

Supporting Information

**Photo-assisted Electrochemical CO₂ Reduction Using a
Translucent Thin Film Electrode**

Phil Woong Kang^a, Jinkyu Lim^a, Robert Haaring^a, and Hyunjoo Lee^{*a}

^aDepartment of Chemical and Biomolecular Engineering, Korea Advanced Institute of
Science and Technology, Daejeon 34141, South Korea

*E-mail: azhyun@kaist.ac.kr

Experimental Section

Additional Data (Figure S1 ~ Figure S12; Table S1)

Experimental Section

Photo-assisted electrochemical reduction cell (PAEC)

Kel-F (polychlorotrifluoroethylene, Aetna Plastic) was selected as a body material for the cell of photo-assisted electrochemical CO₂ reduction (PAEC). A quartz window (31 mm diameter, 3mm thickness) was used to provide a light pathway to the electrode surface. The fully assembled PAEC cell was able to contain 35 ml of electrolyte (1 M KOH). A Xe lamp (300 W, Newport) equipped with a water-cooled sapphire IR filter (Liquid optical filter, Newport), a UV filter (385 nm cut-off, Newport), and an automatic light shutter (Newport) was used as a light source. Light intensity irradiated on the cathode was measured with a power meter (PM400, Thorlab) by placing the photodiode power sensor at the thin film electrode (TFE). The electrode area exposed to the electrolyte was 2.01 cm² (circular, 16 mm diameter). A mixed gas of 90 % CO₂ and 10 % N₂ was introduced as an inlet gas at a rate of 12 sccm through a 1/8 inch line to a gas chamber with a volume of 15 ml. Electrochemical analysis data were obtained through a potentiostat (Zive BP2). A Pt coil (0.5 cm ϕ , 18 cm in length) was used for a counter electrode, and Hg/HgO/1 M NaOH (Re-61AP, ALS) was used as a reference electrode. The gas chromatograph (Micro GC, Inficon) was connected to the gas outline of the PAEC cell. All electrochemical measurements were performed using a potentiostatic technique with voltages of -0.5, -0.7, -0.9, and -1.1 V_{RHE}. Prior to each measurement, the cell was purged with 90% CO₂ (N₂ balance) for 20 min. After applying the voltage, the signal was stabilized for 2 min, then the current with or without light irradiation (300 mW cm⁻²) was recorded. For a durability test, a portion of electrolyte (15 ml) was replaced with cold electrolyte to keep the system within the temperature range of 20 ~ 25 °C every 10 min. The light intensity was 180 mW cm⁻². The electrolyte was completely exchanged every 3 hr.

Preparation of thin film electrode (TFE)

Metal nanoparticles (NP) were deposited on Ag nanowire (NW) by galvanic replacement. Ag NW solution 5.36 ml (1 wt% solution in ethanol, CNvision) was diluted with deionized water (6.59 and 5.81 ml for Au and Pd, respectively) and ethanol (1.23 and 0.45 ml for Au and Pd, respectively). The Ag NW solution 2 ml was diluted with ethanol (11.35 ml) for Ru. The metal precursor (KAuCl₄, 99.99%, Sigma-Aldrich;

K_2PdCl_4 , 98%, Sigma-Aldrich; $RuCl_3$, 98%, Sigma-Aldrich) was dissolved in the same solvent to have a concentration of 25, 25, and 5 mM for Au, Pd, Ru. Right after citric acid was added with a metal to citric acid molar ratio of 1:7, 1:7, and 1:1, for Au, Pd, Ru, respectively, the metal precursor solution (1.83, 3.38, 6.65 ml for Au, Pd, Ru, respectively) was introduced to the Ag NW solution (13.17, 11.62, and 13.35 ml for Au, Pd, Ru, respectively), while stirring at 55 °C. The mixture was stirred at 55 °C for 24 h, washed several times with deionized water and ethanol, then dispersed in ethanol. The final metal concentration was adjusted to be 4 mg ml⁻¹.

In order to fabricate a thin film electrode (TFE), the catalyst solution (8 ml) was mixed with 8 ml of isopropyl alcohol and 43.8 μ l of 5 wt% Sustainion (XA-9, Dioxide Material) and sonicated for 10 min to prepare an ink. The ink was spray-coated onto Al foil (15 μ m, Daehan) to have a metal loading of 0.1 mg cm⁻². The Sustainion (Sustainion XA-9) was further sprayed onto the above film with a loading of 1 mg cm⁻² after drying. The coated Al foil was submerged in 0.1 M KOH (97%, Samchun) solution. A thin film was exfoliated from the Al foil within seconds. The film was scooped and re-submerged in clean 1 M KOH solution for 1 h for activating charge transfer along the Sustainion. For comparison, the same catalyst was spray-coated onto conventional carbon paper (37BC, SGL Carbon) with the same Sustainion coating (1 mg cm⁻²). The film was also treated in 1 M KOH solution for 1 h.

The metal NP/Ag NW catalyst and TFE were observed by transmission electron microscopy (TEM, JEOL-2100F) and field-emission scanning electron microscopy (FE-SEM, Hitachi SU-5000). To obtain a cross-sectional TEM image, the TFE on Al foil was embedded into epoxy resin and cut by microtome (RMC, PT-PC PowerTome Ultramicrotomes). The actual metal content was evaluated by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Avio500, Perkin-Elmer). The metal NP/Ag NW catalyst were drop-casted onto a Si wafer for X-ray photoelectron spectroscopy analysis (XPS, K-Alpha Thermo VG Scientific).

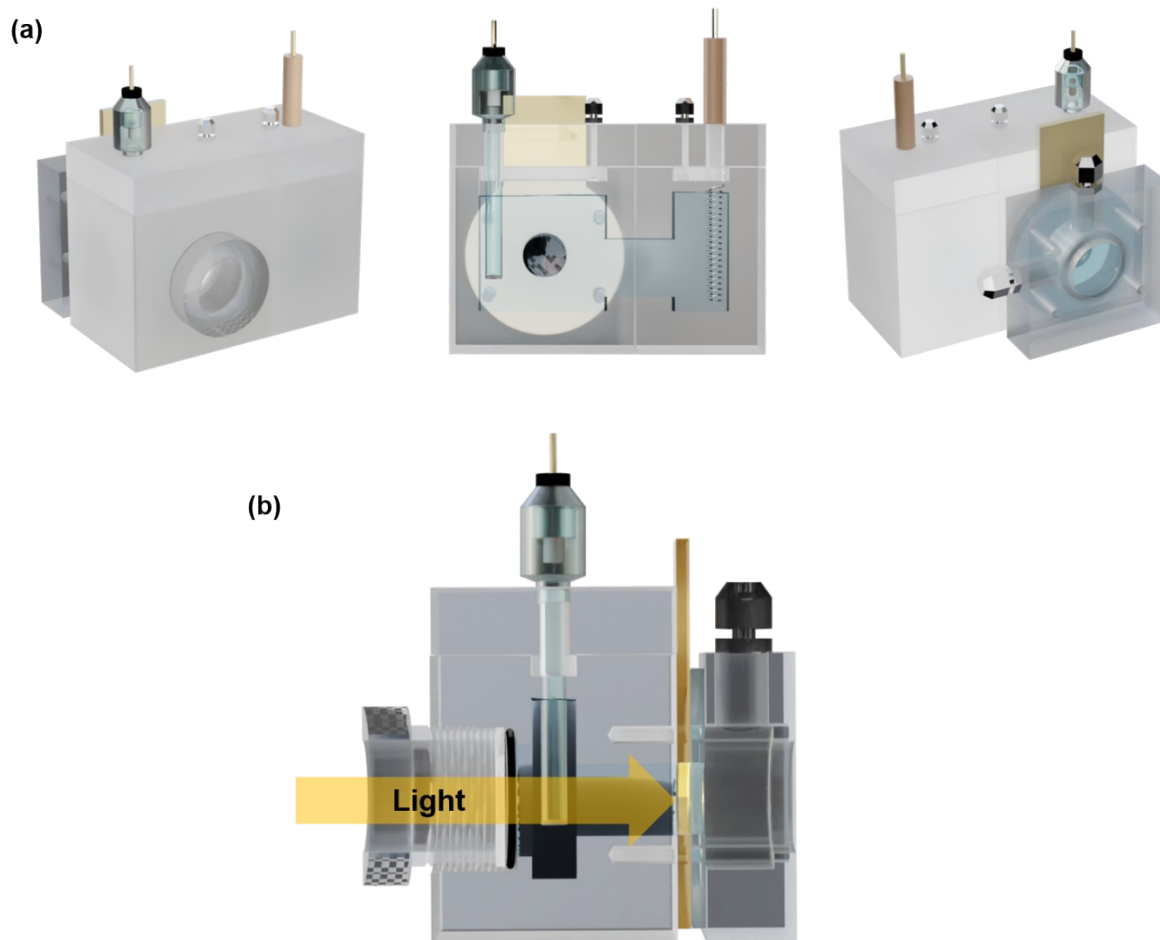


Fig. S1 (a) Graphical representation of a PAEC cell viewed from various directions. (b) A cross-sectional scheme of PAEC cell with light irradiation through front window and electrolyte chamber.

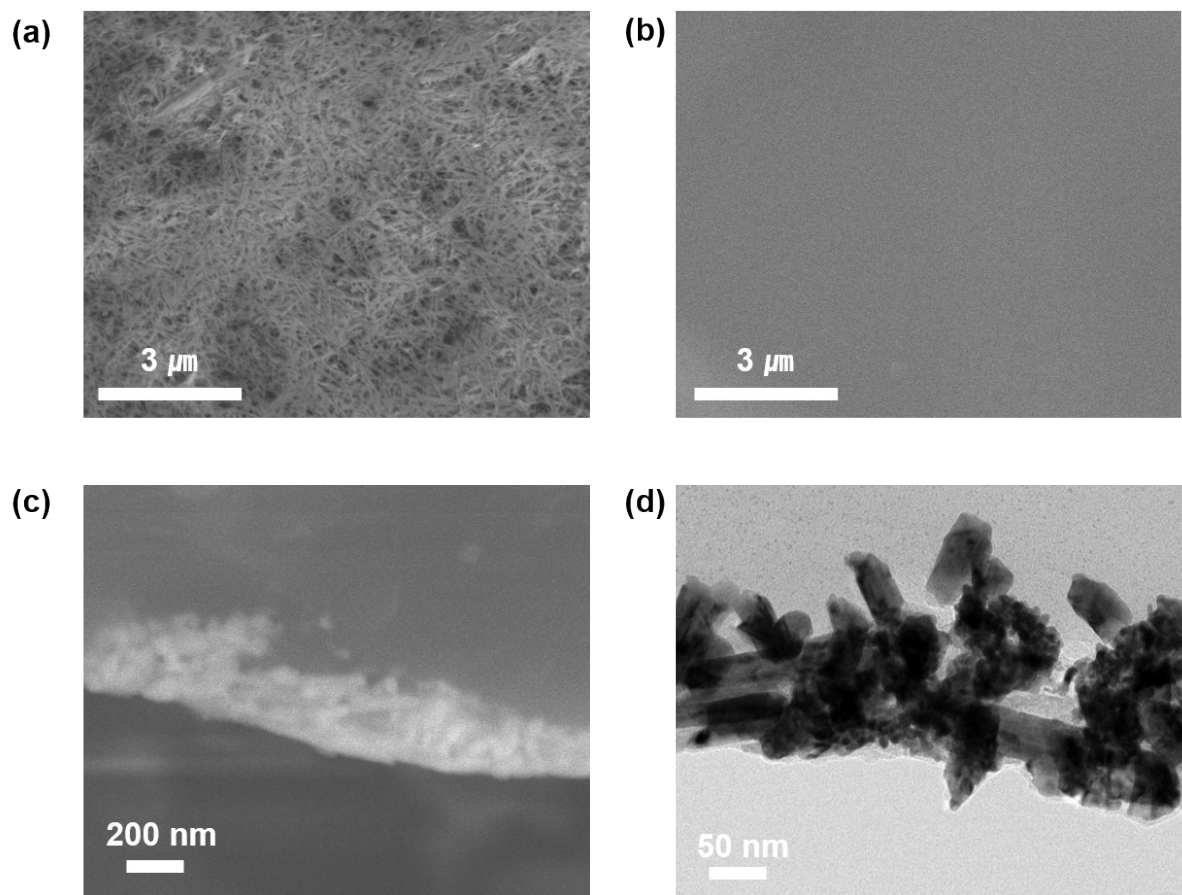


Fig. S2 (a) SEM image of catalyst layer surface on TFE. (b) SEM image of Sustainion surface on TFE before activation in 1M KOH. (c) SEM cross-sectional image of TFE showing catalyst layer and Sustainion layer. (d) TEM ultramicrotome cross-sectional image of TFE showing catalyst layer.

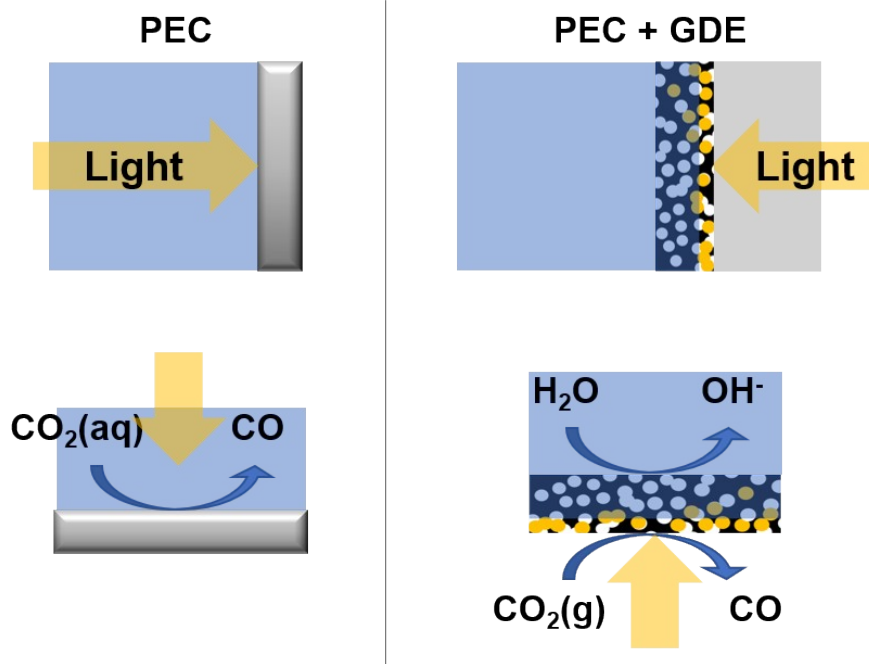


Fig. S3 Conceptual difference between typical PEC and our system combining PEC and GDE.

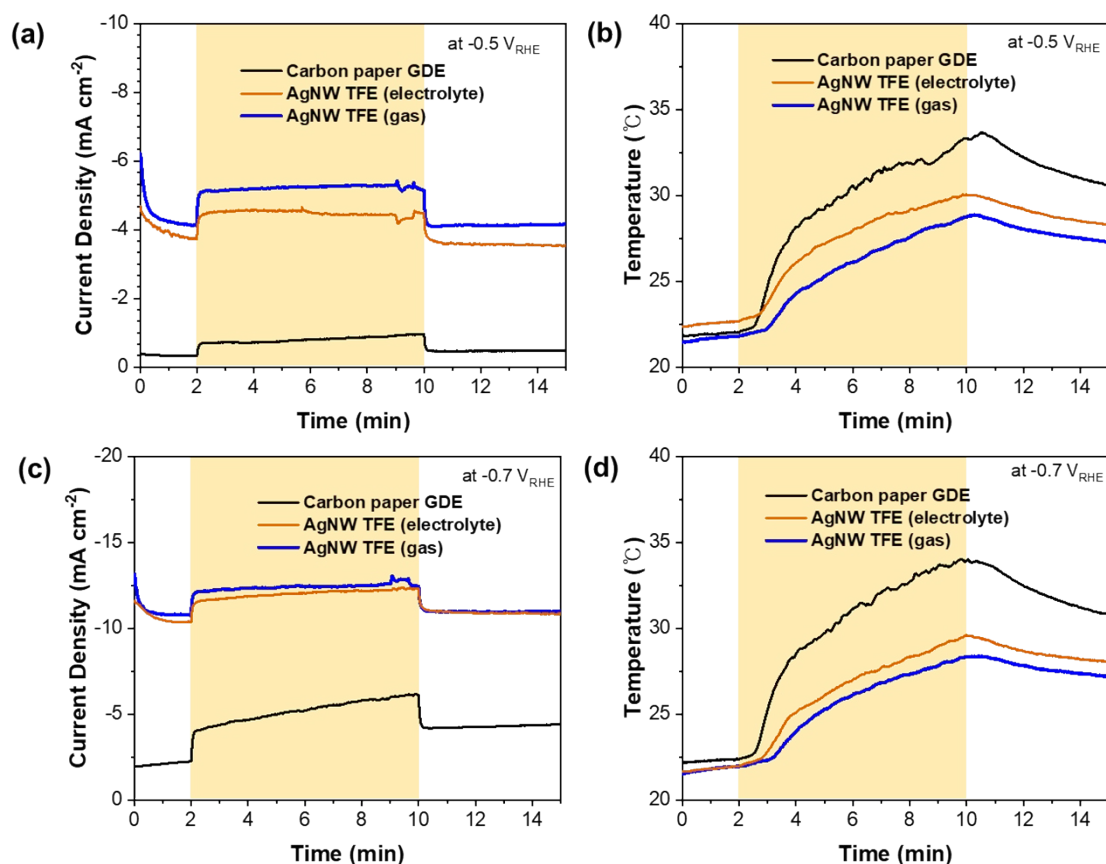


Fig. S4 The changes in the (a, c) current densities and (b, d) temperatures at -0.5 and $-0.7 V_{RHE}$, respectively, for carbon paper GDE and TFE upon light irradiation (yellow region). ‘Ag NW TFE (electrolyte)’ indicates the case when light was irradiated from the side of electrolyte chamber and ‘Ag NW TFE (gas)’ indicates the case when light was irradiated from the side of gas chamber. The light intensity was 300 mW cm^{-2} .

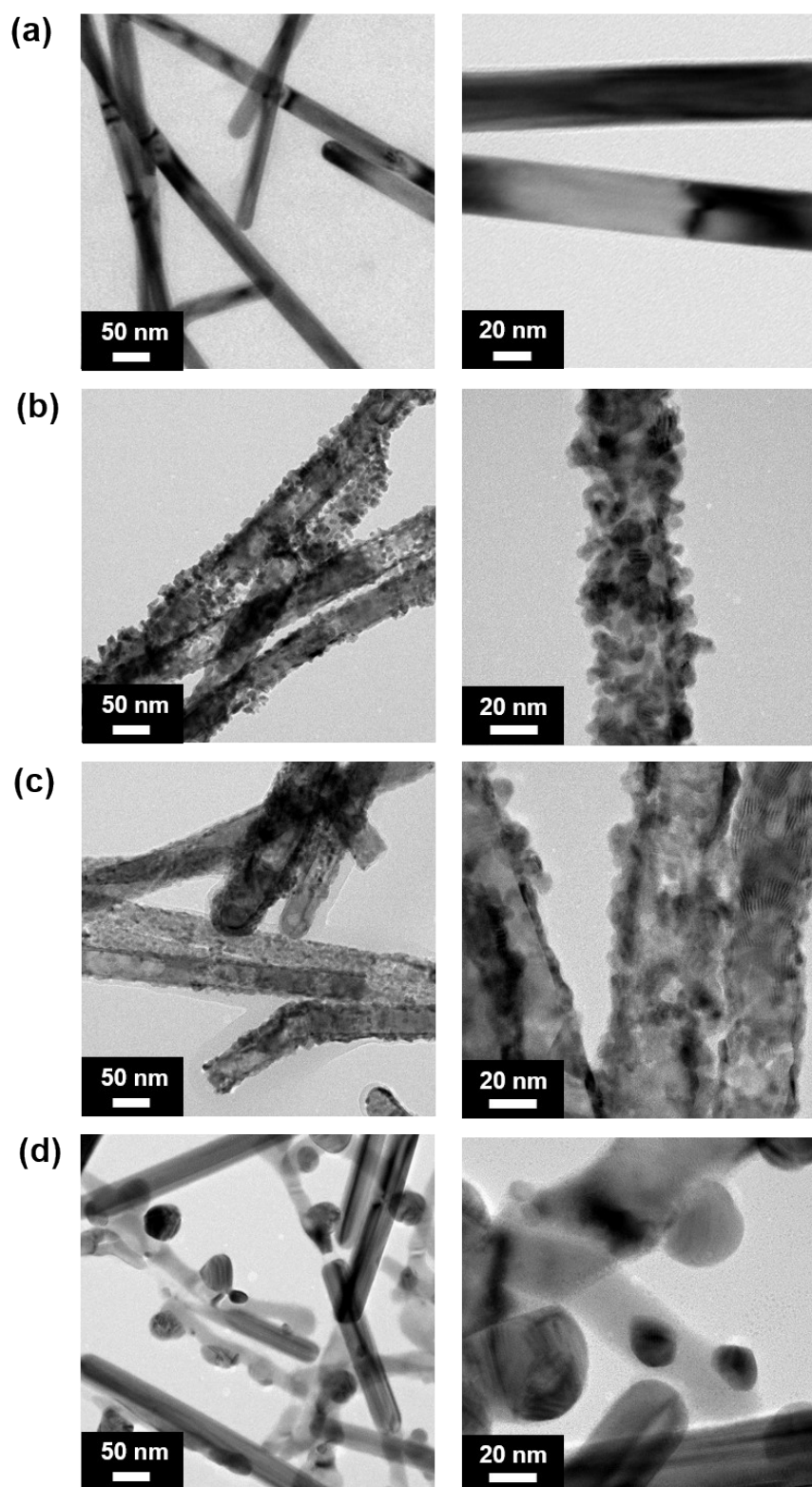


Fig. S5 TEM images of (a) pristine Ag nanowires (Ag NW), (b) Au nanoparticles loaded on Ag nanowires (Au NP/Ag NW), (c) Pd nanoparticles loaded on Ag nanowires (Pd NP/Ag NW), and (d) Ru nanoparticles loaded on Ag nanowires (Ru NP/Ag NW).

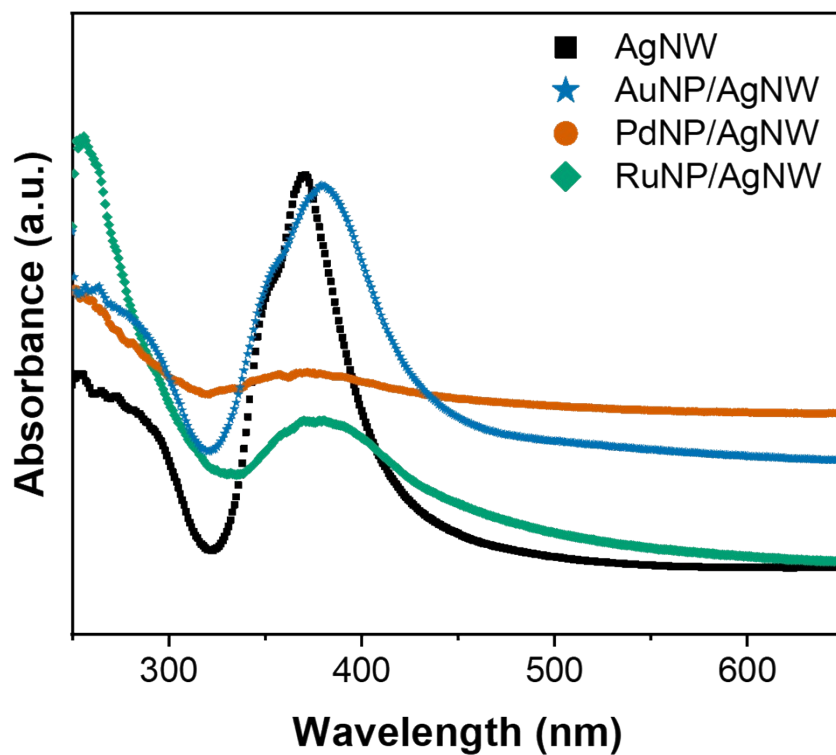


Fig. S6 Ultraviolet-visible (UV-Vis) spectra of metal NP/Ag NW materials dispersed in the solution.

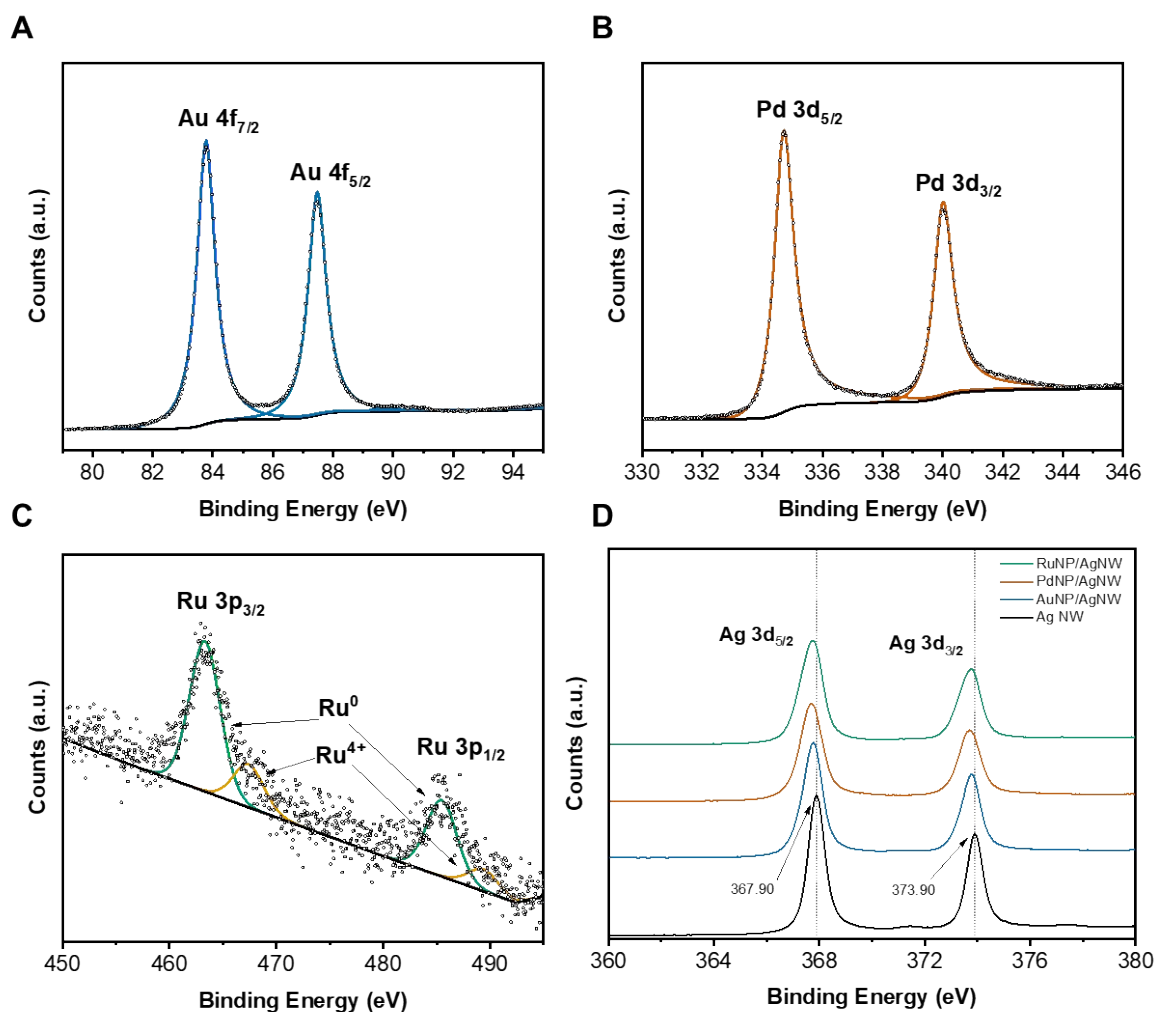


Fig. S7 XPS (a) Au 4f spectra for Au NP/Ag NW, (b) Pd 3d spectra for Pd NP/Ag NW, and (c) Ru 3p spectra for Ru NP/Ag NW. (d) The comparison of XPS Ag 3d spectra for Au NP/Ag NW, Pd NP/Ag NW, Ru NP/Ag NW, and pristine Ag NW.

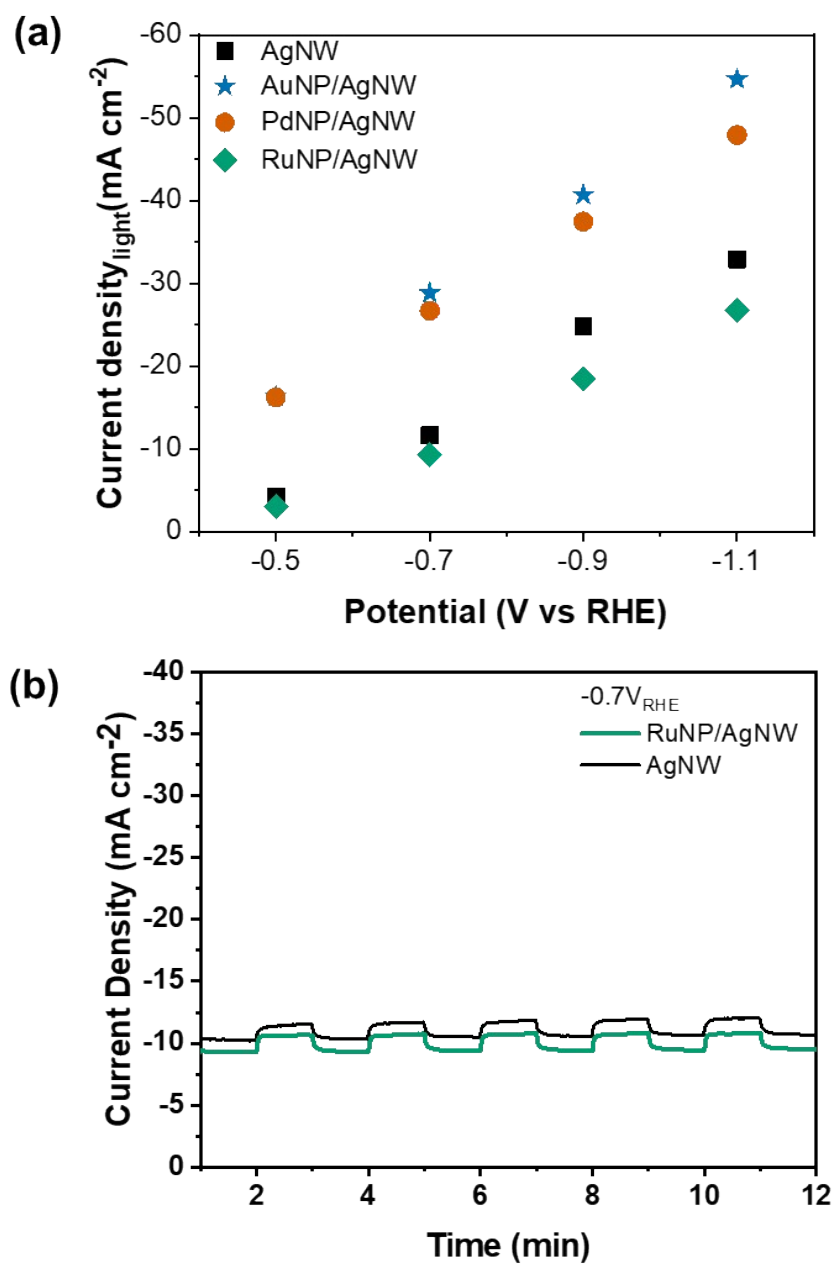


Fig. S8 (a) Current densities with light irradiation (300 mW cm⁻²) for Au NP/Ag NW, Pd NP/Ag NW, Ru NP/Ag NW, and pristine Ag NW catalyst at various potentials. (b) Chronoamperometric analysis on Ru NP/Ag NW at -0.7 V_{RHE} with light on/off cycles.

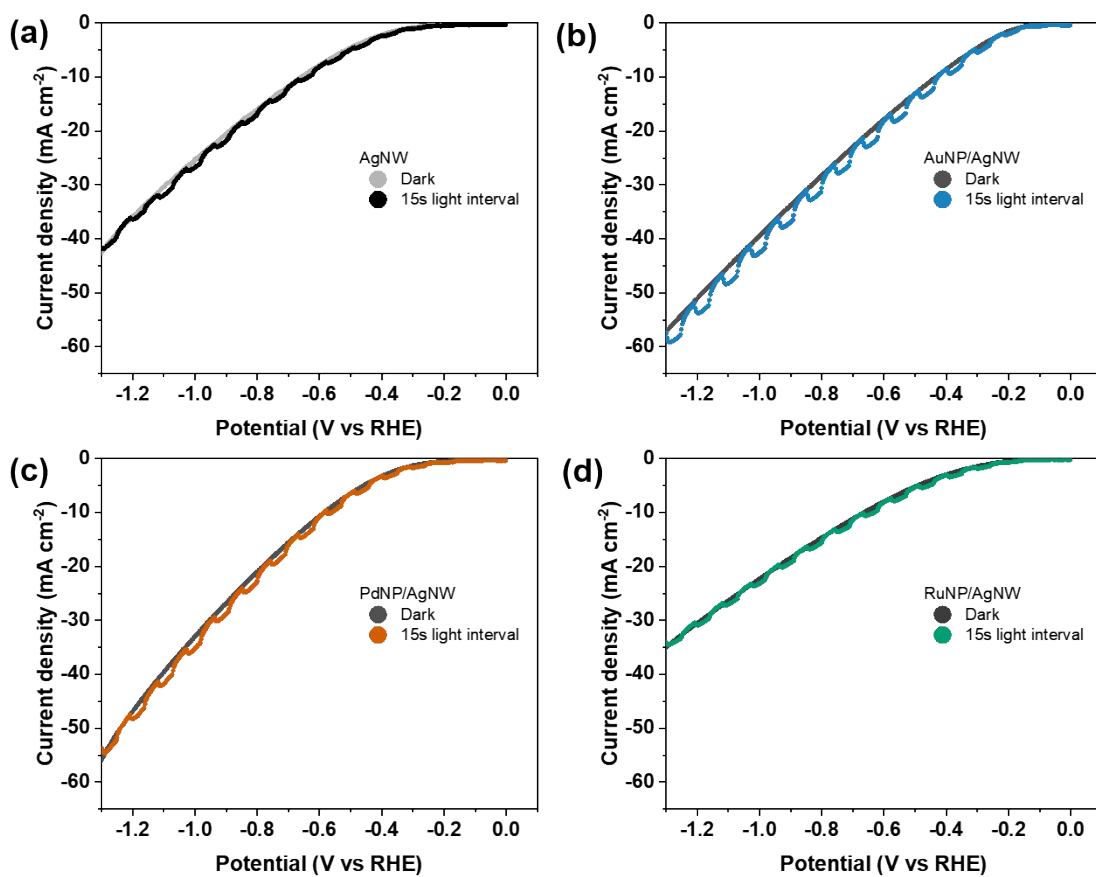


Fig. S9 Linear sweep voltammety curves of (a) Ag NW, (b) Au NP/Ag NW, (d) Pd NP/Ag NW, and (d) Ru NP/Ag NW catalysts with/without light irradiation. Light irradiation intensity was 300 mW cm⁻² with a scan rate of 3 mV s⁻¹.

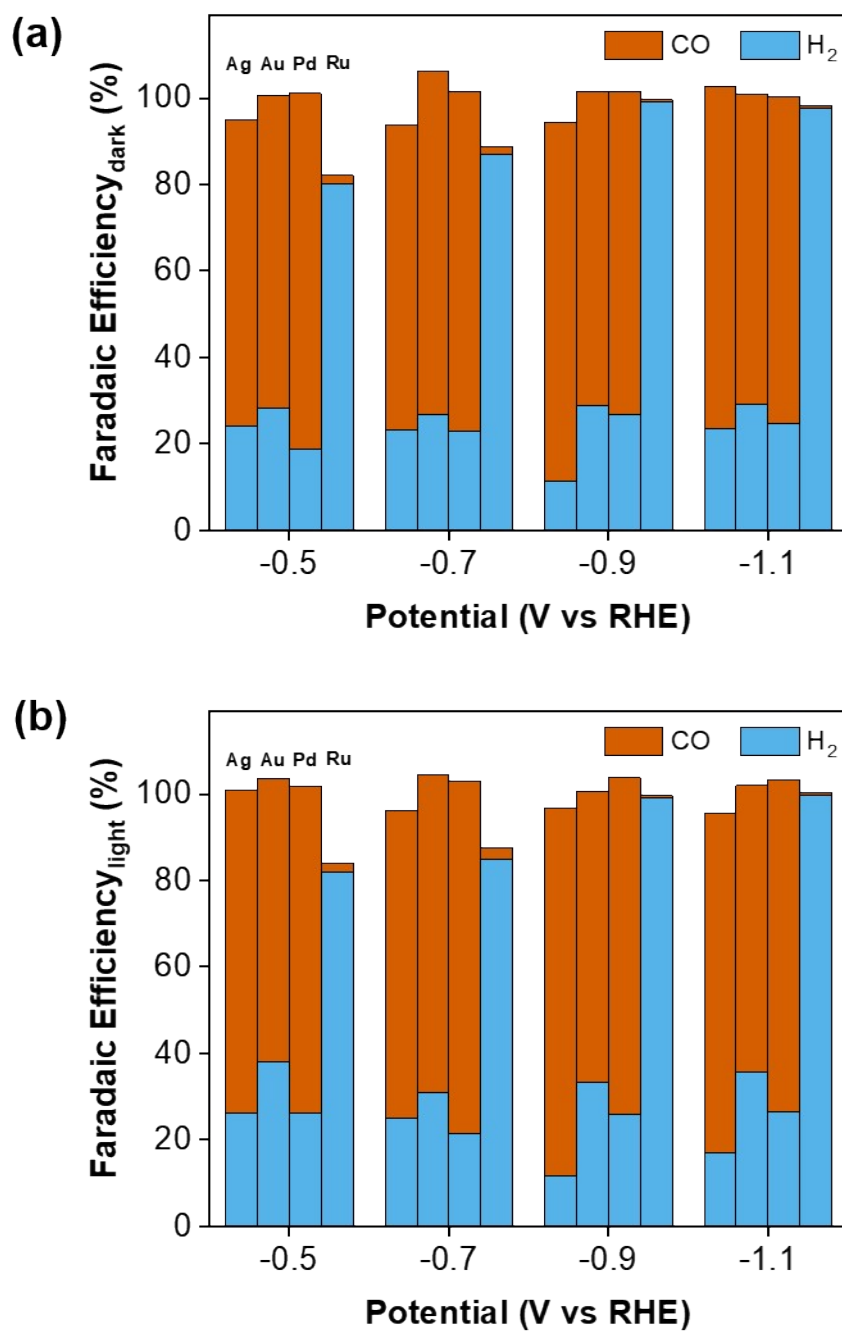


Fig. S10 (a) Faradaic efficiency for CO or H₂ production obtained in Figure 3a. (b) Faradaic efficiency under light irradiation for CO or H₂ production obtained in Figure S7a.

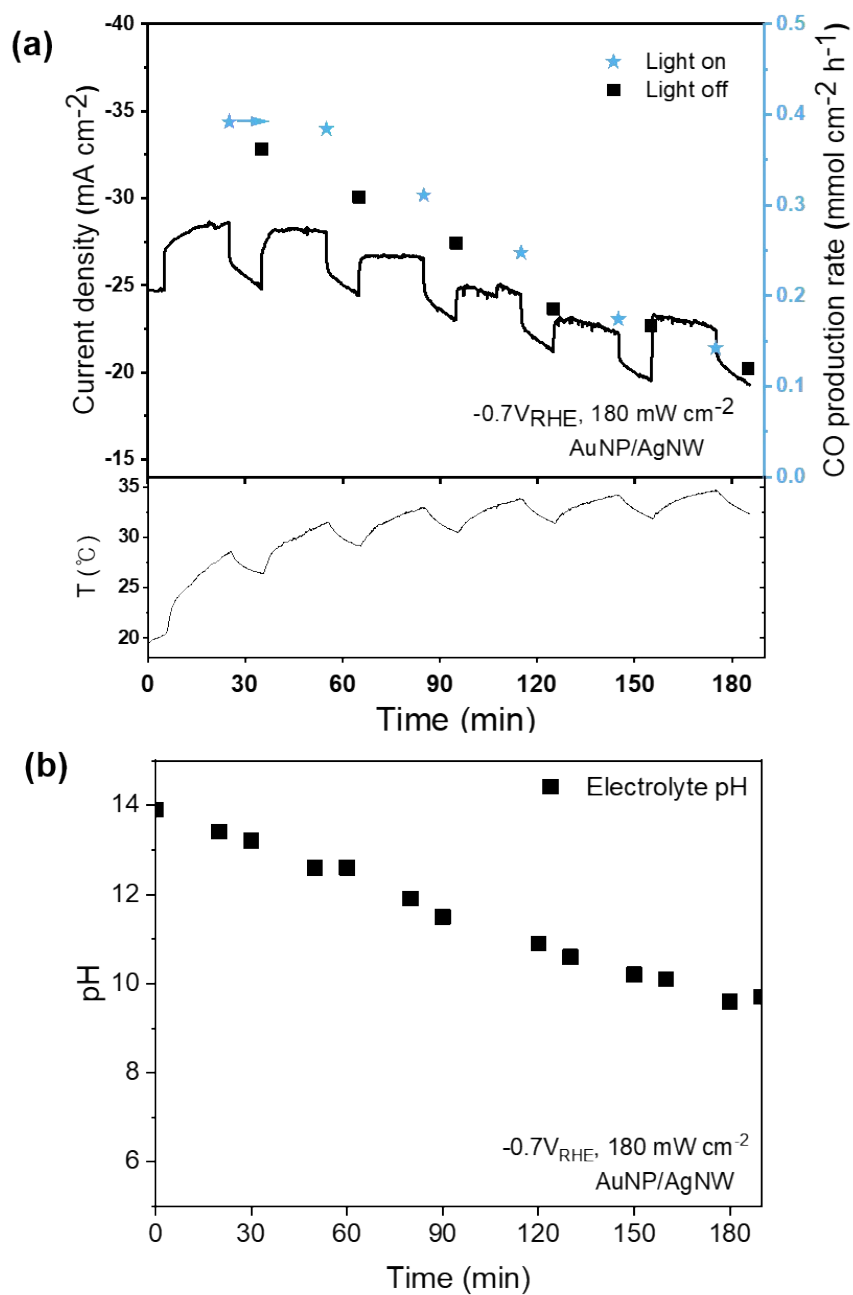


Fig. S11 (a) Chronoamperometric analysis on Au NP/Ag NW catalyst obtained at -0.7 V_{RHE} without partial electrolyte exchange. The changes in current density, CO production rate, and temperature were shown over reaction time. (b) The pH change was monitored in (a).

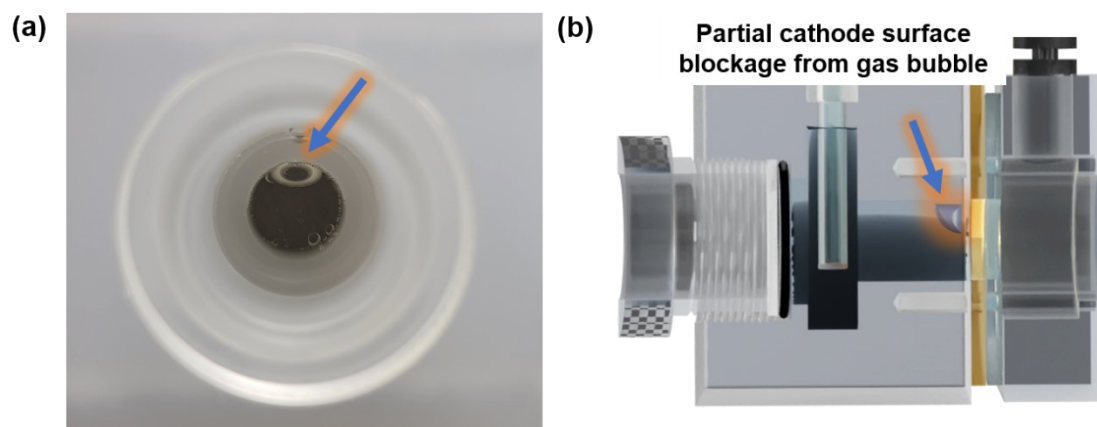


Fig. S12 (a) A photograph showing the formation of gas bubbles on the cathode surface. (b) Graphic representation of the cross section of PAEC cell. Position of the bubble is indicated by blue arrow.

Ref No.	Cathode	electrode area (cm ²)	Applied Potential	Dark Current density (mA/cm ²)	CO ₂ reduction Faradic efficiency (%)	Product distribution (%)	Photo current (mA/cm ²)
This Work	Au NP/Ag NW TFE	2	-0.7V vs RHE	-27.3	79.5	CO(79.5)	-4.2
			-1.1V vs RHE	-48.6	71.6	CO(71.6)	-6.05
1	Ag thin film/Ti/glass slide	1	-1.1V vs RHE	-2.7	68.6	CO(63) HCOOH(4) CH ₃ OH(1.6)	-0.6
2	Cu nanocorals/Ag foil	1	-0.78V vs RHE	-1.0	72	CO(64) C ₂ H ₄ (4) HCOOH(3) C ₂ H ₅ OH(0.5)	-0.3
3	n ⁺ p-Si/Sn-pNWs	-	-0.4V vs RHE	-0.25	70.6	HCOOH(59.2) CO(11.4)	-17.3
4	e-Si/Ag	0.2~0.3	-0.5V vs RHE	0	90	CO(90)	-10.0
5	Si/Bi	1	-0.32V vs RHE	0	95	HCOOH(95)	-4.0
6	ZnTe/ZnO-Au NP	-	-0.7V vs RHE	-9.5	58	CO(58)	-16.0
7	a-Si/TiO ₂ /Au	-	-0.1V vs RHE	0	50	CO(50)	-2.3
8	Ru(MeCN)CO ₂ C ₃ Py-P/TiO ₂ /N,Zn-Fe ₂ O ₃ /Cr ₂ O ₃	1	0.1V vs RHE	0	93	HCOOH(63) CO(30)	-0.2
9	ZnO/ZnTe/CdTe/Au	-	-0.11V vs RHE	0	64	CO(64)	-5.0

Table S1. Photo-enhanced performance in CO₂ electrochemical reduction.

'-' indicates no information provided in the report; the values inside parentheses (product distribution) indicate Faradic efficiency into the specific product; the works denoted with shadows (this work, ref 1 and ref 2) were obtained with plasmonic nanoparticles and the other works were obtained with semiconductor materials; Ref (1) *ACS Energ. Lett.*, 2019, **4**, 1098-1105; (2) *Chem. Comm.*, 2020, **56**, 9970-9973; (3) *J. Mater. Chem. A*, 2018, **6**, 1736-1742; (4) *J. Mater. Chem. A*, 2018, **6**, 21906-21912; (5) *Mater. Today Chem.*, 2019, **11**, 80-85; (6) *Energ. & Environ. Sci.*, 2015, **8**, 3597-3604; (7) *Energ. & Environ. Sci.*, 2019, **12**, 923-928; (8) *ACS Catal.*, 2018, **8**, 1405-1416; (9) *ACS Nano*, 2016, **10**, 6980-6987.