

***In-situ* Observation of the Degeneration Dynamics of Cu Nanowires under Carbon Dioxide Environment**

Xiaobing Hu^{1,2*}, Kun He^{1,2}, Cesar Jared Villa¹, Stephanie M. Ribet¹, Paul J. M. Smeets^{1,2}, Roberto dos Reis^{1,2} and Vinayak P. Dravid^{1,2}

¹ Department of Materials Science and Engineering, Northwestern University, Evanston, IL, USA.

² The NUANCE Center, Northwestern University, Evanston, IL, USA

* Corresponding author: xbhu@northwestern.edu

Atmospheric carbon dioxide (CO₂) levels, the main constituent of greenhouse gases, have been rising steadily since the industrial revolution, creating a global warming effect, with widespread impending environmental consequences. To reduce the concentration of CO₂ in the atmosphere, besides decreasing the emission, conversion of CO₂ to other carbon-based products is an economically and environmentally attractive strategy to reduce greenhouse gas levels. One of the most used conversion techniques is the hydrogenation of captured CO₂, which not only reduces the concentration of CO₂ but also results in the production of fuels and other value-added products [1, 2]. Catalysts play a key role in this hydrogenation reaction to accelerate the reaction kinetics. Among different kinds of metal catalysts, Cu is particularly promising, considering its low cost and high natural earth abundance (67 ppm). To date there are limited high spatial resolution investigations on the degeneration behavior of Cu catalyst particularly under *operando* conditions. Since the CO₂ gas can be regarded as an oxidant, one critical failure mechanism of Cu catalyst is believed to be oxidation. Even though there are numbers of studies related to Cu oxidation in an oxygen environment [3, 4], the failure mechanism of Cu catalysts during the catalysis process under CO₂ environment remains unclear, in part due to the difficulty in achieving sufficient spatial and temporal resolution for an *in-situ* process.

By creating a sealed gas environment in a (scanning) transmission electron microscope (S/TEM) column, the details of the degradation process of the catalyst can be studied in real-time under different gas conditions with sufficiently high spatial and temporal resolution. The thermal stability of catalysts in different gas environments can be mimicked, which provides fundamental insights into understanding the failure mechanism of the catalyst. Herein, we address the failure mechanism Cu nanowires (NWs) under CO₂ atmosphere [5]. By means of *operando* S/TEM observations, the degeneration processes of Cu NW were monitored during exposure to 760 Torr CO₂ pressure and a temperature of 200 °C. We reveal that the oxidation initiates from one end and gradually expands to the other end along the growth direction for a clean Cu NW with a smooth surface (negligible native oxide). When there is significant native oxide and increased surface roughness, this oxidation proceeds from outside to the center along the normal direction of the broad surface. The side-to-side oxidation is comprised of numerous end-to-end oxidation paths at a very localized area as the oxidation process initiates at multiple defect areas. For both the large-scale end-to-end oxidation and localized end-to-end oxidation, the evolution of the Cu/void interface and growth of the oxide layer approximately follows linear kinetics. This work demonstrates how an experiment with an *in-situ* gas holder in a TEM can be used to study the evolution of a nanoscale catalyst, which has implications for many other catalytic systems [6, 7].

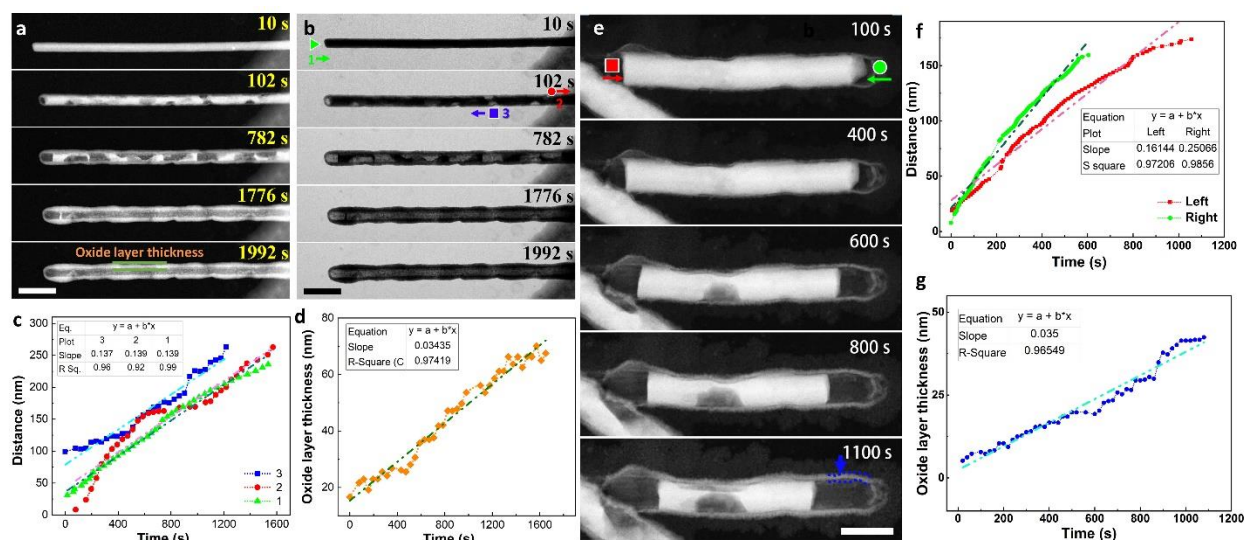


Figure 1. Quantitative analysis of the oxidation dynamics of a Cu NWs with (a-d) rough surfaces and (e-g) smooth surfaces. Simultaneous (a) HAADF and (b) BF image series showing the dynamic morphological change of the Cu NW with rough surface in CO₂ gas environment. Scale bar is 500 nm. (c) Variation of the interfaces position during reaction process. The green, red and blue curves track three different Cu/void interfaces indicated in (b). (d) Thickness changes of the oxidation layer as time extended (0.034 nm/s). (e) HAADF image series showing the oxidation process of single Cu NW with smooth surface. The scale bar is 200 nm. (f) Evolution of the left-end and right-end Cu/void interfaces during the oxidation process. The red curve tracks the evolution of the non-free end interface. Green curve tracks the development of the free right end interface. (g) Evolution of the oxide layer thickness. The blue curve corresponds to oxide layer having the darker contrast as marked by the blue arrow in (e).

Reference:

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