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Low Angle Annular Dark Field Scanning Transmission Electron Microscopy is Sensitive to Oxidation State in CeO_2 Nanoparticles

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Ceria (CeO_2), a rare-earth oxide, can easily capture and release oxygen. This favorable oxygen storage capacity has made it attractive for many applications including catalysis [1]. To study the oxidation and reduction process with high spatial resolution is nontrivial. Scanning transmission electron microscopy (STEM) coupled with electron energy loss spectroscopy (EELS) can be used [2]. However, acquiring atomically resolved EELS data involves expensive equipment, high electron doses and relatively long acquisition times. By comparison imaging techniques require less specialized equipment, lower electron doses, and shorter acquisition times.

Low angle annular dark field (LAADF) STEM image contrast is sensitive to defects. As an extension of this concept and a novel application, LAADF STEM is presented as a technique sensitive to the oxidation state of the cerium ions in CeO_2 nanoparticles. Areas with reduced Ce ions appear brighter by comparison to regions without. In high angle annular dark field (HAADF) STEM this relationship is reversed and regions with reduced Ce ions are comparatively darker. This contrast mechanism was verified through EELS, in-situ measurements, and multislice image simulations. Static displacements due to the increased Ce^{3+} ionic radius disrupt electron channeling and reduce the intensity of the higher-order Laue zones thereby reducing the HAADF signal. The distorted lattice generates additional diffuse scattering which increases the LAADF signal. This contrast mechanism is demonstrated in Figure 1 by comparing LAADF and HAADF images.

LAADF STEM facilitates high spatial resolution measurements on time scales that would be unattainable for STEM EELS. With this approach the oxidation and reduction behavior of CeO_2 nanoparticles were studied. Changes to the nanoparticles were stimulated locally and globally either by using the electron beam directly or by exposing the particles to oxidizing and reducing conditions in an environmental transmission electron microscope. Contrast changes associated with the oxidization and reduction of CeO_2 was observed as well as chemical expansion of the lattice (Figure 2). This change in lattice parameter can be exploited to estimate the extent of reduction. This demonstrates that LAADF STEM imaging may open new avenues for in-situ experimentation to gain insight into dynamic processes [3].

References:

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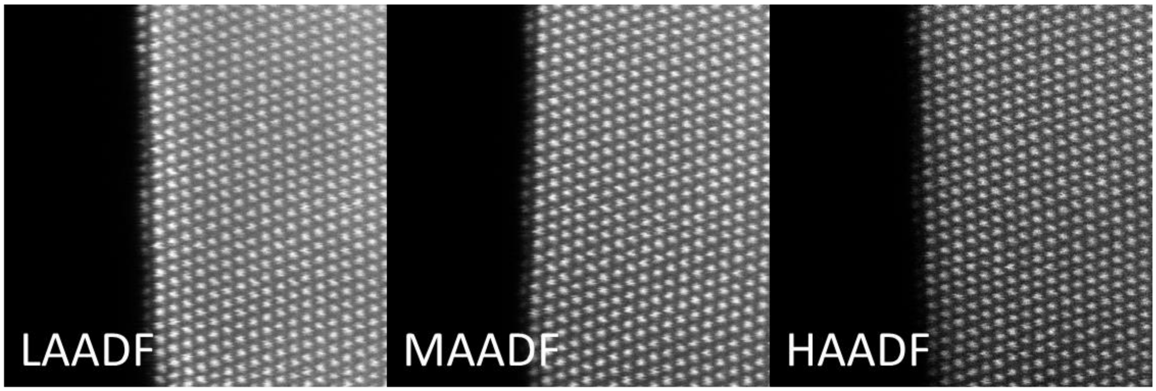

Figure 1. Low angle, medium angle, and high angle annular dark field STEM image from the edge of a truncated octahedral CeO_2 particle. An increase in intensity can be observed at the periphery of the particle in the LAADF image while the decrease in intensity is observed in the HAADF image.

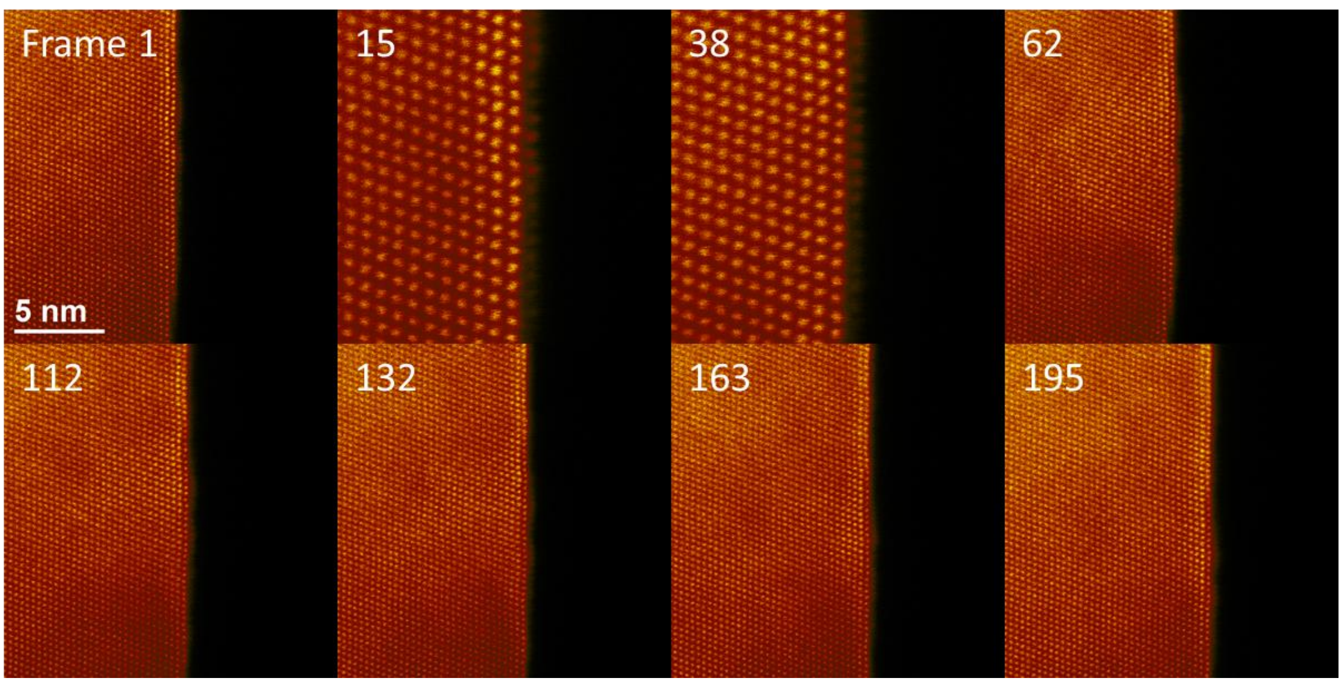

Figure 2. Select frames from a LAADF STEM movie of a particle edge that was reduced by the electron beam (Frames 15 and 38) upon increasing the dose rate (higher magnification). By decreasing the dose rate (lower magnification) the particle recovers (Frames 62-195).