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Direct Observation of Atomic Surface Structures of CeO_2 Nanoparticles

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CeO_2 has a wide range of applications such as catalysts and as electrodes in solid oxide fuel cells due to its unique physical, chemical and electrochemical properties [1,2]. Many of these applications are related to surface structures of CeO_2. For example CeO_2 nanoparticles are used as a catalytic support since surface oxygen vacancies are expected to promote catalytic metal particle dispersion [1]. However, due to the lack of clear observation of oxygen columns using TEM or scanning TEM, atomic surface structures of CeO_2 nanoparticles are under debate. Using high resolution electron microscopy with Argonne Chromatic Aberration-corrected TEM, we are able to observe both Ce and O columns, allowing us to directly observe atomic structures of the (100), (110) and (111) surfaces of CeO_2 nanoparticles.

CeO_2 nanocubes consists 6 dominant flat (100) surfaces, 12 edge (110) surfaces, and 8 corner (111) surfaces. Fig. 1 shows HREM images of the predominantly exposed (100) surface along [110] zone axis. Fig. 1b shows two distinctive surface structures on (100) surface, one is a surface with a Ce termination (yellow bar) and another surface with an O termination (red bar). Thus both O and Ce terminations can exist on the same surface. (100) surface typically has a mixture of Ce, O, and reduced CeO terminations (Fig. 1e). HREM simulation indicates that partial occupancy of the outermost layer occurs at both Ce and O positions, resulting the exposure of the subsurface layer. 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 [3].

HREM image in Fig. 2a shows that the (110) surface consists of flat CeO_{2-x} terminations and small amount of "saw-like" (111) nanofacets indicated by white arrows. For the flat part of the (110) surface, partial surface oxygen vacancies result in two types of termination layers: (110) surface with a CeO2 surface termination and (110) surface with a Ce termination as supported in simulated images in Fig. 2b and 2c. A line profile of the surface layer from A1 to A2 shows more clearly the existence of many surface O vacancies. We observed an average of approximately 30% oxygen vacancies on the flat (110) surface of CeO_2 nanocubes.

The (111) facet is determined as O-terminated by comparing simulated HREM image with the O-terminated surface with the experimental surface contrast, which is in agreement with the previous IR studies and electrostatic considerations for the surface HREM observations of all three surfaces indicate that surface reconstruction, nanofacet, and surface vacancies need to be considered when establishing the structure-catalysis relationship for CeO_2 nanoparticles [4].

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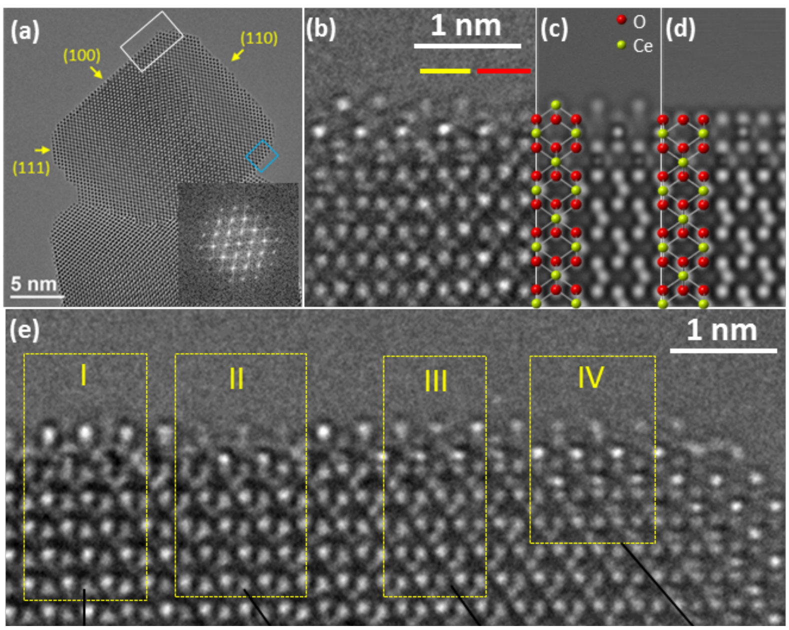

Fig. 1. Atomic structure of (100) surfaces of CeO_2 nanocubes. (a) A HREM image of a typical CeO_2 nanocube along [110]. (b) A magnified HREM image of the (100) surface of (a), highlighted with the blue box. (c)-(d) Simulated HREM images of (b) using Ce and O terminations respectively. (e) A magnified HREM image of the (100) surface of (a), highlighted with the white box. Regions I- IV shows the (100) surfaces with different terminations or occupancies.

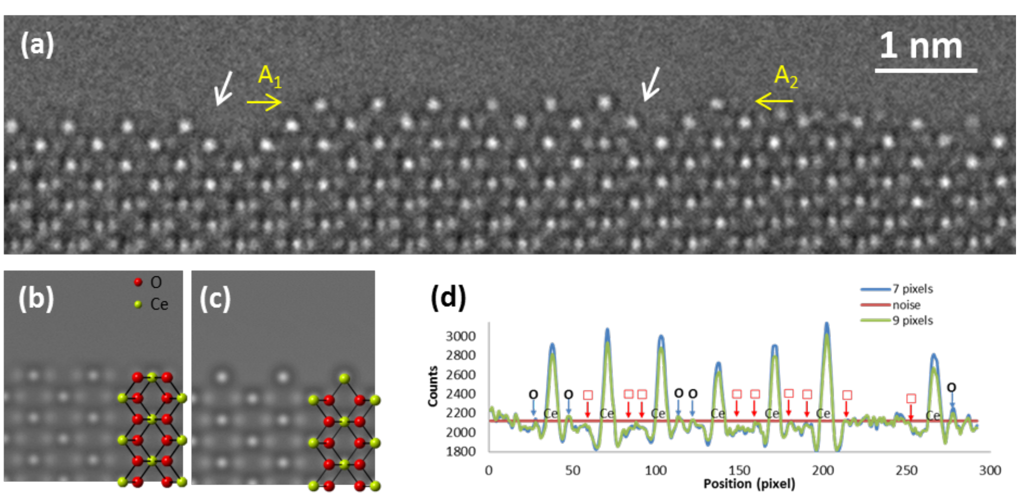

Fig. 2. (110) surfaces of CeO_2 nanocubes. (a) An experimental HREM image on a (110) surface of CeO_2 nanocubes along [110]. The white arrows indicate (111) nanofacets. (b) A simulated HREM image of the CeO_2 (110) surface with a CeO_2 surface termination. (c) A simulated HREM image of the CeO_2 (110) surface with a Ce termination. (d) Integrated line profiles from A1 to A2 indicated in (a). O vacancies are indicated by the squares (□).

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