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1187 – In-situ Atomic-scale Visualization of Autocatalytic Reduction of CuO with H₂

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Metal oxides play an important role in a diverse array of technological applications ranging from heterogeneous catalysis to electronic devices and surface passivation. Oxide reduction is widely used to control the stoichiometry, phase, defects, bonding and atomic scale surface termination of oxides, thereby allowing for tuning their functionalities. Kinetically, two phenomenological models, the “nucleation and growth model” and the “interface model”, have been proposed to explain the oxide reduction process [1-3]. In the “nucleation and growth” model, generation of small nuclei of the reduced phase occurs on the parent oxide surface and the reaction interface increases until growing nuclei coalesce and then decrease, therefore resulting in a sigmoidal dependence of the extent of reaction on time. In the “interface model”, the rapid formation of a uniform and continuous layer of the reduced phase on the parent oxide occurs and the reaction boundary moves inward as the reaction proceeds. The dependence of the reaction rate follows a similar “exponential law” as the in later stage of the “nucleation and growth model”. Despite their difference, a common assumption in both models is that

the reaction is limited by the interface area between the reduced phase oxide and the parent oxide. Using environmental transmission electron microscopy (E-TEM) to visualize hydrogen-induced oxide reduction, here we find that the reaction follows an auto-catalytic process, which differs fundamentally from the two aforementioned kinetic models.

E-TEM allows to observe oxide reduction dynamics by flowing a reducing gas in the sample area while simultaneously probing atomic structure evolution from the outermost surface layer to deeper atomic layers [4,5]. In this work, we employ E-TEM to dynamically resolve atomic structure changes in both the surface and deeper regions of the CuO lattice in response to H₂ induced oxide reduction. The reaction between H₂ and CuO is chosen because of its relevance to various catalytic reactions including the water-gas-shift reaction, methanol synthesis and oxidation and oxidative dehydrogenation of alcohols. Here we show that the CuO reduction occurs via a two-stage process, that is, the slow reaction stage and the fast reaction stage. During the slow reaction stage, the oxide is reduced via the lateral flow of atomic steps. Meanwhile, loss of oxygen from terraces produces oxygen vacancies that migrate onto the subsurface to form an oxygen deficient phase in the subsurface. This results in the fast reaction stage, through which the reduction rate of the oxygen-deficient oxide phase is accelerated.

Fig. 1 is a time sequence of HRTEM images showing the two-stage CuO reduction at $p_{\text{H}_2} \approx 0.5$ Pa and $T \approx 300$ °C. The CuO surface initially exhibits a step-terrace morphology (red line in Fig. 1A) with the surface orientation of $\{110\}$, as revealed from the inset diffractogram. One monolayer of CuO has been reduced from the surface after 16 s via the step flow (the slow stage), seen by comparing the surface configuration with the initial position (red line). The reduction rate during this early stage is $0.03 \text{ nm}^2/\text{s}$ (plot in the righthand column), obtained by measuring the projected CuO area evolution with time. During the middle (Fig. 1B) and later (Fig. 1C) stages, two and three layers of CuO peel off from the surface during the same 16 s period, respectively, indicating an accelerated reaction kinetics (the fast stage). Such accelerated reduction is further confirmed by the faster reduction rate (Right panel in Fig. 1B and 1C). Careful inspections of the inset diffractograms in Fig. 1B and C show the presence of superlattice diffraction spots (red squares) that result from the self-ordering of oxygen vacancy in bulk [4,6,7], pointing to the accumulation of oxygen vacancies upon the oxygen loss from terraces. Density-functional theory calculations suggest a favorable sequential pathway of forming oxygen vacancies in the subsurface and the associated diffusion barriers [4]. The accumulation of oxygen vacancies in the subsurface facilitates the diffusion and the following departure of lattice oxygen from terraces (Fig. 2), therefore speeding up the oxide reduction. These results demonstrate the important effect of sub-surface dynamics on the surface reaction kinetics.

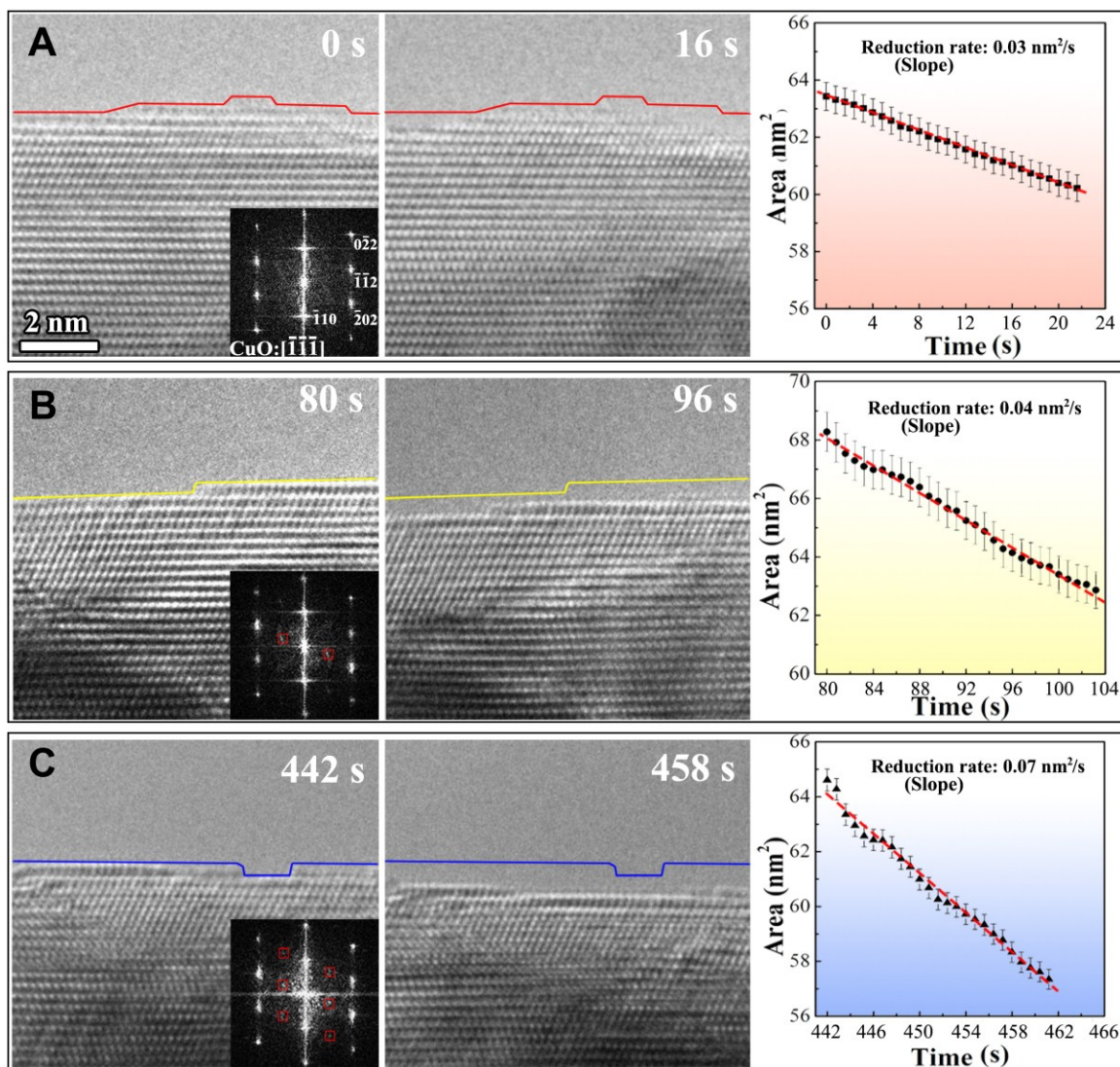


Figure 1. Figure 1 (A-C) Time-resolved HRTEM images at the early (A), middle (B) and late stages (C) of reduction of CuO under $p_{H_2} \approx 0.5$ Pa and $T \approx 300$ °C showing an accelerated reduction, as evidenced by the increased reduction rates in the right column.

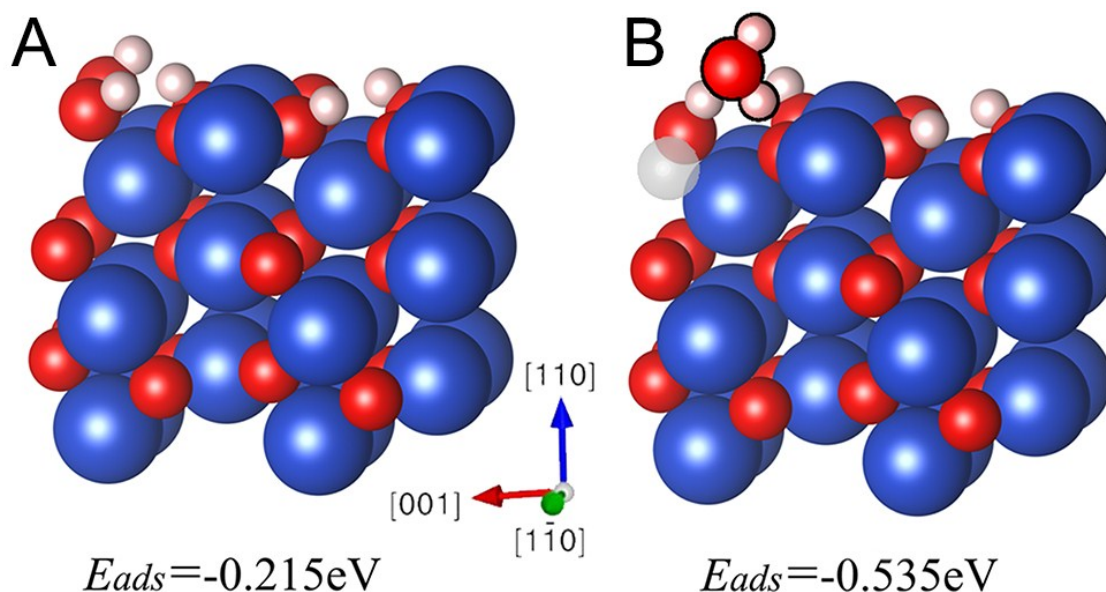


Figure 2. Figure 2 (A) Stable structure of CuO (-110) surface with five H atoms adsorption. (B) Adsorption of the sixth H atom leads to the formation of an H₂O molecule that spontaneously desorbs from the surface, resulting in an oxygen vacancy. Blue, red, pink, and gray balls represent Cu, O, H, and O vacancy, respectively.

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