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In Situ Engineering and Characterization of Photonic Modes in Dielectric Nanocubes

Yifan Wang[1*], Piyush Haluai[1] and Peter A. Crozier[1]

[1.] School for Engineering of Matter, Transport & Energy, Arizona State University, Tempe, AZ, United States.
[*] Corresponding author: ywan1240@asu.edu

Photonic devices rely on materials having high refractive index difference between the photonic structure and the surrounding medium. In sub-micron-sized dielectric particles, which can be considered as cavities, electromagnetic waves with specific wavelengths can be trapped in the form of photonic modes, providing opportunities for energy harvesting and information transfer. To further understand this phenomenon and provide guidance for mode engineering, a systematical experimental study on photonic modes under varying conditions is necessary. Monochromated electron energy-loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) has proved to be a powerful technique to study photonic modes by providing both high energy and spatial resolution [1]. According to the simulation data, photonic modes are strongly dependent on the dielectric properties and the geometry of the material [2]. *In situ* capability grants us the ability to easily modify the morphology inside the microscope enabling the observation of the variation in the photonic mode.

CeO_2 (ceria) is a wide bandgap semiconductor with a high refractive index. For ceria, {111} surfaces have the lowest energy [3]. However, under certain conditions, e.g., in highly basic solution, the preferential growth directions of ceria crystal is <100>. Therefore, we can synthesize ceria nanocubes with {100} surfaces by a hydrothermal method with proper size control [4], and restructure the nanocubes through heating. The morphology evolution process of a ceria nanocube is showed in **Figure 1a**. As the evolution proceeds, the crystal reconstructs and atoms on the {100} surface diffuse and expose {110} and {111} surfaces. Eventually the cube transforms to an octahedron with only {111} surfaces. To parameterize the morphology transformation, we define *d* as truncation depth (**Figure 1b**). By assuming the volume change of the cube is trivial in the process, the shape of truncated cube is solely determined by *d*. **Figure 1c** shows a TEM image with significant edge truncation of ceria cube after *ex situ* heating, marked with red circles.

Such geometry variation will lead to changes in photonic modes, including intensity and energy. Here, we have performed a series of simulations with COMSOL Multiphysics [5] to calculate energy-loss spectra from different degrees of truncation of the edges of a 200nm cube, as showed in **Figure 2a**. An electron beam is set in aloof configuration, 10 nm away from the middle of a truncated cube face. The simulated energy loss spectra for a series of truncation depth *d* are showed in **Figure 2b.** For the spectrum of single cube(*d*=0), multiple peaks are observed below the band gap edge (~3.4eV). With increasing of *d* from 0 to 50nm, redshift of the peaks is observed, as indicated by red arrows. When truncation depth is above certain threshold, i.e., when *d*=100 nm, peaks are diminished or missing, indicated by black arrows. When the cube has transformed to octahedron completely (*d*=180nm), despite the low overall intensity of EELS as such geometry is not scattering favorable (i.e., low energy loss probability), we can still observe a red shift from the peak right at the band gap edge. Based on these results, *in situ* monochromated STEM EELS will be performed in an FEI Titan environmental TEM (ETEM) to observe these changes in photonic modes experimentally by heating up single cubes and aggregates of cubes. The spectra will be taken in aloof configuration to prevent direct interaction between the electron beam and sample. Meanwhile, we can monitor the morphology or composition transformation through STEM or TEM imaging [6].

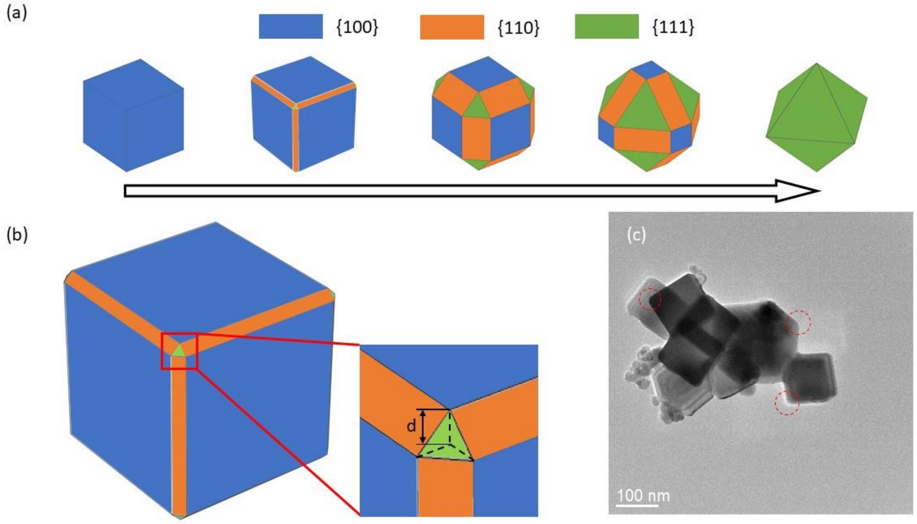

Figure 1. Morphology evolution of ceria cubes. (a) The morphology transformation process by heating at high temperature. The blue, orange and green areas represent the {100} surfaces, {110} surfaces, and {111} surfaces. (b) Image of the intermediate state between cube and octahedron. The depth of truncation **d** is defined in the figure. (c) A TEM image of ceria nanocubes after heating in air at 700°C for 4 hours. Truncation of edge and corner of the cube is observed, indicated by red circles.

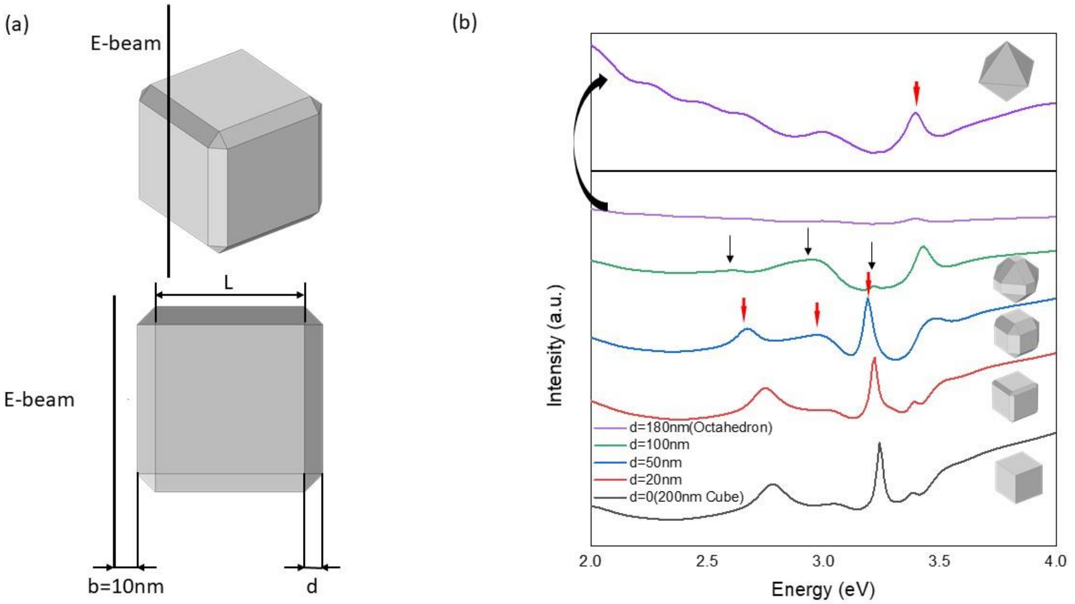

Figure 2. EELS simulation of truncated cubes. (a) Schematic view of simulation configuration. The electron beam is set 10 nm away from the center of one face of the truncated cube. Based on a 200nm

cube, by setting the volume as constant, the geometry of the truncated cube is solely determined by the truncation depth **d**. (b) Energy loss spectra of **d** = 0(200nm untruncated cube), 20nm, 50nm, 100 nm, and 180nm (octahedron) represented by black, red, blue, green, and purple curve. The upper part of the figure exaggerated the purple curve in intensity to show the features. The x axis marks energy loss from 2 eV to 4 eV. The red shifts of the peaks are represented by red arrows, and the diminish of intensity are showed as black arrow.

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