Characterization and dealloying of micelle-nucleated Ag_xAu_y nanoparticles by scanning electrochemical cell microscopy

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Bimetallic nanoparticles (NPs) are highly interesting electrocatalyst materials due to synergistic effects generated by their additional active sites [1], and the ability for tuning their activity by (electro-)chemical dealloying-treatments [2]. Synthesis routes using 0D confinement in micelles give enhanced control over composition and morphology of these bimetallic NPs [3]. However, an unavoidable distribution of catalytic performances and dealloying properties remains among NPs. This calls for electrochemical tools that offer activity measurements at the single-entity level. Scanning electrochemical cell microscopy (SECCM) is such a tool, probing electrocatalytic current locally in a nanodroplet cell, and collecting many data points on one sample that can be post-characterized by *e.g.,* scanning electron microscopy (SEM). This allows a direct correlation between NP activity and morphology/composition. The great potential of SECCM to probe single entities has already been demonstrated in correlative multi-microscopy studies [4] and the technique is being continuously developed further.
In this work, precursor-loaded reverse block co-polymer micelles are electrodeposited on a conductive substrate forming Ag_xAu_y alloy NPs. Electrochemical dealloying of these bimetallic NPs is then used to tune their electrocatalytic activity for the hydrogen evolution reaction. This is done locally with SECCM using a big probe to create areas of NPs in different states of dealloying on a single sample. In a second SECCM experiment, the NPs in the different areas are then characterized as to their specific activity and Ag:Au ratio, followed by co-located SEM. This data is linked with identical-location STEM (scanning transmission electron microscopy) and EDX (energy-dispersive x-ray spectroscopy) at a high number of particles at different dealloying states. Thus, statistical distributions of morphology and composition can be correlated with the statistical distribution of specific activity of dealloyed bimetallic nanocatalysts, paving the way towards a knowledge-based design of electrocatalysts.

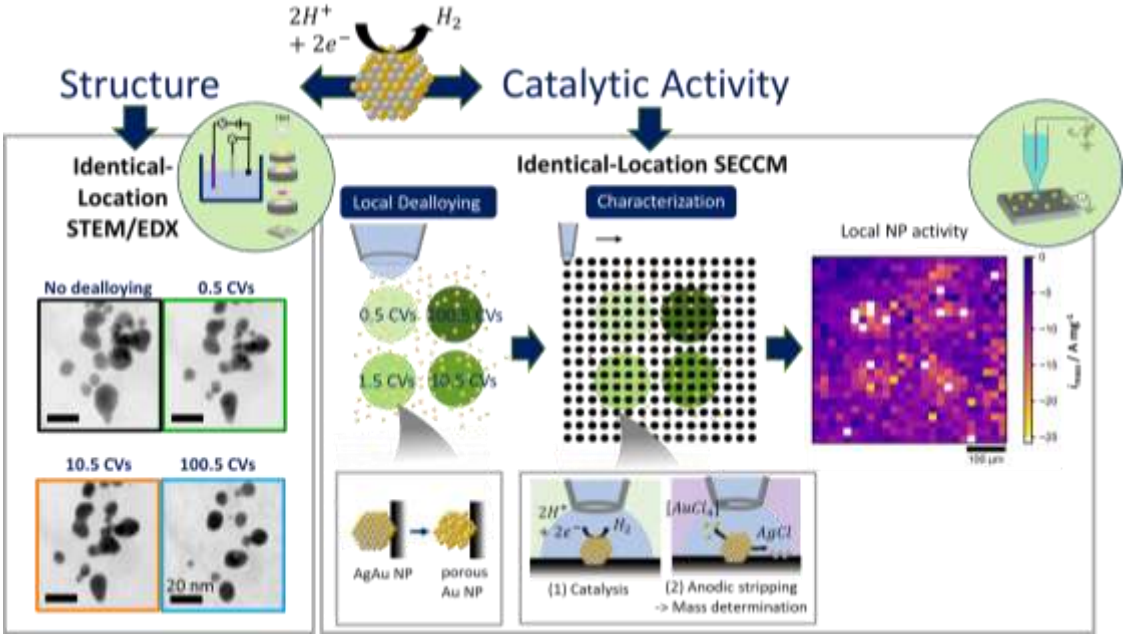

Figure 1. Schematic measurement concept for dealloying of Ag_xAu_y NPs by successive cycling in acid. Left: Identical-location STEM images of NPs at four different dealloying states (numbers of cycles). Right: Local dealloying with big SECCM tip, followed by catalytic activity measurements on many locations with a small tip for statistical analysis

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References

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