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Atomic Surface Structures of Oxide Nanoparticles with Well-defined Shapes

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Recent studies have shown that catalytic activities can be tuned by controlling the shape of nanoparticles such as $SrTiO_3$, CeO_2, and Co_3O_4 [1]. Therefore, determination of surface structure is very important to understand structure-property relationships for these oxide nanoparticles. The Argonne Chromatic-corrected TEM (ACAT) has an image corrector that corrects both spherical (C_s) and chromatic aberration (C_c). C_c correction allows the correction of C_s towards zero to improve resolution without compromising contrast. Using this unique feature, we correct both C_s and C_c to small values to achieve direct structure interpretable HREM images including oxygen atomic columns. In this study, atomic surface structures of $SrTiO_3$, CeO_2, Co_3O_4 nanocubes are observed by using aberration-corrected HREM.

As-prepared $SrTiO_3$ nanocubes have 6 well-defined {100} surfaces. We have shown previously that by tilting $SrTiO_3$ nanocubes to <110> directions, with the oxygen atoms clearly observed using aberration-corrected HREM, we are able to determine surface atomic structure on (100) surface of $SrTiO_3$ nanocubes. HRTEM studies show that the (100) surface of $SrTiO_3$ nanocubes can be SrO, TiO_2-rich reconstructions, or mixed with SrO and TiO_2-rich reconstructions depending on synthetic procedures [2].

CeO_2 nanocubes consists of 6 dominant flat {100} surfaces, 12 edge {110} surfaces, and 8 corner {111) surfaces. Viewing along <110> zone axis allows one to observe atomic structure on (100), (001) and (111) surfaces simultaneously [3]. The (100) surface has a mixture of Ce, O and reduced CeO terminations on the outermost surface. The (110) surface has a combination of reduced flat CeO_{2-x} surface layers and "sawtooth-like" (111) nanofacets. The CeO_2 (111) surface is O-terminated. During HREM observation, the hopping of atoms on the surface is often observed even when the electron beam intensity is reduced to 5×10^2 e/Å^{2}s. Fig. 1 shows the first layer of (111) surface diffuses away under an electron beam irradiation. Several new surface configurations are observed when Ce and O atoms hop on (100), (100) and (111) surfaces.

Co_3O_4 nanocubes consist of 6 dominant flat {100} surfaces and 8 corner {111} surfaces. The inset in Fig. 2 shows the project of Co_3O_4 along [1-10] direction. Oxygen is indicated by red dots. Tetrahedral and octahedral Co sites are indicated by green and blue dots respectively. HRTEM images in Fig. 2 show that (001) terminates at O-Co (at octahedral sites) and (111) terminates at O-Co (at tetrahedral sites).

$SrTiO_3$ nanocubes have ideal surfaces free of surface steps and islands. But CeO_2 and Co_3O_4 nanocubes often show complex surface structures such as sawtooth-like structures. We interpret

this because of difference in surface chemistry since the termination layers of SrO and TiO_2 are charge neutral, but it is not the case for CeO_2 and Co_3O_4 nanocubes [4].

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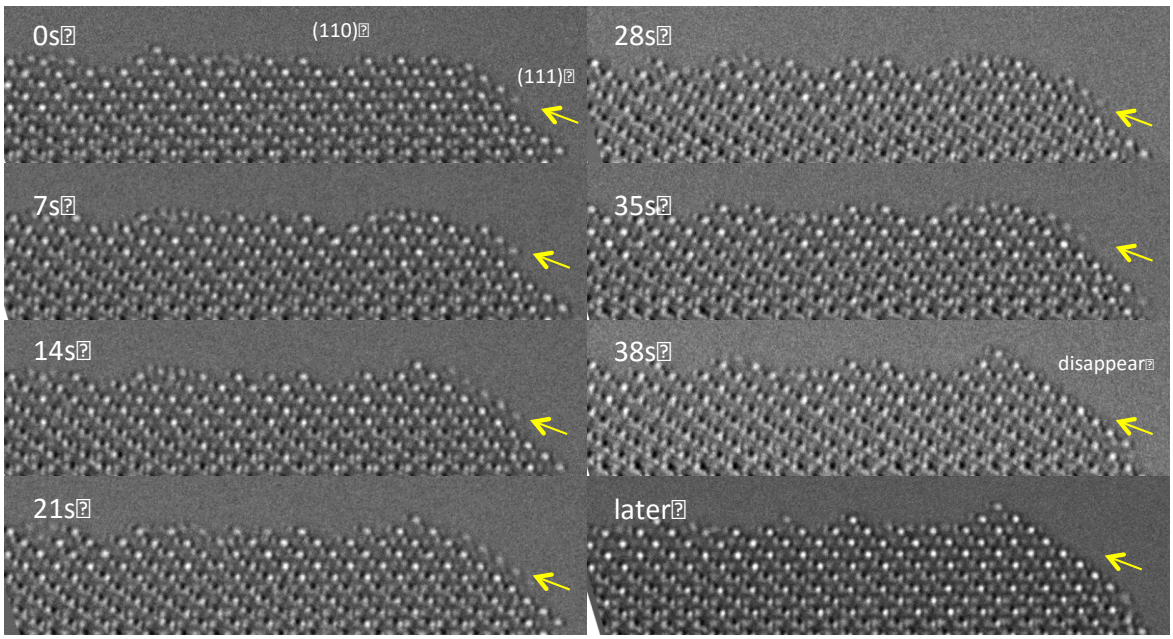

Figure 1. HREM images of {110}/{111} corner of a CeO_2 nanoparticle in selected time frames. The first layer of CeO_2 (111) surface diffuses away completely under an electron beam irradiation.

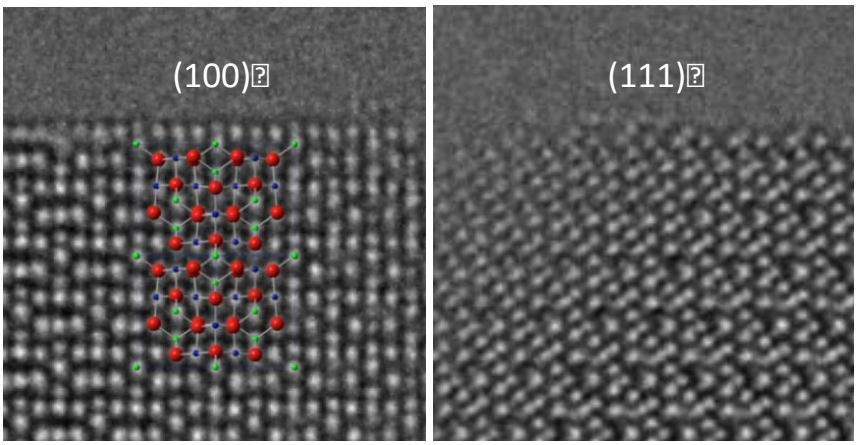

Figure 2. HREM images showing surface atomic structures of Co_3O_4 nanocubes on a) (100), b) (111) surfaces. The red dots represent the oxygen atoms. The blue and green dots represent cobalt at octahedral and tetrahedral sites by atoms with valence +3 and +2.

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