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Meeting-report

A Correlated STEM/APT Study of Multidimensional and Interconnected Multi-element Nanostructures Derived from a Complex Concentrated Oxide

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Complex concentrated oxides (CCOs) are an emerging material class that includes high-entropy oxide (HEOs) and entropy-stabilized oxides (ESOs), whose unprecedented properties stem from disorder-induced distributions in electronic structure and chemistry caused by stabilizing many-cation (typically > 5) solid solutions [1][2]. Integrating these materials into composites with nanoscale tunability will enable tailored (multi)functionality beyond what is possible in a single phase [3]. Here, we demonstrate a novel, highly extensible approach to realize CCO-based nanocomposites with intricate multi-element nanostructures. So-called *hybrid exsolution self-assembly* synthesis is applied to a CCO inspired by $LaFeO_3$—a perovskite commonly modified through chemical doping for use in future electrochemical, sensing, and electro/photocatalysis applications [4]. Using pulsed-laser deposition, we selectively reduce cations in a 6-cation perovskite oxide, inducing defect-interaction-driven exsolution and simultaneous self-assembly of metal nanorods and metal-oxide core-shell nanoparticles, depending on film growth conditions. Nanocomposite synthesis is achieved while maintaining competitive electronic conductivity, and both mechanisms are elucidated via correlated sub-nanoscale electron and atom probes.

A correlated analysis using aberration-corrected scanning transmission electron microscopy (STEM) imaging, energy dispersive X-ray spectroscopy (EDS), electron energy-loss spectroscopy (EELS), geometric phase analysis (GPA) strain mapping, atom probe tomography (APT) with 3D mass spectrometry, and X-ray photoemission spectroscopy (XPS) was performed to elucidate the fundamental nanostructure formation mechanisms underlying the highly tailorable synthesis approach. We show that the method achieves uniform bulk exsolution with short process time and is manipulated by tuning readily accessible PLD conditions. Detailed characterization resolved the impact of increasing oxygen vacancy concentration and varying cation reducibility on nanostructure self-assembly. For example. Metal nanorods grow from bottom of the thin film to top surface, with growth restricted by compressive stress exerted by the matrix in the in-plane direction. Metal-oxide core-shell nanoparticles embedded in the matrix form via seed growth effect triggered by metal nanoparticle formation followed by subsequent reduction of additional mobile cations. This work demonstrates a route towards vast morphological tunability and compositional complexity through nanocomposite design of functional thin films with derived from CCOs. Because this emerging material class includes HEOs and ESOs, this study also lays the groundwork for additional synthetic control and material functionalities arising from tunable configurational entropy [5].

References

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