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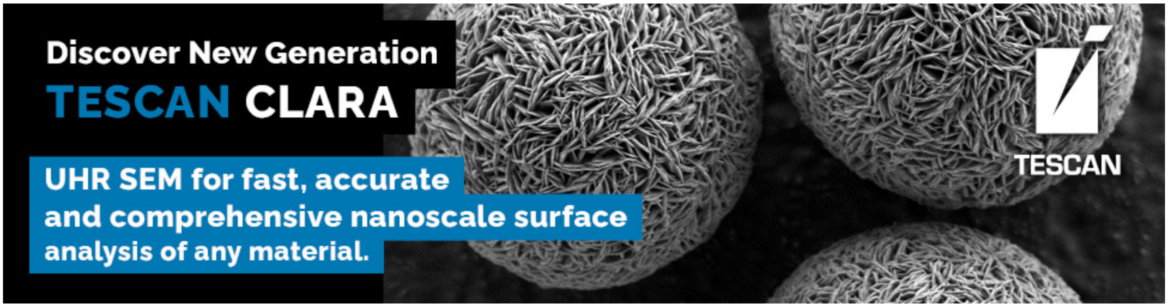

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Operando Electrochemical Liquid-Cell 4D-STEM Studies of Dynamic Evolution of Cu Nanocatalysts for CO_2 Reduction

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Since Cu remains the sole element for CO_2 reduction to valuable chemical products, significant efforts have been devoted to understanding reaction mechanisms of Cu electrocatalysts. However, there remains a longstanding debate over the active state of Cu catalysts, regarding valence state or coordination environments under CO_2RR. For instance, some reports have proposed Cu^+ species and subsurface oxide as possible active sites of oxide-derived Cu electrocatalysts, while others suggested the active state of bulk Cu catalysts is metallic as subsurface oxides are not stable under negative potentials.[1] In this work, we present a comprehensive *operando* correlative study of dynamic evolution of a family of monodisperse Cu NP ensemble (7-18 nm) electrocatalysts under CO_2RR [1]. *Operando* STEM and correlative X-ray methods provide definitive experimental evidence of active Cu sites as metallic Cu nanograins supporting undercoordinated sites for selective CO_2 electroreduction. *Operando* electrochemical liquid-cell scanning transmission electron microscopy (EC-STEM) and low-dose 4D-STEM resolve nanoscale dynamic morphological and structural evolution in thin liquid (~100 nm thick) enabled by electrogenerated H_2 bubbles [2, 3]. *Operando* EC-STEM enables quantitative electrochemistry and simultaneous quantitative STEM imaging, diffraction and spectroscopy at high spatiotemporal resolutions (Fig. 1).

The HAADF-STEM and virtual BF-STEM images show the 7 nm NP-derived loosely connected Cu nanograins formed at 0 V (Figs. 2a-b). 4D-STEM dark-field imaging, based on diffraction spots of 1 (red), 2 (green) and 3 (blue) from a metallic Cu domain in Fig. 2c, yielded a false-color map showing crystal domains with the same/similar crystal orientations resembling those three diffraction spots (Fig. 2d). 4D-STEM composite maps in Fig. 2d clearly show the highly polycrystalline nature of active Cu with fine nanograins. Two particular regions highlight the nanograin boundaries which are either loosely connected (Fig. 2e) or closely overlapped (Fig. 2f). To the best of our knowledge, this observation represents the first report of sub-10 nm nanograin boundaries supporting possible Cu active sites, at an unprecedented spatial resolution enabled by a probe size of ~1 nm. After electroreduction at -0.8 V, the metallic Cu nanograins (50-100 nm) achieved a steady-state closely packed structure (Fig. 2g). A majority of diffraction patterns from Cu domains indicate polycrystalline metallic Cu (Fig. 2h). Few domains show a single-crystal-like metallic Cu feature close to the Cu[110] zone axis (Fig, 2i). False-color dark-field 4D-STEM maps, based on three diffraction spots in Fig. 2i, show that the majority of Cu nanograins are composed of individual grains separated by grain boundaries and/or stacking faults (white arrows, Fig. 2j). This in-depth structural analysis indicates that the dominant active Cu sites, formed at -0.8 V, are closely packed and highly polycrystalline metallic Cu nanograins, relative to loosely connected Cu nanograins formed at 0 V. Upon airflow to repel electrolyte in the EC-STEM cell, metallic Cu nanograins rapidly evolved into single-crystal Cu_2O nanocubes (Figs. 2k-n). Correlated *operando* high-energy-resolution fluorescence-detector (HERFD) X-ray absorption spectroscopy (XAS) reveals dynamic macroscopic changes in valence states and coordination environment. Statistical analysis of interparticle dynamics was probed by *operando* resonant soft X-ray scattering. The strategy described herein can serve as a general platform to resolve the complex nature of nanoscale electrocatalysts under real-time operating conditions across multiple time and length scales [4].

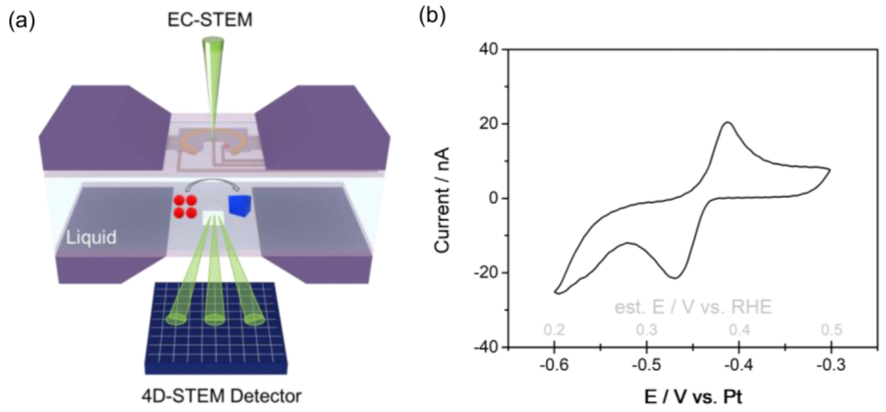

Fig. 1 (a) *Operando* electrochemical liquid-cell STEM equipped with 4D-STEM detector. (b) Cyclic Voltammetry of Cu nanoparticles with well-defined Cu_2O/Cu redox couples. Copyright 2023, American Chemical Society.

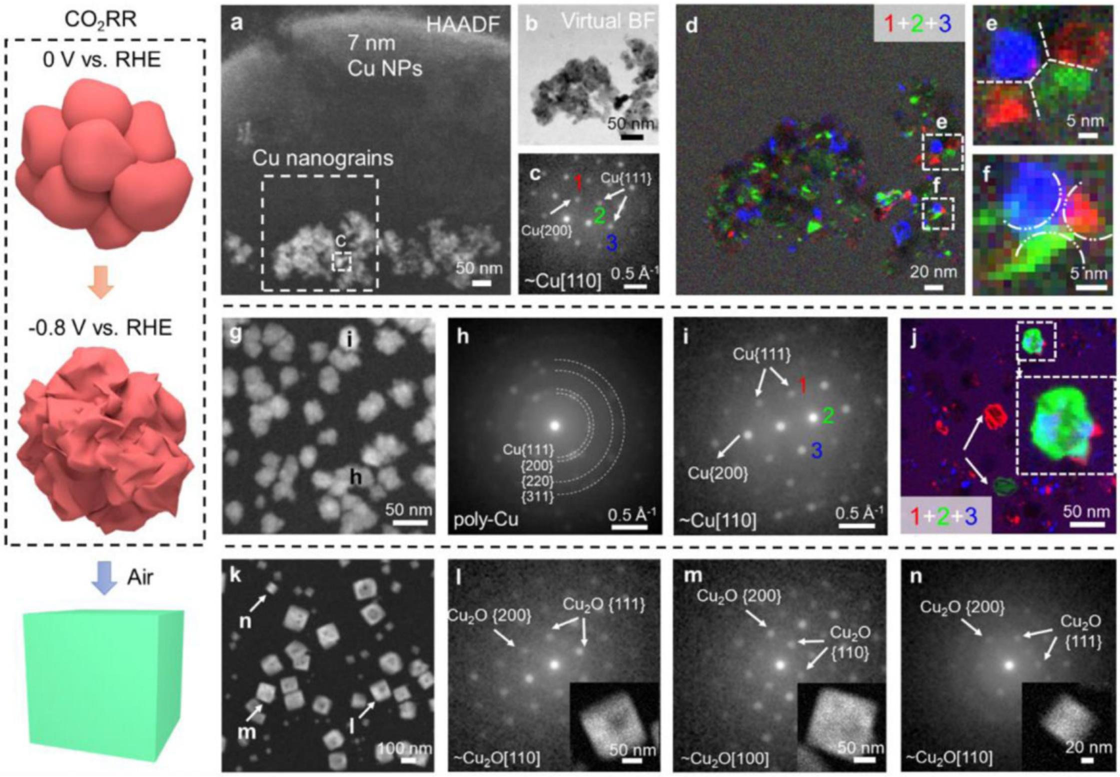

Fig. 2. *Operando* 4D-STEM diffraction imaging of dynamic evolution of Cu nanocatalysts. The left scheme serves as a visual guide of the structural evolution from initial stage of loosely connected (a-e) to steady-state closely packed (g-i) Cu nanograins followed by the rapid formation of Cu_2O cubes (k-n) when exposed to air. Copyright 2023, Springer Nature.

References

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3. Y Yang *et al.*, *ACS Energy Lett.* **7** (2022), p. 1292.
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