Gold Adparticles on Silver Combine Low Overpotential and High Selectivity in Electrochemical CO₂ Conversion

Adnan Ozden, Yanjiang Liu, Cao-Thang Dinh, Jun Li, Pengfei Ou, F. Pelayo García de Arquer, Edward H. Sargent,* and David Sinton*

Cite This: ACS Appl. Energy Mater. 2021, 4, 7504–7512

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Silver (Ag) catalysts enable high selectivity (>90%) in CO₂-to-CO conversion at >100 mA cm⁻²; gold (Au) catalysts are active at lower overpotential, but with lower selectivity (<80%). Here we present an adparticle-functionalized catalyst that combines the benefits of each by uniting Au adparticles on the AgAu interface. Au adparticles modify the lattice and electronic structure of Ag and lower the free energy change required to form *COOH. We demonstrate selective and low-overpotential CO₂-to-CO conversion at >490 mA cm⁻² in a flow cell. In a membrane electrode assembly, the catalyst achieves 90% CO selectivity and 33% CO energy efficiency over 60 h.

KEYWORDS: CO₂ electroreduction, CO production, energy materials, catalyst design, membrane electrode assembly, energy efficiency, carbon efficiency, overpotential

Renewable electricity-powered electrochemical CO₂ reduction (CO₂RR) is a route to the net-zero-emission production of chemicals and fuels that are currently produced via energy- and carbon-intensive industrial processes. Carbon monoxide (CO) is a common industrial feedstock and the input for Fischer–Tropsch-based production of hydrocarbon. CO can also be further reduced to multicarbon products (e.g., ethylene, acetate, and n-propanol) via CO electroreduction process. The conversion of CO₂-to-CO requires fewer electrons and protons (2e⁻/2H⁺) and has been achieved with near-unity selectivities (>90%) at industrially relevant reaction rates (>100 mA cm⁻²).

Electrochemical CO₂-to-CO conversion starts with the formation of *COOH intermediate. Surface adsorbed *COOH is then reduced to *CO via electron transfer and desorbed, as shown in eqs 1–3. An ideal CO₂-to-CO catalyst would provide an adsorption strength that facilitates both *COOH formation and the *CO desorption steps.

\[
\text{CO}_2 + \text{H}^+ (\text{aq}) + e^- + \ast \rightarrow \ast \text{COOH} \quad (1)
\]
\[
\ast \text{COOH} + \text{H}^+ (\text{aq}) + e^- \rightarrow \ast \text{CO}^* + \text{H}_2\text{O} \quad (2)
\]
\[
\ast \text{CO}^* \rightarrow \ast \text{CO} + \ast \quad (3)
\]

Present-day low-temperature CO₂-to-CO conversion is performed on heterogeneous catalysts such as silver (Ag), gold (Au), and palladium (Pd). Ag and Au exhibit the highest selectivities to CO (>80%). Ag can mediate CO₂-to-CO conversion at practical productivities >100 mA cm⁻². However, this high activity comes at the expense of high overpotentials. A practical level of activity (CO partial current density of >150 mA cm⁻²) at low applied potentials (<−1 V versus the reversible hydrogen electrode (RHE)) are required for the practicality of the CO₂-to-CO conversion process. Au achieves CO₂ conversion at lower overpotentials but suffers low selectivity (<90%) at production rates greater than 100 mA cm⁻²; as the hydrogen evolution reaction (HER) takes over. These limitations prevent conventional Au and Ag catalysts from achieving high energy efficiency at industrially relevant reaction rates.

Here we report an activity promoting strategy that combines the selectivity of Ag with the activity of Au, reduces the energy barrier for CO₂ activation, and thereby enables high energy efficiency CO₂-to-CO conversion. Using density functional theory (DFT) calculations, we find that undercoordinated Au atoms at the AgAu interface significantly decrease the formation energy of *COOH (CO₂ + H⁺ + e⁻ → *COOH), reducing the overpotential in CO₂-to-CO conversion.

We implement the Au-doping strategy on planar catalysts (sputtered Ag on porous polytetrafluoroethylene (PTFE) with Au-doping via galvanic replacement, 2D AgAu), and high-surface-area catalysts (Au-doped Ag nanoparticles on 2D AgAu...
and 3D AgAu; see Supporting Information methods for details). In a gas diffusion electrode-based flow cell electrolyzer, 2D AgAu and 3D AgAu catalysts yield CO FEs exceeding 90% at CO partial current densities up to 165 and 350 mA cm\(^{-2}\), respectively. These AgAu catalysts exhibit \(\sim\)200 mV lower onset potentials compared to the undoped Ag controls.

In a membrane electrode assembly (MEA) electrolyzer, the 3D AgAu catalysts enable CO FEs of >90% and CO full-cell EEs of >30% over a wide range of CO partial current densities from 105 mA cm\(^{-2}\) to 240 mA cm\(^{-2}\). The MEA system equipped with a 3D AgAu catalyst enables stable CO electrosynthesis for 60 h at a current density of 200 mA cm\(^{-2}\), with an average CO FE of 90% and average full-cell EE of 33%. At an average current density of 185 mA cm\(^{-2}\), the system also maintains an average single pass CO\(_2\) conversion of 33% for 60 h.

## RESULTS AND DISCUSSION

We analyzed the origins of the limitations of conventional Ag and Au catalysts at practical reaction rates (>100 mA cm\(^{-2}\)): (1) high cathodic overpotential on Ag and (2) high HER activity on Au. Using planar Ag/PTFE and Au/PTFE catalysts, we investigated the CO\(_2\)RR performance in 1 M KHCO\(_3\) over a voltage range of \(-0.41\) and \(-1.36\) V versus the RHE (see Supporting Information experimental procedures for details).

We found that CO partial current density increases with increasing applied potential on both Ag/PTFE and Au/PTFE catalysts (Figure 1a,b and see Supporting Information Tables S1 and S2 for additional experimental details). On Au/PTFE catalyst, the CO FE remains above 90% up to a current density of 60 mA cm\(^{-2}\) and a potential of \(-0.57\) V versus RHE (Figure 1a,b and see Table S1 for additional experimental details). A further increase in the current density results in HER dominating CO\(_2\)RR, and the partial current density is capped at \(\sim\)100 mA cm\(^{-2}\) at \(-0.71\) V versus RHE (58% CO FE at 176 mA cm\(^{-2}\) and at \(-0.88\) V versus RHE) (Figure 1a,b and see Table S1 for additional experimental details). On the Ag/PTFE catalyst, the CO selectivity remains above 90% up to a current density of 120 mA cm\(^{-2}\), albeit with a cathodic overpotential of \(-1.32\) V versus RHE (Figure 1a,b and see Table S2 for additional experimental details). The CO partial current density reaches its plateau of \(\sim\)160 mA cm\(^{-2}\) at \(-1.36\) V versus RHE (86% CO FE at 186 mA cm\(^{-2}\)) (Figure 1a,b).

To provide mechanistic insights into the electrochemical activity of Ag and Au toward CO\(_2\)-to-CO conversion, we carried out density functional theory (DFT) calculations of adsorption geometries and energetics (Figure 1c and see Figures S1–S3 for additional experimental details). The DFT calculations predict that the free energies to form *COOH...
**ΔG** - potential-determining step in CO₂RR - on pure Ag and Au are 1.61 and 1.38 eV, respectively (Figure 1c). Tafel analyses of CO productivities from CO₂ on pure Ag and Au give slopes of 137 and 44 mV dec⁻¹, suggesting that CO₂ + H⁺ + e⁻ → *COOH is the rate-limiting step for CO₂ reduction to CO (see Figure S4 for Tafel slopes). We then sought to find the possible materials structure combinations that would lower the free energy to form *COOH and found that the island models ("i") (i.e., islands of gold particles on Ag—Figures S1 and S2) lower the free energy required to form *COOH, such
that both \( \text{Au}(3 \times 3) - i@\text{Ag}(6 \times 6) \) (0.86 eV) and \( \text{Au}(3 \times 3) - i@\text{Ag}(7 \times 7) \) (0.78 eV) possess smaller \( \Delta G^*_{\text{COOH}} \) than \( \text{Ag}(1.61 \text{ eV}) \) and \( \text{Au}(1.38 \text{ eV}) \) (Figure 1c,d). The presence of undercoordinated Au in the island case led to preferential binding of \( ^*\text{C} \) species. Ag also has a higher affinity for \( ^*\text{O} \) and thus further stabilizes \( ^*\text{COOH} \). The configuration of \( ^*\text{COOH} \) here provides bifunctional binding sites for \( \text{C}^− - \text{Au} \) and \( \text{O}^− - \text{Ag} \)—a feature of the AgAu combination not present in pure Ag or Au cases due to the unstable Ag-bound with \( ^*\text{C} \) and the fully coordinated nature of Au. For island cases, the enhancement in \( U_{\text{L}}(\text{CO}_2\text{RR}) \) outweighs \( U_{\text{L}}(\text{HER}) \) (Figure 1d), due to the undercoordinated Au species. These findings suggest the opportunity to achieve, via AgAu catalysts, the combination of high CO productivity and low overpotential.

Encouraged by the DFT findings, we took the view that by decreasing the \( \text{CO}_2 \) activation barrier and suppressing HER on Ag—via Au islands—we could lower the overpotential toward \( \text{CO}_2 \)-to-CO conversion and thereby attain high EE.

To test this hypothesis, we prepared a set of 2D AgAu catalysts with different morphologies using a galvanic-replacement reaction. The galvanic replacement was performed by immersing Ag/PTFE catalysts in a homogeneous mixture of deionized (DI) water and acetone containing 1 mM AuCl₃ for various durations, from 5 to 30 min (see Supporting Information methods for details). Scanning electron microscopy (SEM) images show the growth of adparticles on the surface of the Ag NPs. 15 min of galvanic replacement between the Ag and Au atoms leads to growth of small islands on the surface of the Ag NPs. Scale bars are 50 and 20 nm, respectively. TEM images of the Au-doped Ag NPs. Scale bars are 100 and 50 nm, respectively. (e, f) TEM images of the Au-doped Ag NPs. Scale bars are 50 and 20 nm, respectively. (g) HAADF-STEM image of the 3D AgAu catalysts. (h) EDX elemental mapping of Ag. (i) EDX elemental mapping of Au. (j) EDX elemental mapping of Au and Ag. Scale bars of HAADF-STEM images and EDX mappings are 50 nm. Note: 3D AgAu catalyst stands for Au-doped Ag NPs supported on planar 2D AgAu catalyst (each with the galvanic-replacement duration of 15 min).
doping (Figure 2c). We detected similar negative shifts and spectra for galvanic-replacement durations ranging from 5 to 30 min, indicating that Au modifies the lattice of Ag prior to forming islands of Au adparticles on the surface. We then carried out in situ X-ray absorption spectroscopy (XAS) measurements and confirmed the alloyed AgAu structures via the extended X-ray absorption fine structure (EXAFS) analysis. Through EXAFS fitting, we found a decrease of Au coordination with galvanic-replacement durations in the range of $10^{-15}$ min, signifying the formation of surface Au adparticles at the AgAu alloy interface under these conditions (Figure 2d,e and see Figures S8–S11 and Table S3 for additional XAS data). With longer replacement durations we observed an increase in the density of Au adparticles (Figure 2d and see Figures S8–S11 and Table S3 for additional XAS data), in agreement with the SEM results (Figure S4).

We assessed the initial CO$_2$RR performance of the 2D AgAu catalysts in a flow cell with 1 M KHCO$_3$ liquid electrolyte (see Figure S12 and Tables S4–S6 for performance data). With galvanic-replacement durations in the range of 0–15 min, the peak CO partial current density increases from 160 to 183 mA cm$^{-2}$, with a reduction in the corresponding cathodic overpotential from $-1.34$ to $-1.16$ V versus RHE (Figure 1a,b and see Tables S4–S6 for additional performance data). Tafel analyses of CO productivities from CO$_2$ on 2D AgAu exhibit a slope of 82 mV dec$^{-1}$, lower than that of Ag (137 mV dec$^{-1}$) (see Figure S4 for Tafel slopes), indicating a faster electron transfer for CO formation. Further extending the duration (from 15 to 30 min) did not improve performance, instead leading to a higher HER activity and a lower peak CO partial current density (see Figure S12 and Tables S6–S8 for additional performance data)—outcomes we attribute to excessive Au surface coverage. Despite the HER activity at low applied potentials ($\sim-0.4$ V versus RHE), the 2D Ag catalyst combines high CO selectivity and low overpotential at reaction rates $>120$ mA cm$^{-2}$ (Figure 1a,b).

To further boost current densities at similar cathodic overpotentials, we sought to extend the reaction interface by translating the Au-doping strategy to a 3D catalyst motif, in which Au-doped Ag nanoparticles (NPs) are supported on 2D AgAu catalysts (see Supporting Information methods for details and see Figure 3 and Figures S13–S16 for the ...
Figure 5. CO$_2$-to-CO conversion performance of 3D AgAu and Ag control catalysts in a catholyte-free membrane electrode assembly (MEA) electrolyzer. (a) CO FE and CO partial current density versus full-cell potential for 3D AgAu and Ag control catalysts. (b) CO EE versus CO partial current density for 3D AgAu and Ag control catalysts. (c) CO concentration (molar ratio) at the cathode outlet versus reactant CO$_2$ flow rate for 3D AgAu catalyst. (d) Single pass conversion of CO$_2$ toward CO versus flow rate for 3D AgAu catalyst. (e) Extended single pass conversion of CO$_2$ toward CO at a constant full-cell potential of $-3.8$ V (an average current density of 185 mA cm$^{-2}$; humidified CO$_2$ with a flow rate of $\sim$15 sccm; 0.1 M KHCO$_3$ anolyte with a flow rate of 15 mL/min; ambient pressure and temperature). The black line represents the full-cell potential recorded during the extended CO$_2$ electrolysis (primary y-axis). Each green circle represents the single pass conversion averaged from three independent samples (secondary y-axis). (f) Extended CO$_2$-to-CO conversion performance of 3D AgAu catalyst at a constant current density of 200 mA cm$^{-2}$ (humidified CO$_2$ with a flow rate of $\sim$80 sccm; 0.1 M KHCO$_3$ anolyte with a flow rate of 15 mL/min; ambient pressure and temperature). The black line represents the full-cell potential recorded during the extended CO$_2$ electrolysis (primary y-axis). Each red square
The 3D AgAu catalysts maintained an SPC of 33% for CO2-to-CO conversion (Figure 5c,d). The 3D AgAu catalyst delivered a cathodic gas stream with a peak 48% CO (molar ratio) and a peak SPC of 34% for CO2-to-CO conversion (Figure 5c,d). When run at an average current density of 185 mA cm⁻², the 3D AgAu catalyst maintained an SPC of 33% during continuous operation (Figure 5e). Although constraining the flow rate of inlet CO2 to 15 sccm results in a decrease in productivity and energy efficiency, the 3D AgAu catalyst maintains a CO partial current density of ~130 mA cm⁻² and a CO energy efficiency of ~25%.

The 3D AgAu catalyst was stable, providing an average CO FE of ~90% and average CO full-cell EE of 32% for over 60 h of continuous operation (Figure 5f). We found, by performing SEM, EDX, and XPS, the catalyst maintained its morphology and composition through the extended CO2-to-CO conversion (see Figures S18 and S19 for the SEM, EDX, and XPS data).

In summary, we present an activity promoting strategy that enables low overpotential and selective CO2-to-CO conversion at industrially relevant reaction rates and EEs. We achieve this by developing AgAu catalysts synthesized through galvanic replacement between Ag and Au. Benefiting from the low energy barrier for formation of a key reaction intermediate (*COO⁻), we achieved onset potential reductions of up to ~200 mV over a wide range of CO partial current densities (100–400 mA cm⁻²). We demonstrated this strategy in both flow cell and MEA electrolyzer formats with neutral-media electrolytes. In an MEA electrolyzer, high-surface-area AgAu catalysts enabled CO FE of >90% and CO full-cell EEs of >30% up to a CO partial current density of 247 ± 6 mA cm⁻². The AgAu catalysts were stable, converting CO2-to-CO conversion for over 60 h at reaction rates (≥185 mA cm⁻²) under both high and low CO2 reactant availability conditions. The AgAu catalyst—in the context of its high selectivity, productivity, energy efficiency, and stability—is among the best low-temperature, neutral-media CO2-to-CO catalysts in literature (see Table S13 for comparison).
Authors
Adnan Ozden — Department of Mechanical and Industrial Engineering, University of Toronto, Toronto, Ontario MSS 3G8, Canada; orcid.org/0000-0003-2714-6408; Email: sinton@mie.utoronto.ca
Edward H. Sargent — Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario MSS 3G4, Canada; orcid.org/0000-0003-0396-6495; Email: ted.sargent@utoronto.ca
Yanjiang Liu — Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario MSS 3G4, Canada
Cao-Thang Dinh — Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario MSS 3G4, Canada; Department of Chemical Engineering, Queen’s University, Kingston, Ontario K7L 3N6, Canada; orcid.org/0000-0001-9641-9815
Jun Li — Department of Mechanical and Industrial Engineering, University of Toronto, Toronto, Ontario MSS 3G8, Canada; Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario MSS 3G4, Canada
Pengfei Ou — Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario MSS 3G4, Canada; orcid.org/0000-0002-3630-0385
F. Pelayo García de Arquer — Department of Electrical and Computer Engineering, University of Toronto, Toronto, Ontario MSS 3G4, Canada; orcid.org/0000-0003-2422-6234

Complete contact information is available at: https://pubs.acs.org/10.1021/acsaem.1c01577

Author Contributions
D.S. and E.H.S. supervised the project. A.O. and C.-T.D. conceived the idea. A.O. and C.-T.D. synthesized the AgAu catalysts and carried out all of the electrochemical experiments. A.O. carried out SEM, TEM, XPS, and XRD measurements. J.L. performed the XAS measurements. Y.L. and P.O. performed the DFT calculations and wrote the corresponding sections. A.O. wrote the manuscript. F.P.G.d.A. contributed to data analysis. All authors discussed the results and assisted during manuscript preparation.

Acknowledgments
We acknowledge financial support from the Ontario Research Fund: Research Excellence Program, the Natural Sciences and Engineering Research Council (NSERC) of Canada. X-ray absorption spectra were performed on SXRM beamlines at the Canadian Light Source (CLS), which is supported by the Canada Foundation for Innovation, Natural Sciences and Engineering Research Council of Canada, the University of Saskatchewan, the Government of Saskatchewan, Western Economic Diversification Canada, the National Research Council Canada, and the Canadian Institutes of Health Research. We acknowledge the Ontario Centre for the Characterization of Advanced Materials (OCCAM) for sample preparation and characterization facilities. J.L. acknowledges the Banting postdoctoral fellowship. D.S. acknowledges the NSERC E.W.R. Steacie Memorial Fellowship.

References


