

In-situ Environmental TEM Observations of Structural Evolution of Oxygenated Cu(110) in CO

Xianhu Sun¹, Jianyu Wang¹, Xiaobo Chen¹, Shuonan Ye¹, Zhilu Liang¹, Judith C Yang², Guangwen Zhou^{1*}

¹Department of Mechanical Engineering & Materials Science and Engineering Program, State University of New York at Binghamton, Binghamton, NY, USA

²Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA, USA

Nearly all metals (except Au) are reactive in their functioning environment and spontaneously develop an oxygenated surface in ambient conditions.¹ This oxygenated surface governs the real-world interactions with the outer environment and plays a key role in heterogeneous catalysis. The oxidizing atmosphere can result in the oxygenation of the metal surface by inducing a sequence of surface restructuring. Meanwhile, the simultaneous presence of the reducing gas, such as CO from the feed gas in the water-gas-shift reaction, may induce de-oxygenation of the surface to form oxygenated compounds that desorb from the surface. Therefore, the competing action of the simultaneously present oxidizing and reducing gases may lead to complex spatial-temporal dynamic changes in the surface structure and composition under the reaction conditions. Atomically identifying the surface structure and composition evolution and associated reaction pathways under such complex reaction conditions is quite challenging. One way of circumventing such complexity is to first produce an oxygenated surface of the metal substrate, which is then exposed to CO to induce the de-oxygenation reaction. Herein, we use this two-step process of in-place preparation of an oxygenated Cu(110) surface by O₂ dosing, followed subsequently by partial de-oxygenation of the oxygenated surface with CO gas flow. The partial de-oxygenation process is dynamically monitored at the atomic scale with environmental transmission electron microscopy (ETEM).

Our ETEM experiments start with flowing O₂ into the TEM column with the gas pressure of 8×10^{-3} Pa at 623 K to burn amorphous carbon contaminant (Fig. 1a). This results in atomically clean Cu(110) facets that subsequently develop into the (2×1)-O missing-row reconstruction (Fig. 1b).² This (2×1) restructuring is characterized by Cu-O-Cu chains growing preferentially along the [001] direction in every other [110]-(1×1) spacing, as shown by the side and top views of the density-functional theory (DFT)-relaxed structure model in Fig. 1c.³ The (2×1)-O reconstruction observed from the in-situ TEM observation in Fig. 1b is confirmed by HRTEM imaging simulation using the DFT-obtained structure model in Fig. 1c. This (2×1)-O is further confirmed by scanning tunneling microscopy (STM) imaging of the Cu(110) surface with the similar O₂ dosing (Fig. 1d).

The Cu(110)-(2×1)-O surface is then exposed to the CO gas flow at 1.6×10^{-2} Pa and 623 K. Fig. 2 illustrates a time-sequence of HRTEM images obtained during the CO gas flow. Fig. 2a corresponds to the initially perfect (2×1) missing-row, showing the presence of 23 Cu-O-Cu columns within the field of view. After the time elapse of 8.8 s, the number of Cu-O-Cu columns decreases to 18 (Fig. 2b), thereby exposing locally the underlying bare (110)-(1×1) surface, as shown schematically by the inset in Fig. 2b. After 0.2 s in Fig. 2c, (3×1)-O reconstruction forms locally, resulting in coexistence of (2×1) and (3×1) as a result of the lateral migration of Cu-O chains to the bare (110)-(1×1) region. This is evidenced by the same number (i.e., 18 peaks) of Cu-O atomic columns in Fig. 2b and 2c. Upon the continued CO flow (Fig. 2d-f), the number of Cu-O chains (peaks) further decreases, and the (3×1) reconstruction becomes more outstanding, indicating the clear trend of the (2×1) → (3×1) transformation in CO.

Oxygen within the Cu-O chains can readily react with CO molecules to produce CO₂ that desorb from the surface in concomitant with gradual removal of surface oxygen. The (2×1) → (3×1) conversion directly reflects the loss of chemisorbed O. Interestingly, the newly formed (3×1) does not convert to (4×1) or (5×1) upon the continued loss of chemisorbed O. Instead, the (3×1) reconstruction maintains locally upon the growth of the bare (110)-(1×1) area (Fig. 2f), suggesting that the (3×1) is a stable surface configuration that may signal the balanced attractive and repulsive interactions between Cu-O-Cu chains. These in-situ ETEM observations provide the microscopic detail of reorganization of Cu-O-Cu chains upon the CO-induced loss of chemisorbed O. Correlated atomistic modeling will be performed to elucidate the CO adsorption, its reaction with chemisorbed O in the Cu-O-Cu chains to form CO₂, and the effect of the resulting oxygen vacancies on the (2×1) → (3×1) transformation.

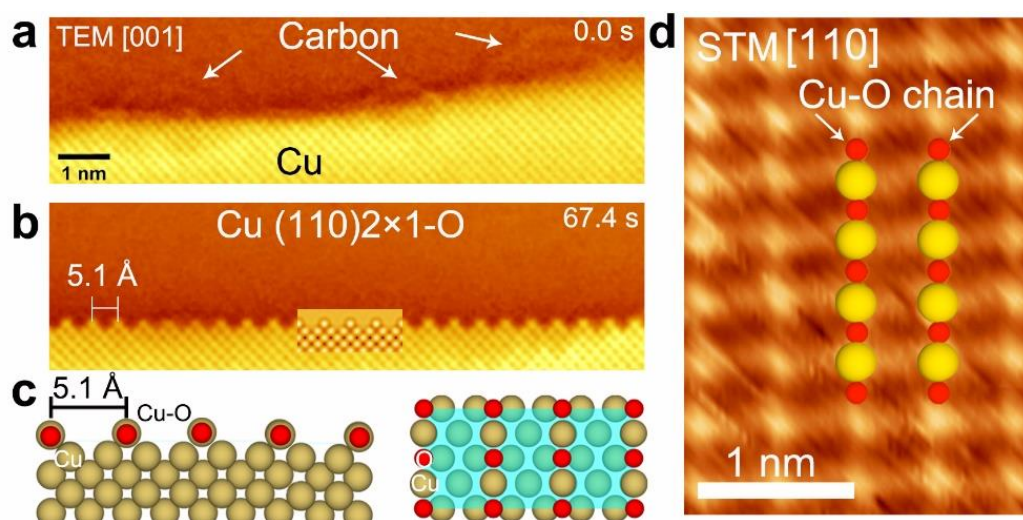


Figure 1 | Formation of Cu (110)-2×1-O reconstruction. **a**, HRTEM image of a pristine Cu (110) facet. **b**, HRTEM image of a Cu (110) after exposure to the O₂ gas flow at $p_{O_2} = 8 \times 10^{-3}$ Pa and $T = 623$ K. Inset is simulated HRTEM image. **c**, Side (left) and top (right) view of Cu (110)-2×1-O atomic models. **d**, STM image of the Cu(110)-(2×1)-O reconstruction.

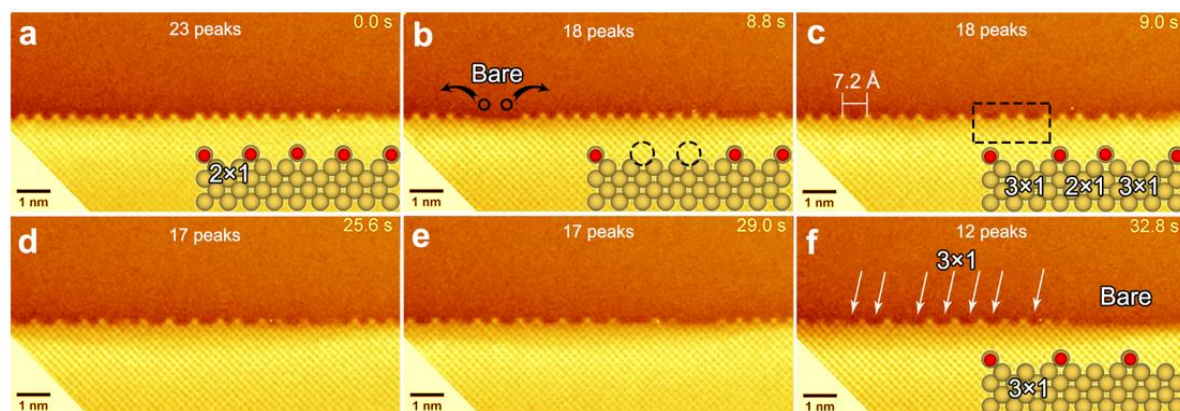


Figure 2 | In-situ TEM observations of the (2×1)-O → (3×1)-O on Cu(110). **a-f**, Time-sequence HRTEM images of Cu (110)-2×1-O reconstruction evolution in CO under $p_{CO} = 1.6 \times 10^{-2}$ Pa and $T = 623$ K.

References:

- [1] Sun, X. *et al.* Atomic- scale mechanism of unidirectional oxide growth. *Adv. Funct. Mater.* **30** (2020), 1906504.
- [2] Li, M., Curnan, M. T., Saidi, W. A. & Yang, J. C. Uneven oxidation and surface reconstructions on stepped Cu(100) and Cu(110). *Nano Lett.* **22** (2022), 1075-1082.
- [3] Li, L., Liu, Q., Li, J., Saidi, W. A. & Zhou, G. Kinetic barriers of the phase transition in the oxygen chemisorbed Cu (110)-(2×1)-O as a function of oxygen coverage. *J. Phys. Chem. C* **118** (2014), 20858-20866.
- [4] This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-SC0001135.