

## Enabling Structure-Property Correlation in Electrochemical Cell Transmission Electron Microscopy Studies of Electrocatalysts

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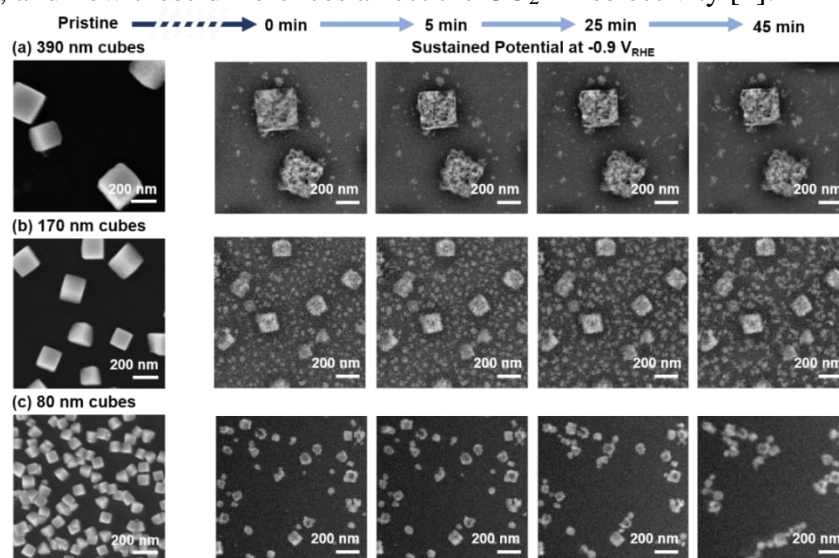
The design of better catalytic materials is crucial to the advancement of several energy and environmental technologies. However, determining how a catalyst's properties are related to its structure is not trivial. Catalysts are known to evolve during reaction, and the features of these dynamical structures must be identified to establish robust structure-property correlation. Probing electrocatalysts for electrochemical conversion reactions is especially difficult due to the limited tools we have for studying materials in a liquid at high spatial resolution. In this case, electrochemical liquid cell transmission electron microscopy (EC-TEM) [1] has the potential to greatly improve our understanding of the catalyst morphologies that exist in a liquid electrolyte and under applied potential. However, simply imaging these dynamical structures is not enough. We also need to relate these structures to their associated properties that are obtained from bulk electrochemical and reaction product measurements, which is also not straightforward.

Here, we address this challenge by focusing on catalyst synthesis strategies that generate model catalysts (1) highly tunable in terms of catalyst surface facet, size and loading and (2) broadly applicable to different support geometries such that we can have near identical electrocatalysts in both EC-TEM and benchtop setups. We illustrate this concept in an example reaction where we studied Cu-based electrocatalysts for the carbon dioxide reduction reaction (CO<sub>2</sub>RR), an important chemical conversion reaction for the revalorization of CO<sub>2</sub>. The catalysts (Cu<sub>2</sub>O cubes) were synthesized by electrodeposition [2] and by tuning the electrodeposition parameters, we were able to control both size and loading of the cubes. Our series of EC-TEM studies using cubes of different sizes (Figure 1) indicated that drastic reconstructions already occurred in a first few minutes of the reaction [3]. Notably, we found that nanoporous cubic frames and re-deposited nanoparticles (NPs) coexisted under reaction conditions. With extended reaction time, the larger cubic frames stayed relatively stable, whereas the re-deposited NPs moved and aggregated into larger clusters. These aggregated structures and the smaller cubes can also detach from the working electrode during reaction.

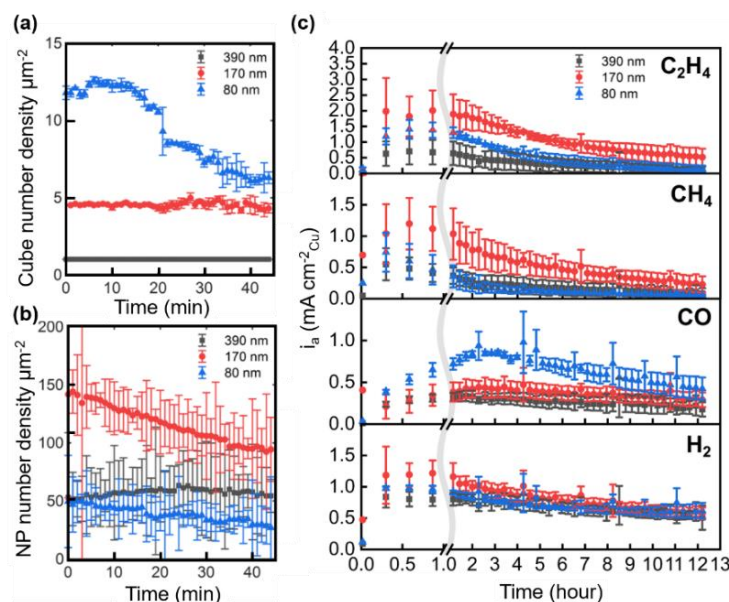
The dynamical behaviour of these differently sized cubes can be further correlated with their time-resolved changes in product selectivity. In Figure 2, we compare the loading of cubes and re-deposited NPs that were extracted from the *in-situ* movies with the partial current densities towards the four main gaseous products, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, CO and H<sub>2</sub>. In general, the overall decrease in product evolution over time correlates with the loss of catalyst particles during reaction. More interesting, our results indicate that the selectivity towards high value products i.e., CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> is sensitive to the restructuring induced loading under reaction conditions. Here, the best performing catalyst is not the one with the highest initial load (80 nm), but the one that has the highest combined loading of cubes and re-deposited NPs. This work highlights how ensemble effects can also arise from morphological changes during reaction.

In the presentation, I will also discuss our recent results using lithographically patterned Cu particle arrays to understand how chemical species in the electrolyte can alter the re-structuring behaviour under

reaction conditions, and how these differences affect the CO<sub>2</sub>RR selectivity [4].



**Figure 1.** Evolution of (a) 390 nm, (b) 170 nm, and (c) 80 nm Cu<sub>2</sub>O cubes at pristine, 0, 5, 25, and 45 min after applying a potential of  $-0.9 V_{RHE}$  in CO<sub>2</sub> saturated-0.1 M KHCO<sub>3</sub>. Each image is an average of 10 frames. The electron flux used is  $3.5 e^- \text{ \AA}^{-2} s^{-1}$ . Modified from [3].



**Figure 2.** Comparing morphological parameters and catalytic performance: (a) The number density of cubes (390 nm: black square, 170 nm: red circle, 80 nm: blue triangle) and (b) the number density of the re-deposited NPs extracted from in situ CO<sub>2</sub>RR experiments collected over 45 min. (c) Faradaic efficiencies of four gaseous products over 12 hours of CO<sub>2</sub>RR at  $-1.1 V_{RHE}$ . Modified from [3].

#### References:

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