Identification of Rapid Oxygen Exchange through Site-Dependent Cationic Displacements on CeO_2 Nanoparticles

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CeO_2 (ceria) and ceria-based materials have many applications in heterogeneous catalysis, largely due to their oxygen exchange properties[1]. Under reducing conditions, ceria releases oxygen through the formation of oxygen vacancies coupled with a cation transition from Ce^{4+} to Ce^{3+}. A lattice expansion (~0.2-0.3Å) occurs once oxygen vacancies are created[2]. The relative ease with which oxygen vacancies are created/annihilated on CeO_2 is strongly dependent on particle surface and size and is an important catalytic property of ceria nanoparticles[3]. Aberration-corrected high-resolution transmission electron microscopy (HRTEM) has been used to image atomic surface structures of CeO_2 nanocubes with both Ce and O atomic columns clearly visible[4]. *In situ* environmental transmission electron microscopy (ETEM) can observe dynamical processes that occur on ceria surfaces in reducing/oxidizing environments. Thus, atomic-level studies of CeO_2 surfaces may enable the reaction pathways and active sites to be determined for oxygen exchange reactions.

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 nanocubes at 40 frames/second and 5000 $e^-/(Å^2s)$. Images were aligned and binned to 10 frames/second to increase signal-to-noise for image processing. MIPAR software and MATLAB codes were used to determine centroid positions and integrated intensities of each Ce atomic column in each 0.1 sec. frame[5]. The root-mean-square-displacement (RMSD) was calculated to quantify the magnitude of displacement of each surface site. Figure 1a) shows a HRTEM image of a sum of 10 frames (1 sec. exposure) of a small (111) facet of a CeO_2 cube in [110] projection in vacuum. Several step edge and corner atoms appear blurred relative to terrace atomic columns as indicated by the white arrows overlaid on the image. Figure 1b) displays the tracks of displacement positions in each frame overlaid on the summed image. In Figure 1c), the calculated RMSD values are overlaid as colored circles according to the magnitude of RMSD. Most surface terrace sites appear stable, while a large degree of displacement (~0.2-0.3Å) was observed at step edge sites and corner sites. The oxygen vacancy formation energies (E_f) at corners and step edges have been calculated to be lower than vacancy formation energies on terrace sites. Consequently, atomic columns shift positions as oxygen is removed from or inserted into the ceria lattice at low E_f sites. These site-specific displacements of Ce atomic column positions suggest variation in local oxygen exchange processes, potentially enabling preferred oxygen exchange sites to be determined[6,7].

References:

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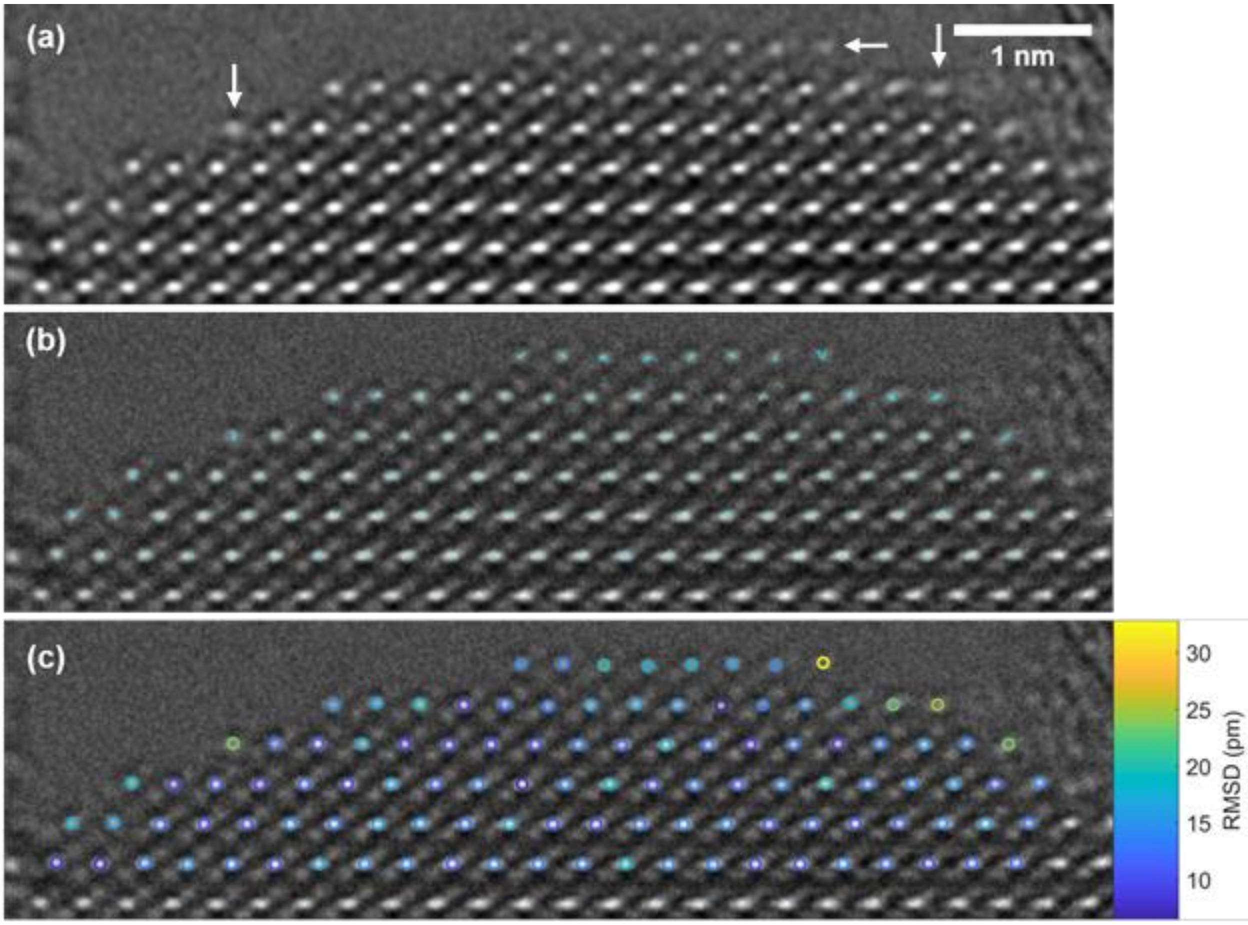

Figure 1. (111) surface of CeO_2 (a) Sum of 10 frames (1 sec. exposure). Ce and O atomic columns visible at surface. (b) Ce atomic column centroid positions in each frame tracked in 10 frames overlaid on a summed image. (c) RMSD of each Ce atomic column position.