Insights into the Structural Dynamics of Cu@Ag Core-Shell Nanoparticles during CO2 Reduction

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Electrochemical CO2 reduction reaction (eCO2RR) is one of the most promising and sustainable approaches to CO2 conversion to reduce atmospheric CO2 concentrations and mitigate the impacts of climate change [1]. For this purpose, the use of metallic nanoparticles (NPs) as electrocatalysis is on the rise, with Cu/Ag bimetallic interfaces being particularly popular for enhancing the eCO2RR towards CO and C2 products [2]. However, the electrochemical performance and product distribution of Cu@Ag core-shell configurations can change drastically under reaction conditions, particularly during the first few minutes of the reaction. In this study, our goal is to reveal the underlying structural changes these NPs experience at the critical first steps of the eCO2RR to understand their structure-properties relationship.

In this study, we utilized EDS analysis and high-resolution electron tomography to characterize the evolution of the Cu@Ag core-shell NP structure. The electrochemical measurements were performed in a homemade two-compartment, three-electrode cell, where the TEM grid was used as the working electrode, allowing for direct observation of the NPs before and immediately after the crucial first minutes of the reaction.

The Cu@Ag core-shell NPs used were found to be oblate and not homogeneously covered by Ag, with atomic-sized pinholes that expose the Cu core. Based on 3D characterization of various nanostructures found after current application, we hypothesized a transformation pathway. We observed an enlargement of these pinholes, most likely caused by the catalytic activity of the Ag shell, resulting in Cu leaching and, subsequently, a complete structural transformation of the NPs. Remarkably, the transformed Cu-Ag core-shell structure almost doubles the production of CO, presumably due to the combined effect of the different structures at various stages of transformation, as these transformations do not occur simultaneously [3].

Through the combined use of electrochemistry and advanced electron microscopy techniques, we have gained a better understanding of the relationship between the structure and electrochemical properties of Cu@Ag core-shell NPs, and how this affects their electrocatalytic performance. This research enhances our knowledge of Cu@Ag core-shell configurations and provides insights into other largely immiscible metal combinations. The study emphasizes the significance of the crystallinity of the central metal nanoparticle in deciding the formation of a complete and uniform second metal shell, which will be the key parameter towards nanoparticle stability.

Graphic:

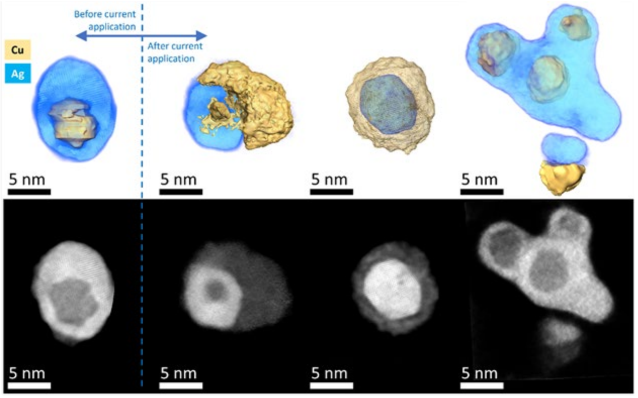

Figure 1. 3D reconstructions and their respective orthoslices through the reconstructed volume for the nanoparticles found before and after the CO2 reduction reaction.

Keywords:

Cu@Ag core-shell, CO2 reduction, Tomography

Reference:

[1] Garg, S. et al. Journal of Materials Chemistry A vol. 8 1511–1544 (2020).
[2] Chen, C. et al. Cu-Ag. Joule 4, 1688–1699 (2020).
[3] Huang, J., Mensi, M., Oveisi, E., Mantella, V. & Buonsanti, R. J Am Chem Soc 141, 2490–2499 (2019).