Determination of Surface Dynamics on CeO$_2$ Nanoparticles using Time-Resolved High-Resolution TEM

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Characterizing the structural evolution of catalyst nanoparticle surfaces can provide insights into the active motifs responsible for catalysis. High-resolution transmission electron microscopy (HRTEM) has been used extensively to study surface dynamics on nanoparticles using *in situ* imaging techniques[1]. Recent advances in imaging detector technology, namely direct detection cameras with fast acquisition modes, have enabled many new materials phenomena to be investigated. With the advent of fast image acquisition, large datasets, otherwise known as "big data", are becoming increasingly common and new developments in data storage, data mining, and processing methods are necessary[2]. Thus, batch processing techniques are essential for reducing processing time and extracting useful information from large, often noisy image datasets. By combining advanced acquisition and processing techniques, time-resolved HRTEM will enable new insights into the structural evolution of nanoparticle surfaces. In this work, we use time-resolved HRTEM to achieve high spatial and temporal resolution of surface atom migration on CeO$_2$ nanoparticles, a material that is used extensively in catalysis applications due to its oxygen exchange properties[3].

An aberration-corrected FEI Titan ETEM equipped with a Gatan K2 IS direct detection camera (with high detection quantum efficiency) was used to image CeO$_2$ nanoparticles at 400 frames/second and 10^4 e$^-$/(Å^{2}s) in vacuum. A single frame of 1/400 second exposure is shown in Figure 1a), and due to the fast acquisition rate, the signal-to-noise ratio of the image was low. To reduce noise in each individual frame, a Kalman filter was applied to an image stack of ~9000 frames and Figure 1b) shows a single filtered image frame. A Kalman filter is a computationally light, recursive filtering technique which adapts at each time step to significantly reduce noise in each frame. MIPAR, a commercially available software with a recipe-based image processing method, was used to identify atomic column positions and quantify column intensities[4]. Using MIPAR's batch processing feature, each image from the ~9000 image stack was analyzed to produce a mask of atomic columns (Figure 2a)) that was used to generate measurements, including the position, area, intensity mean, and integrated intensity of each atomic column, from the unfiltered image frames. The integrated intensity quantization of each atomic column is overlaid on the image in Figure 2b) and was used to estimate the number of atoms within each column. With this approach, atoms within the small CeO$_2$ nanoparticle were tracked with 1/400 second temporal resolution for ~30 seconds. Additional details outlining the batch processing workflow and relating the atomic movement on the CeO$_2$ nanoparticle surface to oxygen exchange processes will be presented[5].

References:
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[5] We gratefully acknowledge support of NSF grant DMR-1308085, the use of ASU's John M. Cowley Center for High Resolution Electron Microscopy and use of the K2 IS camera courtesy of Gatan.
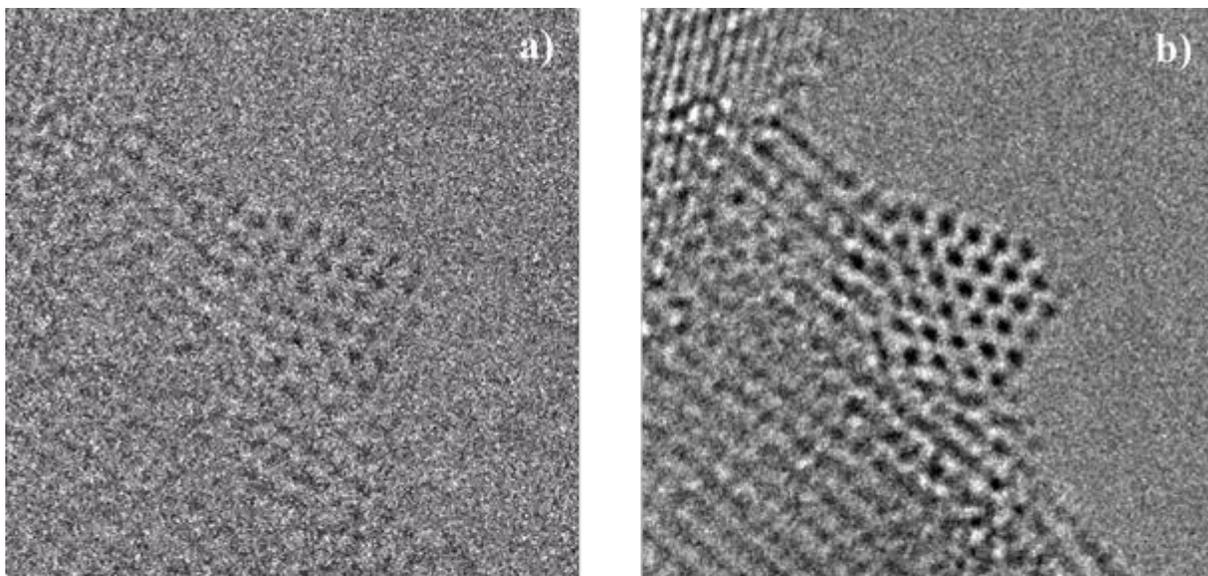
Figure 1. HRTEM images of a CeO_2 nanoparticle in (111) projection. a) 1/400 second-exposure raw image b) Kalman-filtered image of raw image from a).
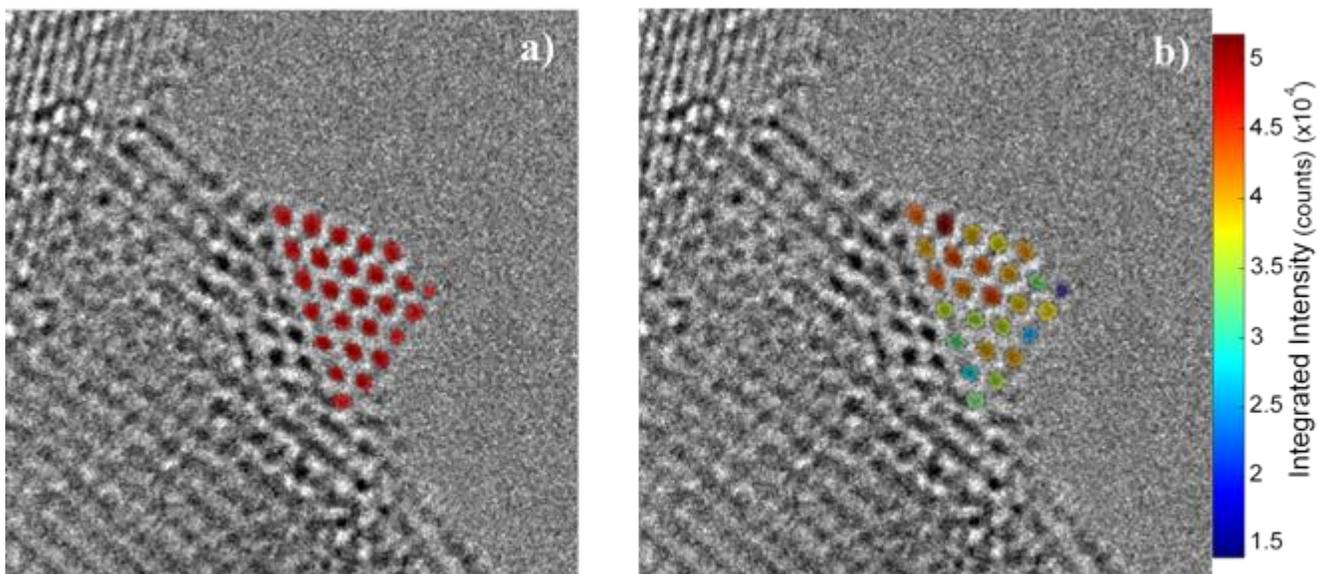

Figure 2. a) Atomic column detection mask (red) determined through image batch processing in MIPAR b) Atomic column integrated intensity overlaid on image.