## Precise active sites for a unique performance: cluster catalysts in the electrochemical CO<sub>2</sub> conversion

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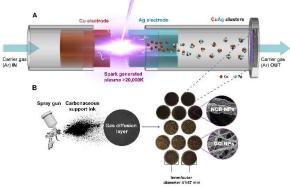
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## Abstract

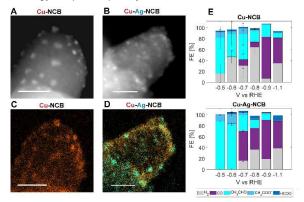
The electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR), is a promising technology to store renewable energy in chemical bonds. Unfortunately, Cu is the sole element that can catalyze CO<sub>2</sub>RR to C<sub>2</sub>-products. Further, both bulk Cu and Cu nanoparticles lack product selectivity.<sup>1</sup> Very recently, CuAg nanosurface alloys have been investigated as selective electrocatalysts to convert CO<sub>2</sub> to C<sub>2</sub>-products.<sup>2</sup> Notably, enhanced selectivity's to C<sub>2</sub>-products could be achieved but waned over time due the loss of the active site.<sup>2</sup> As cluster reactivity is greatly affected by size, elucidating the size effect is of tremendous fundamental importance. Unfortunately, cluster production methods with size control and high yields remain challenging. Here, we report a simple, scalable method to produce (bi)metallic clusters (~1 nm) via spark ablation (**Figure 1**).



**Figure 1.** Schematic illustration of the spark ablation (A) and immobilization (B) of the Cu(-Ag) oxide clusters on heteroatom doped carbonaceous (N-doped carbon and graphene oxide) support gas diffusion layer-based composites.

] that in situ, the clusters become fully metallic and maintain atomicity during the reaction. Our method shows

that using spark ablation, (bi-)metal oxide clusters free of ligands can be produced and successfully immobilized on carbonaceous supports offering a completely new design strategy for (electro)catalysts.



**Figure 2.** (A-D) STEM(-EDXS) images of the Cu and Cu-Ag oxide clusters on NCB support. E) Product distribution in CO2RR of the catalyst on the left.

## References

- Koolen, C. D.; Luo, W.; Züttel, A. ACS Catal. 2022, 948–973. https://doi.org/10.1021/acscatal.2c03842.
- Koolen, C. D.; Oveisi, E.; Zhang, J.; Li, M.; Safonova, O. V.; Pedersen, J. K.; Rossmeisl, J.; Luo, W.; Züttel, A. Nat. Synth 2023, 1–11. https://doi.org/10.1038/s44160-023-00387-3.



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