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### **Metal exsolution and nanoparticle self-assembly dynamics at complex oxide surfaces**

Metal exsolution attracts much attention for the synthesis of nanostructured catalysts. Thermal reduction of doped perovskite parent oxides induces the migration of reducible cations from the oxide bulk to the surface and results in the self-assembly of metallic nanoparticles that serve as catalytic centers. Ideal exsolution-type catalysts therefore dynamically adapt with respect to the oxygen chemical potential. The parameters that influence the kinetics of nanoparticle exsolution, however remain an open question in the scientific community. Furthermore, little is known about the origin of stability limitations of exsolved nanoparticles that are typically anchored at the oxide support.

We employ epitaxial thin films model systems with atomically defined surfaces to investigate the exsolution response of Ni in  $\text{SrTi}_{0.9}\text{Nb}_{0.05}\text{Ni}_{0.05}\text{O}_{3-\delta}$  and  $\text{SrTi}_{0.95}\text{Ni}_{0.05}\text{O}_{3-\delta}$  of respective *n*-type and *p*-type defect chemistry. Here, we study the mass transfer of dopants towards the surface as well as the morphological evolution of the nanostructured catalysts. Our thin film approach enables to study differences in the exsolution behavior on the basis of well-defined (001) surfaces eliminating uncertainties regarding the complex microstructure and anisotropy of ceramic oxides and the presence of secondary surface phases.

In order to assess the dynamic changes at the catalyst surface during metal exsolution, we conduct advanced *in-situ* spectroscopy and scattering analyses. In particular, we employ a recently developed synchrotron-based technique that allows for the simultaneous analysis of the chemical and structural evolution of the solid-gas interface based on coupled *in-situ* ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and *in-situ* ambient pressure grazing incidence X-ray scattering (AP-GIXS). Our investigations show that the defect chemistry of the near-surface region determines the dynamics of the exsolution response, where the formation of space charge regions at the perovskite surface plays a major role for the process.

We conclude that the mass transfer during metal exsolution and therefore the nanoparticle self-assembly at the perovskite surface is surface-controlled by interaction with the energy landscape of the complex oxide surface. Derived from our investigations, we propose a mechanistic model that describes how metal exsolution is mediated by the surface defect chemistry and we demonstrate surface engineering of the topmost atomic layers can be utilized as a novel strategy for the active control of the exsolution behavior. Moreover, our observations indicate that the different nature of the surface potential may influence the stability of exsolved nanoparticles.