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# Single Atom Motion on $CeO_2$ Nanoparticle Surfaces Imaged by Aberration Corrected HRTEM

G. Möbus, Z. Saghi
Dept. Engineering Materials, University of Sheffield, Mappin Street, Sheffield S1 3JD, UK

Single atoms have been successfully imaged in both TEM and STEM. Isolated heavy atoms on carbon film [1], heavy dopants in a light matrix [2], or monolayers of graphene in plan view [3] are prime examples. Rather than imaging static sceneries, dynamic movements of atoms can be recorded by insitu TEM, e.g. for graphene and for fcc metal surfaces [3-4]. Here we present atomic motion induced by electron irradiation on $CeO_2$ surfaces of nanoparticles. Within the widely found octahedral morphology of ceria nanoparticles, analysed by tomography in our earlier work [5], we find a fraction of particles exhibiting small but regular capped corners of {100} facet orientation linking the {111} type main facets (Fig 1). Aberration corrected TEM (Sheffield double-corrected JEM-2200FS-AC) has been used close to Gaussian focus at vanishing Cs. Each particle is a member of a larger cluster. Observation under typical FEGTEM imaging conditions ($2^{nd}$ smallest CA) is stable until the beam is converged to ~twice the field of view, ~ 40 nm. At first, the initially continuous carbon film is found to perforate locally, thereby freeing the particle of interest from any background noise. While the quantification of atomic scale contrast is massively facilitated by the absence of the support, focus determination is challenging, and there is also a risk of mistilts if the orientation of the entire particle cluster is changing.

Upon exceeding an intensity threshold, atomic surface movements appear, starting within the {100} caps, and also affecting steps and islands on {111} facets. In contrast, flat {111} and the rarely observed {110} facets remain stable, in agreement with molecular modelling [6]. Within an observed 2 min. sequence of images every 2 s (Fig 1), the major atomic movements appear reversible, and involve little ablation of cerium. However, initial oxygen loss on the presumably O-terminated {100} could play a role. The square pyramidal cross-sections are ideal to test atom counting in the final three monolayers where we find (on average) lateral numbers of $CeO_2$ units of 1, 3, and 5. The Ce atom numbers per column are then likely the same in depth and width, and can be quantified by relating profile intensity plots to discrete threshold levels (Fig 2), based on the contrast (max-min), independent of black-white reversals. By reference to the intensity jumps from 1 - 4 times a basic count unit, we can successfully identify locations corresponding to a single count unit, realised mainly by single Ce atoms, respectively single ceria molecular units. It should be noted that movements of high contrast spots within a 2 s interval would comprise the movement of entire columns of ~ 3 atoms, while the redistribution of gray-levels, such as from Fig 1a.9 to 1a.10 involves the movement of one single atom.

In a second series of experiments under similar but slightly underfocused imaging conditions (Fig 3, black/white reversed compared to Fig 1), a different type of facet development is observed: Atomic steps on both {111} facets merge to form a triangle of inward {111} facets of 2 units length. This is reminiscent of inward facets for the Marks' decahedron common in Au nanoparticles, however, no grain/twin boundaries are involved here. The driving force is entirely the elimination of the less stable {100} termination. [7]

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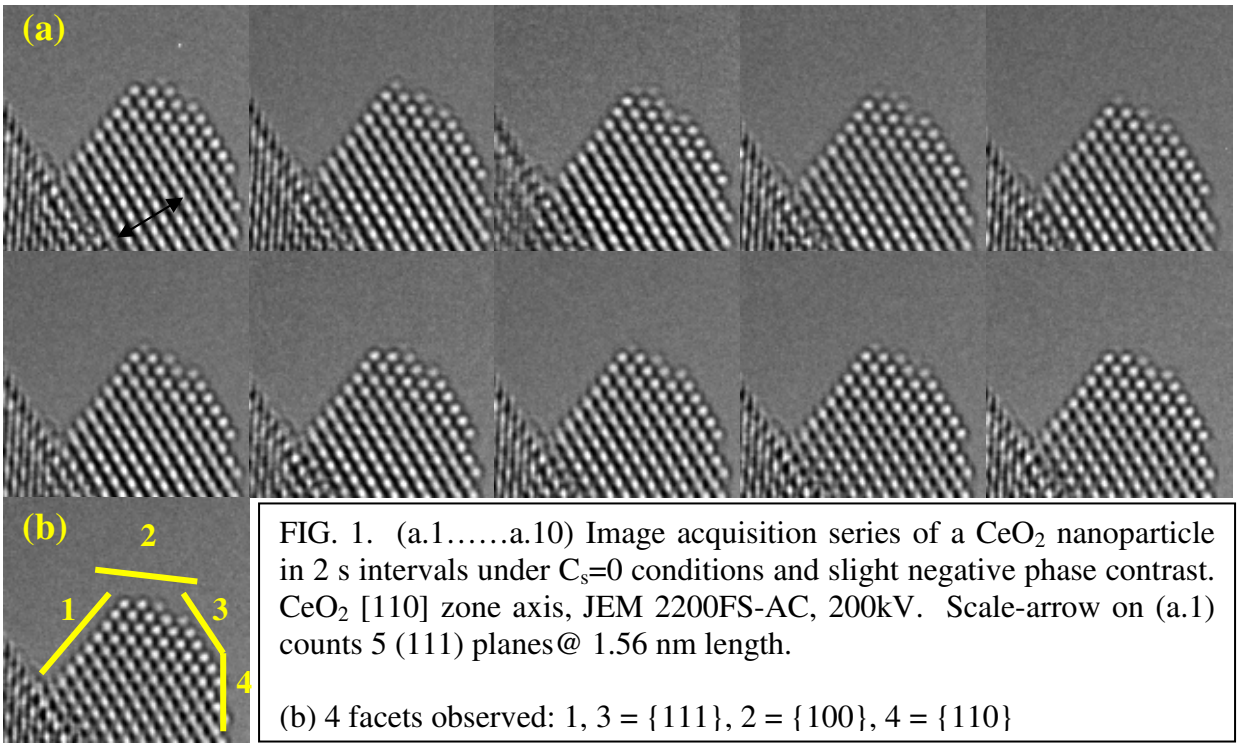
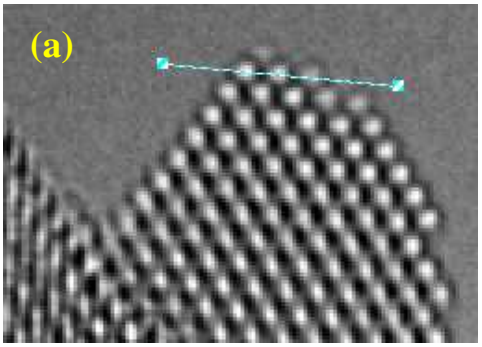



FIG. 1. (a.1……a.10) Image acquisition series of a $CeO_2$ nanoparticle in 2 s intervals under $C_s$=0 conditions and slight negative phase contrast. $CeO_2$ [110] zone axis, JEM 2200FS-AC, 200kV. Scale-arrow on (a.1) counts 5 (111) planes@ 1.56 nm length.

(b) 4 facets observed: 1, 3 = {111}, 2 = {100}, 4 = {110}



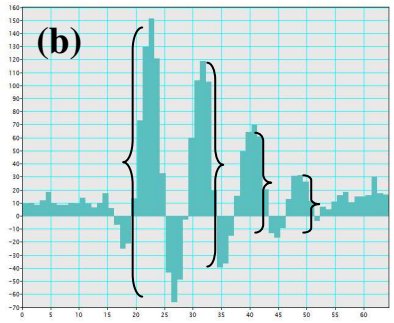




FIG. 2. (a) Magnified from Fig 1(a.9) with line profile along {100} of 2.7 nm. (b) Background subtracted intensity trace with contrast changes (max – min) in discrete multiples.

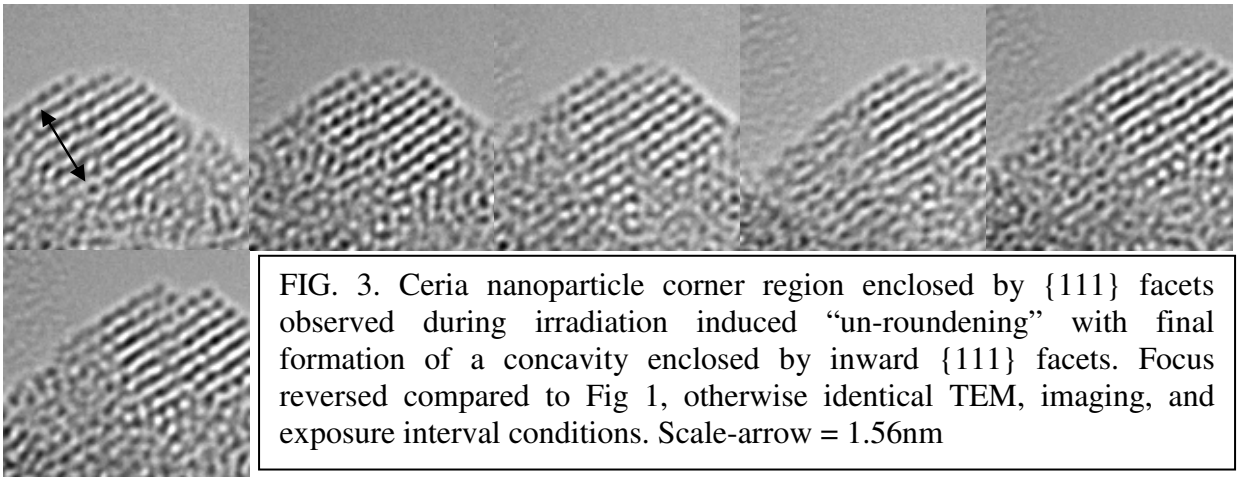


FIG. 3. Ceria nanoparticle corner region enclosed by {111} facets observed during irradiation induced "un-roundening" with final formation of a concavity enclosed by inward {111} facets. Focus reversed compared to Fig 1, otherwise identical TEM, imaging, and exposure interval conditions. Scale-arrow = 1.56nm

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