

Supporting Information

Enhanced Electrochemical CO₂ Reduction Selectivity by Application of Self-Assembled Polymer Microparticles to Silver Electrode

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1. EXPERIMENTAL METHODS

Materials:

Polystyrene (PS, $M_w=18.1$ k) was purchased from Polymer Source, Inc., Canada. Tetrahydrofuran (THF) and potassium bicarbonate (KHCO_3) were purchased from the Fujifilm Wako Pure Chemical Corp. All chemicals were used without further purification. Silver (Ag) foil was purchased from the Nilaco Corp. Carbon paper (CP: TGP-H-060) was purchased from Toray Industries, Inc.

Fabrication of a self-assembled PS-coated Ag foil (SA-PS/Ag-foil) electrode:

PS was dissolved in THF at a concentration of 1 mg/mL, after which the self-assembled PS-modified Ag foil (SA-PS/Ag-foil) electrode was prepared by the dip-coating method.¹ In this process, the THF solution containing the PS (100 μL) was added to ultra-pure water (40 mL: 18 $\text{M}\Omega\cdot\text{cm}$), after which the substrate (a section of Ag foil) was dipped into the mixture and then withdrawn upward. After the substrate was lifted above the beaker it was left to dry in air.

Fabrication of a self-assembled PS-coated Ag/CP (SA-PS/Ag/CP) electrode:

An Ag layer was deposited onto a section of carbon paper (50 \times 50 mm^2) using radio frequency magnetron sputtering, employing a load lock-type sputtering instrument (SPK-404L, Canon Tokki Corp.) in conjunction with an Ag target and Ar plasma. The thickness of the Ag layer was controlled to approximately 200 nm by adjusting the sputtering time based on calculation of the deposition rate. A rectangular specimen was cut from the coated CP to serve as the Ag/CP electrode (20 \times 20 mm^2).

The self-assembled PS-modified Ag/CP (SA-PS/Ag/CP) electrode was prepared by the dip-coating method in the same manner as the SA-PS/Ag-foil specimen.

The drop-cast PS-modified Ag/CP electrode was prepared by the drop-cast method using 100 μL of a solution of PS in THF (1 mg/mL).

Fabrication of high-density PS microspheres on the Ag foil:

The PS microspheres were prepared by the SORP method.² In this process, PS was first

dissolved in THF at a concentration of 1 mg/mL, after which 1 mL of pure water was added dropwise to the THF solution over a 1 min time span. The THF was subsequently evaporated to obtain the polymer particles by precipitation. The resulting high-density PS microspheres were deposited on the Ag foil by drop-casting using a 100 μ L quantity of the microsphere dispersion.

Characterizations:

The fabricated electrodes were observed using both scanning electron microscopy (SEM: Hitachi High Technologies, SU3500) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FT-IR: Thermo Scientific Nicolet iS50) with a Ge crystal in contact with the sample.

Contact angles were determined using a contact angle meter (Drop Master DM-501; Kyowa Interface Science Co., Ltd.).

A potentiostat/galvanostat (SP-50, Bio-Logic Science Instruments) or a bi-potentiostat (2325, ALS Co., Ltd.) was used for electrochemical measurements. During this process, the sample electrode (combined with Ta foil as a contact material), Pt foil and a Ag/AgCl electrode (RE17, EC Frontier Co., Ltd.) were used as the working, counter and reference electrodes, respectively. CO₂ reduction was conducted at -1.6 V vs. Ag/AgCl (-1.1 V vs. RHE).

The electrolysis cell for electrocatalytic CO₂ reduction consisted of an anode and a cathode, separated by a cation membrane (Nafion® 117, DuPont Co., Ltd.) or a cation membrane combined with an anion membrane (ASE, Astom Co., Ltd.) as shown in Figure S1, together with a CO₂-saturated 0.5 M aqueous solution of 0.5 M KHCO₃ (pH 7.6) as the electrolyte. The amounts of CO and H₂ in the gas phase were determined by *in situ* measurements using a flow reactor combined with a gas chromatograph (GC). The flow reactor (GS-5100, GL Sciences Inc.) was equipped with an autosampler for *in situ* analyses and was directly connected to a GC system (GC-2014, Shimadzu Corporation) equipped with Porapak-N and MS-13X columns. The GC was calibrated using a CO₂-based standard gas containing approximately 100 ppm H₂, N₂, O₂, CO and hydrocarbons. At the start of each experiment, a flow of CO₂ was applied at 20 mL min⁻¹ for 20 min to saturate the electrolyte and to remove air in the reactor. The amounts of gaseous products were estimated by multiplication of the concentration of products determined using the GC, the flow rate and the measurement interval (20 min).

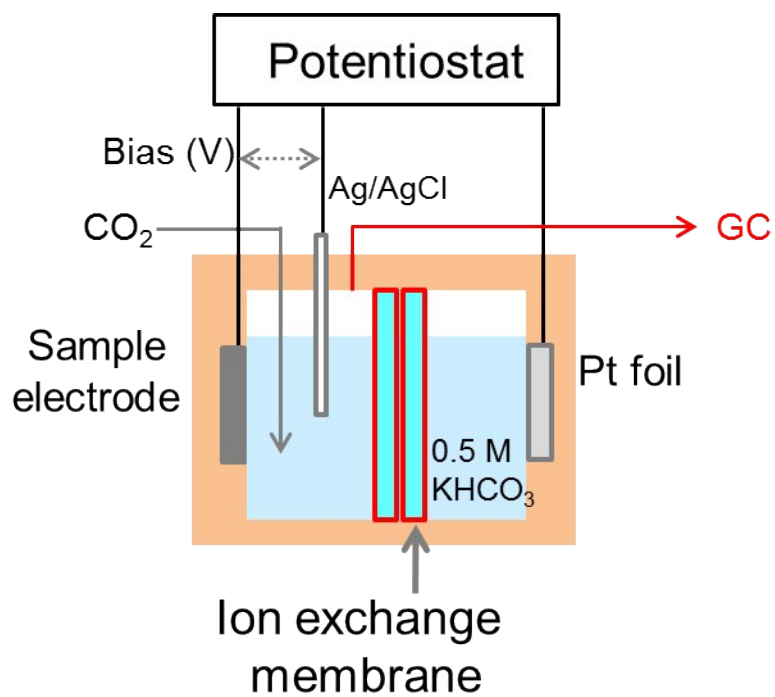


Fig. S1 Schematic illustration of flow cell for electrocatalytic CO₂ reduction.

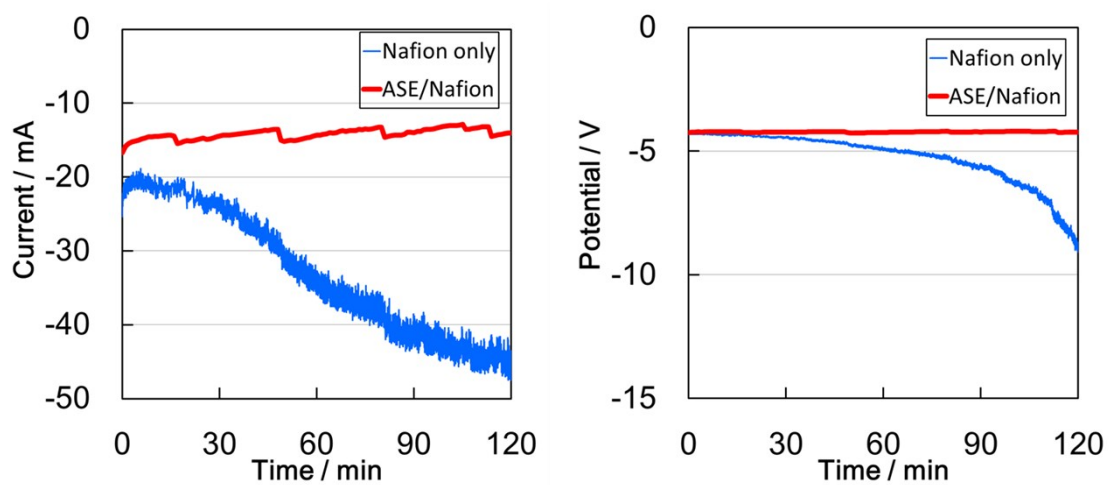


Fig. S2 Time courses of current and potential between working and counter electrodes using different membrane types with Ag foil electrode under potentiostatic conditions (applied bias of -1.6 V vs. Ag/AgCl). Ag foil (Ta foil), Ag/AgCl and Pt foil were employed as the working, reference and counter electrodes, respectively. The electrolyte was a CO₂-saturated 0.5 M KHCO₃ solution.

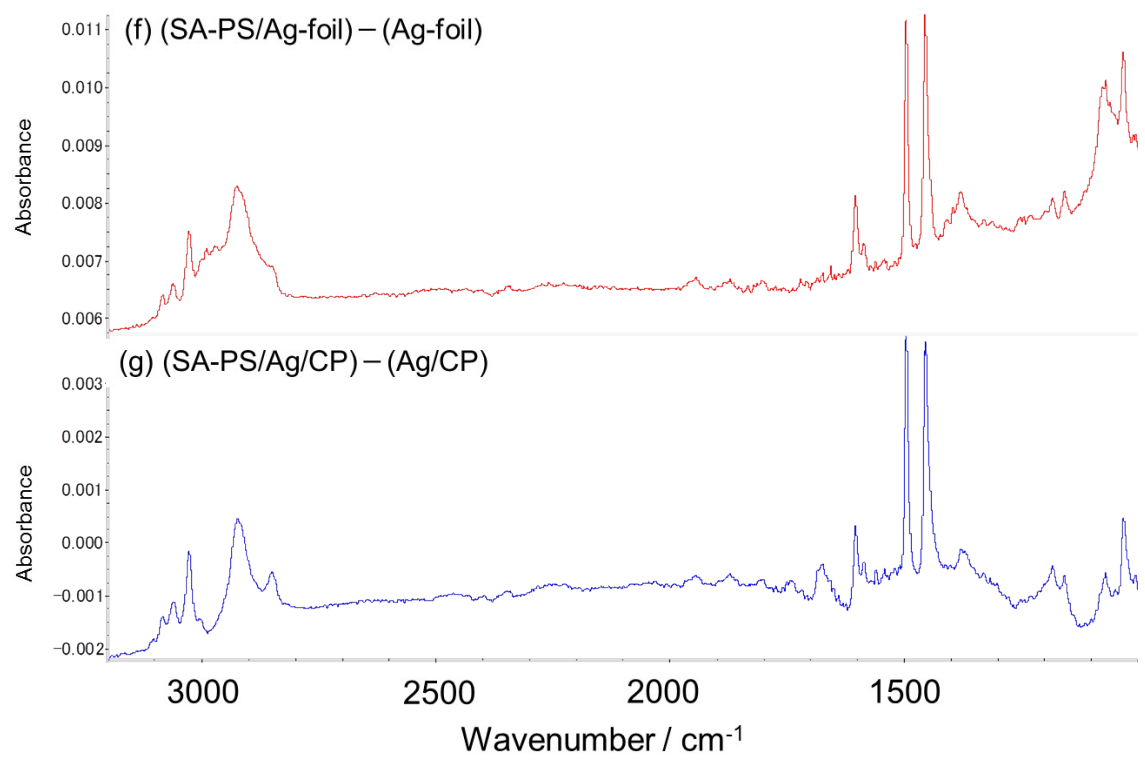
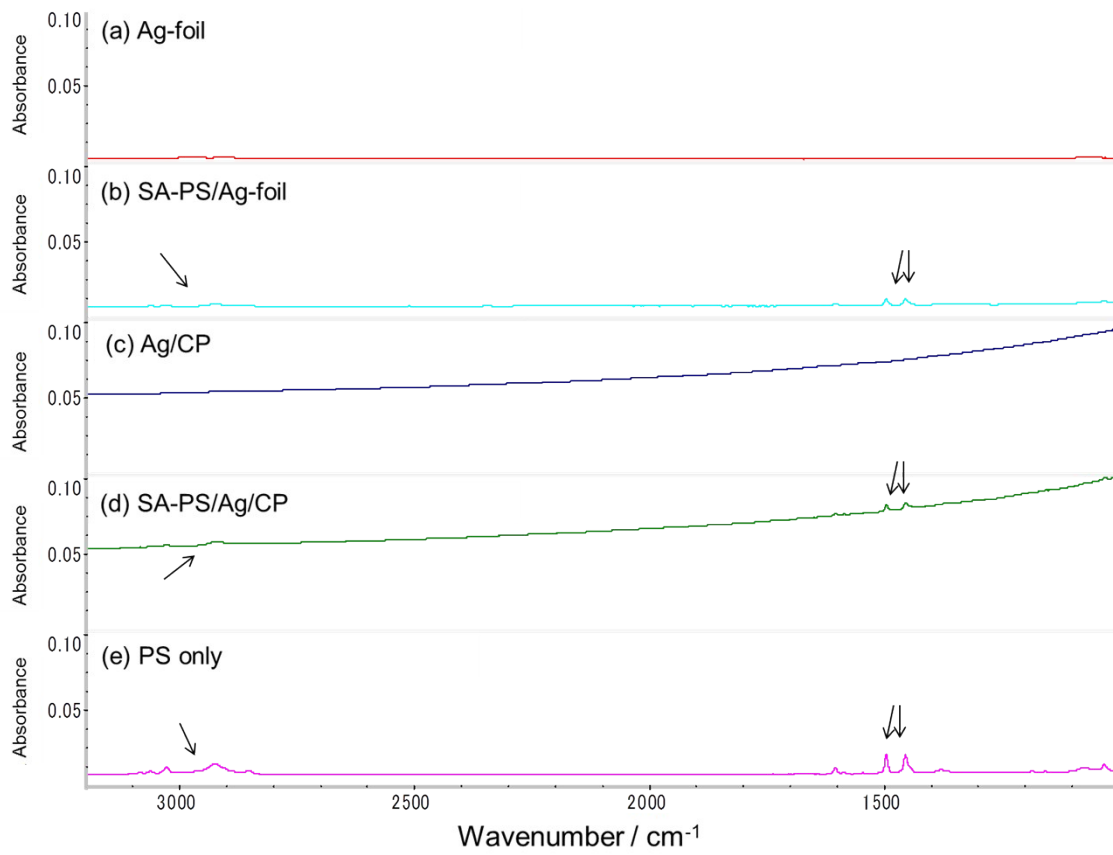


Fig. S3 FT-IR spectra of (a) Ag foil, (b) SA-PS/Ag-foil, (c) Ag/CP, (d) SA/PS/Ag/CP and (e) PS. Difference FT-IR spectra between (f) SA-PS/Ag-foil and Ag foil and (g) SA-PS/Ag/CP and Ag/CP. The FT-IR spectra of the Ag foil and Ag/CP show no peaks, while the SA-PS/Ag-foil and SA-PS/Ag/CP spectra exhibit peaks those were assigned to aromatic C-H stretching vibration (3000 cm^{-1}), aromatic C=C stretching vibration (1500 and 1450 cm^{-1}) absorption. These results confirm that the Ag foil and Ag/CP were successfully coated with PS.

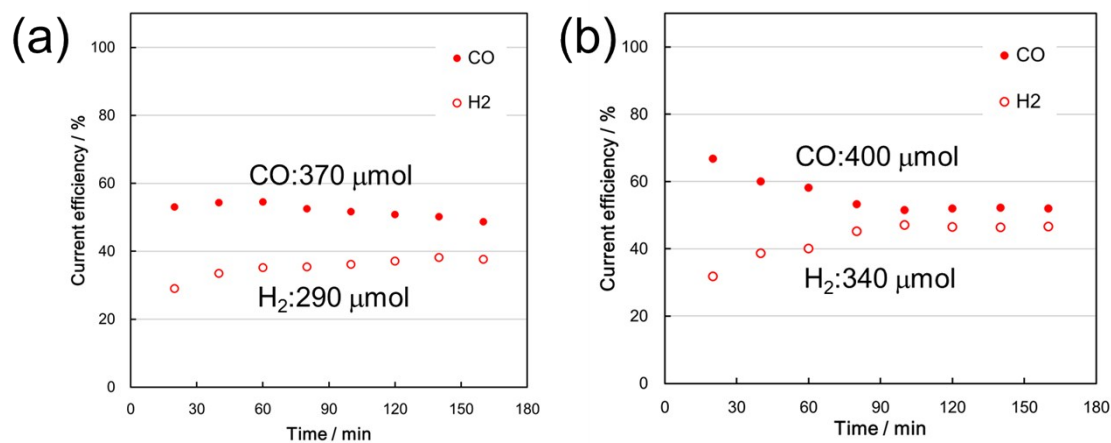


Fig. S4 Results for CO₂ reduction using self-assembled PS modified Ag-foil cells with CO₂-saturated 0.5 M KHCO₃ solution as electrolyte. The amounts of gaseous products at 3 h and the current efficiencies observed during CO₂ reduction at -1.1 V vs. RHE are presented for (a) Ag foil and (b) self-assembled PS-modified Ag foil.

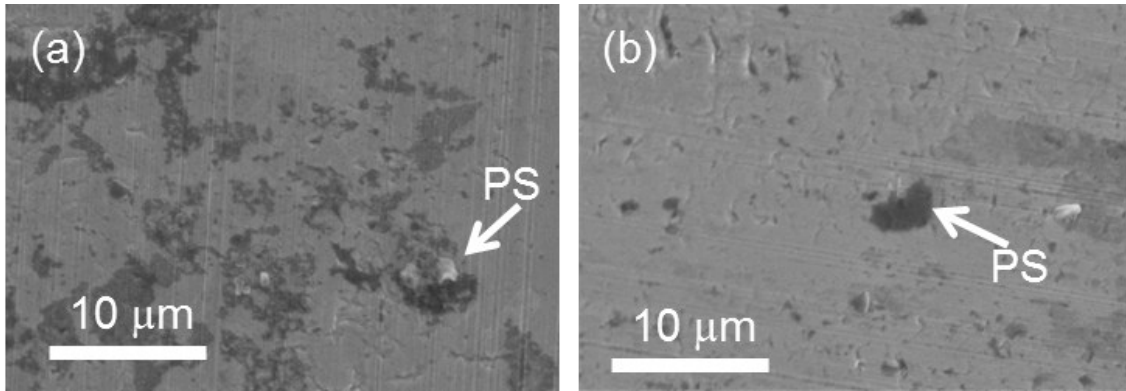


Fig. S5 SEM images of self-assembled PS-modified Ag foil after (a) 1 h and (b) 3 h reaction time.

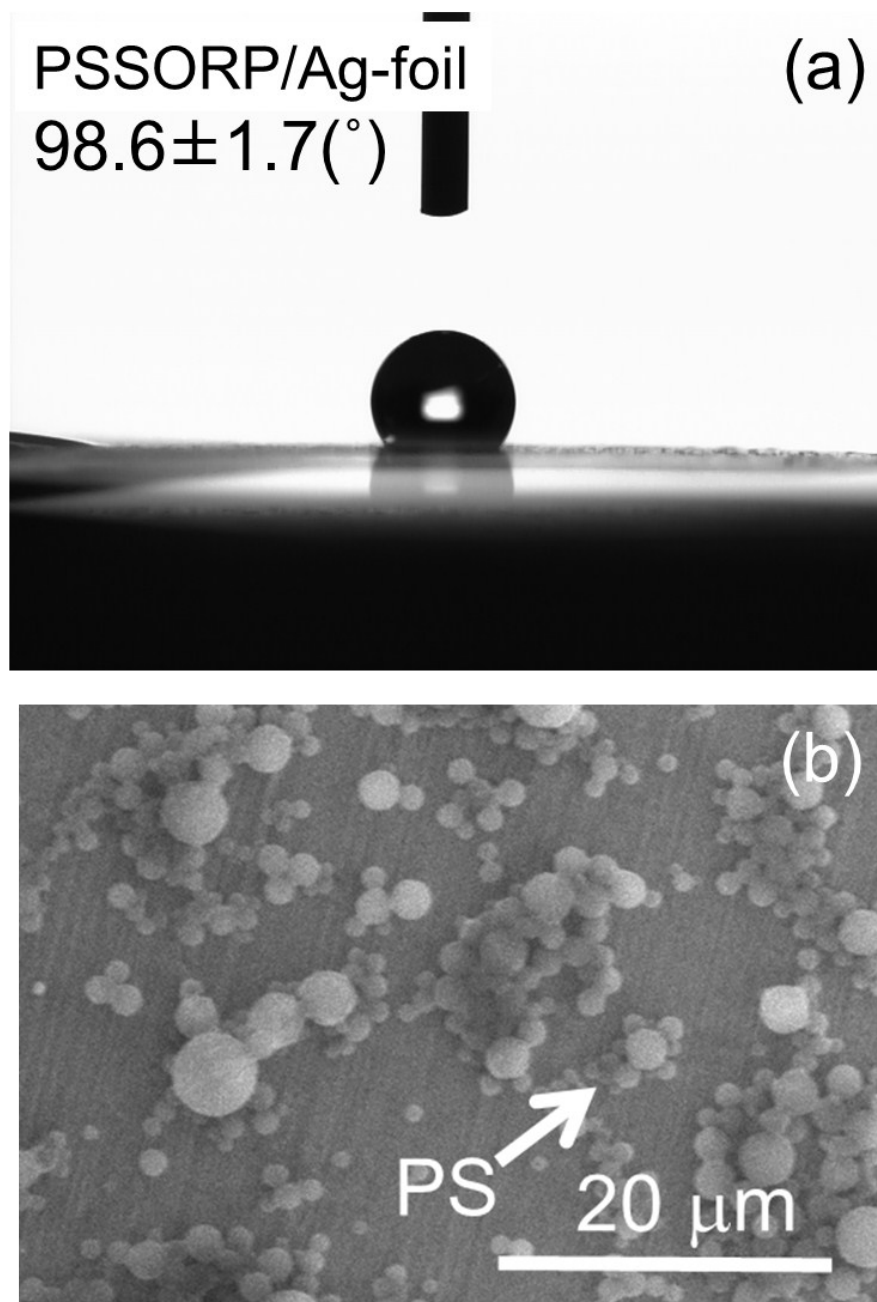


Fig. S6 (a) Water contact angle for Ag foil coated with PS produced by SORP method via drop-casting and (b) SEM image of this material.

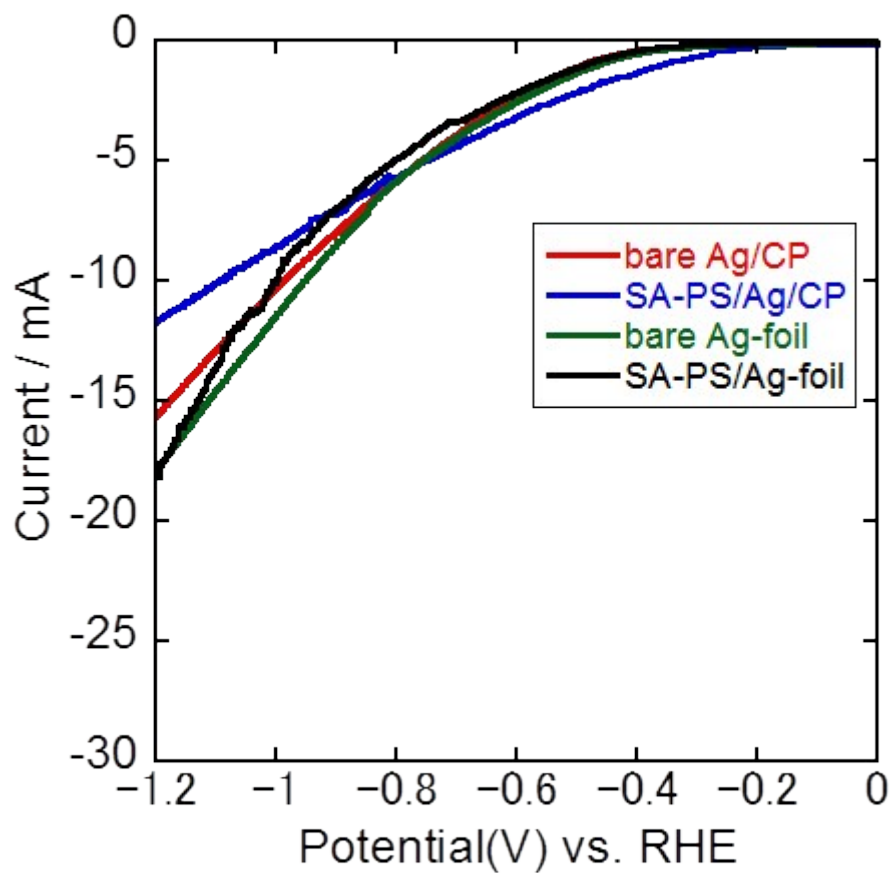


Fig. S7 Current-potential characteristics of bare Ag-foil, SA-PS Ag-foil, bare Ag/CP and SA-PS/Ag/CP electrodes at following 3 h reaction time.

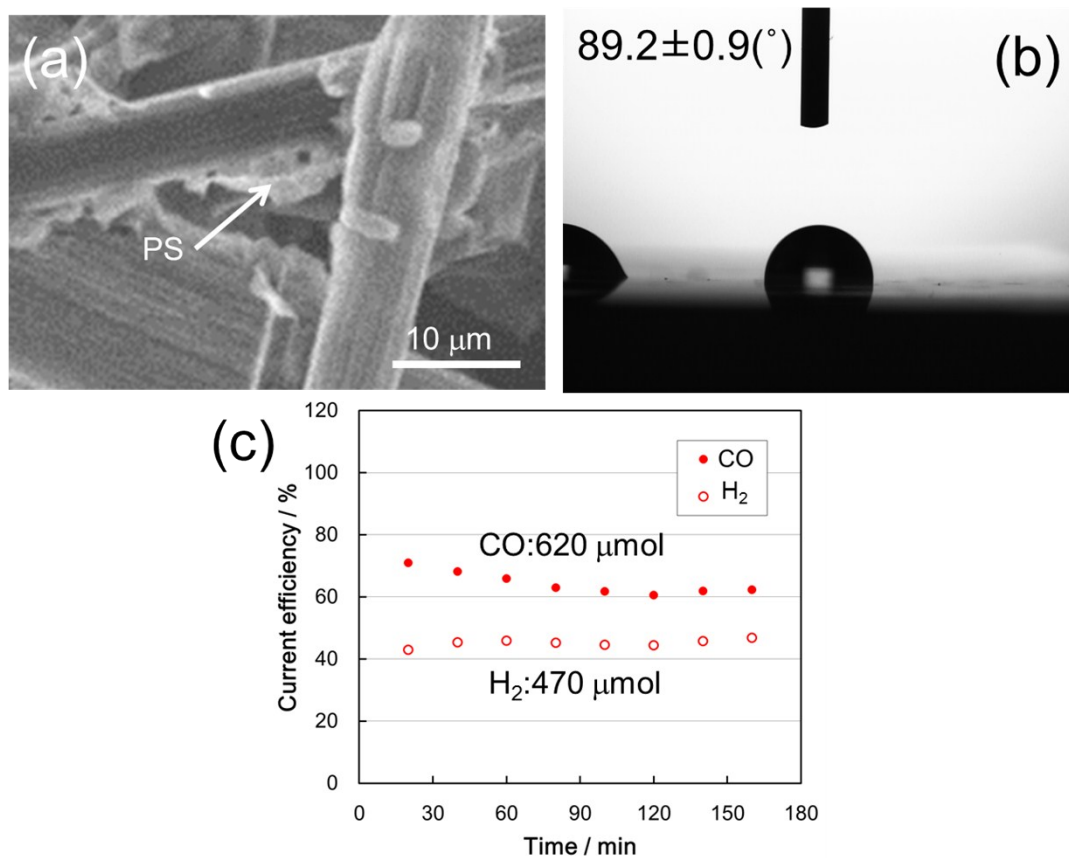


Fig. S8 (a) SEM image of PS drop-cast Ag/CP, (b) water contact angle on PS drop-cast Ag/CP, and (c) Amount of gaseous products and current efficiencies at -1.1 V vs. RHE during CO₂ reduction using PS drop-cast Ag/CP cell.

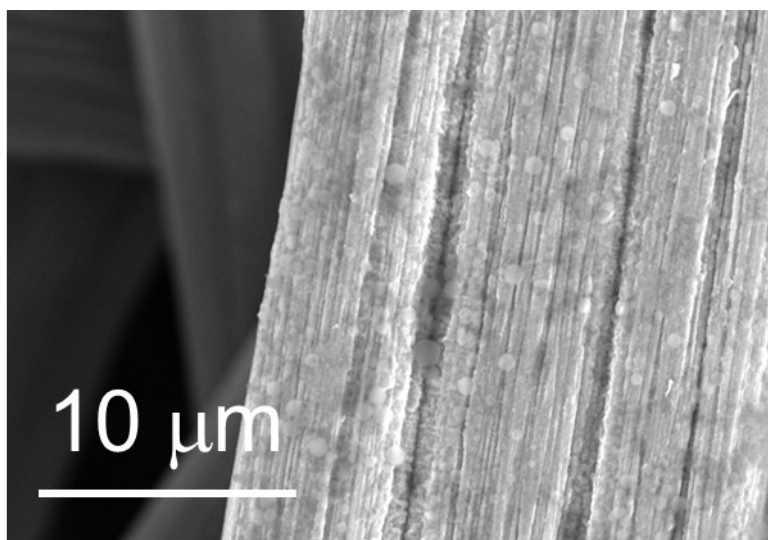


Fig. S9 SEM image of self-assembled PS-modified Ag/CP following 3 h reaction time.

References

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