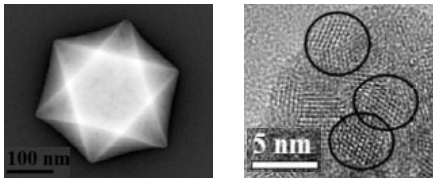
Exploring Nanostars

Self-assembled oxide superoctahedra featured on Crystal Growth & Design *cover*

The evolution of a self-assembled, oxide superoctahedral structure has been elucidated *for the first time*, and this unique finding was featured on the cover of *Crystal Growth and Design* – a journal ranked first in the field based on impact factor. For these studies, researchers at the Department of Energy's EMSL and their collaborators from the University of Central Florida and the Defence Academy of the United Kingdom used a combination of experimental tools at UCF and EMSL as well as theoretical tools at the Cambridge-Cranfield HPC facility to study cerium oxide. Because cerium oxide is crucial for solid oxide fuel cells, solar cells, catalysis, and biomedicine, understanding its nanostructures is vital to improve their performance in those applications.



Cerium oxide forms octahedral superstructures (TEM image at left) composed of octahedral nanoparticles (HRTEM image at right; circles indicate individual nanoparticles).

To characterize the superstructures, the research team applied high-resolution transmission electron microscopy and fast-Fourier transform analysis. HRTEM yielded structural and morphological information. FFT analysis allowed the researchers to study a specific sample area of interest such that crystallographic information from even single nanoparticles could be derived. Integrating the team's experimental data with atomistic modeling revealed a stepwise process for superstructure formation. Importantly, the process occurred naturally – at room temperature and pressure and without surfactants. First, cerium oxide molecules form individual octahedral nanoparticles that are shaped like two pyramids stuck together at their bases. This step was successfully predicted by molecular dynamics simulations, and that prediction was confirmed experimentally. Next, the octahedra stack tightly together via fractal self-assembly to yield superoctahedral structures. Understanding the orientation of the interfaces between two adjoining octahedral nanoparticles is particularly important. These interfaces may have a low or high energy conformation – in other words, the surfaces of the nanoparticles may lie against one another more or less comfortably. A high-energy interface is prone to defects that may act as potential reaction sites, making the defects favorable for improved performance.

Scientific Impact: Understanding the factors that control oxide nanostructure size, shape, and self-assembly enable the design of new materials with improved properties for energy, catalytic, or biomedical applications. The types of information obtained in these studies demonstrate the importance of EMSL's capability development to enable the design and growth of increasingly complex materials and their characterization with unprecedented (atomic level) resolution.

Societal Impact: The ability to understand and tailor nanomaterials with better properties can lead to sustainable, greener energy prospects; environmental protection; and the detection, treatment, and prevention of diseases using nanomedicine.

For more information, contact EMSL Communications Manager Mary Ann Showalter (509-371-6017).

Reference: Kuchibhatla SVNT, AS Karakoti, DC Sayle, H Heinrich, and S Seal. 2009. "Symmetry-Driven Spontaneous Self-Assembly of Nanoscale Ceria Building Blocks to Fractal Superoctahedra." *Crystal Growth & Design* 9(3)1614-1620. DOE:10.1021/cg801358z

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