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ELECTRONIC SUPPLEMENTARY INFORMATION

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S-1 Details of experimental procedures

S-2 Supplementary figures

S-1 Details of experimental procedures

1) Electrode preparation

The Ag electrodes were prepared from Ag foil (Alfa Aesar, 99.998%, 0.25 mm in thickness). The Ag foil was mechanically polished and sonicated with DI water prior to the making of electrodes. The apparent electrode size used for the electrolysis was 3.2 cm².

Most silver salts are insoluble in water. As silver nitrate has the highest solubility among silver compounds, we chose NaNO₃ (0.1M, aqueous) as electrolyte for anodization. Anodization was conducted with platinum as the counter electrode and Ag/AgCl as the reference electrode. A Solartron SI 1287 Electrochemical Interface was used to apply potential (0.45, 0.50, 0.55, 0.60, 0.65, 0.70, and 0.90 V) to the Ag sheet electrode and to control the charge (3, 5, 5.5, 6, 7, and 10 coulombs respectively) for anodization. Anodization was conducted in neutral (pH7) 0.1M NaNO₃ electrolyte and in pH3 0.1M NaNO₃ electrolyte, respectively. Diluted HNO₃ (~1%) was used to adjust the pH.

2) Electrochemical characterization and products analysis

The Solartron SI 1287 Electrochemical Interface was used for all the electrochemical experiments including cyclic voltammetry (CV), potentiostatic, and galvanostatic sweeps. Experiments were performed in a two-chamber cell using platinum as the counter electrode and Ag/AgCl as the reference electrode. KHCO₃ (0.1M, aqueous) was used as the supporting electrolyte. CO₂ was purged through the electrolyte for at least 15 minutes before starting each experiment. The pH of the electrolyte saturated with CO₂ was measured to be 6.8. All potentials were measured versus the Ag/AgCl reference electrode. Overpotential was calculated using the equation: η = (-0.0103-0.0591*pH-0.197) - E (vs. Ag/AgCl).

Before the electrochemical tests for each electrode, 5 cycles of CVs at a scan rate of 25 mV/sec over an applied potential range of -0.5 to -1.5 V (vs. Ag/AgCl) were run to condition the electrodes.

Electrolysis tests were conducted using potentiostatic sweeps. The electrolysis was terminated after 10 coulombs of total charge were transferred. During the electrolysis, the electrolyte in both compartments was stirred at a rate of 500 rpm using a magnetic stirrer. Gas phase product was sampled from the headspace of the electrochemical cell chamber using a gas-tight syringe (Hamilton). A Thermo Scientific Trace GC Ultra gas chromatograph equipped with a VICI pulsed discharge detector and SUPELCO CarboxenTM 1010 PLOT

column was used for quantifications. Ultra high purity (>99.999%) Helium was used as carrier gas.

The Tafel plot data was collected under potentiostatic sweeps. The potentiostatic method measured steady-state currents at various applied potentials descending from -1.0 to -1.4 V vs. Ag/AgCl (corresponding to 0.3 to 0.7 V overpotential) at a 0.05 V step. For each potential, a steady state was considered to be achieved when the current change fell to <5.0%.

3) SEM

JEOL JSM-7800 field emission scanning electron microscopy (SEM) was used to characterize the surface and cross section of the electrodes. The JEOL IB-09010CP Cross Section Polisher was used to prepare the cross section specimen.

4) Electrochemical surface area measurement

The electrochemical surface area measurement was conducted in a three electrode cell using a Pt counter electrode and an Ag/AgCl reference electrode. The electrolyte was 0.1 M KOH aqueous solution (N₂ saturated) with pH of 12.6. After electrochemically reduction at -1.34 V vs. Ag/AgCl (i.e., -0.40 V vs. RHE) for 10 minutes, the electrodes were oxidized at 0.21 V vs. Ag/AgCl (i.e., 1.15 V vs. RHE), which was believed to only form a monolayer of Ag₂O or AgOH (Q. Lu, J. Rosen, Y. Zhou, G. S. Hutchings, Y. C. Kimmel, J. G. Chen and F. Jiao, **Nat. Commun.**, 2014, **5**, 3242). By comparing the amount of electrons passed during the oxidation process, the relative chemical surface areas between different Ag electrodes were obtained.

5) XRD

Grazing incidence X-ray diffraction (XRD) patterns were obtained with a Rigaku Smartlab X-ray diffractometer using Cu K α radiation ($\lambda = 1.5405$ Å). Data was collected using a scan rate of 1°/min. The grazing incidence angle used was 0.5°.

6) **XPS**

X-ray photoelectron spectroscopy (XPS) spectra were acquired with a PHI 5000 VersaProbe II X-ray photoelectron spectrometer using an Al K α source. Survey scans (with 187.85 eV pass energy at a scan step of 0.8 eV) and high resolution (O 1s), (Ag 3d) and (C 1s) scans (with 23.5 eV pass energy at a scan step of 0.1 eV) were performed.

S-2 Supplementary Figures



Fig. S1. CO Faradaic efficiency for anodization in pH3 0.1M NaNO₃ electrolyte (anodization potential is 0.6 V vs. Ag/AgCl and charge is 5.5 coulombs).



Fig. S2. Morphology of anodized Ag electrodes. (a) SEM of the surface of the an-Ag (anodization: at 0.6 V for 5.5 coulombs in neutral 0.1 M NaNO₃ electrolyte). (b) SEM of the surface of the poly-Ag. (c) SEM of the cross section of the an-Ag.



Fig. S3. (a) A typical cyclic voltammogram of Ag over the range of 0 to 1.60 V vs. RHE. The current peak observed at about 1.15 V corresponds to a monolayer formation of Ag₂O or AgOH. Current transit at constant potential of 1.15 V vs. RHE for an-Ag (b) and poly-Ag (c). The charge required to oxidize one monolayer of an-Ag is about 5 times as large as that of poly-Ag.



Fig. S4. Grazing incidence XRD patterns of Ag electrodes anodized under various conditions, which are marked as xxxV-xxxC-pHxxx corresponding to anodization potential (V)-anodization charge (C, coulombs)-electrolyte pH. The intensity was normalized to the (111) peak.



Fig. S5. O 1s and Ag 3d XPS spectra of Ag electrodes anodized (a) under different potential while the charge was fixed at 5 coulombs and (b) with different charge while the potential was fixed at 0.6 V. Anodization was conducted in a neutral (pH7) 0.1M NaNO₃ electrolyte.



Fig. S6. O 1s and Ag 3d XPS spectra of anodized Ag electrodes after 5 cycles of CV conditioning electrolysis (at a scan rate of 25 mV/sec over an applied potential range of -0.5 to -1.5 V vs. Ag/AgCl). For comparison, XPS spectra of unanodized poly-Ag and as-anodized Ag (anodized at 0.6 V for 5 C) are also included in the figure. No Ag oxide was found on the surface of any of the samples after conditioning electrolysis (The spectra for other electrodes anodized at other conditions are not shown here).