

Investigating the Behavior of Cu-based Catalysts During Electrochemical CO₂ Reduction with Liquid Cell Electron Microscopy

See Wee Chee, Aram Yoon, Rosa Aran-Ais, Ruben Rizo, Philipp Grosse and Beatriz Roldan Cuenya
Fritz Haber Institute of the Max Planck Society, Berlin, Berlin, Germany

The electrochemical reduction of CO₂ (CO₂RR) into useful hydrocarbons is a promising strategy towards the sustainable conversion of renewable energy. By turning emitted CO₂ back into a condensed form, it further closes the artificial carbon cycle. Research efforts in CO₂RR, have been focused on finding electrocatalysts that are selective towards the desired products, such as ethylene, ethanol, 2-propanol, which can be used directly as fuels and base chemicals for the chemical industry. The main challenge with designing optimal electrocatalysts for this reaction is that it is inherently complex with several reaction pathways and multiple possible reaction products. It is known that Cu is the only catalytic material that produces the desired C₂-C₃ products in substantial amounts [1], but the reaction also requires a high overpotential and is, thus, energy inefficient. Research over the years have shown that the selectivity is highly dependent on the morphological features of the electrocatalyst, including the shape, size and exposed surface facets [2]. However, we still have limited insight into the stability of these features during reaction, which hampers the practical implementation of CO₂RR as a technology.

Liquid cell electron microscopy can allow us to visualize the dynamical structures of working nanoparticle catalysts in an electrolyte and under electrified conditions [3]. In this talk, I will present recent work at the Fritz Haber Institute studying the dynamics in Cu nanoparticle (NP) catalysts for electrochemical CO₂RR using liquid cell electron microscopy. To understand the intrinsic behavior of these shaped controlled NPs without the influence of surfactants, we used an electrochemical synthesis method that was developed by our department using alternating potentials and CuSO₄ solutions containing Cl⁻ ions for stabilizing the cubic morphology. In Figure 1(a), we present *in situ* results illustrating the electrochemical deposition process, where Cu NPs of different shapes are first deposited at reductive potentials, whereas at moderate oxidizing potentials, we observe the selective dissolution of the non-cubic NPs. Repeated cycling between the two potentials increases the number of retained cubic NPs. Then, the electrolyte is switched to the CO₂-saturated 0.1 M KHCO₃ solution by flowing the solution for 30 mins at open circuit potential. After that, a reductive potential of -0.7 V was applied to these nanoparticles. Figure 1(b) shows the results from one such experiment where a few different processes were observed at the same time, nanoparticle motion, nanoparticle dissolution and the growth of dendrites during the application of potential. These results suggest a high mobility of Cu species on the surface of the Pt electrode.

In addition to these microscopic observations, I will discuss our on-going efforts to complement these *in situ* experiments with chemical analysis and spectroscopy in order to investigate the behavior of bimetallic electrocatalysts.

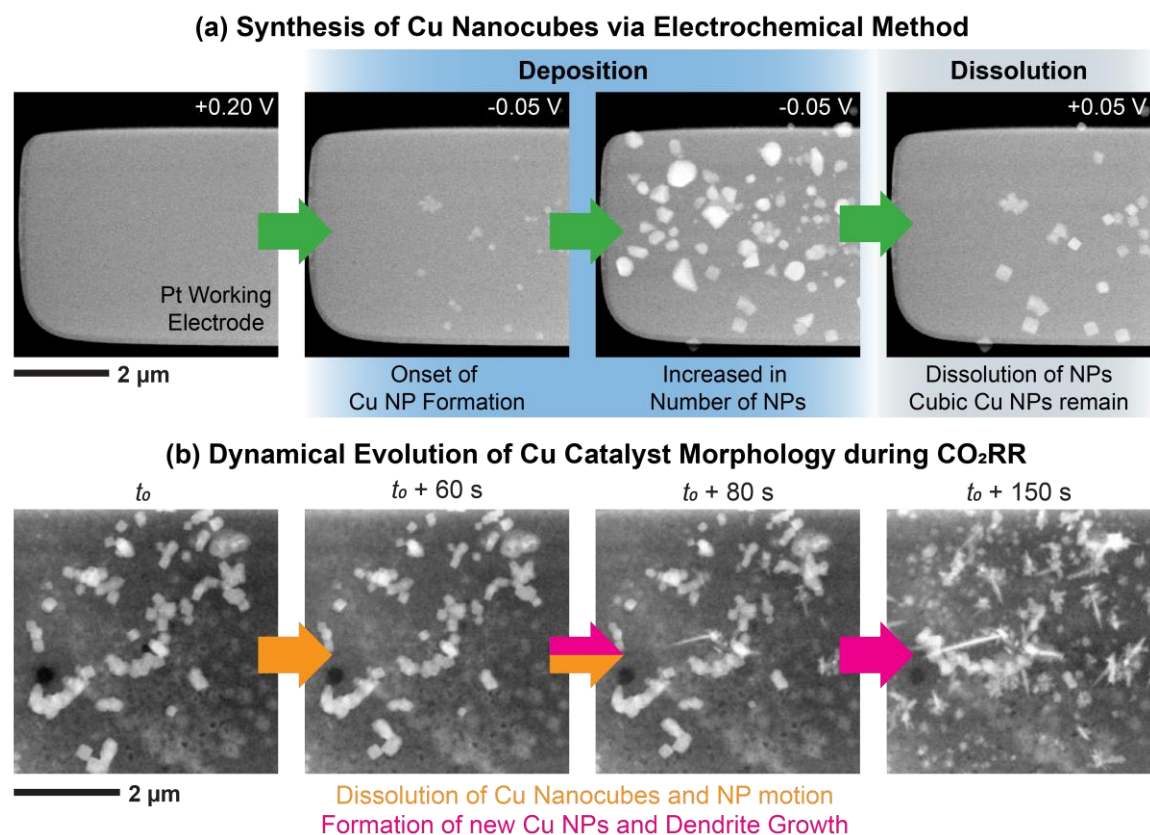


Figure 1. (a) Image sequence describing the formation of Cu nanocubes through an alternating electro-deposition protocol with a 5 mM CuSO₄ + 5 mM KCl solution, where we first see the deposition of nanoparticles of different shapes at reductive potentials, followed by the selective dissolution of non-cubic nanoparticles at oxidative potentials. (b) Image sequence describing the dynamical evolution of Cu nanocubes synthesized with the method described in (a) in 0.1 M CO₂-saturated KHCO₃ and at an applied potential of -0.7 V.

References

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- [2] D. Gao *et al.*, *Nat. Catal.*, 2, 3, 198–210, 2019.
- [3] F. M. Ross, *Science*, 350, aaa9886, 2015.