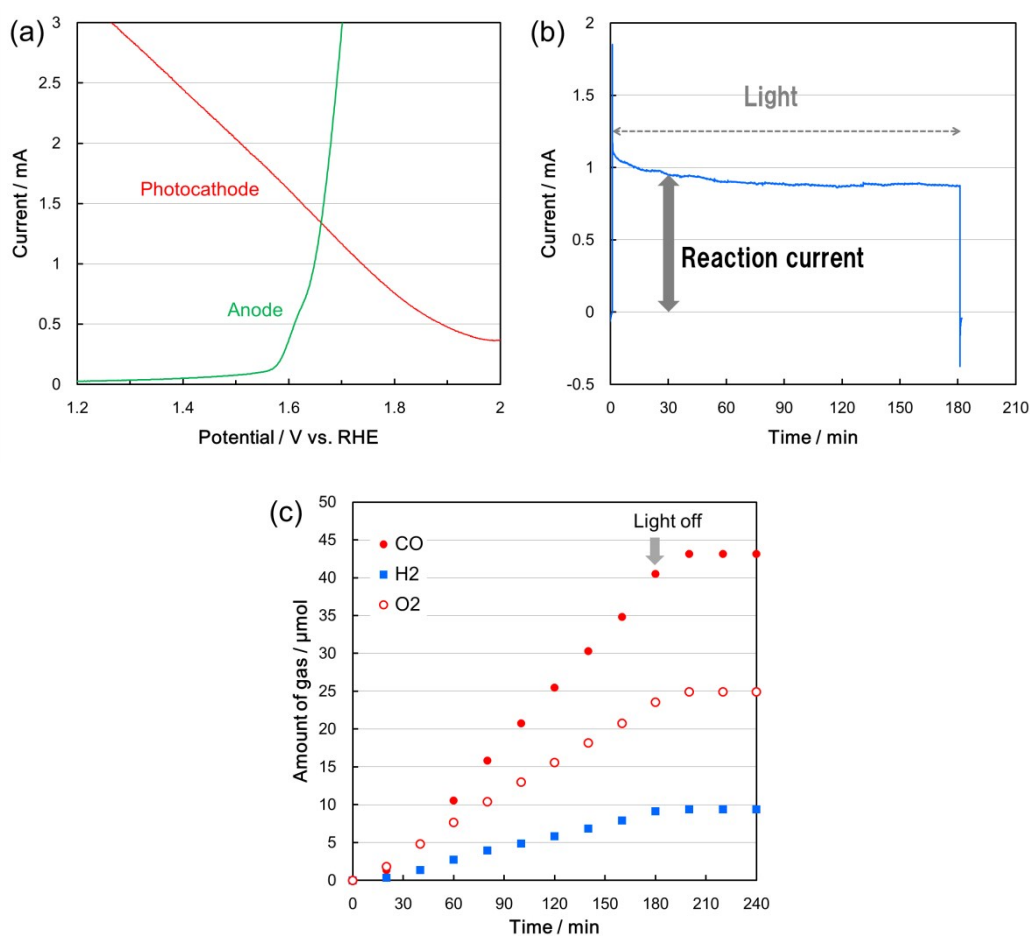


Figure S7. Results for solar driven CO₂ reduction using a photocathode for CO₂ reduction and an anode for water oxidation in a one-compartment reactor. The photocathode consisted of a [Mn-MeCN] electrode (ca. 1 cm²) and a 3jn-a-Si cell as a light absorber. The anode was a Ni(OH)₂ deposited β-FeOOH:Ni/a-Ni(OH)₂ electrode (ca. 8 cm²). The electrolyte was CO₂ saturated 0.1 M KBB solution. The CO₂ flow rate was 40 mL min⁻¹ (a) Current-potential characteristics of the photocathode and the anode under simulated solar light (1SUN, AM1.5, 1 cm²). Time courses for (b) the current under potentiostatic conditions (applied bias 0 V) and (c) the amount of gaseous products observed during solar-driven CO₂ reduction using the combination of photocathode and anode.

References

1. M. Bourrez, F. Molton, S. Chardon-Noblat and A. Deronzier, *Angewandte Chemie International Edition*, 2011, **50**, 9903-9906.
2. T. M. Suzuki, T. Nonaka, K. Kitazumi, N. Takahashi, S. Kosaka, Y. Matsuoka, K. Sekizawa, A. Suda and T. Morikawa, *Bull. Chem. Soc. Jpn.*, 2018, **91**, 778-786.