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 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 (Cs) and chromatic aberration (Cc). Cc correction allows the correction of Cs towards zero to improve resolution without compromising contrast. Using this unique feature, we correct both Cs and Cc 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 terminated on the outermost surface. The (110) surface has a combination of reduced flat CeO2-x 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 5x10^2 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.** 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$_3$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.