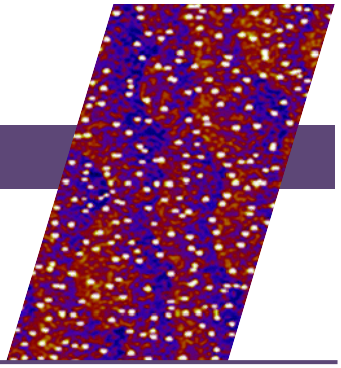
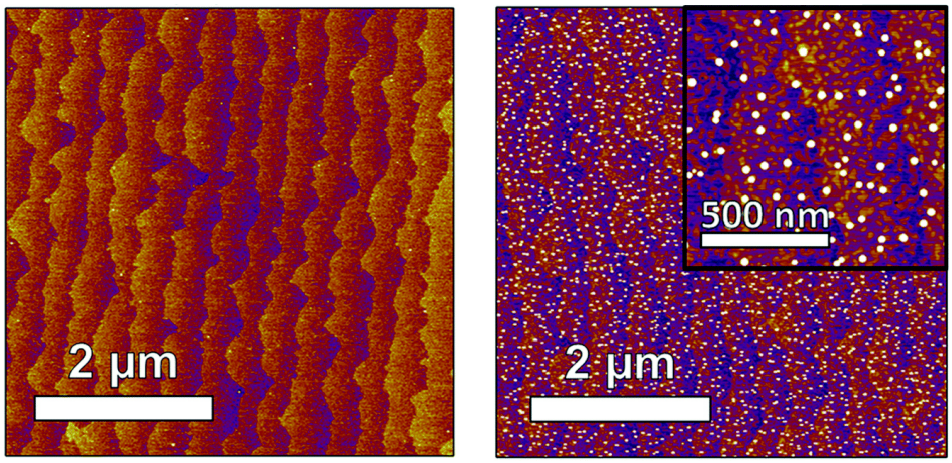
Watching Nanoparticle Chemistry and Structure Evolve





Atomic force microscope images of nickel- and niobium-co-doped strontium titanate, before (left) and after (right) thermal treatment in a reducing (H_2) atmosphere. After treatment, bright features consistent with the formation of nickel nanoparticles are observed.

Scientific Achievement

Using a multimodal approach developed at the Advanced Light Source (ALS), researchers learned how chemical properties correlate with structural changes during nanoparticle growth.

Significance and Impact

The work will enable a greater understanding of the mechanisms affecting the durability of nanoparticles used to catalyze a broad range of chemical reactions, including clean-energy reactions.

Catalyzing technological progress

In applications ranging from chemical synthesis to energy storage, catalysts enable chemical reactions to run at more favorable temperatures, pressures, or in general, with lower energy requirements. For example, catalysts enable the efficient splitting of water to generate hydrogen, which can then be used as a clean, decarbonized fuel.

For such applications, nanoparticles on the surface of a transition-metal oxide work well as catalysts, but they are susceptible to coarsening, agglomeration, and other forms of degradation, shortening their usable lifetime. In this work, researchers applied a technique they developed at the ALS to simultaneously study the chemistry and structure of catalyst materials as they form, a capability that will help scientists identify strategies for improving nanoparticle durability.

Understanding nanoparticle exsolution

A process called "exsolution" has shown significant promise for controlling nanoparticle size, shape, distribution, and stability. Briefly, the process involves causing dopant atoms in a host matrix to migrate to the surface and gather to form nanoparticles. This is done by heating the host material under reducing conditions (i.e., in a reducing gas such as hydrogen). Exsolution from metal oxide hosts produces highly stable metal nanoparticles that are often partially embedded in the oxide surface and show high activity for the oxygen evolution reaction (OER), a key step in many electrochemical reactions, including water splitting.

Here, the samples studied were thin films of $SrTi_{0.9}Nb_{0.05}Ni_{0.05}O_{3-\delta}$ (STNNi). When STNNi is heated in H_2 gas, the Ni atoms migrate to the surface and form nanoparticles. Before the reducing treatment, such samples are inactive with respect to the OER. After treatment, the system becomes active, despite a relatively small amount of Ni doping.

Correlated photoemission and scattering

To better understand the chemical and structural transformations occurring in the Ni nanoparticles during exsolution, the researchers applied a technique they developed at ALS Beamline 11.0.2, dubbed Ambient-Pressure PhotoEmission and X-ray Scattering (APPEXS). This new capability, currently available only at the ALS but being developed at other facilities

around the world, allows simultaneous ambient-pressure x-ray photoelectron spectroscopy (APXPS) and ambient-pressure grazing-incidence x-ray scattering (APGIXS) measurements, enabling the correlation of chemical and structural changes, respectively, as the nanoparticles grow.

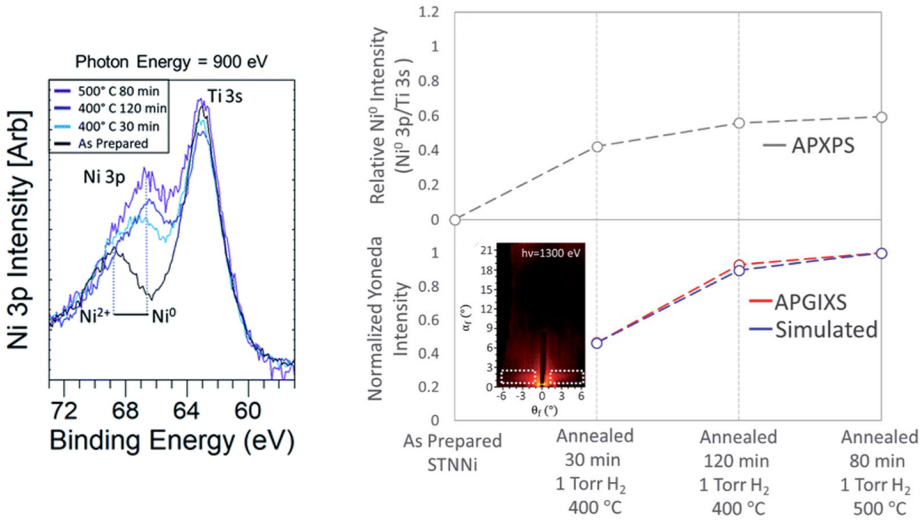
The researchers also used scanning probe microscopy to establish that nanoparticle exsolution occurred and obtain boundary information about particle morphologies and distributions for use in computer modeling. The elemental composition of the Ni nanoparticles was supported by nanoprobe x-ray absorption spectroscopy at the Advanced Photon Source.

The exsolution solution

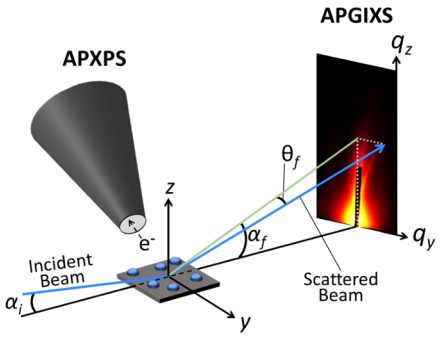
The correlated data showed that, as nanoparticle size and structure evolved, the surface Ni component transformed from oxide to metal, while the bulk of the STNNi film was not affected. Particle morphology simulations based on the scattering data revealed that the particles grew larger and adopted a compressed shape as exsolution proceeded.

The work serves as an important proof of principle for studies of exsolved materials as they're grown or during reactions, and it opens up new avenues for studying complex systems in realistic environments.

The researchers are now exploring collaborations to apply this technique to diverse scientific areas, including atmospheric science, microelectronics, corrosion science, hydrogen storage, and other heterogeneous catalytic systems.



Left: APXPS data from the STNNi sample shows that, after treatment, the Ni 3p feature shifts from 68 to 66.5 eV, characteristic of a transition from Ni^{2+} to Ni^0. At the same time, the Ni 3p intensity increases notably compared to the Ti 3s peak, indicating that the surface becomes increasingly enriched in Ni^0. Right: The top graph shows relative Ni enrichment at the STNNi surface as a function of the reducing treatment (from the APXPS data). Bottom graph shows the correlated APGIXS (red) and simulated (blue) intensity of a feature called the Yoneda line (see dashed boxes in inset) that can be used to assess roughness and/or inhomogeneities in planar systems.



APPEXS experimental layout. In APXPS experiments, incident x- rays are absorbed at the sample surface, resulting in the emission of photoelectrons that reveal chemical information. Incident x- rays that don't get absorbed but instead scatter away from the sample are also detected through the APGIXS technique, providing information about sample structure.

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Publications: H. Kersell, M.L. Weber, L. Falling, Q. Lu, C. Baeumer, N. Shirato, V. Rose, C. Lenser, F. Gunkel, and S. Nemšák, "Evolution of surface and sub-surface morphology and chemical state of exsolved Ni nanoparticles," *Faraday Discuss.* **236**, 141 (2022), doi:10.1039/D1FD00123J.

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