Tracking Atomic Scale Oxygen Exchange in Dynamic Structure of CeO_2 Nanoparticle Surfaces

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Oxygen exchange reactions play a critical role in many energy conversion processes that are important for renewable energy, chemical synthesis and other technologies. For instance, gaseous oxygen is reduced to oxygen ions at the cathode interface and then diffuses through a solid oxide electrolyte to oxidize fuel molecules at the anode in solid oxide fuel cell (SOFC) [1]. Oxygen exchange reactions are complex and consist of multiple steps including O_2 absorption/desorption, molecular dissociation/association, electron transfer, and incorporation/removal oxygen into or from surface vacancies. Electroceramic oxides, such as CeO_2 and ceria-based materials, are ideal candidates for oxygen exchange applications, because of the unique ability of changing Ce oxidation states while maintaining stable structures; which enables the conversion to a nonstoichiometric oxide easily and reversibly during the oxygen exchange and transport process [2]. Due to the complexity of the multi-step oxygen exchange reaction, the surface exchange kinetics and detailed oxygen exchange mechanisms are not well understood. To improve material performance, it is desirable to develop a deeper understanding of the atomic level processes that regulate oxygen exchange and transport. Time resolved *in-situ* aberration-corrected TEM was used to observe atomic level variations in the oxygen vacancy creation/annihilation rates on CeO_2 nanoparticle surfaces.

With the observation of the relaxation of the adjacent cations and the intensity changes in anions, the frequency of adjacent cation displacement can be associated with the oxygen vacancy activity. Images were acquired using Gatan K2 IS direct electron detector operated at 20 frames/second with FEI Titan ETEM 80-300. Time series image stacks were aligned by cross-correlation for drift correction and re-binned twice for noise reduction in digital micrograph. A Gaussian blur filter with a 2-pixel radius was applied on time series image stacks in image J for smoothing purposes. The displacement of Ce cation column and O anion column in time series image stacks with picometer precision were tracked using 2D elliptical Gaussian fitting in custom MATLAB script written by B. D.A. Levin [3].

Figure. 1a showed an AC-TEM image of CeO_2 (111) surface in the [110] projection with 1s total exposure time at room temperature. One important observation is that the surface Ce column is more diffused than bulk Ce column, especially at the step edge site. Same observation can be found in the O column. The standard deviation of the position of each Ce and O column was measured to quantify the average displacement from its mean position during each time series image stacks, which shown in **Figure. 1b&c**. Surface Ce columns, such as step edges and interface boundaries sites, showed significantly larger standard deviations (20-25pm) than non-surface Ce columns. In comparison, O columns at surface or sub-surface could be more active than non-surface columns. **Figure 2** showed the relationship between Ce column displacement and neighboring oxygen column intensity changes at a specific step edge site. A strong Ce column displacement indicated possible oxygen vacancy creation/annihilation process occurred, which correlates with changes in the oxygen column intensity in some cases.

References:

[1]Adler, S. B., Chemical Reviews, 104(2004), 4791–4844.
[2]Trovarelli, A. in “Catalysis by ceria and related materials” (Imperial College Press, London), 25
[3]Levin, B. D. A. L., arXiv:1909.07477(2019), https://arxiv.org/abs/1909.07477 (accessed 02,20,2020)
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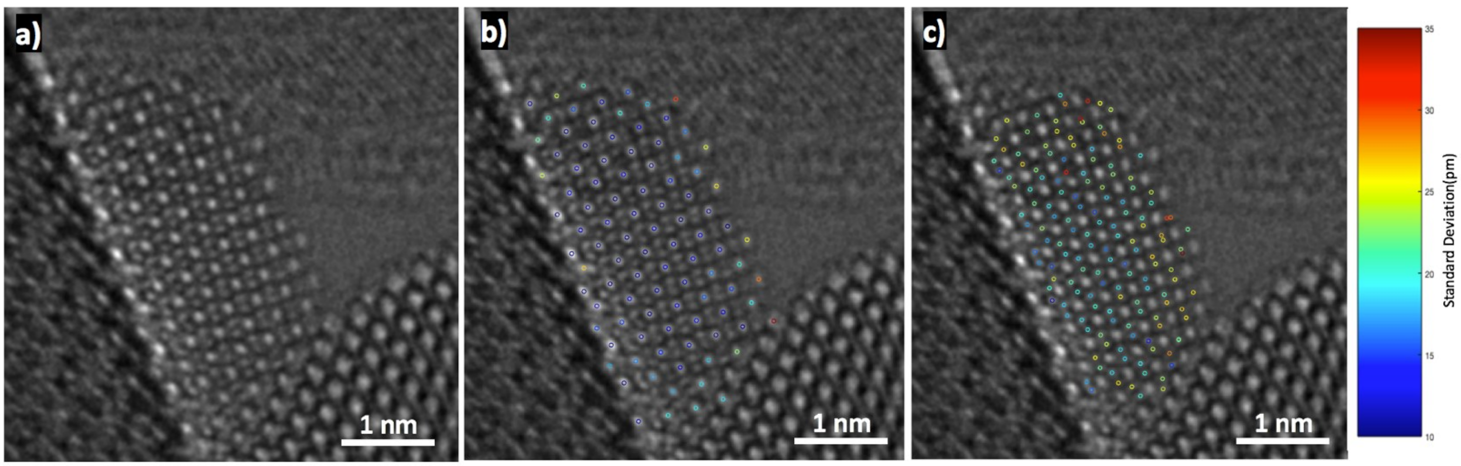

Figure 1. a) AC-TEM image of CeO_2 (111) surface in the [110] projection with 1s total exposure time at room temperature. Standard deviation in column position over sequence of 20 frames each 1/20s exposure time indicated by colored markers overlaid on atomic column of b) cerium and c) oxygen

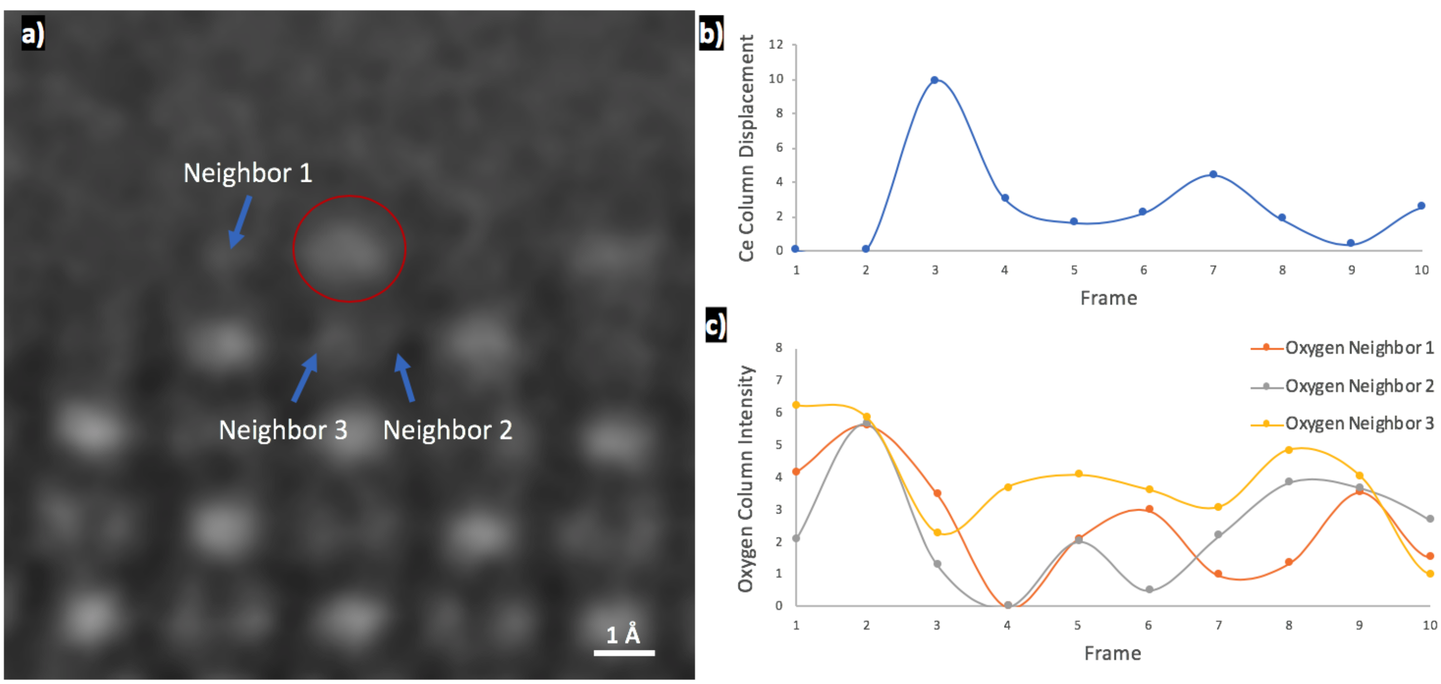

Figure 2. a) AC-TEM image of CeO_2 (111) surface in the [110] projection with 1s total exposure time at room temperature. Selected step-edge atom is circled in red. b) Ce column displacement in 10 frames c) O column intensity in 10 frames