

## Dynamic Restructuring during Processing: Approaches to Higher Temporal Resolution

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Non-equilibrium dynamic structural fluctuations occur during many materials synthesis and processing conditions. Atoms can diffuse across a surface and spontaneously self-assemble to form quasi-stable non-equilibrium phases. The fundamental atomic scale processes taking place on the surface are not well understood and many intermediate structures may form with similar Gibbs free energies separated by low kinetic barriers [1]. Describing the structural evolution of the system in space and time is a major challenge which may be tackled with aberration corrected, *in situ* electron microscopy, allowing atomic columns to be located with picometer precision. Recently introduced direct electron detectors offer fast time resolutions and high detection quantum efficiencies. In practice, combining both high spatial and temporal resolution remains challenging, and careful consideration must be given to signal-to-noise and electron flux. High temporal resolution may compromise spatial precision due to degradation in signal-to-noise but may also reveal rapid structural fluctuations at the atomic level. Approaches to high temporal resolution are illustrated below for *in situ* imaging of metal and ceramic nanoparticles under vacuum and in the presence of reactive gas.

We are investigating structure-reactivity relationships for CO oxidation using *operando* TEM [2]. Figure 1 shows a CO oxidation catalyst consisting of Pt nanoparticles on the (100) surface of a CeO<sub>2</sub> nanocube recorded with a FEI Titan environmental transmission electron microscope (ETEM) in 1 Torr of CO at room temperature with an exposure time of 0.75s. In Figure 1a, the Pt particle shows lattice fringes and a well-defined orientation relationship exists between the metal particle and the oxide support. Figure 1b shows the same particle at a different time in which the fringe contrast in the Pt particle is almost completely absent. Many other Pt particles also show image contrast which oscillates between uniform flat contrast and lattice fringe contrast. The absence of fringe contrast or speckle contrast associated with disorder is indicative of the Pt particle undergoing dynamic restructuring. This restructuring takes place under reaction conditions at a frequency significantly faster than the detector readout rate.

To gain greater insight into dynamic structural re-arrangements, it is necessary to make measurements at higher temporal resolution. The Gatan K2 direct electron camera now allows readout rates in excess of 1000 frames per second (fps) with detection quantum efficiencies close to unity. However, for atomic resolution imaging, a typical electron flux of 1000 e<sup>-</sup>/Å<sup>2</sup>/s would yield an average intensity of only 1 e<sup>-</sup>/Å<sup>2</sup> per frame at millisecond time resolution, which is inadequate to yield even a qualitative description of atomic level structural fluctuations. To address this issue, it is necessary to increase the electron flux. Figure 2 shows a sequence of images from a CeO<sub>2</sub> nanoparticle recorded with a time resolution of 10 ms at room temperature with an electron flux of 10<sup>5</sup> e<sup>-</sup>/Å<sup>2</sup>/s. The Ce surface cations (imaged with dark contrast) are highly mobile, resulting in a surface that is constantly undergoing reconstruction. For CeO<sub>2</sub>, the low energy (111) surfaces are prominently featured in all dynamic configurations, while higher energy surface structures spontaneously form and dissolve as the system

evolves. Figure 2 shows that quasi-stable configurations are separated by less stable short-lived transition forms. The transition form is characterized by local streaking or diffuse atomic column contrast in the image, indicating rapid translational motion or oscillatory behavior between configurations, presumably of similar energy and separated by low energy barriers  $E_a$ . At higher time resolutions (not shown), the motion of individual columns can be resolved, but the signal-to-noise is degraded [3]. Noise reduction methods can be helpful but may also introduce artifacts. The energy to overcome kinetic barriers between states may come from either thermal fluctuations or the electron beam. The displacement rate for thermal processes varies as  $\exp(-E_a/kT)$  whereas displacement rates for both knock-on and radiolytic processes vary as  $1/E_a$ . Thus, regardless of the energy transfer mechanism, the rate of local activity is a measure of variations in the local surface activation energy. This suggests that, even when high electron fluxes are employed to achieve high temporal resolutions, it should be possible to make at least qualitative correlations between local activation energies and structural fluctuations. The practical issues associated with acquiring and processing high temporal resolution data will be discussed.

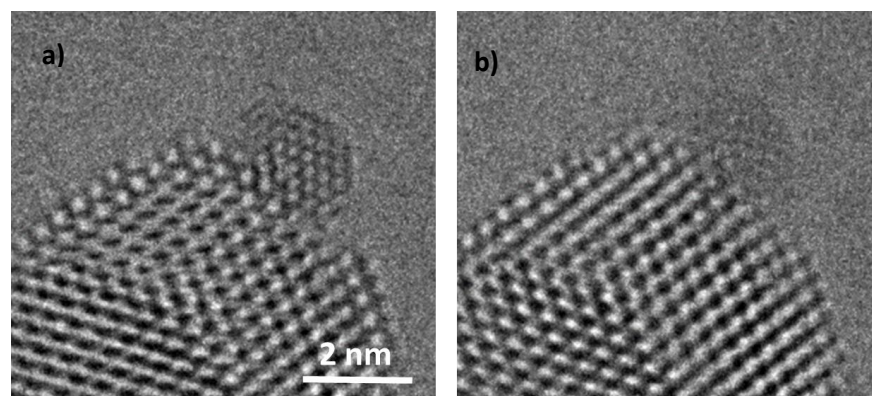
## References

[1] P. M Ajayan et al, Phys Rev. Lett. **60** (1980) 585-587.

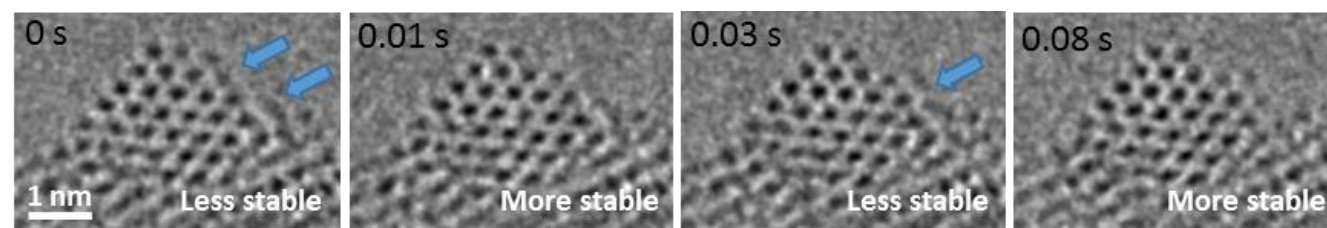
[2] J. Vincent et al., (these proceedings)

[3] E.L. Lawrence et al, (these proceedings)

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**Figure 1.** a) Pt nanoparticle on  $\text{CeO}_2$  in CO at room temperature showing clear Pt fringes. b) Same particle at a different time showing loss of fringe contrast due to rapid dynamic reconfiguration.



**Figure 2.** Series of images recorded from  $\text{CeO}_2$  nanoparticle at 100 fps showing the transformation between more stable and less stable configurations. Blue arrows indicate diffuse/streaked atomic columns, which highlights the instabilities during that frame's exposure.. Numbers show time between frames.