

***In Situ* Study of Cu Oxidation in gas environment**

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Due to the increasing emission of CO₂ from different anthropogenic activities, the conversion from CO₂ to high-value multi carbon (C₂₊) production catalytic system has become the focus of interest for obtaining sustainable high-value multi carbon production by hydrogenation of captured CO₂. [1] Currently, even though there are numbers of studies related to the synthesis of catalysts, the failure mechanism of catalysts during the catalysis process remains unclear. By introducing the *in situ* gas system to the (scanning) transmission electron microscope (S/TEM), the details of the catalyst degradation process can be studied in real-time at different gas environments. The thermal stability of catalysts in different gas environments could be mimicked. Among different kinds of noble metal catalysts, Cu has attracted more attention in the catalysis field since its low cost and unique applications in converting carbon dioxide/carbon mono oxide to C₂₊ [2]. Therefore, the stability of different Cu polymorphs catalysis is critical for the engineering application.

Herein, this study addresses the failure mechanism of Cu in water vapor and CO₂ gas at 200 °C. By mean of *in situ* gas S/TEM, the oxidation processes of Cu nanowire (NW), and Cu nanosheet (NS) were monitored during exposure to CO₂ at 760 Torr and water vapor at 14 Torr at 200 °C. The time-sequential image series and videos reveal that the failure of the Cu catalyst is mainly caused by oxidation. The oxidation of Cu is dependent on surface facet and purity since Cu is easy to be oxide and there is always a native oxide on the surface. The morphology of Cu NW is shown in Figure 1(a). Based on the selected area diffraction (SAD) pattern shown in Figure 1(b), the growth direction of Cu NW is along. For the Cu nanowire, the oxidation initiated from one end and gradually expanded to another end along the growth direction of the NW, as shown in Figure 2. However, we also observed that this oxidation process can proceed from outside to inside along the normal direction of the broad surface. The detailed studies confirm the relationship between the oxidation path and the surface oxide. When there is no surface oxide in the Cu NW, the oxidation of Cu NW prefers the end to end path. When there is a lot of surface oxides, the oxidation follows the outside to inside path. Electron energy loss spectrum (EELS), energy dispersive spectrum (EDS) and SAD are used to confirm the phase and element evolution during the *in situ* gas study. The Cu nanosheet (NS) is easier to be oxidized compared to the Cu nanowire since there is more surface exposed to the gas environment. The oxidation of Cu NS prefers to start at the {110} facet which is the edge of the nanosheet. This study suggests the pristine condition of the Cu surface likely plays a key role in the degeneration process of the catalysts [3].

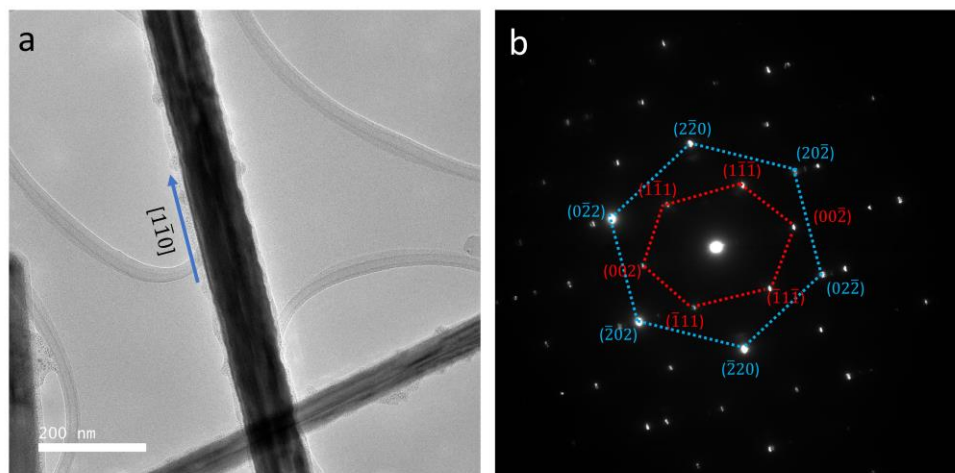


Figure 1. TEM image of Cu nanowire (a) and the corresponding selected area diffraction pattern (SAD) (b). The zone axes of yellow pattern is [111] and the zone axes of red pattern is [110]. The faces () are shared by red and blue patterns.

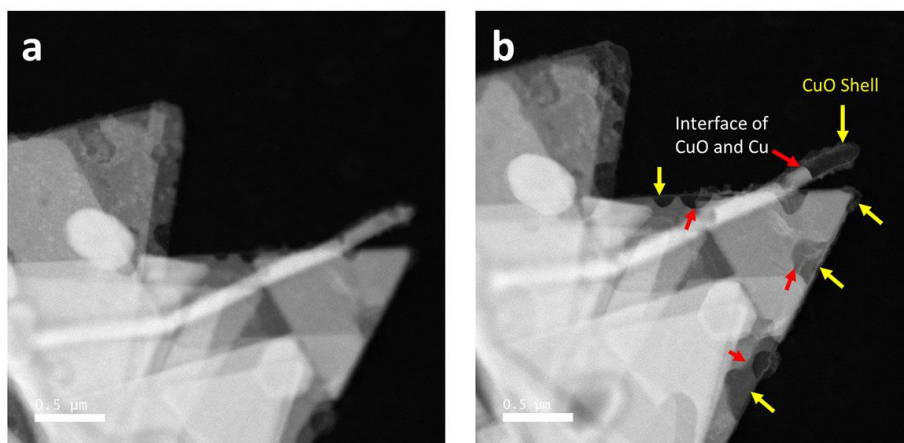


Figure 2. The oxidation of Cu nanowire and Cu nanosheet in CO₂ gas environment. Before oxidation (a) and in the middle of oxidation. The yellow arrows indicate the CuO shell, and the red arrows indicated the Cu and CuO interfaces.

References

- [1] C Liu, B Yang, E Tyo, S Seifert, J Debartolo, B Von Issendorff, P Zapol, S Vajda, and La Curtiss, *Journal of the American Chemical Society*, **137**(27) (2015). p. 8676-8679.
- [2] W Luc, X Fu, J Shi, J-J Lv, M Jouny, B H Ko, Y Xu, Q Tu, X Hu, J Wu, Q Yue, Y Liu, F Jiao and Y Kang, *Nature Catalysis* **2**(5) (2019). p. 423-430.
- [3] This work made use of the EPIC facility of Northwestern University's NUANCE Center, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205); the MRSEC program (NSF DMR-1720139) at the Materials Research Center; the International Institute for Nanotechnology (IIN); the Keck Foundation; and the State of Illinois, through the IIN. We thank Yijing Kang and Xianbiao Fu for contributing to the sample preparation. We gratefully acknowledge Rainer Straubinger and Jennifer McConnell from Protochips Co. for the technical support. We acknowledge Protochips Co. in the establishment of *in situ* gas system in NUANCE center at Northwestern University.