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Harnessing High Temporal Resolutions to Explore Fluxional Behavior on CeO_2 Nanoparticles under Reducing Conditions

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State-of-the-art, commercially available, direct electron detectors can acquire TEM image series at up to 1000 frames per second (fps), capturing 1 ms snapshots of a materials system undergoing dynamic structural re-arrangement. In materials science in general, and catalysis in particular, this time regime may provide information on reaction paths, mechanisms or intermediate and metastable states of an evolving system. For example, fast structural re-arrangements at the atomic level under reaction conditions, known as fluxional behavior, are of increasing interest in catalysis [1]. Unfortunately, characterizing these dynamic events in the presence of gases and external stimuli without sacrificing either temporal or spatial resolutions is still a major challenge due to signal-to-noise (SNR) limitations.

To mitigate the SNR limitations, we have employed a high electron beam dose to drive chemical change in CeO_2 nanoparticles. Time-resolved *in situ* TEM images show the fluxional behavior of nanoparticles in strong reducing conditions during illumination with a fluence rate of 120,000 $e^{-}Å^{-2}s^{-1}$ [2]. This electron fluence has been previously reported to induce surface CeO_2 reconfigurations at room temperature [3]. The 8913 frames time-series has been acquired in a Gatan K2 IS direct electron detector at 400 frames per second (2.5 ms each, 22.8 s in total), to track the evolution of CeO_2 fluxionality. New methodologies have been developed to deal first with large volume of data (almost 9,000 frames) and track atomic column positions and intensities in very noisy conditions [4, 5].

A summed image (22.28 s) showing the average structure of the nanoparticle under consideration is shown in Figure 1a. At its top surface, two faint atomic columns (pointed with red arrows) are vaguely visible. The weak intensity suggests that the contribution of these two columns to the average image is very low, indicating a low frequency of occupancy throughout the entire time series. Improving the time resolution to 50 ms by binning a smaller number of frames (20 frames) reveals the presence of very dynamic surface atomic columns, leading to structural re-arrangements of the nanofacet (Figure 1b, green arrows). The atomic configuration at these locations is changing from frame to frame, indicating that the lifetime of the structures is very low at this time scale (50 ms). Finally, temporal resolution has been improved to 2.5 ms per frame, as shown in Figure 1c. In addition to the surface reconfigurations happening on the 2.5 ms time frame, subsurface transformations are also observed with the appearance of local column streaking in the planes shown in the blue boxes (round shape on the left, blurred and streaked on the right). This image streaking may be related to the presence of shearing planes triggered by the electron beam removal of oxygen. Further analysis will be carried out to correlate the cationic migration observed at the top surface, where creation and annihilation of oxygen vacancies are required to allow cationic mobility, with the existence of local shear planes due to the lack of oxygen [6].

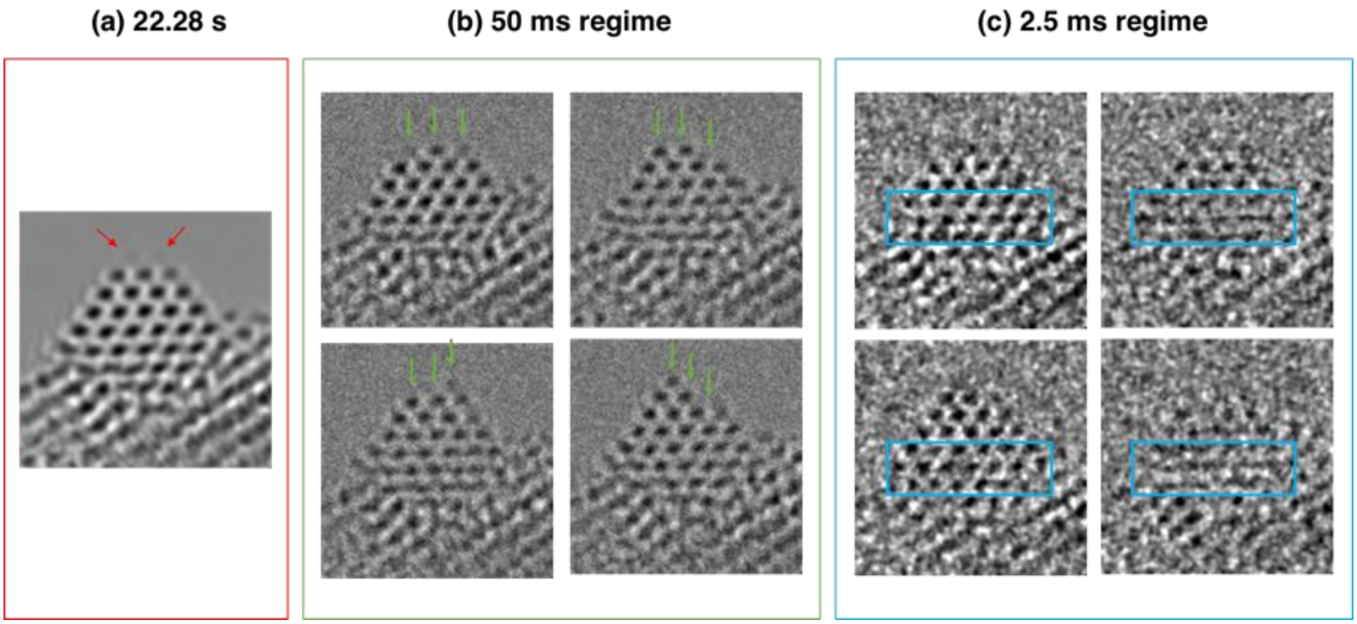

Figure 1. Subsets of the *in situ* TEM data illustrating the CeO_2 nanoparticle in a (110) orientation at different time resolutions. (a) Summed image of the 8,913 frames, leading to a 22.28 s image. (b) 20-frame average images, corresponding to a time resolution of 50 ms. (c) Single frames of the time series, acquired at 2.5 ms.

References:

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