Supporting information for

Solar-driven simultaneous electrochemical CO_2 reduction and water oxidation using perovskite solar cells

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Affiliation

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Supplemental Experimental Procedures

Electrochemical deposition of Au dendrite

Au dendrite electrode was prepared by electrodeposition on an Au foil substrate (1 cm^2, 250 μm thickness, 99.99 % Au, Aldrich) with Pt counter electrode. The solution for electrodeposition was composed of 1.0 mM $HAuCl_4$ and 0.5 M H_2SO_4 (Aldrich) and in 80 ml DI water. The Au foil was mechanically polished and ultrasonically cleaned with acetone, ethanol, and deionized water. Isolation adhesive films cover the outer part of the Au electrodes to prevent the unintended reaction. Stainless steel clamps held onto the stacked electrodes with a constant pressure during the deposition time. Chronoamperometry was applied to obtain the deposits from the mixture solution at −0.3 V(*vs.* Ag/AgCl reference electrode). Electrodeposition was carried out in a stationary electrolyte solution without stirring or protective gas bubbling. After 120 s of electrolysis, the electrode was taken out and washed with deionized water several times. Special care was taken when the electrode was removed from the solution so that the shear force between the solution and electrode surface did not break the dendrites.

Electrodeposition of Co-Pi electrode

The previous report followed the electrodeposition of the Co-Pi electrode.[1] Co-Pi electrode was prepared by electrodeposition on an FTO glass substrate with Pt counter electrode. The solution for electrodeposition was composed of 0.5 mM of $CoSO_4$ in 40ml of 0.1 M KPi (pH 7). Before the electrodeposition, the precursor solution was degassed by bubbling with N_2 for an hour with vigorous stirring. Electrodeposition was proceeded at 1.1 V (vs Ag/AgCl reference electrode) until 15 C/cm^2 passed.

Characterization of physical properties

The physical characteristics of the prepared Au dendrite and Co-Pi electrode were analyzed using X-ray diffraction (XRD), a field emission scanning electron microscope (FE-SEM), an energy dispersive X-ray spectrometer (EDS), and X-ray photoelectron spectroscopy (XPS). The XRD patterns were obtained by thin-film XRD (RIGAKU D/MAX-RC) using the radiation from a Cu Kα source at 30 kV and 60 mA. The prepared electrodes' surface morphology and composition were observed using the FE-SEM (Hitachi S-4800) equipped with EDS (Horiba) at an acceleration voltage of 5.0 kV.

Electrochemical test

Electrochemical activities were measured by using an electrochemical analyzer (CHI 750D, CH Instruments Inc.). The standard calomel electrode (SCE) and Pt gauze (Sigma, 99.9%) were used as reference and counter electrodes. Electrolyses were performed on a fuel-cell-like two-compartment electrochemical cell separated by a piece of SELEMION anion exchange membrane and Nafion proton exchange membrane (Fig. S8) For the measurement of catalytic activity for CO_2 reduction, the electrolyte was N_2- or CO_2-bubbled 0.5 M $KHCO_3$ (Sigma-Aldrich) aqueous solution (pH 7.1 − 7.2), in which an analytical grade of water (HPLC Certified Solvent, Burdick&Jackson) was used. The results in N_2-bubbled electrolytes were included only for comparison with those of CO_2-bubbled electrolytes. Each compartment contained 10 ml of electrolyte. The electrochemical conversion of CO_2 at various constant potentials (*i.e.,* from −0.3 to –0.9 V *vs.* RHE) was performed in a CO_2-bubbled 0.5 M $KHCO_3$ aqueous solution. To measure catalytic activity for water oxidation, an electrolyte was N_2-bubbled 0.1 M KPi buffer (pH 7). The electrochemical water oxidation at various constant potentials (*i.e.,* from 1.55 to 1.85 V *vs.* RHE) was performed in an N_2-bubbled 0.1M KPi buffer (pH 7) solution. For the galvanostatic electrochemical test, Au dendrite and Co-Pi were used

for cathode and anode, respectively. Electrolyte for CO_2 reduction was CO_2-bubbled 0.5 M $KHCO_3$, and electrolyte for water oxidation was N_2-bubbled 0.1 M KPi buffer. All potential measured SCE and converted to the RHE reference scale using E (*vs.* RHE) = E (*vs.* SCE) + 0.241 V + 0.0591 V*pH except galvanostatic system. Galvanostatic CO_2 conversion and water oxidation system was tested from 2.2 to 2.9 V in CO_2-bubbled 0.5 M $KHCO_3$, and electrolyte for water oxidation was N_2-bubbled 0.1 M KPi buffer for cathode and anode, respectively. Voltage is directly applied to each electrode without a reference electrode. The Nafion membrane separates each reaction compartment to transport protons generated from the anode by water oxidation reaction. Also, each gas product produced by the reactions is collected separately and analyzed by two individual gas chromatography (GC) simultaneously. Solar to fuel experiment is conducted with the same method as galvanostatic CO_2 reduction and water oxidation system without applied voltage.

Gas product analysis

Gas products from the CO_2 reduction were analyzed by using 7890 Agilent gas chromatography (GC) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Carboxen-1000 columns (12390-U, Supelco) were used for both TCD and FID, respectively, and Ar (99.999%) was used as a reference gas. Before beginning the electrochemical CO_2 reduction reaction, CO_2 (99.99%) was purged for 30 min. CO_2 was continuously purged into the reactor and vented to the sampling loops with 6 sccm of gas flow velocity. This flow contains the gas products from electrochemical CO_2 reduction. When two gas sampling valves collected the product-gas at the same time, one collected gas that flowed to the TCD for detecting H_2 and CO_2, while the other collected gas sample that passed through the methanizer and then was analyzed by FID for detecting CO. Oven temperature was changed from 80 °C to 225 °C during the analysis. Aliquots were collected every 18 min during the

reaction. Gas products from the water oxidation were analyzed by using the same model as CO_2 reduction equipped only with TCD. Molecular Sieve 5A packed columns were used for TCD, and Ar (99.999%) was used as a reference gas. Before the electrochemical test, the electrochemical cell was purged with Ar (99.999%) for 30 min. Ar was continuously purged into the reactor and vented to the sampling loops with 6 sccm of gas flow velocity. This flow contains the O_2 from electrochemical water oxidation. The oven temperature was fixed at 30 ^oC during the analysis. Aliquots were collected every 5min during the reaction.

Perovskite solar cell fabrication

An F-doped SnO_2 (FTO, Pilkington, TEC 8) substrates were chemically etched with zinc powder and dilute HCl solution and cleaned by sonication in deionized water, acetone, and ethanol. A dense blocking layer of TiO_2 (bl-TiO_2, ~70 nm in thickness) was deposited onto an FTO substrate by spray pyrolysis, using a 20 mM titanium diisopropoxide bis(acetylacetonate) solution (Aldrich) at 450 °C to prevent direct contact between the FTO and the hole-conducting layer. A 150 nm thick mesoporous (mp)-TiO_2 film was deposited by spin-coating for 50 s at 2500 rpm onto the bl-TiO_2/FTO substrate using 50 nm particle TiO_2 paste diluted in ethanol and calcinated at 500 °C for 1 h in the air to remove the organic components. To deposit perovskite absorbing layer, $(FAPbI_3)_{0.95}(MAPbBr_3)_{0.05}$, the perovskite precursor solution was prepared by dissolving 889 mg ml^{-1} of $FAPbI_3$, 30 mg ml^{-1} of $MAPbBr_3$, and 30 mg ml^{-1} of MACl in DMF/DMSO (8:1 v/v) mixed solvent. Then, the solution was then coated onto the mp-TiO_2/bl-TiO_2/FTO substrate by two consecutive spin-coating steps, at 1000 and 5000 rpm for 3 s and 15 s, respectively. 1 mL ethyl ether was poured onto the substrate during the second spin-coating step. Then, the resultant substrate was heated on a hot plate at 150 °C for 10 min. For deposition of hole-transport materials, a PTAA (poly(triarylamine), MS Solution)/toluene (10.5 mg/ 1 ml) solution with an additive of 3.5 μl of Li-bis(trifluoromethanesulfonyl) imide

(Li-TFSI)/acetonitrile (340 mg/ 1 ml), 3.5 µl of 4-tert-butylpyridine (TBP) was spin-coated on $(FAPbI_3)_{0.95}(MAPbBr_3)_{0.05}$/mp-$TiO_2$/bl-$TiO_2$/FTO and at 2000 rpm for 30 s. Finally, the Au counter electrode was deposited by thermal evaporation. The entire unit cell size is 25 mm x 25 mm. Four active areas with a size of 4 mm x 4 mm were fabricated on the unit cell by superposing FTO and Au electrodes. Photovoltaic performance was measured by masking the active area with a metal mask (0.0935 cm^2).

Photostability of perovskite solar cell

The photostability test was performed with encapsulated devices employing PTAA. The devices were encapsulated using a getter-dispersed polymer-metal barrier films. The device with an FTO/Bl-TiO_2/mp-TiO_2/$(FAPbI_3)_{0.95}(MAPbBr_3)_{0.05}$/PTAA/Au was kept under AM 1.5 G simulated sun light in nitrogen (N_2) filled the chamber. The device temperature in the chamber was maintained between 25 ^oC by the cooling system. PCEs of devices were recorded using a source meter (Keithley 2420) for 12 hours.

1. W. Kanan Matthew and G. Nocera Daniel, *Science*, 2008, **321**, 1072-1075.

Figure S1. XRD result of Au dendrite electrode

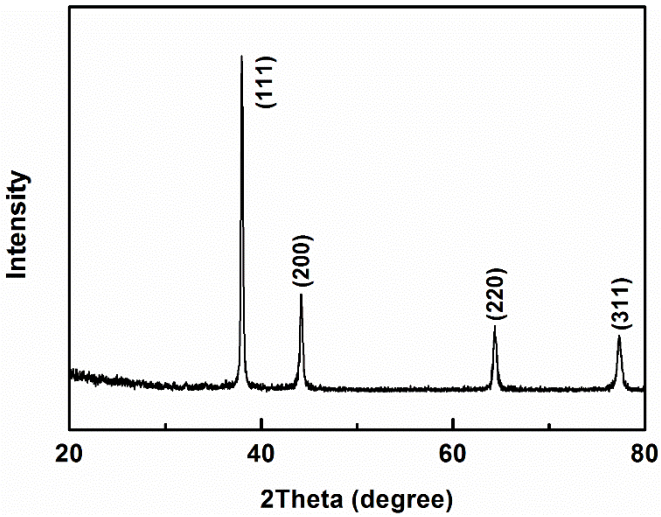


Table S1. Electrochemical CO_2 reduction test details on Au dendrite and foil

Au dendrite

Voltage	H_2 efficiency (%)	H_2 productivity (μmol)	CO efficiency (%)	CO productivity (μmol)
0.2	88.55	5.75	12.8	0.83
0.3	60.59	9.91	39.82	6.51
0.4	45.95	15.64	53.24	18.13
0.5	31.29	13.69	70.86	30.99
0.6	15.73	9.70	86.61	53.44
0.7	14.15	11.46	85.16	68.98
0.8	10.22	9.59	90.88	85.19
0.9	11.89	14.86	90.21	112.76

Au foil

Voltage	H_2 efficiency (%)	H_2 productivity (μmol)	CO efficiency (%)	CO productivity (μmol)
0.2	102.54	3.33	0	0.00
0.3	101.36	8.29	0	0.00
0.4	102.65	17.47	0	0.00
0.5	90.26	19.74	6.11	1.34
0.6	84.59	26.09	10.69	3.30
0.7	65.26	26.43	32.78	13.28
0.8	41.36	19.41	61.72	28.93
0.9	20.66	12.91	80.47	50.29

Figure S2. Capacitance measurement and roughness factor of Au dendrite and foil

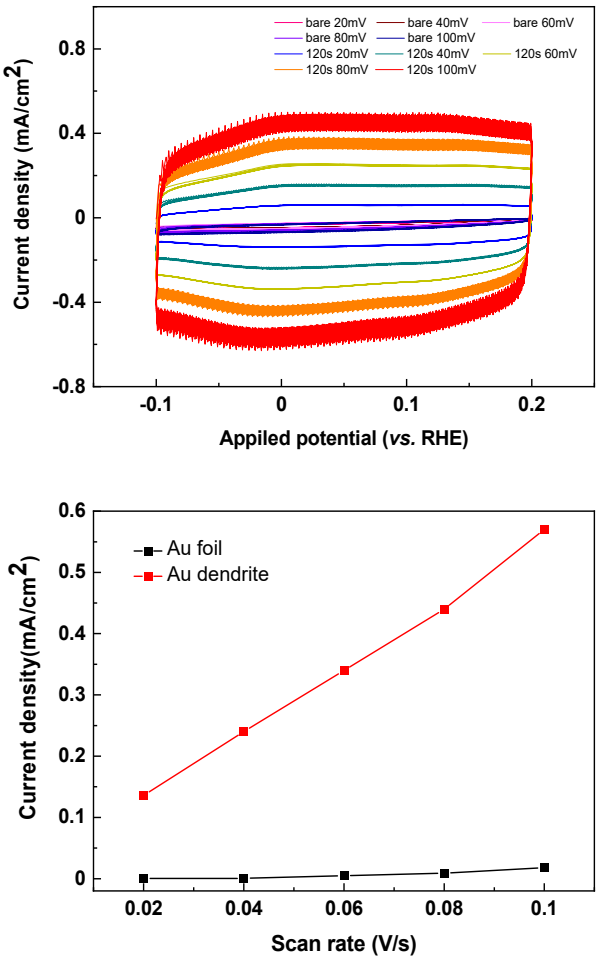


Figure S3. Electrochemical impedance spectroscopy of Au dendrite and foil

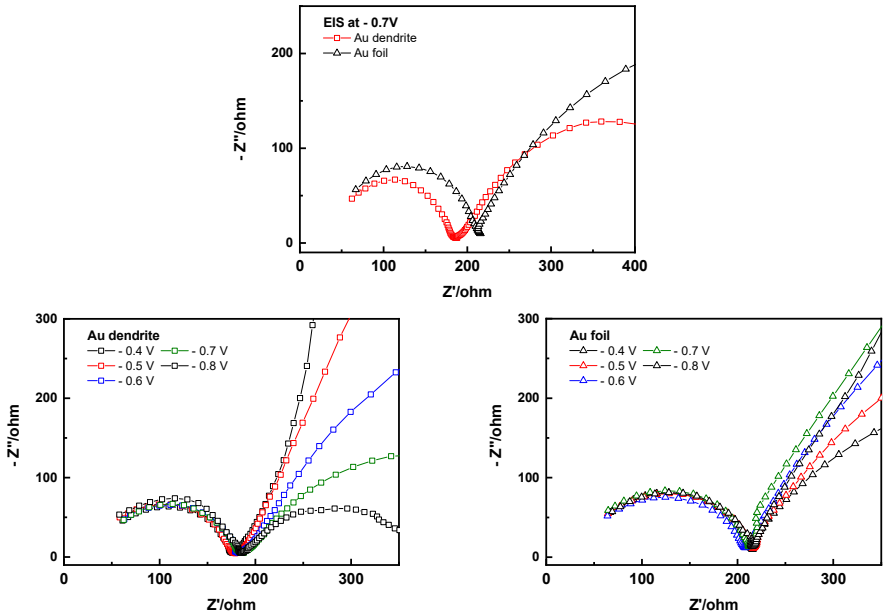
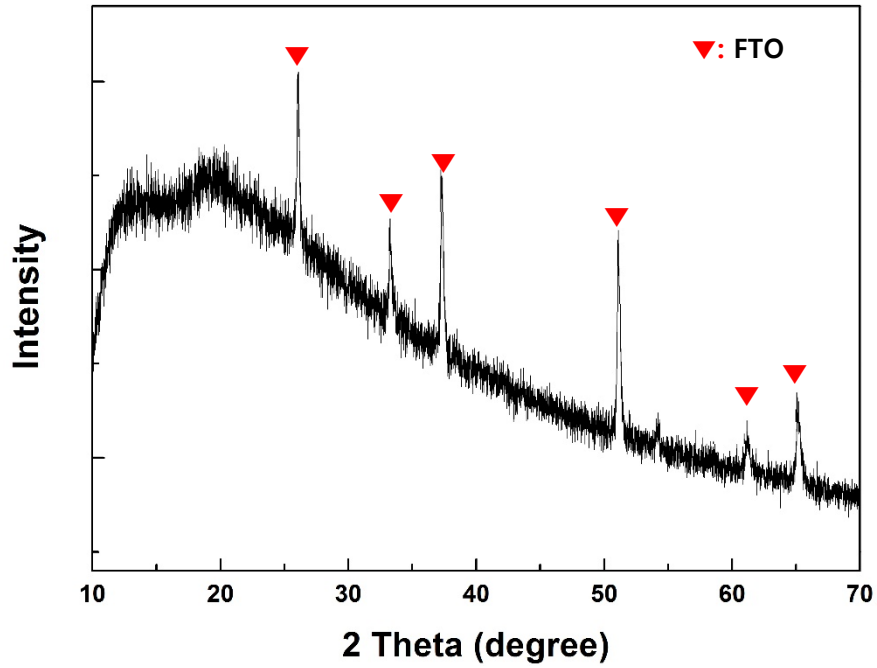
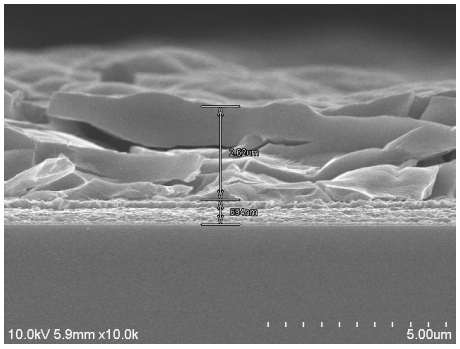


Table S2. Details of electrochemical impedance spectroscopy of Au dendrite and foil

	Au foil			Au dendrite		
	Electrolyte R (Ω)	Ohmic R (Ω)	Charge transfer R (Ω)	Electrolyte R (Ω)	Ohmic R (Ω)	Charge transfer R (Ω)
- 0.4 V	45.94	177.5	7070	48.89	138.4	1910
- 0.5 V	45.89	177.2	3488	43.84	141.2	1568
- 0.6 V	44.84	176.3	1737	49.32	140.4	613
- 0.7 V	44.64	172.9	884.7	49.46	140.7	280.5
-0.8 V	45.64	179.5	524	48.75	140.5	151.1

Figure S4. XRD result (top) and SEM image (bottom) of Co-Pi electrode





Element	Weight%	Atomic%
O K	40.43	66.16
P K	12.90	10.91
K K	9.76	6.54
Co K	36.90	16.39
Totals	**100.00**	

Table S3. Electrochemical water oxidation details on Co-Pi electrode

Voltage (V) (vs. RHE)	**O_2 efficiency (%)**	**O_2 productivity (μmol)**
1.55	0	0
1.65	87.2	4.85
1.75	92.3	9.95
1.85	93.1	15.4

Figure S5. The galvanostatic current of Au S and Au L electrode for 2 hours

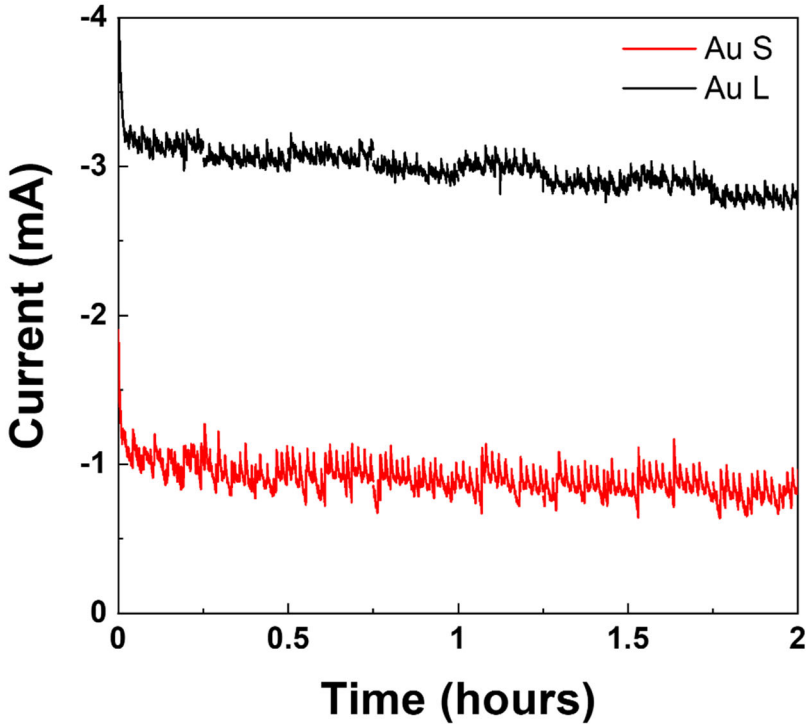


Figure S6. The galvanostatic current of Au S and Co-Pi electrode in the range from 2.2 V to 2.9 V

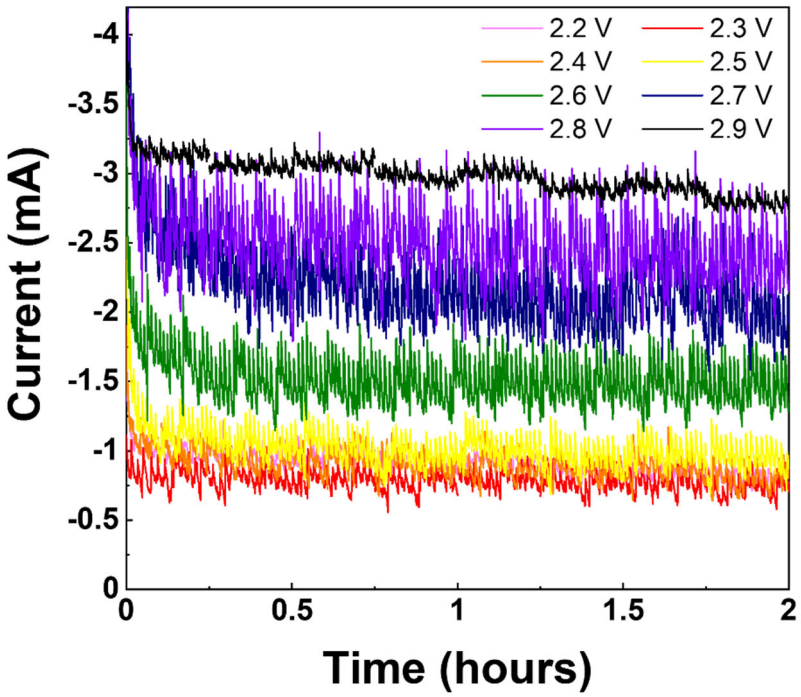


Figure S7. Photostability test of perovskite solar cell for 12 hours

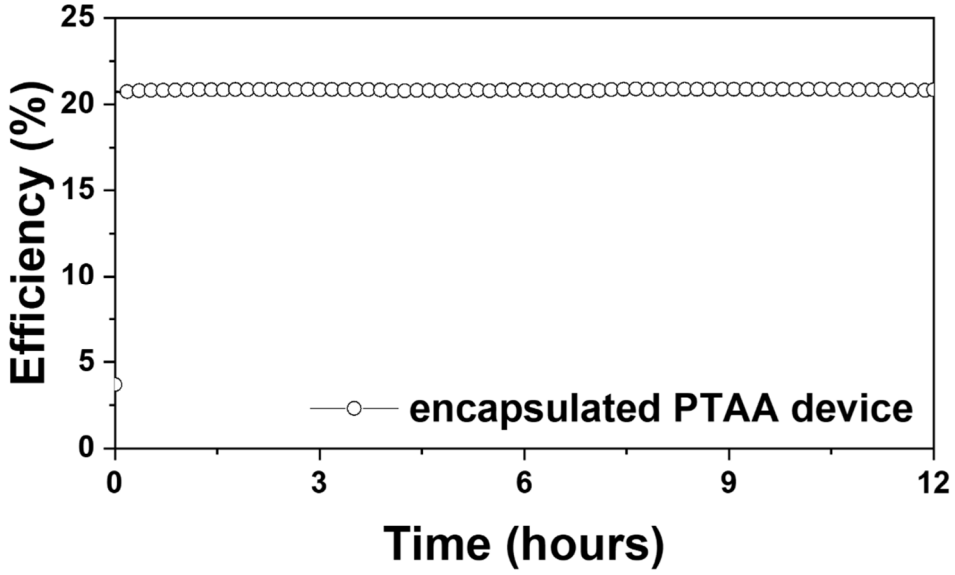


Figure S8. Schematic illustration of reactor separated by membrane

