Atomic Surface Structures of Oxide Nanoparticles with Well-defined Shapes

Jianguo Wen¹, Yuyuan Lin², Huaping Sheng¹, Lifen Wang¹, Dean J. Miller¹, Zili Wu³, Kenneth R. Poeppelmeier²,⁴, and Laurence D. Marks²

¹Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL
²Department of Materials Science & Engineering, Northwestern University, Evanston, IL
³Chemical Science Division & Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee,
⁴Department of Chemistry, Northwestern University, Evanston, IL

Recent studies have shown that catalytic activities can be tuned by controlling the shape of nanoparticles such as SrTiO₃, CeO₂, and Co₃O₄ [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 (C₅) and chromatic aberration (C₇). C₇ correction allows the correction of C₅ towards zero to improve resolution without compromising contrast. Using this unique feature, we correct both C₅ and C₇ to small values to achieve direct structure interpretable HREM images including oxygen atomic columns. In this study, atomic surface structures of SrTiO₃, CeO₂, Co₃O₄ nanocubes are observed by using aberration-corrected HREM.

As-prepared SrTiO₃ nanocubes have 6 well-defined {100} surfaces. We have shown previously that by tilting SrTiO₃ 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 SrTiO₃ nanocubes. HRTEM studies show that the (100) surface of SrTiO₃ nanocubes can be SrO, TiO₂-rich reconstructions, or mixed with SrO and TiO₂-rich reconstructions depending on synthetic procedures [2].

CeO₂ 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 CeO₂ₓ surface layers and "sawtooth-like" (111) nanofacets. The CeO₂ (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 5x10²² e⁻/Å² 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.

Co₃O₄ nanocubes consist of 6 dominant flat {100} surfaces and 8 corner {111} surfaces. The inset in Fig. 2 shows the project of Co₃O₄ 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).

SrTiO₃ nanocubes have ideal surfaces free of surface steps and islands. But CeO₂ and Co₃O₄ 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$_3$O$_4$ nanocubes [4].

References:
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![Figure 1](https://example.com/figure1.png)

**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](https://example.com/figure2.png)

**Figure 2.** HREM images showing surface atomic structures of Co$_3$O$_4$ 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.