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Dose-rate-dependent damage of cerium dioxide in the scanning transmission electron microscope

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ABSTRACT

Beam damage caused by energetic electrons in the transmission electron microscope is a fundamental constraint limiting the collection of artifact-free information. Through understanding the influence of the electron beam, experimental routines may be adjusted to improve the data collection process. Investigations of CeO_2 indicate that there is not a critical dose required for the accumulation of electron beam damage. Instead, measurements using annular dark field scanning transmission electron microscopy and electron energy loss spectroscopy demonstrate that the onset of measurable damage occurs when a critical *dose rate* is exceeded. The mechanism behind this phenomenon is that oxygen vacancies created by exposure to a 300 keV electron beam are actively annihilated as the sample re-oxidizes in the microscope environment. As a result, only when the rate of vacancy creation exceeds the recovery rate will beam damage begin to accumulate. This observation suggests that dose-intensive experiments can be accomplished without disrupting the native structure of the sample when executed using dose rates below the appropriate threshold. Furthermore, the presence of an encapsulating carbonaceous layer inhibits processes that cause beam damage, markedly increasing the dose rate threshold for the accumulation of damage.

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1. Introduction

In the transmission electron microscope damage to samples introduced through interactions with the high energy electron beam can limit measurement precision, resolution, and sensitivity. The processes that cause damage can be classified as being either elastic or inelastic in nature. A commonly encountered elastic damage process is ballistic or “knock-on” damage, which results from a direct transfer of momentum from the incident electrons to the nuclei of the atoms in the specimen. Radiolytic damage originates from inelastic interactions between the incident beam and electrons within the specimen, in which the potential energy of an excited atomic state is converted into atomic displacement. A more complete discussion on damage mechanisms has been reviewed elsewhere [6,7,16,18].

To limit the extent of such damage, the microscope operator can control a given set of experimental parameters, such as accelerating voltage, dose (electrons per unit area), and dose rate (dose per unit time) [5]. A critical dose defines the threshold above which a detectable amount of damage is produced within the sample. When the onset of damage occurs at a critical dose this means that low dose rates, short exposure times, or combinations thereof will limit damage. However, radiation-intense metrology, such as spectrum imaging and tomography, tests low-dose practices and emphasizes the need for understanding the mechanisms of electron beam damage and identifying techniques to mitigate such damage.

Cerium dioxide (CeO_2) has been the focus of several reports studying electron beam damage, which has been tracked using electron energy loss spectroscopy (EELS) to detect changes in the Ce $M_{4,5}$ edges [2,11,12,32,37]. The native oxidation state of the Ce ions in bulk CeO_2 is $+4$, although the presence of a reduced surface region has been commonly reported using scanning transmission electron microscopy (STEM)-EELS [12–14,35,38]. As the electron beam interacts with the sample the Ce oxidation state will reduce to $+3$. Results from dosimetry experiments have provided critical dose values for which a detectable change in the cerium oxidation state was observed [11,12,32]. This indicates that collecting artifact free data from CeO_2 under dose intensive conditions would be problematic. However, recent studies by Turner et al. [35] and Goris et al. [13] hint the onset of beam damage in CeO_2 may be dictated by some relationship other than a critical

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dose. Both studies involved high dose experimentation on CeO_2 but, notably, also specifically reported that no measurable change in the sample was observed.

In an attempt to understand this apparent contradiction, a series of experiments were performed on CeO_2 nanocubes. The nanocubes were exposed to a high energy electron beam using a series of dose rates while changes to the structure and chemistry of the nanocubes were monitored using low-angle and high-angle annular dark field STEM (LAADF- and HAADF-STEM, respectively) imaging and EELS measurements of the Ce $M_{4,5}$ edge. STEM imaging can be used to observe any changes to the structure such as the formation of voids or changes to the crystallographic phase. Additional information can be gained using annular dark field STEM imaging when the crystal is oriented (e.g., along a high-symmetry zone axis) to promote electron channeling. In this case, changes to the local crystal structure disrupt the electron channeling process, and alter the intensity in the resulting image. This technique has been used to identify strain fields around interfaces and line defects [31,39]. It is also sensitive to point defects [27,29] and has been used to identify regions in CeO_2 nanoparticles that were reduced [19]. By using this imaging technique in combination with EELS we were able to quantitatively assess the effects of electron beam irradiation in CeO_2 nanocubes. We found dose rate to be the primary factor governing the reduction of CeO_2 in the electron microscope. Below the critical dose rate threshold, no detectable damage accumulates. As a result, there is no well-defined critical dose, rather the dose necessary to observe a change in the oxidation state depends on the dose rate used for observation.

2. Experimental procedures

CeO_2 nanocubes were synthesized using wet chemical methods according to a previous literature report [34]. Briefly, 9.60 g sodium hydroxide (NaOH) and 0.868 g of $Ce(NO_3)_3$ were dissolved in 50 mL H_2O (Nanopure H_2O) with a resistivity of approximately 18.2 $M\Omega \cdot cm$ and sonicated for 10 min. The solution was heated at 180 °C for 24 h in a Teflon®-lined autoclave. Afterwards, the samples were cooled to ambient temperature and washed with Nanopure H_2O. The solution was centrifuged three times at 837.8 rad/s for 5 min and dried in an oven at 60 °C overnight to obtain a dry CeO_2 powder. The particles were dispersed in water and deposited onto copper grids coated with carbon films and allowed to dry. The samples were cleaned using a low energy, inductively coupled plasma with a composition of 25% O_2 and 75% Ar. This was done to remove sources of hydrocarbon contamination and prevent the buildup of carbon as the sample was irradiated. The plasma treatments lasted 5–20 s in length and were found to eliminate electron-beam-induced carbon deposition, but did not severely degrade the support film. Images taken before and after a plasma treatment indicate that no obvious restructuring of the nanocube occurred.

STEM data was collected using an aberration-corrected FEI Titan 80-300 operating at 300 kV. LAADF and HAADF images were acquired using the same detector by changing the camera length such that the inner collection semiangle was $\approx$ 28 mrad and $\approx$ 88 mrad, respectively. The convergence semiangle used was $\approx$ 14 mrad. EELS measurements were collected using an imaging energy filter (Gatan, Tridiem 865). The collection semiangle was $\approx$ 11 mrad and a dispersion of 0.2 eV/ch was used. The FWHM of the zero loss peak was $\approx$ 1.0 eV to $\approx$ 1.4 eV. To access the range of dose rates used in the experiments the gun lens focus was adjusted to change the probe current without interruption.

For all irradiation experiments, a 1024×1024 raster with a per-pixel dwell time of 1 μs was used. EELS spectra were recorded approximately every 30 s or 60 s. A spectral acquisition time of 3 s was used, during which the electron beam was scanned over the entire square raster pattern encompassing the particle approximately three times; as a result, the measurement indicates the spatially-averaged oxidation state of the entire particle. Each image frame of the raster was recorded and stored except in experiments that lasted longer than 15 min. In those cases, images were recorded and stored approximately every minute because of the limitations related to storing the large volume of data in temporary memory. The electron dose rate ($e\,nm^{-2}\,s^{-1}$) was calculated by dividing the probe current by the area of the raster. This is a time-averaged value, reflecting that each point of the specimen is not continuously illuminated, rather only momentarily once every complete raster. The cumulative dose ($e\,nm^{-2}$) was calculated by multiplying the dose rate by the elapsed time. The probe currents were measured using the microscope's fluorescent screen that had been previously calibrated using a pico-ammeter.

The ratio of the integrated intensity of the Ce M_5 to the Ce M_4 peak – the "white-line" ratio – was calculated by taking the second derivative of the spectra and integrating the positive portion of each edge. This procedure was implemented in Digital Micrograph using a publicly available script [24]. The uncertainty of these measurements is defined through the following relationship,

$$\delta W = W\sqrt{\left(\frac{\sqrt{N_1}}{N_1}\right)^2 + \left(\frac{\sqrt{N_2}}{N_2}\right)^2}$$

where W is the white-line ratio and N_1 and N_2 are the integrated intensities of the Ce $M_{4,5}$ edges.

3. Results

We monitored the changes to an individual CeO_2 nanocube as a function of dose rate and cumulative electron dose. The nanocube (Fig. 1), approximately (32–33) nm on a side, was oriented along the [001] zone axis. In Fig. 2 the ratio of the integrated intensity of the Ce M_5 to the Ce M_4 peak (M_5/M_4) – the white-line ratio, which is sensitive to oxidation state – is plotted as a function of dose. Each curve represents a different dose rate and all these data were obtained from the same nanocube. Several minutes elapsed between the start and stop of each experiment. Here we can observe that total dose does not correlate to changes in the M_5/M_4 ratio; rather *dose rate* is the key factor. At a dose rate of 2.97×10^5 $e\,nm^{-2}\,s^{-1}$ the nanocube was exposed to a dose of 9.03×10^8 $e \cdot nm^{-2}$ after which no discernable change had occurred to the white-line ratio or to the fine structure of the Ce $M_{4,5}$ edges (Fig. 2b). By comparison, when dose rates of 7.28×10^5 $e\,nm^{-2}\,s^{-1}$, 1.10×10^6 $e\,nm^{-2}\,s^{-1}$, and 1.37×10^6 $e\,nm^{-2}\,s^{-1}$ were used, an increase in the white-line ratio was observed, indicating the reduction of Ce, even though the cumulative doses were lower. In addition, changes in the fine structure of the Ce $M_{4,5}$ edges could be observed at these dose rates (Fig. 2c). This includes a shift to lower energies, a reduction in the satellite peak intensities, and the change in the relative peak intensities, all of which are characteristic features of a transition from the +4 to +3 Ce oxidation state [11]. At the extreme of 1.37×10^6 $e\,nm^{-2}\,s^{-1}$, an almost immediate change to the white-lines ratio was observed. The initial data point had a white-lines ratio of $\approx$ 1.0; this is larger than the average starting value ($\approx$ 0.94) of all the other measurements, suggesting that reduction of the nanocube had occurred almost immediately as it was exposed to the beam. After a dose of 4.12×10^7 $e\,nm^{-2}$ the white-line ratio had a value of $\approx$ 1.05 and increased to $\approx$ 1.14 at a dose of 1.67×10^8 $e\,nm^{-2}$. These doses are $\approx$ 4.6% and $\approx$ 18.5% of the total dose that caused no change to the white-line ratio when using a