

CARBON DIOXIDE REDUCTION

Geometry aids green carbon electrochemistry

Nanoscale texture of electrocatalysts, enabled by the tools of nanoscience, is emerging as an important lever for the control of electrochemical reaction pathways.

Adam J. Rondinone and Jingsong Huang

In October, the Intergovernmental Panel on Climate Change released Special Report 1.5 (SR1.5)¹, which details the state of the science and policy recommendations for the mitigation of climate change and reminds us that a suite of new technologies will be needed to fully replace our current fossil energy infrastructure. Accordingly, the recycling of CO₂ is one of the main aims in the fields of environmental and energy research; by developing means to convert the greenhouse gas to valuable fuels or chemical feedstocks, we might simultaneously achieve the goals of mitigating CO₂ emissions, reducing reliance on fossil sources and storing energy for later use. Biomass technology is extremely promising and already mature for some products, however alternatives will be needed to complement what biomass cannot replace. For over 40 years scientists have investigated electrochemical catalysis as a way to synthetically convert CO₂ to reduced molecules; if successful, this can be a way to store off-peak renewable electricity in the form of non-battery chemical energy for later use. Mixed results have been observed so far, due to challenges with selectivity, efficiency and reaction rate.

The conversion of CO₂ to any molecules with two or more carbon atoms requires the formation of a carbon–carbon bond — a crucial step that is one of the most difficult to achieve electrochemically. Like heterogeneous catalysis, electrochemical catalysis relies on random collisions of reactant molecules with each other and the electrode surface. The time that a reactant molecule is available for reaction in a volume is termed the ‘residence time’, which is a critical input for the reaction mechanism. The first reduction product of CO₂ may be either formate or CO; of these, CO is the key intermediate in the production of higher hydrocarbons or oxygenates in an electrochemical setting². CO tends to adsorb favourably on some metal surfaces such as copper, but the residence time simply isn’t long enough on a flat surface to allow a high percentage of oligomerization, which limits production of molecules with three

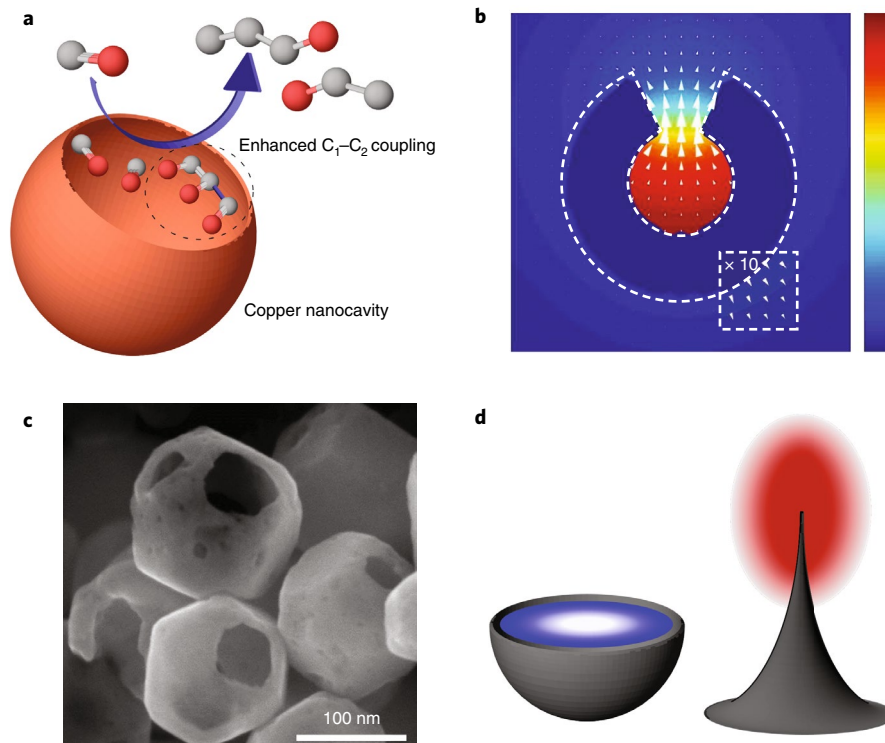


Fig. 1 | Utilizing the nanoscale texture of electrocatalysts to direct product selectivity in electrochemical catalysis. **a**, Conceptual schematic of a nanocavity that promotes C₃ product formation via nanoconfinement of C₂ intermediates (grey, C; red, O). **b**, Results of finite-element method simulations showing high C₃ concentration (red is higher concentration than blue) and flux distribution (arrows) in the nanocavity due to the longer residence time of precursor molecules. **c**, Scanning electron microscopy image of open copper nanocavity structure. **d**, Nanoscale texture of electrocatalysts including negative and positive curvature can suppress or enhance electric field strength in the electric double layer. Panels **b** and **c** adapted from ref. ³, Springer Nature Ltd.

or more carbon atoms (C₃₊ molecules). The search for alternative metals and alloys that might improve oligomerization has so far been unsuccessful.

Now, writing in *Nature Catalysis*³, Sinton, Sargent and colleagues show, through simulation-based rational design of the nanoscale texture of an electrocatalyst, that C₃ product formation is promoted via nanoconfinement of C₂ intermediates. They used subtle chemical and electrochemical processes to synthesize copper particles with tunable nanocavities (Fig. 1a–c). The

copper nanocavities were used to reduce CO electrochemically in a hybrid vapour–liquid phase electrolysis cell. Although both the exterior and interior surfaces of copper particles were active towards CO reduction, the researchers demonstrated that the confinement effect exhibited by the interior nanocavities could lengthen the residence time of C₂ intermediates and increase oligomerization, thereby producing a higher percentage of C₃ alcohol than previously reported. The nanocavities therefore served as nanoflasks for reactions by trapping

intermediates inside for a longer duration. This strategy may be coupled with existing solar cell and CO₂-to-CO conversion technologies to reduce CO₂ to cost-effective renewable C₃ products.

The result is important because it demonstrates a critical point — that nanoscale or mesoscale texture can be a useful tool in the control of electrochemical processes. Electrochemical catalysis has, for many years, been focused on other aspects of the reaction pathway such as variability in oxidation states at the surface, double layer formation, chemisorption and physisorption energies. The typical electrochemical volcano plot does not take into account texture or confinement; in fact, most electrochemists want to avoid texture at all costs, and go to great lengths to polish and flatten surfaces because the texture will confound rate studies by introducing anomalous electric fields. However, a growing body of evidence suggests that texture is a useful lever to tune reaction kinetics and selectivity and even to search for novel reaction pathways^{4–6}.

Texture can provide the means to control diffusion and residence time through confinement, as shown by Sinton, Sargent and colleagues³, but can also change the electric field strength under electrochemical bias if the texture is reduced to an even smaller scale, thereby influencing electrochemical reactions^{7,8}. Texture at the nanometre-scale can be realized by the controlled formation of nanocavities in conducting surfaces, a task only made possible with the development of nanoscience tools and strategies. A prominent example is nanoporous carbon, which demonstrates the utility of nanocavities for supercapacitors⁹, where the negative curvature, especially at the

nanometre-scale, reduces electric field strength at the electrode surface (Fig. 1d, left) and makes a Faradaic (electron transfer) reaction less likely to occur, thus allowing higher surface charge density Q at elevated voltage V and accordingly higher energy density ($\frac{1}{2}QV$) to be achieved¹⁰. Alternatively, high positive curvature at the sharp tip of nanoneedles or nanospikes will increase the electric field^{4,5} and make Faradaic reactions more likely to occur (Fig. 1d, right)¹¹. The strong electric field may alter the frontier orbital energies of refractory reactants with a negative electron affinity, such as CO₂, and also lower the overpotential needed for electrochemical reductions through field electron emission¹², thereby improving reaction energy efficiency. These factors make it possible to directly reduce CO₂ to hydrocarbon or oxygenate by one-pot synthesis instead of using CO as the feedstock^{5,6}.

Looking forward, advances will still need to be made before these types of catalyst can be put to commercial use. One challenging aspect of using metallic catalysts under reductive conditions is their tendency to electrochemically reconstruct, which will slowly but detrimentally evolve the texture towards a different and perhaps less useful morphology. It is likely that novel alloys or multilayer structures will be necessary to mitigate reconstruction while maintaining the right chemisorption energies. However, these are solvable materials science problems.

This work convincingly demonstrates the principles necessary to electrochemically produce heavier hydrocarbons or oxygenates, but the ultimate goal is to produce even heavier molecular weights that approximate gasoline, diesel, or the myriad components of crude oil. Looking at

heterogeneous catalysis as a model, further implementation of confinement could be an option — perhaps in a sequential manner — to trap molecules in a reactive setting where oligomerization is more likely to occur until the intermediate is no longer able to remain in the pore due to its increased size. Possibly, confinement could be incorporated as a step in a sequential catalysis scheme wherein heavy oligomeric intermediates produced by confinement become preferred reactants for unconfined reaction sites. The key challenge will be to find the right reaction mechanisms to achieve targeted products (selectivity) without sacrificing overpotential (efficiency) or reaction rates (activity). □

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