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Atomic motion on various surfaces of ceria nanoparticles in comparison

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Abstract: Aberration corrected HRTEM has been successfully applied to image the atomic motion at the edges and surfaces of nanoparticles of ceria of various types under electron irradiation. Here we identify movements not only on {100} facets, but also on {110} and even {111} facets, previously considered stable. However, the degree of movement varies strongly and HRTEM is evidently the preferred technique to measure relative stability at high spatial resolution as it does not require extended surfaces as in scanning probe microscopy (SPM) or chemical methods. The advantage of aberration correction shows in suppression of contrast from the carbon support films and the absence of delocalisation fringes at particle edges, apart from improving point resolution.

1. Introduction

The efficiency of a nanoparticle as a catalyst is strongly influenced by its surface reactivity, which in turn depends on its surface irregularities, atomic steps, majority of crystal orientations exposed etc. Ceria is one such example, utility of which as a catalyst [1,2] originates from surface oxygen content. The catalytic activity and mobility of Ce and O ions on the surface of ceria nanoparticles is linked with how strongly each atom is bound to the surface with the order of binding energy being: {111} > {110} > {100} [3]. So it would be highly beneficial to study relative activities of ceria low index surfaces experimentally. High resolution transmission electron microscopy (HRTEM) has been used effectively in nanoparticle studies as it gives direct information on surface instabilities and reconstruction of nanocrystals [4]. Recent developments (e.g. aberration corrected TEMs and modern CCD cameras) have made in-situ observation of atomic hopping possible including structural transformations in gold at elevated temperatures, e.g. [5, 6]. Here we report the use of aberration-corrected bright-field phase-contrast TEM in monitoring atomic movements in oxide crystals. In extension of our earlier work studying motion exclusively on small facets of {100} type [7], a comparison of {111}, {110}, and large faces of {100} is presented, and some motion is now identified on each of them.

2. Experimental details

Both commercial CeO$_2$ (Sigma Aldrich) nanopowder and specifically hydrothermally prepared CeO$_2$ nanocrystals [8] were used for measurements in this work. The former are predominantly of octahedral shape with only small caps [9] (see Figures 1, 2 and 4), while the latter are tuned to show a maximum fraction of cube-faces (see Figure 3).

Aberration corrected TEM with spherical aberration close to zero and near Gaussian focus has been used in standard imaging conditions. As Ce provides mixed amplitude/phase contrast even at the smallest thicknesses due to its high atomic number, images with vanishing weak-phase contrast were found to provide the best single-atom visibility and minimized carbon background. Image series were

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automatically acquired in 2 s intervals using a GatanUltrascan 2kx2k camera. Gatan Digital Micrograph and ImageJ softwares were used for post-processing of the images. Experiments for figures 1 and 2 were obtained on the Sheffield JEOL JEM-2200FS-AC at 200kV, while experiments for figures 3 and 4 used the Sheffield JEOL JEM 3100 R005 at 300kV.

3. Results and Discussion

Figure 1: (a) Ceria nanocrystals with \{100\}, \{110\} and \{111\} facets, (b) Time series (at 0, 20, 38, 40 and 44 s) of bigger particle (left) and the corresponding profile plots of the 1st monolayer. (scale bar = 1 nm); C-film ablated by e-beam.

Figure 1(a) shows the bright field overview of two epitaxially adjoining faceted ceria octahedral nanocrystals. While the tiny \{100\} facet of the right hand side particle has been analysed in detail in [7], we demonstrate here that the hopping phenomena observed can be generalised to the much larger \{100\} facet of the bigger particle (left hand side), and are therefore not corner-effects.

Figure 1(b) shows some representative images of the time series taken for a length of 2 min (60 images). During the length of recording \{111\} facets remained stable while the \{100\} facet underwent major atomic hopping processes as indicated by the accompanying profile plots. This kind of high instability of \{100\} facets compared to adjoining stable \{111\} facets is directly dependent on variable surface oxygen contents/vacancies on these surfaces which strongly influences the ceria surface chemistry. In particular we assume \{100\} surfaces semi-occupied with oxygen to suppress surface dipoles [7]. The variable surface occupancy of the top monolayer due to Ce-hopping, should lead to variations of lattice constant in the 2nd monolayer: A similar line profile was taken on the second monolayer, in order to measure interatomic distance. Difference between two consecutive Gaussian peak centres would give corresponding inter atomic distance. Using the first two frames in figure 1(b), corresponding to 0 and 20 s, we find atomic positions 1, 4 and 5 on the top monolayer undergoing major changes in terms of atomic visibility and corresponding plot intensity. As a consequence, the interatomic distance below Pos. 1 increases from 0.39 ± 0.005 nm to 0.405 ± 0.005 nm. Pos. 4 also loses atoms from frame 1 to 2 and again the corresponding interatomic distance below increases from 0.382 ± 0.005 nm to 0.41 ± 0.005 nm. Pos. 5 seemingly gains a large number of atoms and the projected Ce-Ce distance below decreases from 0.438 ± 0.005 nm to 0.426± 0.005 nm. In summary, when there is no atoms/less atoms present in the first monolayer the corresponding position in the second monolayer becomes a virtual exposed 1st monolayer which reconstructs by expansion, also accounting for the larger Ce$^{3+}$ ionic radius in these oxygen depleted (reduced) top layer positions.

Figure 2(a) shows an overview of another particle of the same system, this time with two \{111\} facets, enclosing a small \{110\} facet now. A part of the time series (Fig 2(b)) clearly shows that the \{110\} surface reconstructs itself into \{111\} facets under the e-beam. Atomically flat and smooth facets are not always the most stable surfaces, and it is established, that through formation of dislocations a faceted or a stepped surface can be preferred by such a system [10]. Surface oxygen content (or depletion of oxygen
depending on the system and the environment) plays an important role in such reconstruction of the surfaces [11]. So it is evident that in this case the relatively unstable \{110\} surface transforms into a faceted surface covered by more stable \{111\} faces, as predicted in [3]. Similar reconstruction, albeit on larger scale, has also been reported by Nie et al [12], as below a critical thickness ceria forms \{111\} faceted islands when ceria was deposited on sapphire as a thin film.

![Figure 2](image2.png)

Figure 2: (a) Ceria nanocrystal with \{110\} and \{111\} facets, (b) Time series (at 0, 8, 18, 24, 26, 30, 32, 40, 46 and 50 s) (scale bar = 1 nm). C-film ablated by e-beam. Contrast inversion between (a) and (b) to facilitate comparison with experiment I (Figure 1).

![Figure 3](image3.png)

Figure 3: (a, b) Two time steps from a time series of mainly cube-shaped nanoparticles with dominant \{200\} facets; amorphous C contrast suppressed via Cs = 0, JEOL-JEM-R005. (c) Java EMS simulation corresponding to ROI, dashed on (a): Defocus +14 nm, thickness 1.5 nm. Unit cell (white box) with all Ce atom columns appearing as black spots.

It is important to clarify whether cuboid ceria surfaces with \{100\}-type faces larger than \{111\} behave in the same way. Fig 3(a, b) confirms extensive atomic hopping on \{100\} on a hydrothermal specimen with mainly cubes, while for the first time (minor) hopping on the adjacent \{111\} face, probably due to overspill of atoms from the very active corner region, is observed (see [13] for further details).

![Figure 4](image4.png)

Figure 4: (a) A ceria nanocrystal imaged along [112] zone axis, (b, c) experimental and JEMS simulated section (dashed region on (a)) with corresponding profile plots.
4. JEMS simulation
To confirm the relative orientations of unit cells, the positions of Ce columns, and the local thickness of various regions of interest, High Resolution TEM (HRTEM) image simulations were employed using Java EMS software [14,15]. For the [110] ceria images of Figure 3, simulations were done for a range of defocus values starting from -25 to +25 nm in steps of 5 nm. For the center of the dashed region on Figure 3a, Figure 3c shows a match with defocus value of +14 nm and thickness of 1.5 nm. The other simulation parameters were used as follows: energy spread 0.3 eV/ defocus spread 3.0 nm, incoherent envelope (MTF/vibrations) fitted to 0.05-0.06 (preliminary guess only), while the beam convergence envelope is of negligible influence for any setting of 0.5mrad or smaller. To confirm visibility of even finer details in the ceria structure, simulations of [112] zone axis are added. Figure 4(a) represents the HRTEM images of a ceria nanocrystal imaged along [112] direction. Simulation parameters used were similar except for the defocus value which was +25 nm and the thickness of the ROI was found to be 8.0 nm. Profile plots corresponding to the experimental image (Fig 4(b)) shows apparent dumbbell contrast of the white spots along the dotted line and same is confirmed by the simulation as well. Ce positions are in corners and edge centres of the unit cell, oxygen would coincide with the “dumbbells”, however this is coincident and not atomic contrast, as it rapidly fluctuated with focus.

5. Conclusions
Electron beam irradiation appears to be a promising probe in measuring or establishing the relative functional activity of different nanoparticle surfaces in comparison, as it probes one individual face of one nanoparticle rather than a wide average as with chemical, SPM or X-ray methods. Here we found exceptionally high Ce mobility, linked to oxygen deficit, for extended {100} ceria facets, but also mobility on {110} and to a minor degree on {111}. The importance of aberration correction to suppress Fresnel fringing and support film contrast and the ability to tune to maximum contrast for Ce-columns is confirmed.

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