Supporting information

Cascade Reactions in Nanozymes: Spatially Separated Active Sites inside Ag Core-Porous Cu Shell Nanoparticles for Multistep Carbon Dioxide Reduction to Higher Organic Molecules

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Materials

All chemicals were obtained from commercial suppliers and used without further purification. Poly(vinylpyrrolidone) Mₙ 55,000, sodium chloride (≥99.5%), L-ascorbic acid (≥99.0%), poly(ethylene glycol) methyl ether Mₙ 5,000, hydrazine solution 35 wt% in water, Nafion® 117 solution (~5% in a mixture of lower aliphatic alcohols and water), methanol (HPLC grade), potassium hydrogen carbonate (≥99.9%), anhydrous dimethyl sulfoxide (≥99.9%) and carbon monoxide, carbon dioxide, methane, ethane, ethylene and acetylene were purchased from Sigma-Aldrich/Merck. Ag nitrate (≥99.5%), sodium hydroxide (≥98.0%), Cu (II) nitrate (≥99.0%), ethanol (100%) and acetone (≥99.8%) were purchased from Chem-Supply Pty Ltd Australia. Nitric acid (69%) was purchased from VWR International Pty Ltd. Deuterium oxide (99.9%) was purchased from Cambridge Isotope Laboratories Inc.

Methods

All glassware was rinsed with concentrated nitric acid then Milli-Q water. All aqueous solutions were prepared using Milli-Q water.

Ag cores synthesis

Ag cores were synthesized according to a literature procedure. Briefly, 0.425 g poly(vinyl pyrrolidone) Mₙ 55,000 and 0.425 g Ag nitrate were dissolved in 100 mL water. To this solution, 1.0 mL 5.0 M sodium chloride was added under magnetic stirring. Further stirring for 15 min in the dark led to the formation of a colloidal suspension of AgCl nanoparticles. A solution containing ascorbic acid (100 mL, 50 mM) and sodium hydroxide (13 mL, 0.5 M) was prepared. To this solution, 12.5 mL of freshly prepared AgCl colloids were added under magnetic stirring with further stirring for 2 h in the dark. Using a centrifuge at 6000 rpm (4226 rcf) for 7 min, the reaction mixture was washed twice with water and concentrated to 14 mL and stored in the dark at 4 °C.

Porous Cu coating on Ag cores

Ag-core porous Cu-shell nanoparticles were synthesized using Ag cores synthesized as previously described with a procedure modified from the literature. Briefly, poly(ethylene glycol) methyl ether Mₙ 5,000 solution (60 mL, 2 wt%), Ag nanoparticles (4.0 mL of the previously prepared suspension) and Cu(NO₃)₂ (1.0 mL, 0.1 M) were mixed under stirring. To this solution, hydrazine (31.8 µL, 35 wt%) was added and left stirring for 3 min. Using a centrifuge at 4000 rpm (1878 rcf) for 15 min, the reaction mixture was separated, and the product was washed twice with water. Then using a centrifuge at 5000 rpm (2935 rcf) for 15 min, the reaction mixture was washed twice with ethanol and dried at 50 °C.

Porous Cu nanoparticles synthesis

Porous Cu nanoparticles were synthesized in a similar procedure to the Ag-core porous Cu-shell nanoparticles, without the addition of Ag cores. Briefly, poly(ethylene glycol) methyl ether Mₙ 5,000 solution (6.0 mL, 2 wt%) and Cu(NO₃)₂ (100 µL, 0.1 M) were mixed under stirring. To this solution hydrazine (3.18 µL, 35 wt%) was added and left stirring for 3 min. Using a centrifuge at 4000 rpm (1878 rcf) for 15 min, the reaction mixture was separated, and the product was washed twice with water. Then using a centrifuge at 5000 rpm (2935 rcf) for 15 min, the reaction mixture was washed twice with ethanol and dried at 50 °C.

TEM

For low magnification imaging, TEM samples were prepared by dipping carbon coated Cu grids in a colloidal solution of nanoparticles and allowing them to dry. Low magnification TEM analysis was performed on a Phillips CM200 (200 kV, field emission gun).

High resolution transmission electron microscopy was performed with a JEOL microscope (JEM-2800) equipped with Schottky-type emission source working at 200 kV, Gatan OneView camera.
(4kx4k, 25FPS) to obtain images with a resolution of 0.09 nm. Energy dispersive spectroscopy elemental mapping was performed using double silicon drift detectors, with a solid angle of 0.98 steradians with a detection area of 100 mm².

**Electrode preparation**

Plain carbon cloth – 1071 HCB purchased from fuel cell store³ was cut into square pieces with a 2 x 2 cm² area and contacted, sonicated in acetone for 10 min and then dried in a 120 °C oven. To ensure comparability across measurements and to avoid different electrochemical behavior due to varying substrate contributions, precisely controlled particle loading on the substrate was employed. An ink suspension with a concentration of 5 mg·mL⁻¹ particles in methanol and 1 % (v/v) Nafion® 117 5 wt% solution was prepared. An aliquot of 336 µL of this suspension was cast dropwise onto a carbon cloth suspended in air by self-closing tweezers. The cloth was left to dry in air, resulting in an absolute loading of 1.68 mg of particles per cloth.

**Electrochemical setup**

H-cell and O-ring fitted clamp electrodes were purchased from TianJin AIDA Science-Technology Development Co. Ltd⁴ with custom made Teflon volume-reducing blocks was employed for CO₂ reduction experiments. A Fumasep anion exchange membrane, purchased from Fuel Cell Store⁵. CO₂ (Supagas, ultra-high purity) was pre-bubbled through water prior to entering the cathode compartment. The gas flowrate was set to 1.5 sccm using a needle valve according to a 50 sccm flow meter purchased from Aalborg⁶, which measured the flow from the exhaust of the cathodic compartment. The cathodic and anodic compartments were filled with KHCO₃ (15 mL, 0.1 M), pre-treated by -1.4 V vs. Ag|AgCl|sat. KCl overnight and pre-bubbled with vigorous CO₂ bubbling for 30 min.

The working electrode was carbon cloth connected to a platinum clip and the reference electrode was a custom-built Ag|AgCl|sat. KCl electrode. For every experiment a new working electrode and fresh electrolyte were employed. Platinum mesh was used as the counter electrode. Chronoamperometry was run for 2 h at a fixed potential using an Autolab potentiostat controlled with Nova 2.1.2 software. On-line gas product quantification and liquid product analysis were performed before and after electrocatalysis. Potentials were converted from vs. Ag|AgCl|sat. KCl to vs. RHE using the following formula:

\[
E_{\text{RHE}} = E_{\text{Ag|AgCl|sat.KCl}} + 0.059 * \text{pH} + E^{\circ}_{\text{Ag|AgCl|sat.KCl}},
\]

where pH = 6.8 and \( E^{\circ}_{\text{Ag|AgCl|sat.KCl}} = 0.199 \) vs. SHE.

Liquid products were analyzed using ¹H-NMR. 500 µL aliquots of electrolyte from the cathode compartment were taken before and after electrocatalysis. Each aliquot was mixed with 100 µL of DMSO in D₂O stock solution. The DMSO in D₂O stock solution was prepared by mixing 5.0 µL DMSO with 10 mL D₂O. NMR aliquots were investigated on Bruker Avance III HD 400 MHz NMR with 64 scans and 16 s recycle delay, using DMSO as the internal standard. Product quantification was performed via the internal DMSO standard to determine the concentration of CO₂ reduction products.

Gas products were analyzed using gas chromatography. SRI 8610C multiple gas analyzer #5 gas chromatograph was purchased from SRI Instruments⁷ and calibrated using carbon monoxide, carbon dioxide, methane, ethane, ethylene and acetylene [1% (w/w) each component in nitrogen aerosol of 4 L, analytical standard] for calibration. Hydrogen calibration was performed using a gas mixture of carbon monoxide, carbon dioxide, hydrogen, methane and oxygen [1% (w/w) each component in nitrogen, cylinder of 14 L, analytical standard]. Automatic injection of 1.0 mL gas aliquots was taken from the cathode exhaust after 45 min.
**Figure S1.** TEM of AgCu nanozymes. TEM images and size distribution histogram showing Ag-core porous Cu-shell structures with an average diameter of 145 nm (s.d. = 15 nm, n = 70). Differences in contrast allow for the distinction of Ag cores and Cu shells.

**Figure S2.** SAED of AgCu nanozyme. a) SAED pattern of b) area used for SAED. c) Indexing shows that the SAED pattern is characteristic of face-centered cubic Ag and cubic Cu$_2$O.

| ED spots | Measured d Å | d(hkl) Ag Å | hkl | d(hkl) Cu$_2$O Å | hkl |
|----------|--------------|-------------|-----|------------------|-----|
| a        | 2.35         | 2.3590      | 111 |                  |     |
| b        | 2.04         | 2.0440      | 200 |                  |     |
| c        | 1.45         | 1.4450      | 220 |                  |     |
| d        | 1.24         | 1.2310      | 311 |                  |     |
| e        | 1.18         | 1.1796      | 222 |                  |     |
| f        | 3.02         | 3.020       | 110 |                  |     |
| g        | 2.45         | 2.465       | 111 |                  |     |
| h        | 2.14         | 2.135       | 200 |                  |     |
| i        | 1.51         | 1.510       | 220 |                  |     |
| j        | 1.29         | 1.287       | 311 |                  |     |

Reference: ICDD 04-007-8790 (PDF 00-004-0783) for Ag; ICDD 04-007-9767 (PDF 00-005-0667) for Cu$_2$O.
Figure S3. Anodic stripping of Ag from AgCu nanozymes. a) cyclic voltammogram of nanozymes in 50 mM KSCN, with three sweeps from 0 to +1 V vs. Ag/AgCl/3 M KCl @ 25 mVs.\textsuperscript{-1}, b) EDX elemental mapping of Ag (green) and Cu (red) for the nanozyme after anodic stripping, c) STEM image of nanozyme after anodic stripping of Ag with a scan indicated by the dotted red lines d) the line scan of post-anodic-stripping nanozyme. Cyclic voltammetry shows a large oxidation signal in the first scan, which is presumed to account for the oxidation of the Ag. EDX elemental mapping shows that the Ag is no longer confined to the core of the nanozyme, indicating diffusion of Ag out of the core and redeposition onto the exterior of the nanozyme. STEM imaging shows a central region, which is darker than the as-synthesized nanozyme (see Figure 1a), indicating a hollow nanozyme structure, with a line scan indicating that the post anodic stripping nanozyme exhibits a hollow core-shell structure.

Figure S4. a) STEM, b) SEM and c) EDX elemental mapping of Ag (green) and Cu (red) of nanozymes after anodic stripping. STEM imaging shows loss of initial core-shell structure (see Figure 1a) with no localisation of high contrast Ag to the center of core-shell particles, which is consistent with EDX elemental mapping showing Ag deposited outside of nanozyme Cu shells.
Figure S5. a) Chronoamperogram of nanozyme catalysts during CO$_2$RR. Chronoamperograms were recorded for 2 h at different applied potentials vs. Ag|AgCl|sat. KCl. b) SEM image of the carbon cloth electrode after electrochemical CO2RR experiment.
Figure S6. H$_2$, HCO$_2^-$ and CH$_4$ product formation rates for nanozymes at different potentials vs. RHE. H$_2$ evolution increases significantly at -0.65 V vs. RHE, at the same potential that C$_3$H$_8$O drops in the nanozyme window (see Figure 2). Further increase of H$_2$ production at -0.7 and -0.8 V vs. RHE indicate the competition of H$_2$ for CO$_2$RR. Formate production on the nanozyme peaks at -0.70 V vs. RHE and decreases at -0.80 V vs. RHE. CH$_4$ detection shows trace amounts between -0.55 V and -0.70 V vs. RHE with measurable production by CO$_2$RR at -0.80 V vs. RHE.

Figure S7. Ratio of n-propanol to propionaldehyde is derived from the integration of peaks resolved at 0.780 and 0.775 ppm, which are characteristic of the two products.\textsuperscript{6}
**Figure S8.** TEM of porous Cu nanoparticles. TEM images and size distribution histogram showing porous Cu nanoparticles with average diameter of 89 nm (s.d. = 19 nm, n = 84).

**Figure S9.** $\text{C}_3\text{H}_8\text{O}$, $\text{C}_2\text{H}_6\text{O}$, $\text{C}_2\text{H}_4$, $\text{CO}$, $\text{H}_2$, $\text{HCO}_2^-$, $\text{CH}_4$ product formation rates for porous Cu control nanoparticles at different potentials vs. RHE. Note the lack of production of $\text{C}_3\text{H}_8\text{O}$ on the porous Cu nanoparticles at -0.60 and -0.65 V vs. RHE, where $\text{C}_3\text{H}_8\text{O}$ is detectable for the nanozyme at these potentials. Another significant difference in the formation rates for the porous Cu nanoparticles is the decrease of CO production at -0.80 V vs. RHE, where the nanozyme exhibits increased CO production instead.
Figure S10. $\text{C}_3\text{H}_6\text{O}$, $\text{C}_2\text{H}_5\text{O}$, $\text{C}_2\text{H}_4$, $\text{CO}$, $\text{H}_2$, $\text{HCO}_2^-$, $\text{CH}_4$ product formation rates for a second batch of nanozyme particles at different potentials vs. RHE, confirming the previously observed potential window, in which the nanozymes promote the cascade reaction.