Understanding the Growth Mechanism of CeO_2 Nanocrystals by Comparison of Experimental and Simulated HAADF-STEM Images

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In recent years, ceria and doped-ceria anisotropic nanocrystals (NC's) have been produced by a variety of solution-based synthetic routes. The motivation in producing ceria-based NCs with controlled morphology is to develop high surface area catalyst supports with well-defined exposed crystal planes that exhibit optimal catalytic activity. Understanding the growth mechanism of CeO_2 NC's is vital to designing nanostructured functional materials.

In this study, CeO_2 NC's were synthesized using aqueous cerium (III) nitrate solution in the presence of oleic acid (OLA) stabilizing agents [1]. The CeO_0 NC's produced are denoted as Ce-1 ([OLA]/[Ce_{+3}] molecular ratio = 4) and Ce-2 ([OLA]/[Ce_{+3}] molecular ratio = 8) respectively. A wide variety of characterization techniques have been applied to these materials, such as XRD, FT-IR, TGA and TEM. Here a combined experimental and theoretical high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) study is presented to illustrate its unique potential in revealing the structure and morphology of CeO_2 NC's. The results obtained provide deeper insights into the possible growth mechanisms of CeO_2 NC's.

A typical polyhedral NC from the Ce-1 sample (Fig. 1(a)) exhibits {100}- and {111}-type termination facets viewed along the <011> projection. The bright spots in HAADF-STEM images correspond to Ce atomic columns. From the experimental micrograph, a 3D atomic model (Fig. 1(b)) has been constructed using the MEGACELL [2] software. In order to evaluate the accuracy of the model, HAADF-STEM image simulation using this model structure was performed with the xHREM suite [3] as shown in Fig. 1(c). Both the experimental and simulated HAADF-STEM images show good agreement in terms of shape, as well as the 'top-hat' line intensity profiles taken along the arrowed line indicated on the NC (Figs. 1(d) & (e)). When the [OLA]/[Ce_{+3}] molecular ratio is increased to 8, a more developed cube-like CeO2 NC (Fig. 2(a)) is generated. It shows {100}- and {110}-type termination facets when viewed along the <001> projection (Fig. 2(a)). Similarly a 3D model structure of this NC was built (Fig. 2(b)), and the corresponding HAADF image simulation (Fig. 2(c)) was performed. The experimental and simulated images (Figs. 2(a) & (b)) look very similar except that there is an intensity reduction toward the center of the NC in the former as indicated by the red arrow in Figs. 2(a) & (d). It is well known that the image intensity in HAADF is dependent upon several parameters, including the atomic number and sample thickness. Since contrast from the Ce atoms dominate, fewer projected Ce atoms are present at the center of the NC, rendering a cube-like NC with concave surfaces. The intensity ratio between the most and least intense coumns in Fig. 2(a) is ~ 1.557. The approximate depth of the surface concavities can be inferred by image simulation as shown in Fig. 3. As deduced from the exterior crystal dimension in Fig. 2(a), there are 11 atoms in most of the Ce columns. Using the xHREM suite, Ce column intensity as a function of the number of Ce atoms can be simulated as shown in Fig.

3(a). By comparing the intensity of columns with varying numbers of Ce atoms, the intensity ratio of 11 Ce atoms to 6 Ce atoms (~ 1.578) matches well with the intensity ratio observed in Fig. 2(a). This indicates that 5 Ce atoms at most are missing in each column close to the center of the NC, corresponding to 2-3 missing atoms on each face. This finding is supported by the fact that extra Ce planes are visible at the {100} termination facets of the NC (Fig. 2(a)). Based on the experimental and simulated HAADF data, two plausible NC formation mechanisms are proposed in Scheme 1.

References

[1] M.A.L. Cordeiro, *et al*., *Chem. Mater*., **25 (10),** (2013),2028.
[2] D.G. Stroppa *et al*., *Ultramicroscopy*, **111,** (2011), 1077.
[3] K. Ishizuka, *Ultramicroscopy*, **90,** (2001), 71.

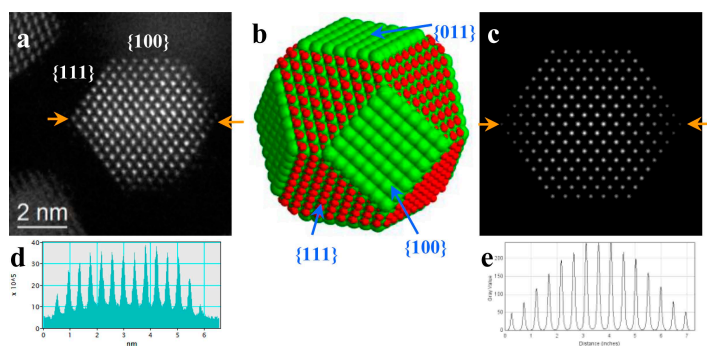**Figure 1**. (a) HAADF-STEM micrograph of a typical polyhedral NC in sample Ce-1 showing {100} and {111}- type termination facets in the <011> projection; (b) 3D atomic model derived from (a) built using MEGACELL; (c) the corresponding HAADF-STEM image simulation; (d) and (e) intensity profiles taken along the line indicated by the orange arrows in (a) and (c), respectively.
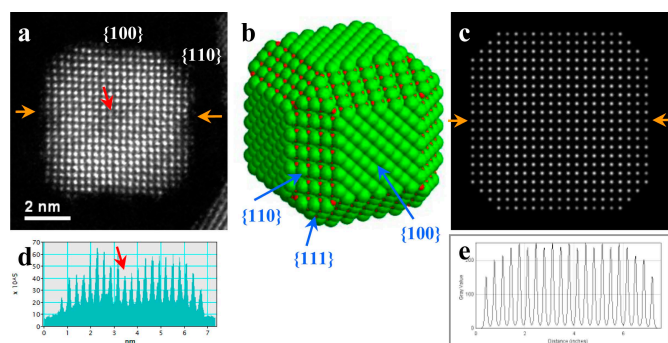

Figure 2. (a) HAADF-STEM micrograph of a typical cube-like NC in sample Ce-2 showing {100} and {110}-type termination facets in the <001> projection; (b) 3D atomic model derived from (a) built using MEGACELL; (c) the corresponding HAADF-STEM image simulation; (d) and (e) intensity profiles taken along the line indicated by the orange arrows in (a) and (c), respectively.
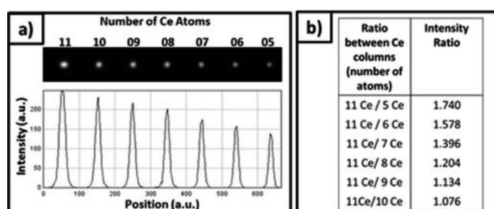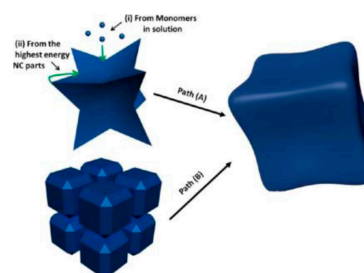

Figure 3. (a) HAADF-STEM simulation of Ce column intensity as a function of the number of Ce atoms per column, and (b) intensity ratios between 11 Ce atoms and a decreasing number of Ce atoms in each column.

Scheme 1. Two possible growth mechanisms for the CeO_2 NC morphology shown in Figure 2(a).