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Real-Time Imaging of Surface Dynamics on CeO_2 Nanoparticles using Time-Resolved Aberration-Corrected TEM

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Oxygen exchange on CeO_2 (ceria) nanoparticle surfaces is often the rate limiting step in technological applications [1], and a nanoparticle's shape, size, surface composition, and surface atomic arrangement can all influence catalytic activity, meaning that each individual nanoparticle may have its own intrinsic chemical and physical properties. Consequently, the ability to accurately and quantitatively characterize nanocatalysts to locate 'active' sites is necessary to understand and tailor their behavior. In addition to differentiating between the functionally-relevant active structures and the passive spectator structures on a catalyst, the structural motifs may change during a single 'turnover' event of a chemical reaction [2]. An accurate description of a nanoparticle's surface structure therefore requires a technique that combines atomic spatial resolution with sensitivity to changes in the structure during a reaction. Advances in aberration-corrected TEM (AC-TEM) have vastly improved image resolution and quality, and the recent development of direct electron detectors has led to significantly improved performance in read-out speed and noise reduction over CCD imaging cameras [3]. Here, we demonstrate the use of *in situ* time-resolved AC-TEM on a CeO_2 nanoparticle to directly observe dynamic surface reconstructions with atomic spatial resolution and 2.5 ms time resolution.

An aberration-corrected FEI Titan ETEM equipped with a Gatan K2 IS direct detection camera (with high detective quantum efficiency) was used to image a ~2 nm CeO_2 nanoparticle at 400 frames/second and 10^5 $e^-/(Å^2 s)$ in vacuum ($<10^{-6}$ Torr). The position of each Ce atomic column in the nanoparticle in each 2.5 ms image frame was determined by fitting a 2D elliptical Gaussian to each lattice site. Local lattice expansions and contractions were observed on the (100) surface over short time periods (~0.2 s), and Figure 1 shows a representative expansion and contraction event over 0.5 s. Each image in Figure 1 is a 12.5 ms exposure image (five 2.5 ms images summed together). The distance between Ce atomic columns on the bulk-terminated (100) surface is 3.825 Å. As shown in Figure 1a, the distance between two (100) surface Ce atomic columns is 3.27 Å at 0.16 s, expands to 5.03 Å after 0.21 s (Figure 1b), and contracts back to 3.52 Å after an additional 0.2 s (Figure 1c). The separation distance between the two (100) surface Ce atomic columns highlighted in Figures 1a-c was determined for each 2.5 ms frame in the 0.5 s image sequence and is shown in Figure 1d. The blue points indicate measurements from each frame, the solid black line is a 5-period moving average trendline, and the dashed green line indicates the bulk-terminated (100) separation distance (3.825 Å). The blue windows represent the five image frames that were summed together to create Figures 1a-c. The expansion of the atomic columns occurs rapidly and is shown with 2.5 ms time resolution in Figure 2. In Figure 2a, the distance between the two (100) surface atomic columns is 3.77 Å. After 2.5 ms, the three surface atomic columns are absent from the image (Figure 2b). The surface lattice may be in a 'transition state' where the atoms in the surface columns are dynamically rearranging, causing weak image contrast that is undetectable or below the noise level of the imaging camera. In the next frame (Figure 2c), the contrast from the surface atomic columns is visible again, with the separation distance between the two atomic columns increasing to 4.43 Å. The expansion continues to

4.93 Å after an additional 2.5 ms, shown in Figure 2d. Although individual image frames of Figure 2 are quite noisy, we can still extract information about the precise time over which the surface lattice expansion took place. The local lattice expansion and contraction behavior was cyclical, occurring several times over the full set of experimental images (~20 s), and is likely related to surface oxygen exchange processes. Further details outlining intensity quantification to observe rapid atom migration will be presented [4].

References:
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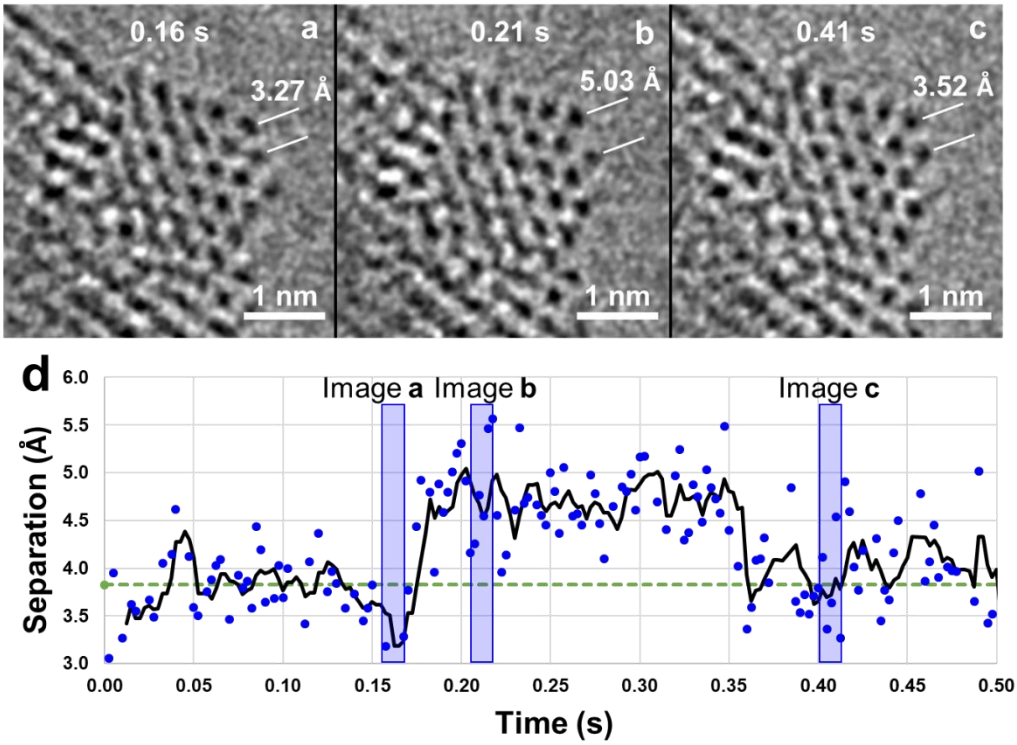

Figure 1. a-c) 12.5 ms exposure images demonstrating a local surface lattice expansion on the CeO_2 nanoparticle. **d)** Measurement of the separation of the two marked surface Ce atomic column over a 0.5 s image sequence.

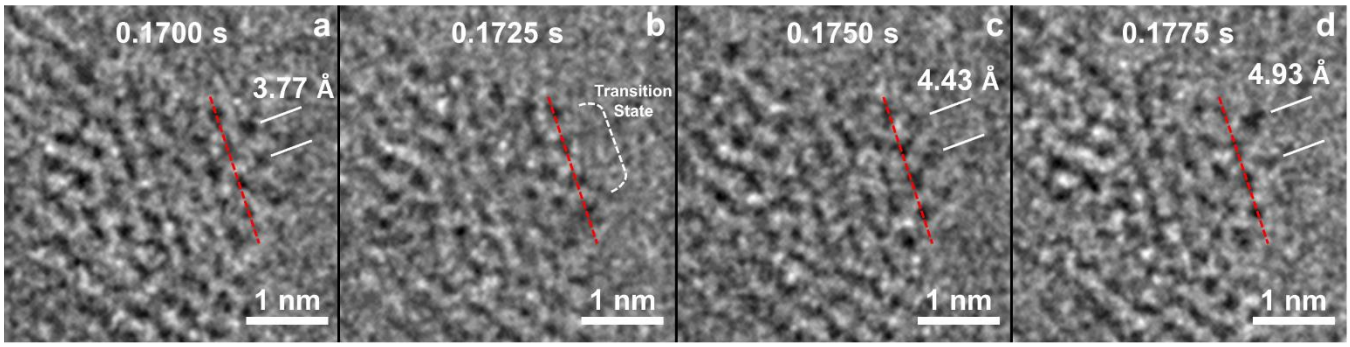

Figure 2. Images of local (100) surface expansion of CeO_2 nanoparticle with 2.5 ms time resolution. The dashed red line in each frame provides a guide to the eye for referencing the surface dynamics.

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