Supplemental Information

Hierarchically 3D Porous Ag Nanostructures Derived from Silver Benzenethiolate Nanoboxes: Enabling CO₂ Reduction with a Near-Unity Selectivity and Mass-Specific Current Density over 500 A/g

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Experimental Details

Materials
Silver nitrate (AgNO₃, 99.85%, Acros Organics), sodium chloride (NaCl, 99.99%, Fisher Chemical), sodium bromide (NaBr, 99.99%, Acros Organics), poly(vinylpyrrolidone) (PVP, \(M_w\approx55000\), Sigma Aldrich), and potassium hydrogen carbonate (KHCO₃, 99.99%, Acros Organics) were used as received. Thiophenol (99%, Acros Organics), ethylene glycol (EG, Fisher Chemical), ethanol (190 proof), and acetone were used without further purification. De-ionized (DI) water was used for preparing all aqueous solutions.

Synthesis of silver benzenethiolate (AgBT) nanoboxes
The synthesis started with the preparation of ternary silver halide (AgCl₀.₅Br₀.₅) nanocubes by following the procedure reported elsewhere. In a typical preparation of AgCl₀.₅Br₀.₅ nanocubes, 2.5 g of PVP was first dissolved in 12 mL of EG in a 50-mL three-necked flask with the assistance of vigorous stirring. To this solution was added 10.2 mg of NaCl and 18.4 mg of NaBr powders. The solution was purged with nitrogen gas and then a nitrogen blanket maintained the inert atmosphere above the solution. The flask was covered with an aluminum foil to prevent any possible undesirable light-induced reactions. The solution was then heated up to 60 °C and maintained at this temperature until all salts were dissolved. 1 mL EG solution of 0.34 mol/L AgNO₃ was added to the warm solution at a rate of 1 mL/min using a syringe pump. Mixing AgNO₃ with halide ions triggered the precipitation reaction to form AgCl₀.₅Br₀.₅ nanocubes. The reaction lasted 2 hours to ensure the completion of nanocube growth. The nitrogen atmosphere, the temperature of 60 °C, and magnetic stirring of 300 rpm (with a stir bar of 19.1 mm × 9.5 mm) were maintained throughout the entire synthesis. The product solution was transferred to a 50-mL centrifuge tube, followed by the addition of 20 mL of ethanol. The solution was then sequentially vortexed and centrifuged at 6000 rpm for 20 min. The supernatant was discarded, and the nanocubes settled at the bottom of the centrifuge tube were re-dispersed in 20 mL of ethanol. The new dispersion was centrifuged again at 6000 rpm for 10 min. The recovered nanocubes were dispersed in 5 mL of ethanol for preparing AgBT nanoboxes. A solution of thiophenol (HBT, 0.049 M) was prepared by mixing thiophenol and ethanol at 1:200 (V/V) ratio. 15 mL of the thiophenol solution was then added to the dispersion of AgCl₀.₅Br₀.₅ nanocubes, followed by
vortexing for 2 min. The dispersion was placed in the dark for 24 h to complete the transformation of the AgCl$_{0.5}$Br$_{0.5}$ nanocubes to AgBT nanoboxes.

The success of synthesizing AgBT nanoboxes relies on the two-fold functions of the AgCl$_{0.5}$Br$_{0.5}$ nanocubes, i.e., regulating the concentration of freestanding Ag$^+$ at a constant low level to control the growth kinetics of AgBT and serving as physical template to regulate the geometry of the growing AgBT into nanoplates and nanoboxes. The lower solubility product of AgBT ($K_{sp} = 2.4 \times 10^{-21}$ mol$^2$ L$^{-2}$) than those of AgCl and AgBr ($K_{sp} = 1.77 \times 10^{-10}$ and $5.35 \times 10^{-13}$ mol$^2$ ·L$^{-2}$ for AgCl and AgBr, respectively, in water at 20 °C) represents the driving force of the transformation reaction of AgCl$_{0.5}$Br$_{0.5}$ to AgBT. For example, a typical reaction transforms AgCl$_{0.5}$Br$_{0.5}$ nanocubes with an average edge length of 160 nm (Figure S1) gradually to AgBT nanoplates on the surfaces of the AgCl$_{0.5}$Br$_{0.5}$ nanocubes and finally to hollow nanoboxes made of pure AgBT (Figure S2 and S3). Each hollow box is constructed from assembly of six rigid AgBT nanoplates interconnected orthogonally (Figure S3C). The XRD pattern of the AgBT nanoboxes exhibits a quintuplet of peaks corresponding to different orders of reflection of the same lattice, which indicates the AgBT nanoplates are crystallized in a layered crystalline structure with an interlayer distance of 14.1 Å (Figure S3D).

**Electrochemical reduction of AgBT nanoboxes**

In a typical process, 5 mL dispersion of the AgBT nanoboxes prepared in the previous step was centrifuged at 6000 rpm. The collected AgBT nanoboxes were then washed with copious ethanol, followed by centrifugation. The clean AgBT nanoboxes were dispersed in 1 mL of ethanol, forming an ink of precursor for preparing the eCO$_2$RR catalyst. An aliquot of 20 μL of the ink was then loaded onto a freshly polished glassy carbon electrode with a size of 0.9 cm × 0.8 cm (i.e., 0.72 cm$^2$ in area). The ink was dried for 30 min in a vacuum oven set at 60 °C. This electrode was used as the working electrode in a homemade three-electrode cell connected to a CHI 604E electrochemical workstation. A Ag/AgCl electrode immersed in a saturated KCl aqueous solution was used as the reference electrode and a Pt wire as the counter electrode. The electrochemical cell was composed of two compartments separated with a Nafion 115 (DuPont) membrane, which allowed the permeation of ions but prevented the diffusion of gas molecules. The purchased Nafion membrane was pretreated by soaking a piece of 4 cm × 4 cm sheet in DI water for 4 hours followed
by soaking it in hot water at 80°C for 1 hour. The working electrode and reference electrode were placed in one compartment and the counter electrode in the other compartment. Both compartments were filled with 0.1 M KHCO$_3$ aqueous solution, which was purged with high-purity CO$_2$ for 30 min. Applying $-1.2$ V (vs. RHE) bias to the working electrode reduced the assembled AgBT nanoboxes to 3D porous Ag nanostructures on the glassy carbon electrode. The reduction lasted until 2 coulombs of charges were passed through the cell, ensuring the complete transformation of the AgBT nanoboxes to Ag.

**Electrochemical reduction of CO$_2$**

After the complete transformation of AgBT nanoboxes to 3D porous Ag nanostructures, an additional 30-min purge of CO$_2$ was applied to remove any possible gaseous products (e.g., CO, H$_2$) from the electrochemical cell. The compartment containing the working electrode was then sealed while the CO$_2$ flow was continued above the electrolyte solution to maintain constant saturation of CO$_2$ in the electrolyte. Linear sweep voltammetry (LSV) was performed from 0 V to $-1.2$ V (vs. RHE) at a scan rate of 10 mV·s$^{-1}$. In a quantitative measurement, the CO$_2$ flow was stopped, ensuring all reduction products to be in the electrochemical cell compartment. The electrochemical reduction was carried out by applying an appropriate potential until 0.5 coulomb or 1.0 coulomb of charges passed through the electrochemical cell. The entire procedure was repeated for the measurement at a different potential by freshly preparing the catalyst with the fresh precursor ink. The potential values reported in the manuscript were calibrated to the values against the RHE (reversible hydrogen electrode) according to

$$\text{Potential (V vs. RHE)} = \text{Applied potential (V vs. Ag/AgCl.sat. KCl)} + 0.199 \text{ V} + 0.0592 \times \text{pH}. $$

**Materials characterization**

Scanning electron microscopy (SEM) images were obtained using a FEI QUANTA 450 scanning electron microscope. Each SEM sample was prepared by placing one droplet of ethanolic dispersion of nanoparticles on a piece of silicon wafer. The droplet was then dried in a fume hood at ambient condition and in the dark. Energy dispersive X-ray spectroscopy (EDS) and imaging were performed in the same microscope with the X-Max$^N$ 50 spectrometer (Oxford instruments). The SEM images of Ag nanostructures on glassy carbon electrodes were taken by directly placing
the electrodes in the SEM microscope. The same samples were also characterized by XRD using a Bruker D8 diffractometer with a Cu Kα (λ = 1.540 Å) target. The 2θ was set in the range of 3–70 degrees and the scan rate was 0.4 degree/min. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-1400 electron microscope. The sample of electrochemically reduced AgBT was prepared by adding an ethanol drop on to the electrode of reduced AgBT followed by exfoliation of material directly using a TEM grid. The Fourier transform infrared (FTIR) spectroscopy was studied with the use of Thermo Scientific Nicolet iS5 FTIR spectrometer equipped with Thermo Scientific iD5 attenuated total reflectance (ATR) accessory.

**Analysis of the products generated from the electrochemical reduction**

In a typical analysis of the electrochemical reduction products, 100 μL of gas was sampled using an airtight syringe from the headspace of the compartment containing the working electrode. The gas sample was analyzed using a Agilent 7820A gas chromatography (GC) system equipped with a thermal conductivity detector (TCD). The GC peak areas of CO and H₂ were used to calculate the partial current densities and Faradaic efficiencies of individual products. The quantitative analysis was calibrated with the standard gases (Scott Mini-Mix). Nuclear magnetic resonance (NMR) spectroscopy was used to analyze the liquid products formed and dissolved in the electrolyte. A sample was prepared by adding 0.500 mL of the electrolyte in a NMR tube. To the NMR tube was added 0.200 mL of 5 mM Dimethylsulfoxide (DMSO) solution dissolved in deuterated water that served the internal standard.

**Determination of the amount of Ag catalysts**

An aliquot of 50 μL of the ink (AgBT nanobox dispersion in ethanol) was digested by mixing with 400 μL of concentrated HNO₃ in a 15-mL disposable centrifuge tube (Fisher). After the complete digestion, the solution was diluted by adding DI water to a total volume of 14.00 mL. The concentration of Ag⁺ in the solution was measured using inductive coupling plasma-atomic emission spectroscopy (ICP-AES).

The concentration of Ag⁺ in the prepared dispersion = 15 μM

Amount of Ag⁺ in the prepared dispersion = 15 μM × 14.00 × 10⁻³ L = 0.21 μmol
Amount of Ag in the ink which was used for preparing 3D porous Ag nanostructure catalyst

\[
\begin{align*}
&= 0.21 \text{ μmol} \times (20 \text{ μL} / 50\text{μL}) \\
&= 0.084 \text{ μmol}
\end{align*}
\]

Mass of Ag catalyst on the electrode

\[
\begin{align*}
&= 0.084 \text{ μmol} \times 107.87 \text{ g mol}^{-1} \\
&= 9.06 \text{ μg}
\end{align*}
\]

Estimation of electrochemically active surface area (ECSA)

To evaluate the exposed surface originated from the porous nature of the catalyst, the ECSA measurements were performed by following a the reported procedure.\(^{9,10}\) Typically, measurement was carried out in a 25-mL electrochemical cell containing 20 mL aqueous solution of 5 mM Pb(NO\(_3\))\(_2\), 10 mM HNO\(_3\), and 10 mM KCl. A platinum wire and a Ag/AgCl/saturated KCl electrode were used as the counter and reference electrodes, respectively. A glass carbon electrode fully coated with different Ag nanostructures, including the hierarchically 3D porous Ag nanostructures, citrate capped Ag nanoparticles, and thermally reduced Ag nanoparticles, was used as the working electrodes. Cyclic voltammetry (CV) was then measured by scanning the potential in a range of −0.45 V to 0 V (vs. Ag/AgCl) at a scan rate of 0.1 V/s. The measured CV graph exhibited a peak corresponding to the submonolayer deposition of Pd during the under-potential deposition (UPD). The integrated peak area (highlighted in the CV graph below) was used to calculate the ECSA using the following equation:

\[
\text{ECSA} = \text{Peak area} \times \text{constant} / (\text{scan rate})
\]

The constant corresponding to the monolayer deposition of Pd on Ag is \(1.67 \times 10^{-3} \text{ cm}^2/\mu\text{C}\) (Anal. Chem., 1997, 69, 4660-4664).

The ECSA of the hierarchically 3D porous Ag nanostructures shown in Figure 1 is 71 cm\(^2\)/mg, which is ~2 orders higher than that of thermally reduced Ag nanoparticles shown in Figure 3A (0.185 cm\(^2\)/mg) and ~70 times higher than that of citrate capped-Ag nanoparticles shown in Figure 3D (1.0 cm\(^2\)/mg).
Computational methods

To provide more in-depth information on electrochemical processes at the microscopic level, first-principles calculations have been performed using density functional theory (DFT) and the projector augmented wave (PAW) method as implemented in the Vienna ab Initio Simulation Package (VASP). The meta-GGA SCAN density functional, which is known to predict accurate geometries and energies of diversely bonded systems including metallic and van der Waals bonds, is used to evaluate the molecule adsorption on metal surfaces. A $2 \times 2 \times 1$ Monkhorst-Pack k-point mesh and a plane wave basis set with an energy cut-off of 520 eV are used. The calculations of molecule adsorption are performed in $4 \times 4$ supercells of Ag(111) surface in order to minimize the effect of adsorbate-adsorbate interaction. Four atomic layers of Ag are simulated with the geometry of the bottom layer fixed to mimic the bulk property. A vacuum distance of 14 Å is imposed to avoid the interlayer interactions. Atomic structures are relaxed until the final force exerted on each atom is less than 0.02 eV/Å and the change in total energy is less than $10^{-4}$ eV. Dipole corrections are included for all the surface slab calculations.

It is well known that the hydrogen adsorption free energy ($\Delta G_{H^*}$) is the most important factor for describing the HER activity in acidic solutions. While in alkaline solutions, besides the thermodynamic free energy $\Delta G_{H^*}$, the kinetic barrier for water dissociation represents another factor that may govern the overall reaction rate. The material design can be achieved by a balance between the water dissociation and the relative $H^*/OH^*$ adsorption free energies. When benzenethiolate ions ($C_6H_5S^-$) are adsorbed on the Ag surface (i.e., the surface of the 3D porous Ag nanostructures shown in Figure 1), the adsorption free energy $\Delta G$ for hydrogen varies and is computed as $\Delta G_{H^*} = E_{H^*} - \frac{1}{2} E_{H_2} - E^*$, where $E_{H^*}$, $E_{H_2}$, and $E^*$ are the total energies of the adsorbed system, the gas phase species, and the surface, respectively. For hydrogen adsorption, we include the zero point energy and vibration entropy corrections as adopted in Ref. 14.

We compared calculations using both the RPBE functional and SCAN functional. Calculations with the RPBE functional shows that $\Delta G_{H^*}$ on a Ag (111) surface is around 0.56 eV, which is consistent with the results in the literature. The calculations based on the SCAN functional give rise to a $\Delta G_{H^*}$ of 0.31 eV on the Ag (111) surface, which represents a slightly stronger binding of
hydrogen. Moreover, the meta-GGA functional SCAN can capture a large amount of intermediate-range van der Waals interaction, which is crucial for accurately determining the adsorption configurations of the benzenethiolate ions ($\text{C}_6\text{H}_5\text{S}^-$). For instance, due to the lack of van der Waals interaction, RPBE incorrectly predicts that the molecule desorbs from the surface after hydrogen adsorption. Therefore, the calculations using the SCAN functional have been used to compare the H adsorption on clean Ag surface and the benzenethiolate-modified Ag surface.
**Figure S1.** SEM image of AgCl$_{0.5}$Br$_{0.5}$ nanocubes.

**Figure S2.** XRD patterns of the products taken at different times after mixing thiophenol with AgCl$_{0.5}$Br$_{0.5}$ nanocubes. The vertical lines at the bottom represent the XRD pattern of AgCl$_{0.5}$Br$_{0.5}$ calculated from the standard XRD patterns of AgCl and AgBr using the Vegard equation.
Figure S3. (A) Schematic illustration and SEM images of nanoparticles at different stages involved in the transformation of AgCl\textsubscript{0.5}Br\textsubscript{0.5} nanocube to AgBT nanobox. (B) SEM images of one AgBT nanocube taken from different angles. (C) SEM image of the as-synthesized AgBT nanoboxes assembled on a Si substrate. (D) XRD patterns of the AgBT nanoboxes and AgCl\textsubscript{0.5}Br\textsubscript{0.5} nanocubes.
Figure S4. XRD pattern of the 3D porous Ag nanostructures that were prepared from electrochemical reduction of the AgBT nanoboxes. The pattern well matches the standard XRD pattern (red bars) of face-centered cubic Ag crystal, indicating that the AgBT nanoboxes were completely reduced to Ag.
Figure S5. SEM images of the AgBT nanoboxes on a glassy carbon electrode (A) before and (B) after reduced by flowing different amounts of electrons: (B) 0.5 C, (C) 1 C, and (D) 2 C in an electrochemical cell. The applied potential was -1.2 V (vs. RHE). The scale bar in (A) also applies to (B-D). The scale bar in (A) applies to all images.

Figure S6. Cyclic voltammogram of the bulk Pd deposition and the monolayer deposition of Pd at 0.1 V/s on Ag, which was used as the working electrode.
Figure S7. The ATR-FTIR spectra of the porous Ag (red curve) and ethanolic solution of BT (blue curve).

The observation of peaks corresponding to the aromatic C=C stretching (1575, 1474, and 1436 cm\(^{-1}\)) and aromatic C-H stretching (2918 and 2850 cm\(^{-1}\)) confirms the presence of BT molecules on the Ag surface of porous Ag nanostructures. Peaks corresponding to the thiol molecule are indicated by the dotted lines. Other peaks of the blue curve correspond to the ethanol, which was used to dilute BT. Peaks centered at 1087 and 1044, 3329 and 1732 cm\(^{-1}\) are attributed to the C-H, O-H stretching and C-O stretching of the residual ethanol, respectively.
Figure S8. Digital photo of the H-type electrochemical cell.
Figure S9. (A) GC chromatograms of a typical gas sample taken from the eCO$_2$RR product and the commercial reference gas mixture that was used for qualitative and quantitative analysis of the gas product. (B) 1H NMR spectrum of the electrolyte after eCO$_2$RR. The broad peak centered at 4.6 ppm corresponds to water in the electrolyte and the sharp CH$_3$-S peak originates from the internal standard, DMSO. The blowup inset indicates the absence of any coupling of methyl groups and functional groups, which implies the absence of possible liquid products of eCO$_2$RR (e.g., methanol, ethanol, etc.).

Figure S10. Area-specific current density of eCO$_2$RR using the 3D porous Ag nanostructures of Figure 1B as catalyst.
Figure S11. (A) Area-specific current densities and (B) Faradaic efficiencies of forming individual species using the bare glassy carbon electrode.
Figure S12. EDS spectra of (black) the 3D porous Ag nanostructures formed from electrochemical reduction of the AgBT nanoboxes and (red) the aggregated Ag nanoparticles formed from thermal reduction (or thermal decomposition) of the AgBT nanoboxes at 350 °C in N₂ atmosphere. The absence of S peak for the thermally reduced Ag nanoparticles indicates that thermal process prevents the re-adsorption of thiophenol. Two spectra were offset vertically for visual clarity.
Figure S13. Area-specific current densities of forming individual product species using the thermally reduced Ag nanoparticles as catalyst.

Figure S14. (A) Time-dependent area-specific current density at a $-0.75 \text{ V (vs. RHE)}$. (B) Stability of cyclic voltammetry (CV) curves after 10,000 cycles. The 3D porous Ag nanostructures of Figure 1B were used as the catalyst. The characterization was performed using the CO$_2$-saturated 0.1 M KHCO$_3$ (aq) electrolyte. The scan rate of applied potential was 1 V/s for CV measurement.
Table S1. Summary of Ag catalysts for eCO₂RR

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Maximum FE for CO formation (%)</th>
<th>Area-specific current density for CO formation at FE&gt;90% (mA/cm²)</th>
<th>Mass-specific current density (A/g)</th>
<th>[KHCO₃]</th>
<th>Ref.</th>
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<tr>
<td>5 nm Ag/C</td>
<td>84.4</td>
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<td>53.8 (at 0.7 V)</td>
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<td>Polycrystalline Ag</td>
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<td>N/A</td>
<td>0.1 M</td>
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<tr>
<td>Nanoporous Ag foil</td>
<td>92</td>
<td>18</td>
<td>0.2 (at 0.5 V)</td>
<td>0.5 M</td>
<td>17</td>
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<tr>
<td>Electro-deposited Ag</td>
<td>62</td>
<td>2.5</td>
<td></td>
<td>0.5 M</td>
<td>18</td>
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<tr>
<td>Triangular Ag Nanoplates</td>
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<td>1.25</td>
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<td>19</td>
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<td>18*</td>
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<td>0.23~1.5</td>
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<td>0.1 M</td>
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<tr>
<td>Br-derived porous Ag foil</td>
<td>96.2</td>
<td>11.5</td>
<td>0.5 M</td>
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<td>Ag nanowire array</td>
<td>91</td>
<td>~4.92</td>
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<td>0.12</td>
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<td>0.1 M</td>
<td>26</td>
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<td>Silver inverse opal</td>
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<td>PON-Ag</td>
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<td>Hierarchical 3D porous Ag</td>
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<td>5.3</td>
<td>502 (at 1.03 V)</td>
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<td>This work</td>
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Note:

* represents the estimated values from the current density plots.
References


