Influence of the Defect Structure on the Exsolution Behaviour of Nickel in Epitaxial $SrTi_{0.9}Nb_{0.05}Ni_{0.05}O_{3-\delta}$ Perovskite Oxide Thin Films

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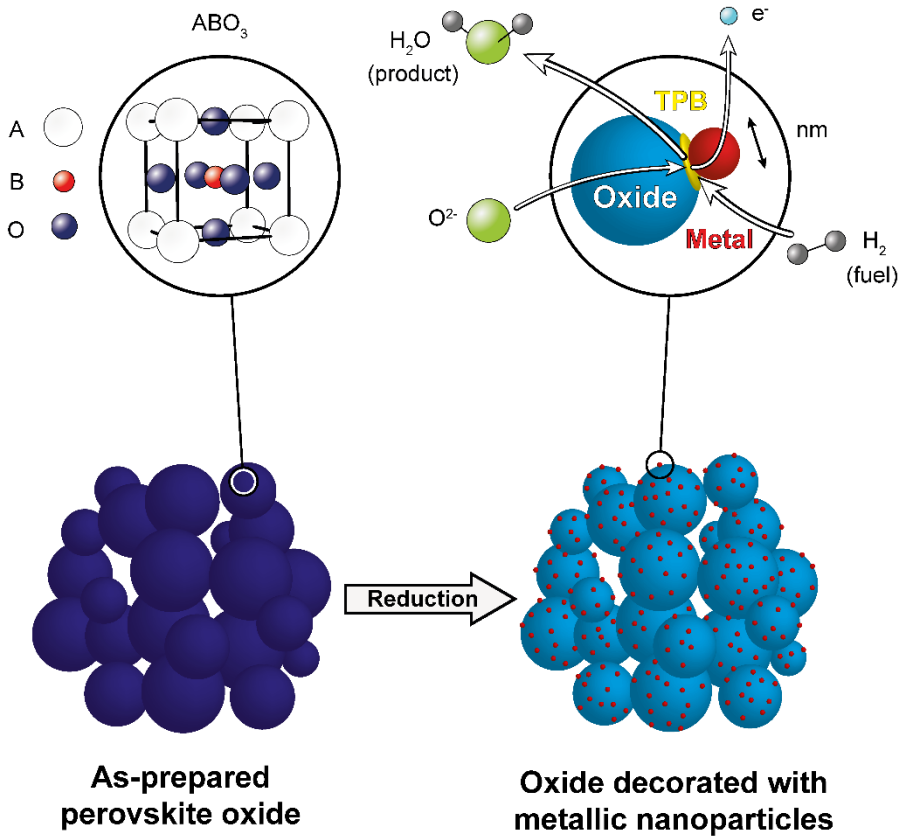
M. L. Weber, M. Wilhelm, L. Jin, U. Breuer, C. Lenser, F. Gunkel, N. H. Menzler, R. Dittmann, R. Waser and O. Guillon

Metal exsolution

Synthesis of supported nanoparticles by metal exsolution

Idealized concept



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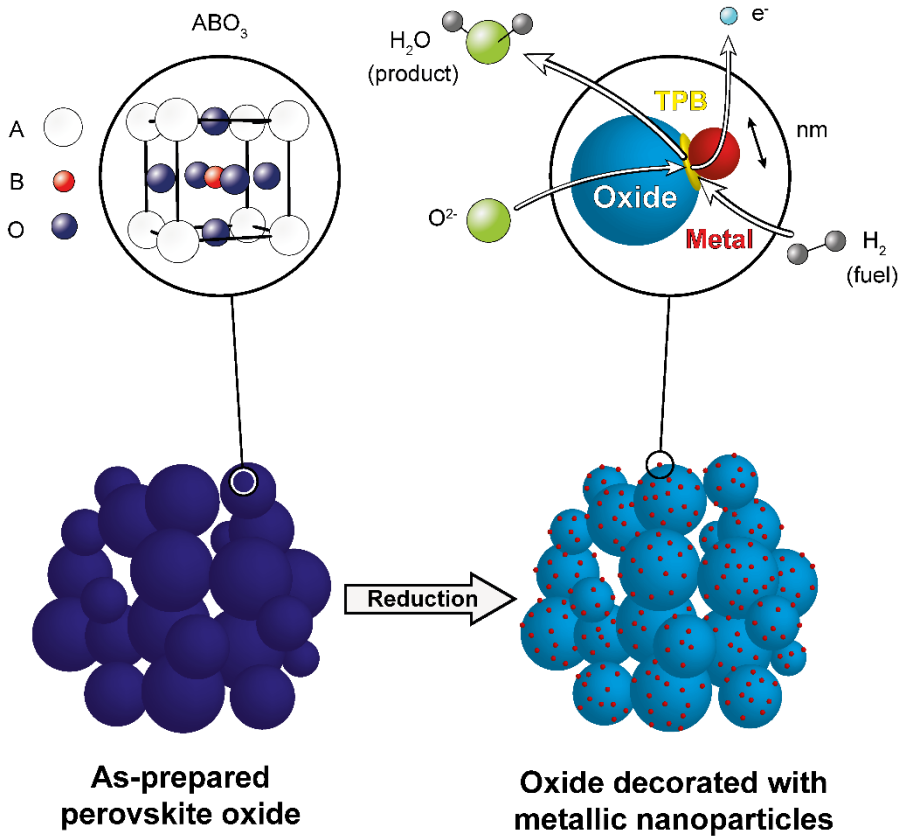
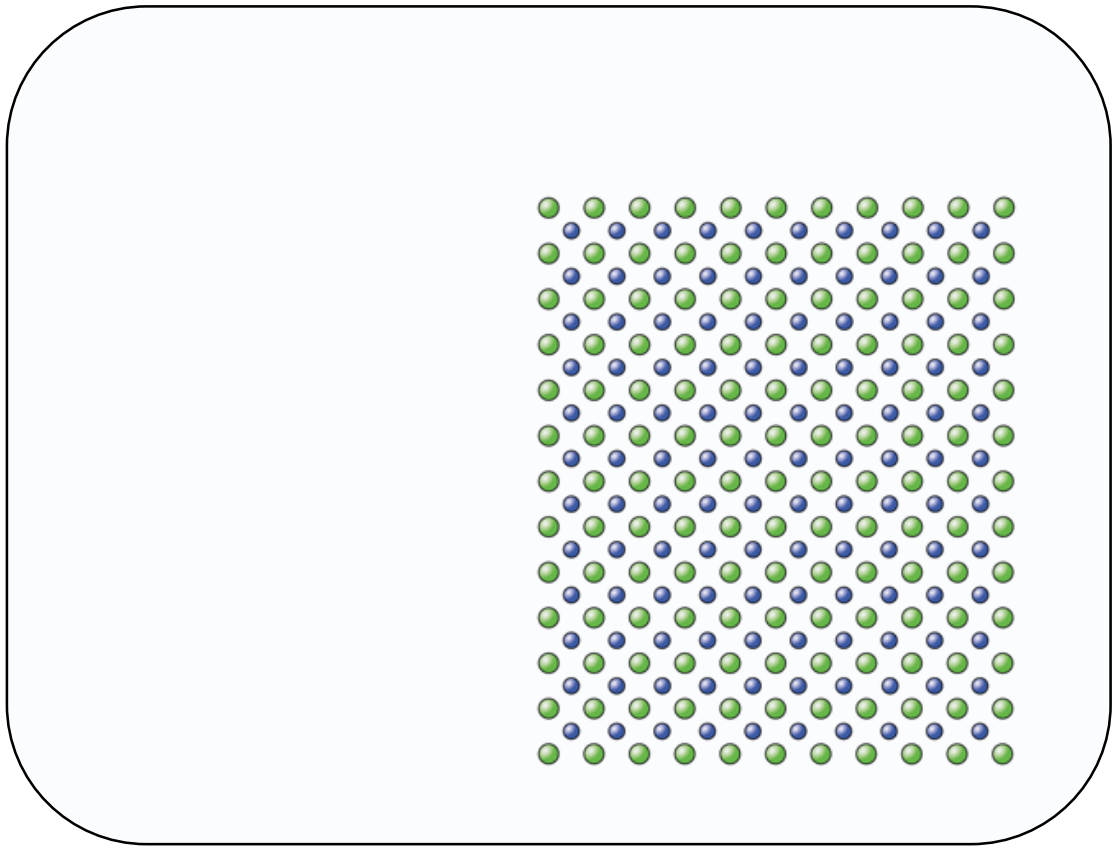


Exsolution process



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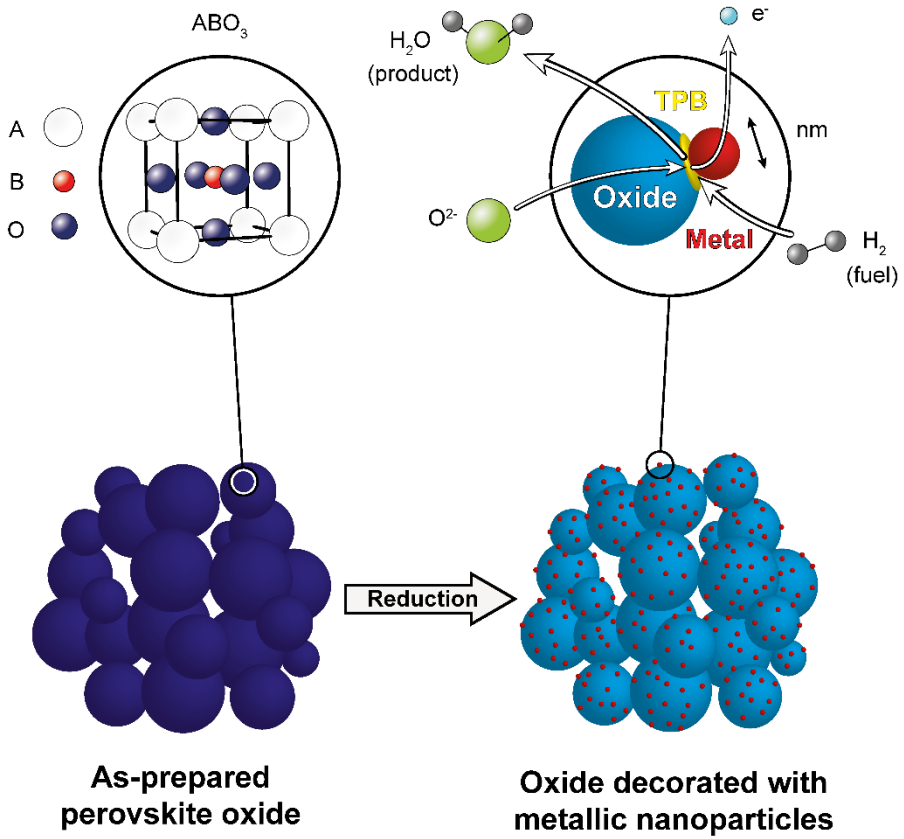
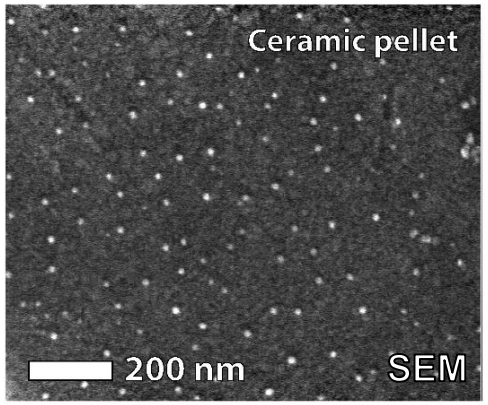
Metal exsolution

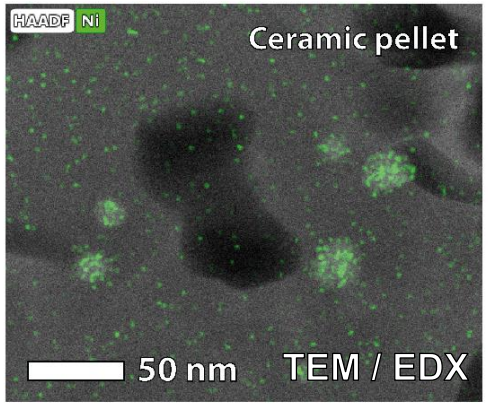
Thin film approach

Idealized concept



Ceramic $SrTi_{0.9}Nb_{0.05}Ni_{0.05}O_{3-\delta}$





Metal exsolution

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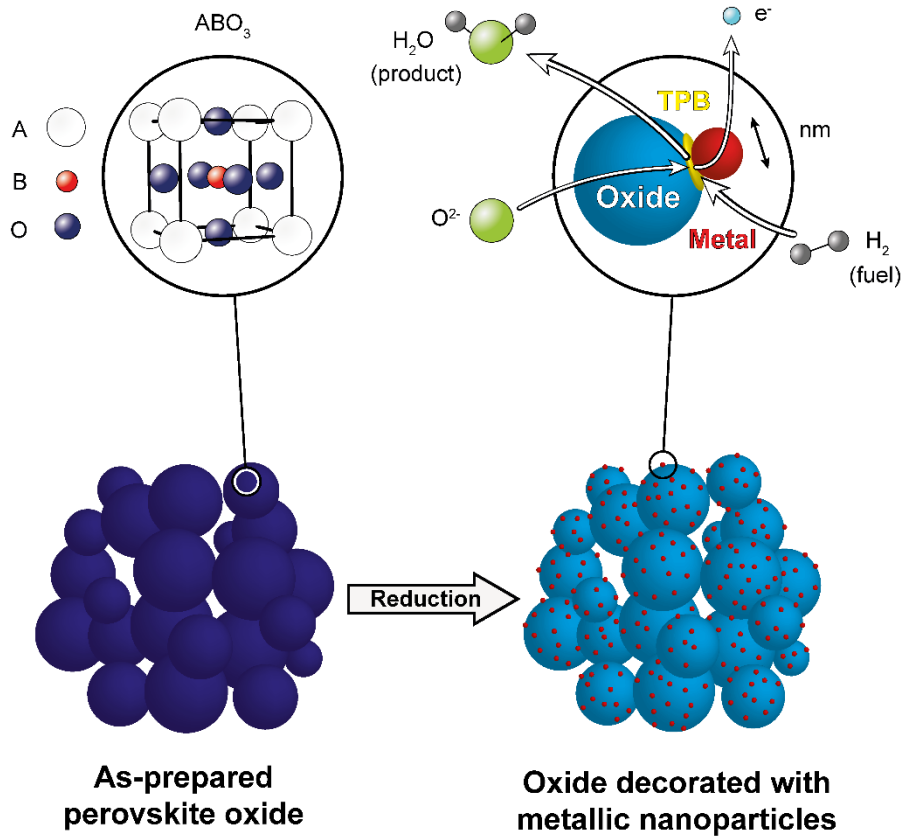

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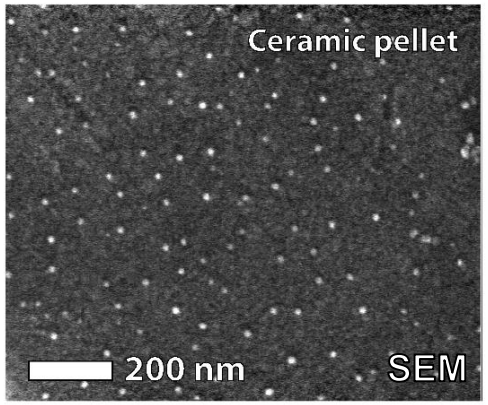
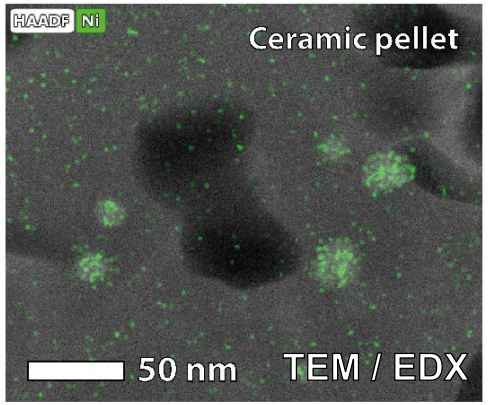
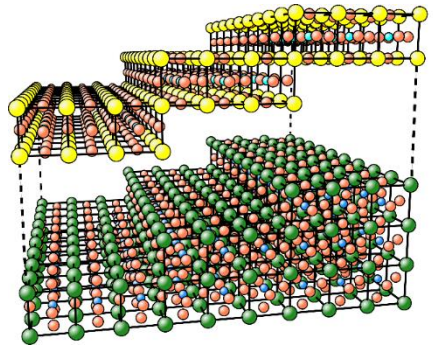


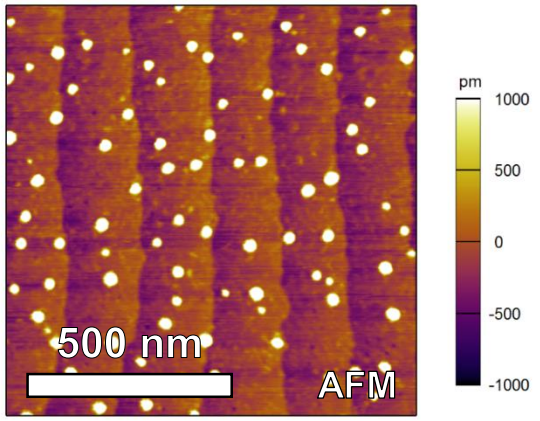


Epitaxial model sytems

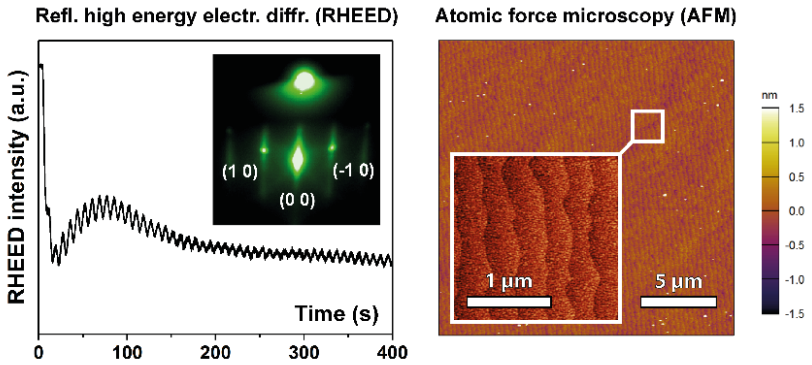


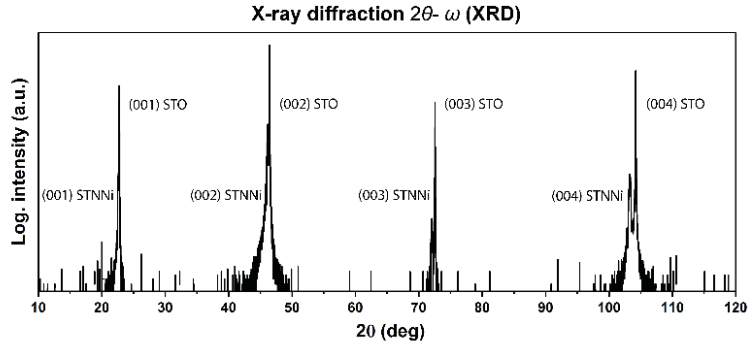
[Moritz L. Weber and Felix Gunkel, *Journal of Physics: Energy* **2019** *1* (3), 2515-7655]

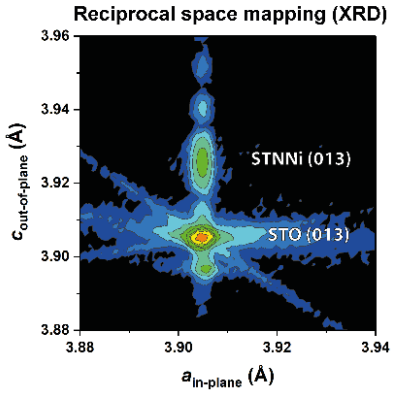
30 u.c.

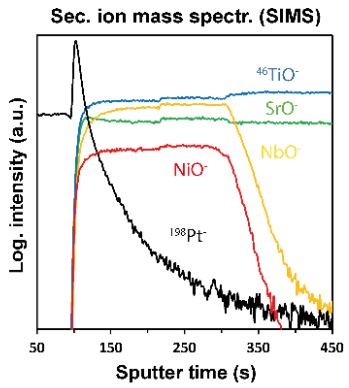


Metal exsolution



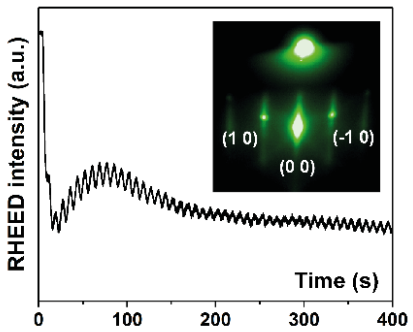




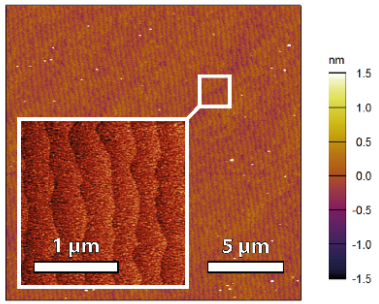


Metal exsolution

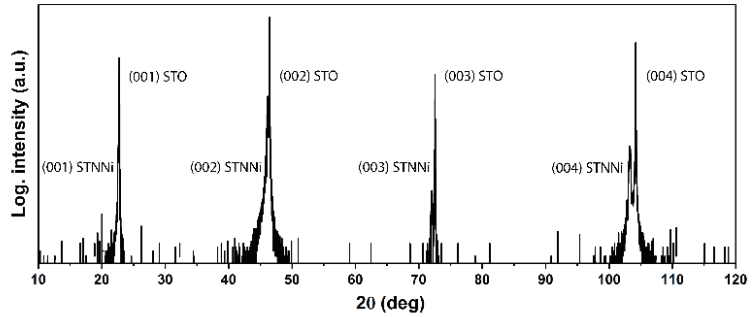
Refl. high energy electr. diffr. (RHEED)



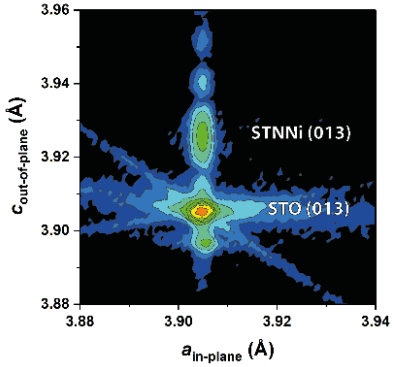
Atomic force microscopy (AFM)



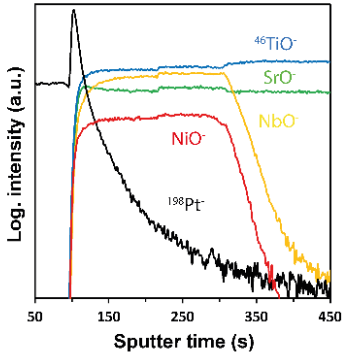
X-ray diffraction 2θ- ω (XRD)



Reciprocal space mapping (XRD)



Sec. ion mass spectr. (SIMS)



Reduction

(800°C, 15h, 4% H_2 / Ar)

Thin film thickness 50nm

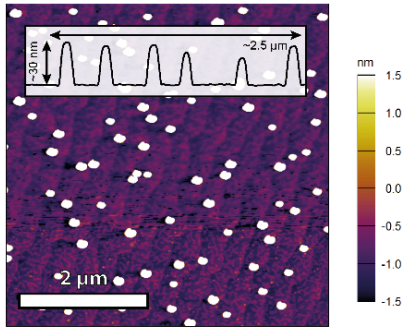
Deposition with monolayer precision

High control of material properties:

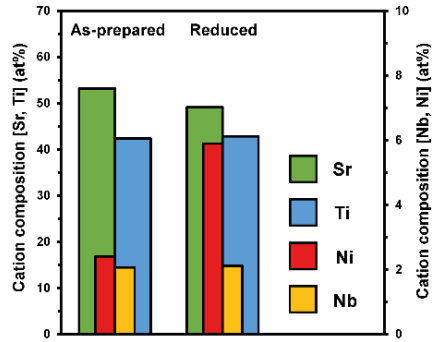
- Smooth surface
- Crystal orientation
- Strain state
- Defect structure…

Well-defined model systems for exsolution studies

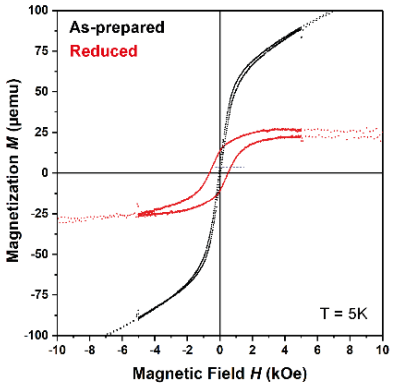
Atomic force microscopy (AFM)



X-ray photoelectron spectr. (XPS)



Vibrating sample magnetometer (VSM)



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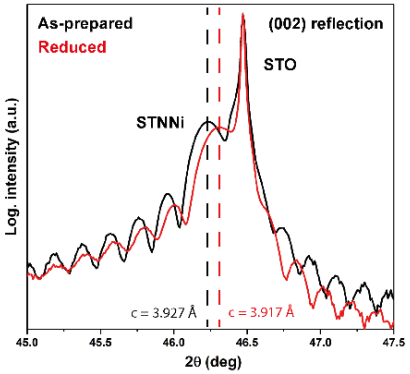
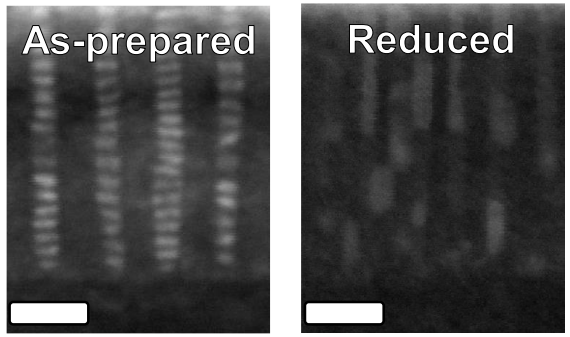


- Formation of highly dispersed nanoparticles
- Ni enrichment at the surface
- Magnetic transition to the ferromagnetic state
- Shift in the *c*-lattice parameter visible
- Release of Ni from the thin film lattice and the formation of metallic nanoparticles

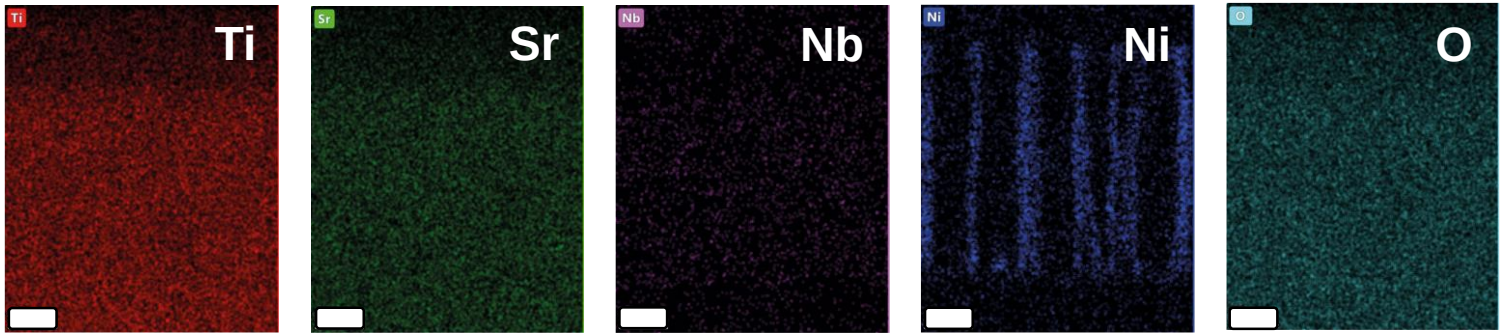
Metal exsolution

Structural properties – accomodation of Ni within the host lattice

TEM dark-field imaging



Energy dispersive X-ray spectroscopy (EDXS)



Scale bars: 20nm

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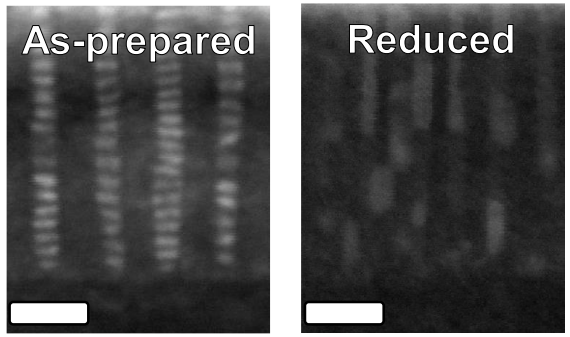

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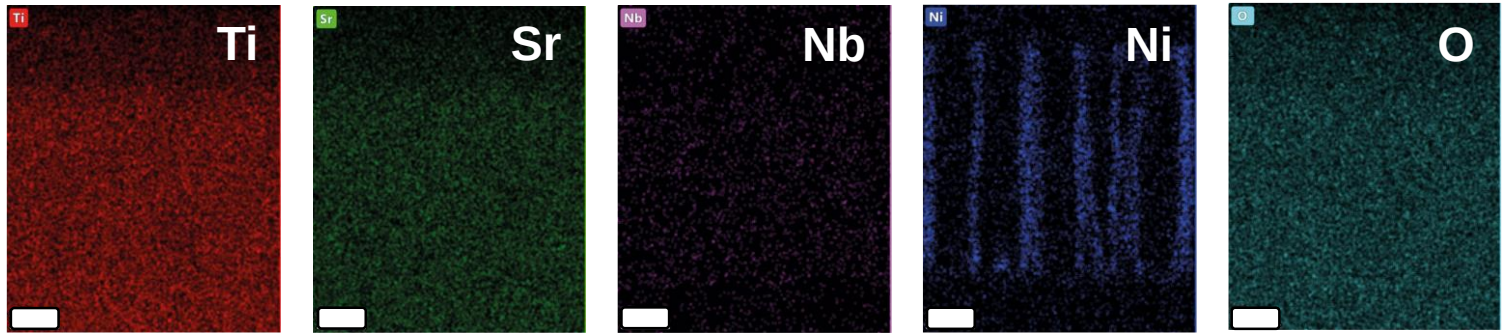
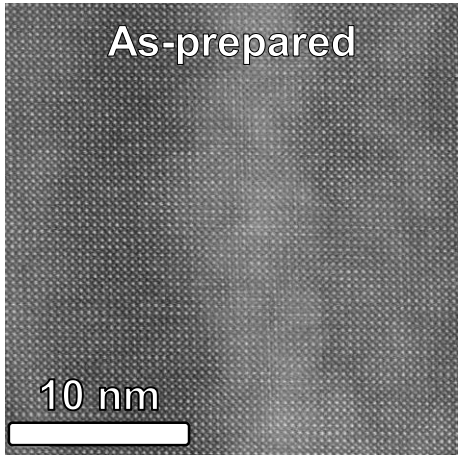


Scale bars: 20nm

HR-STEM



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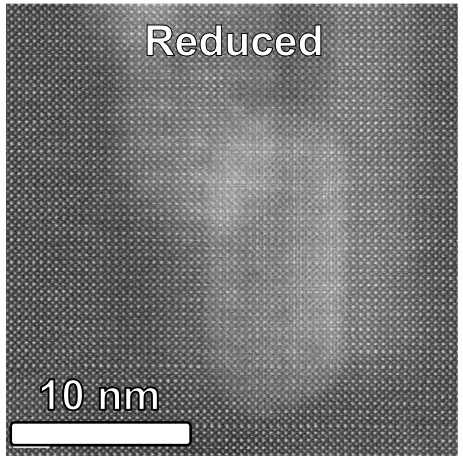

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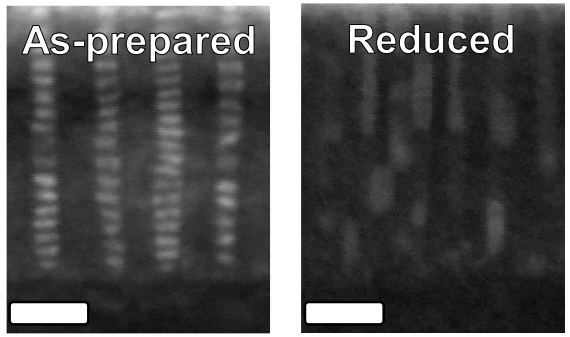

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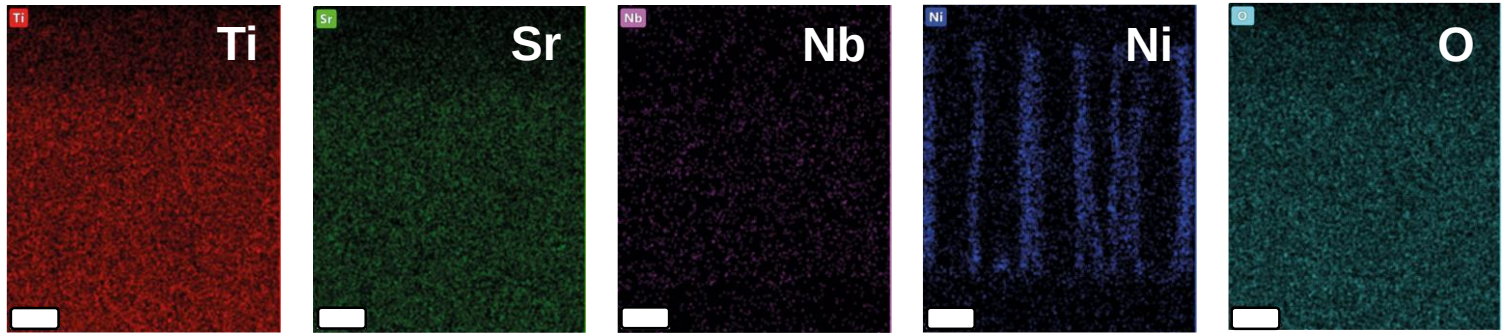
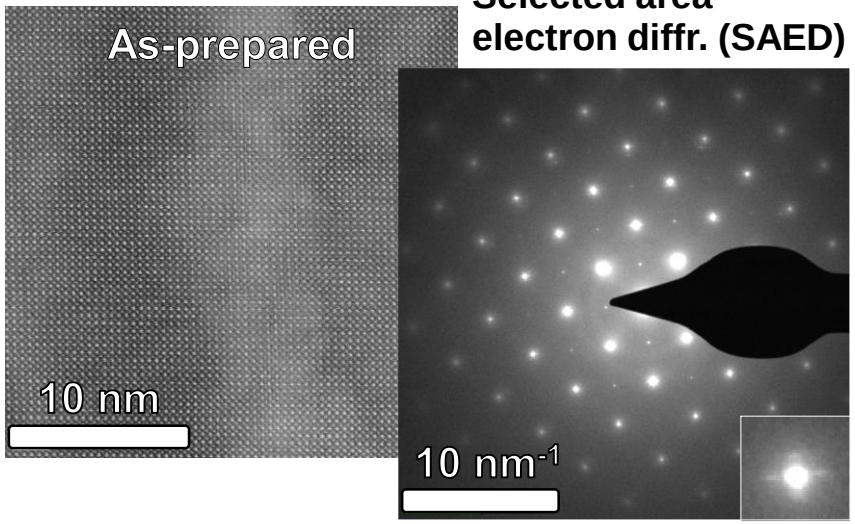


Scale bars: 20nm

HR-STEM | **Selected area electron diffr. (SAED)**



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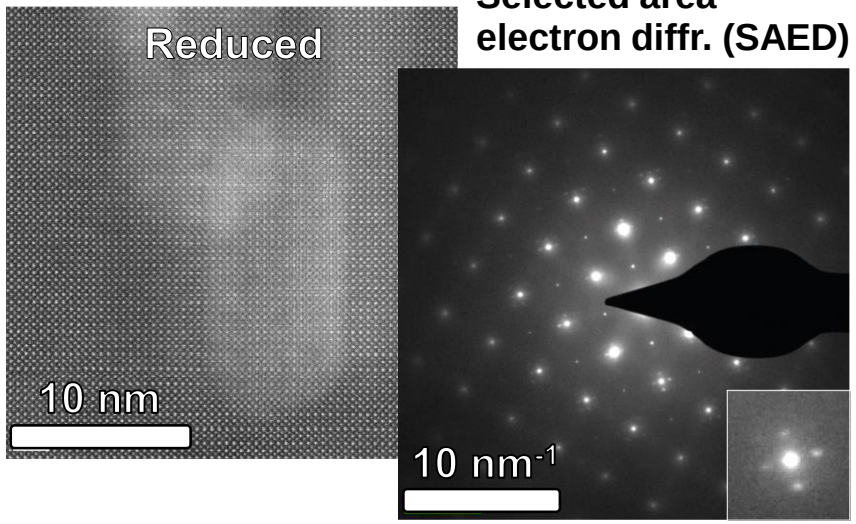

Phase separation of Ni-rich nanostructures on the nano-scale

Nanostructures reside in domain matching relationship within the host lattice

Phase transition and reorganization of Ni-rich phase upon reduction

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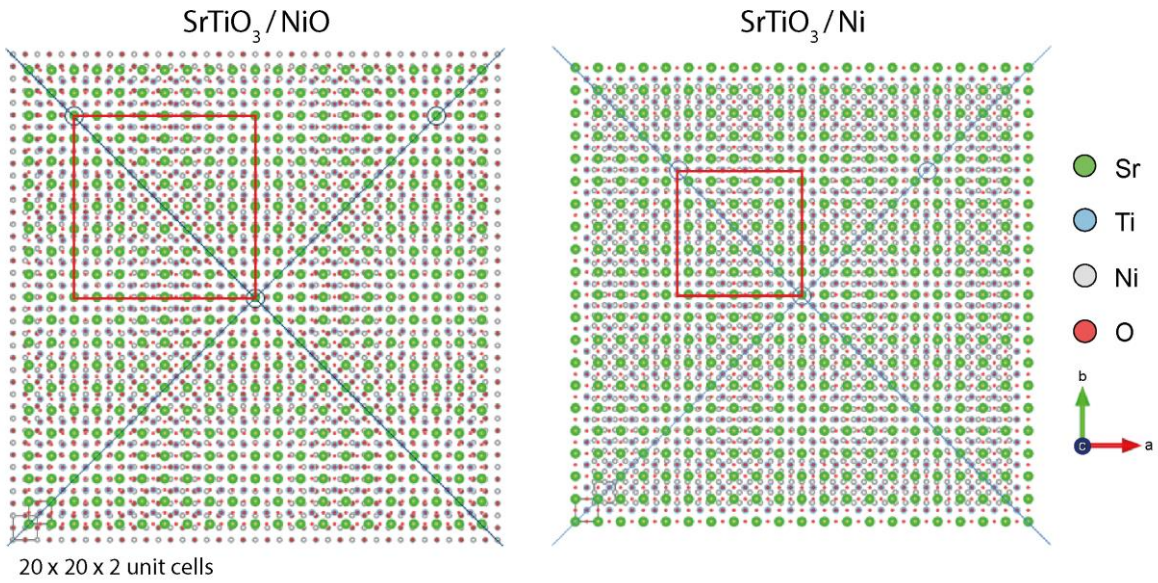
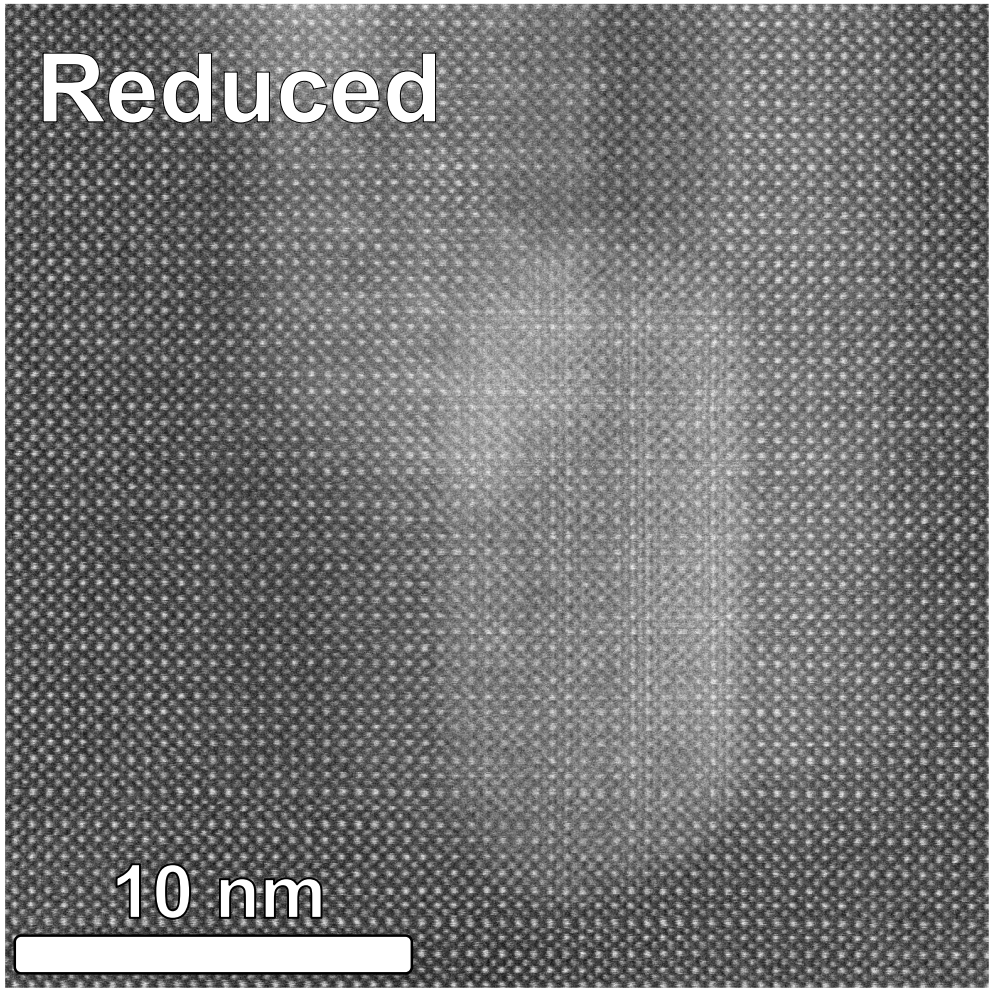
Metal exsolution

Structural properties – domain matching epitaxy



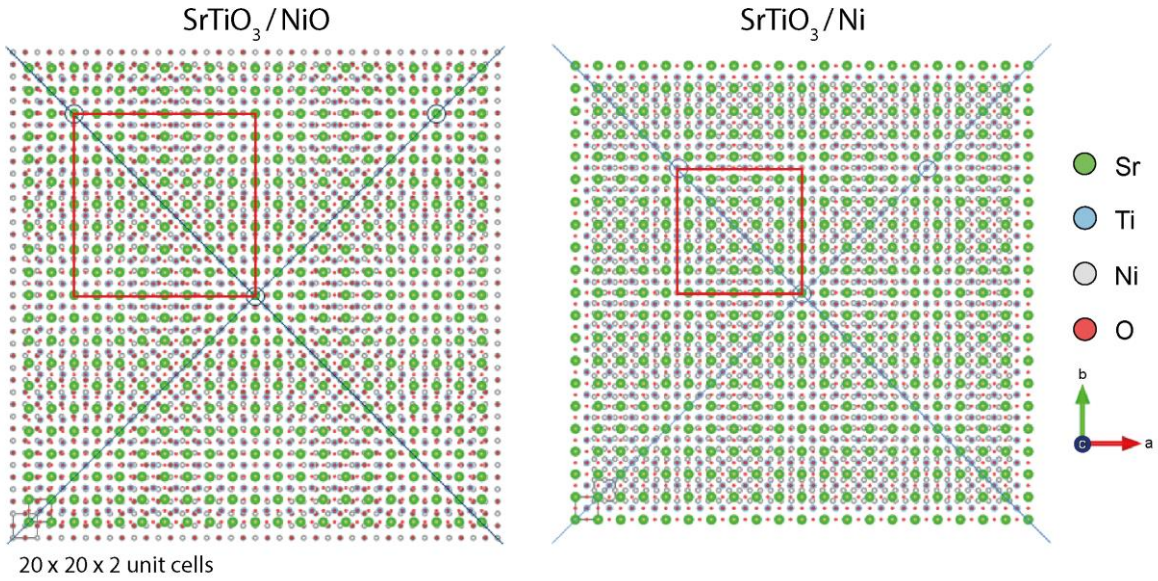


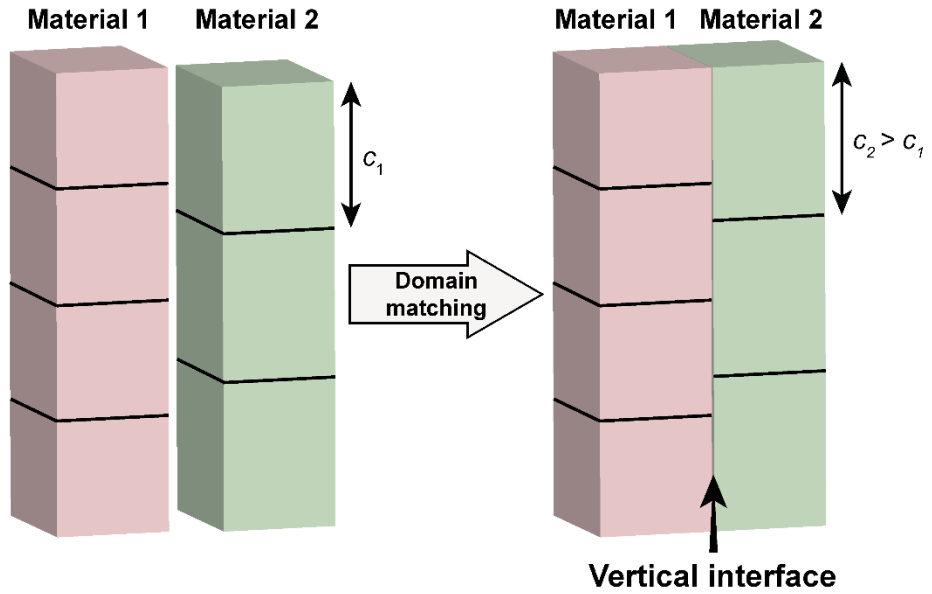
Coincidence site lattice model (CSL)

Material	Lattice parameter (Å)	Periodicity *n*	*F* (%)
STN(Ni)	3.91	~8	0.18 %
NiO	4.178	~7.5	
STN(Ni)	3.91	~5.5	-0.1 %
Ni	3.581	~6	

Metal exsolution

Structural properties – domain matching epitaxy





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- Structural properties determined by nature of the **semi-coherent vertical interface**
- Minimum CSL misfit, interfacial area, elastic stiffness tensors, díslocation density

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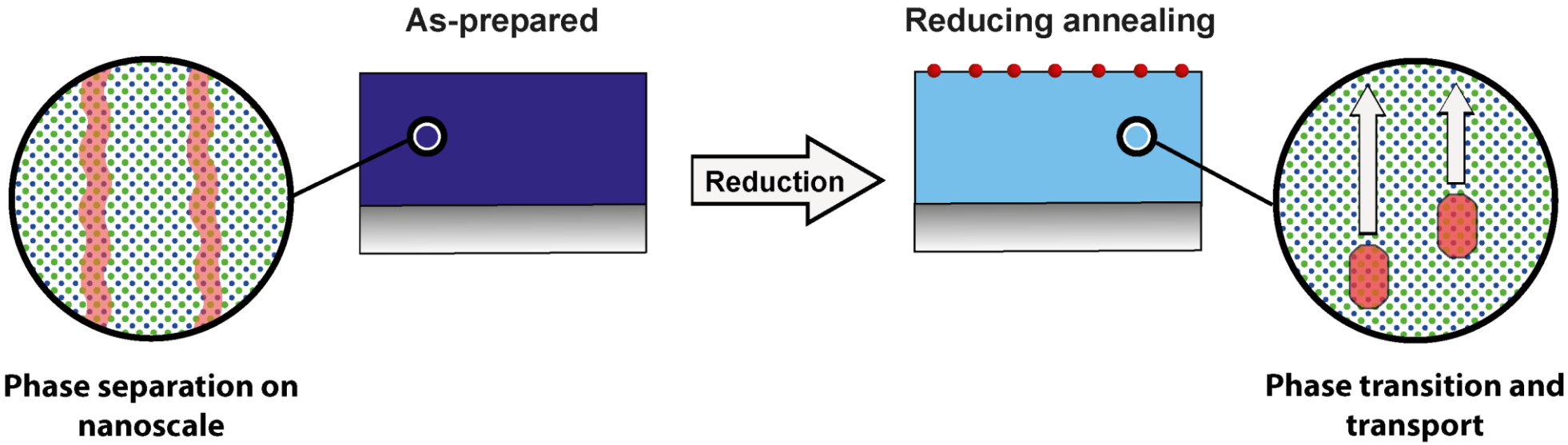
Metal exsolution

Structural properties – accomodation of Ni within the host lattice



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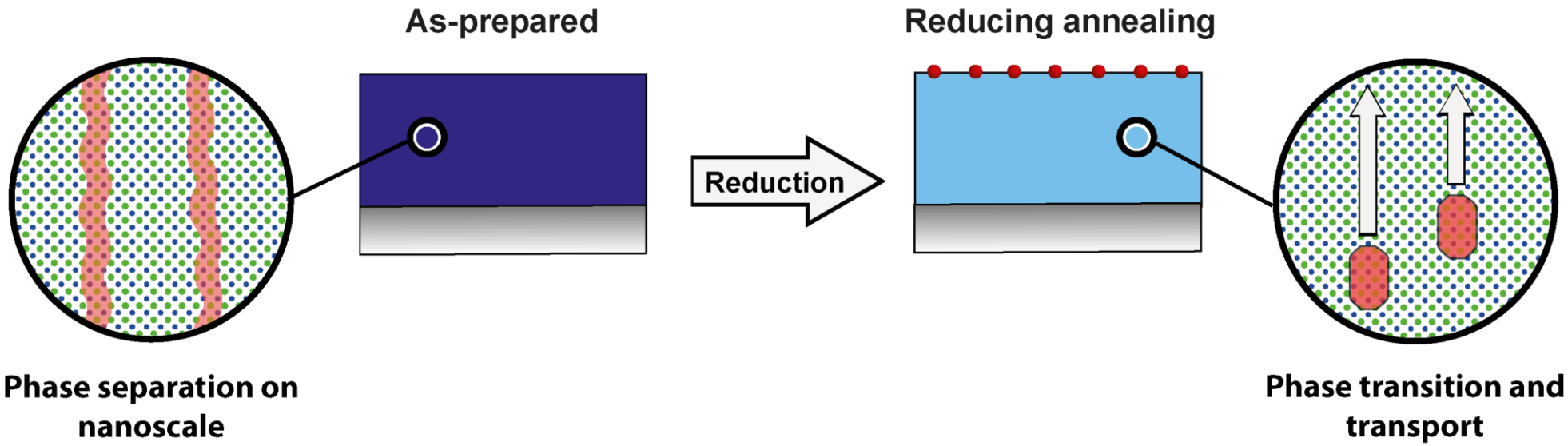
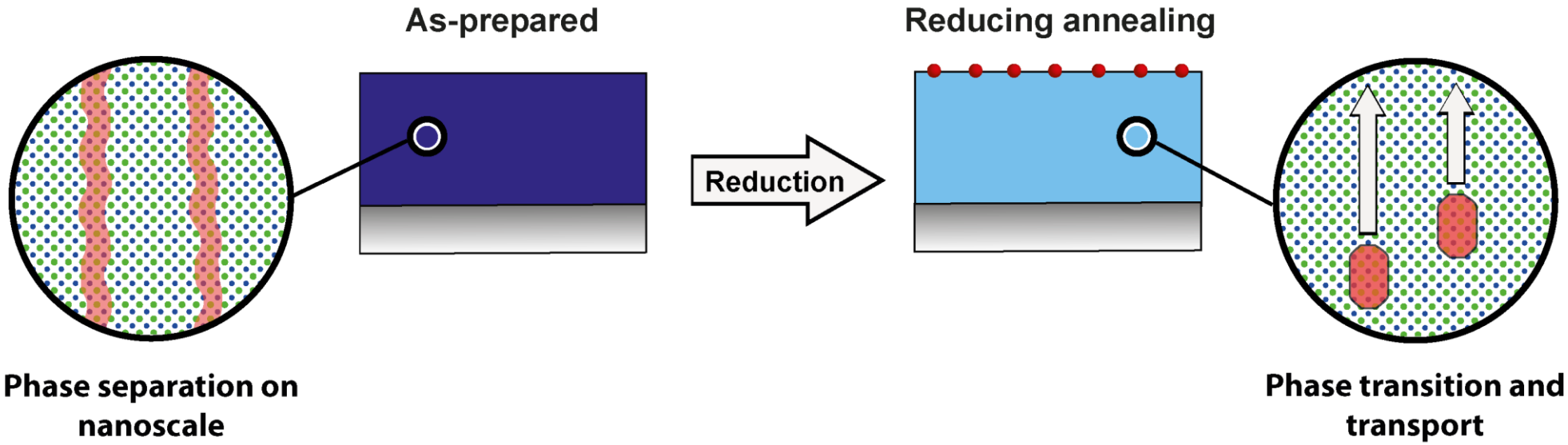


1) Nanoscale phase separation

→ Exsolution of pre-formed nuclei as alternative exsolution pathway

Metal exsolution

Structural properties – accomodation of Ni within the host lattice



1) Nanoscale phase separation

→ Exsolution of pre-formed nuclei as alternative exsolution pathway

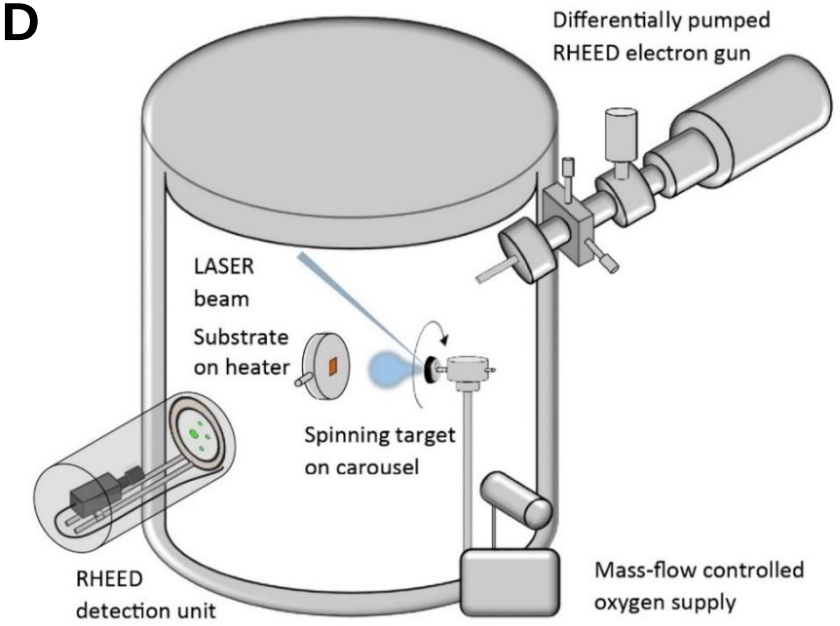
2) Decoupled nucleation and transport

→ Investigation of nanoparticle transport as isolated process

Metal exsolution

Influence of defect structure on metal exsolution

PLD

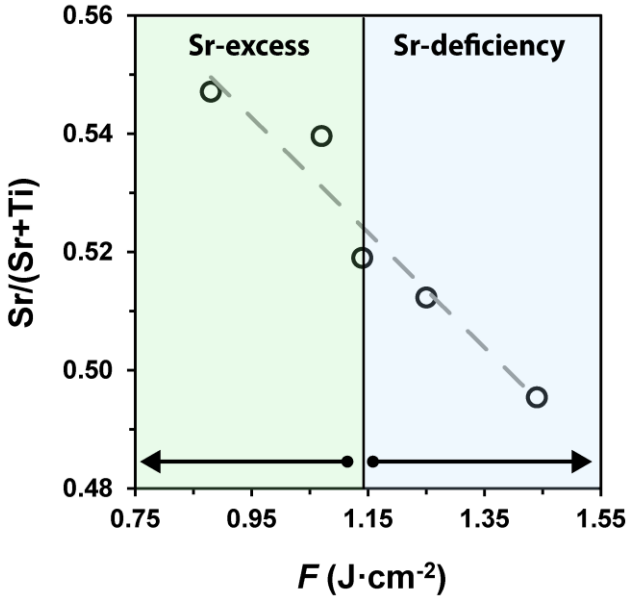


Tailoring the thin film defect structure based on the applied laser fluence *F*

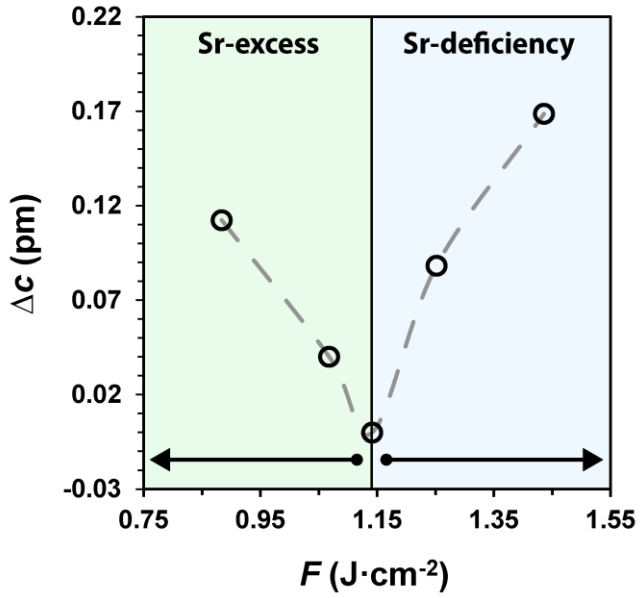
→ Amount and initial velocity of ablated species

→ Plasma plume dynamics (e.g. scattering processes)

XPS



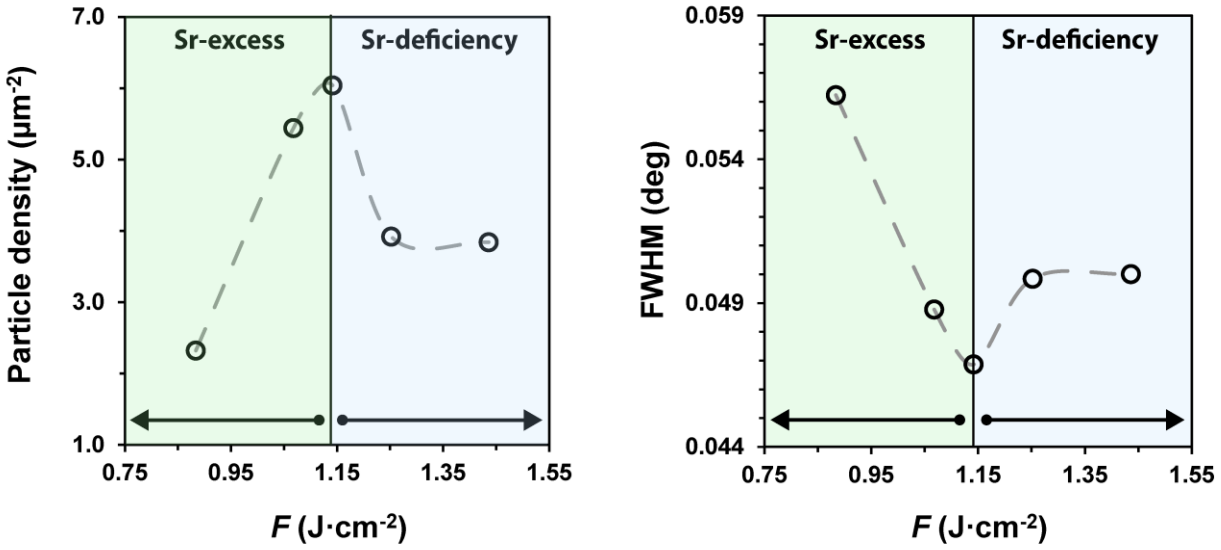
XRD

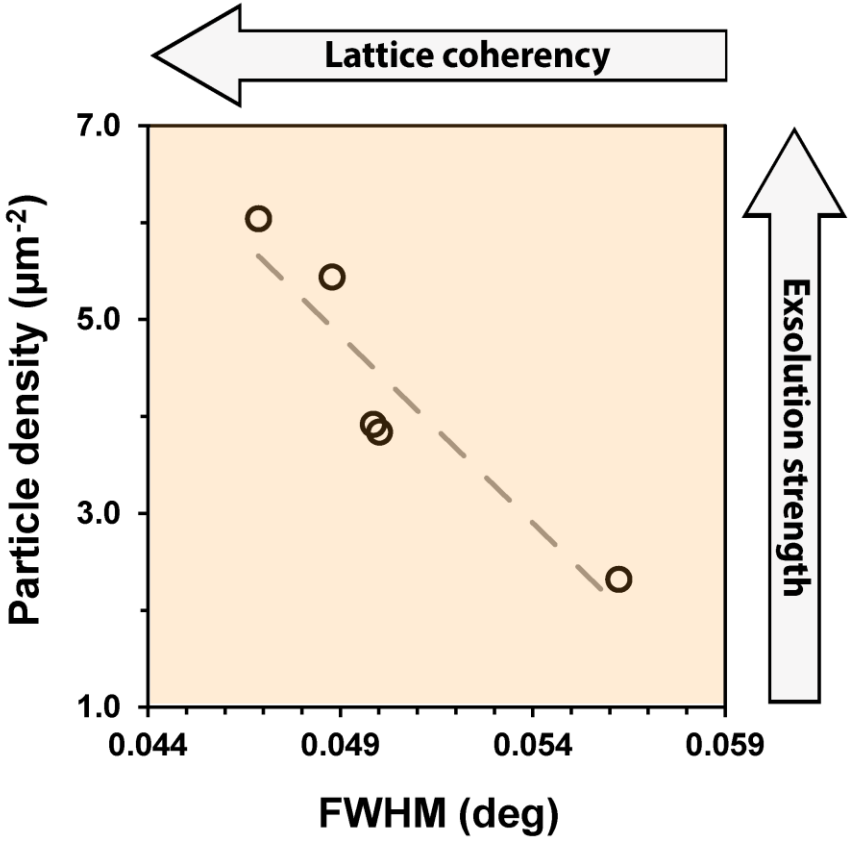


→ Incorporation of non-stoichiometry and respective defect structures resulting in systematic change in host stoichiometry and expansion of the *c*-lattice paramter

Metal exsolution

Influence of defect structure on metal exsolution





→ Highest nanoparticle density for stoichiometric thin films

→ Non-stochiometry i.e. defect incorporation results in distortions of the host lattice and loss of lattice coherency

→ High lattice coherency of the host lattice promotes metal ecsolution to the perovskite surface

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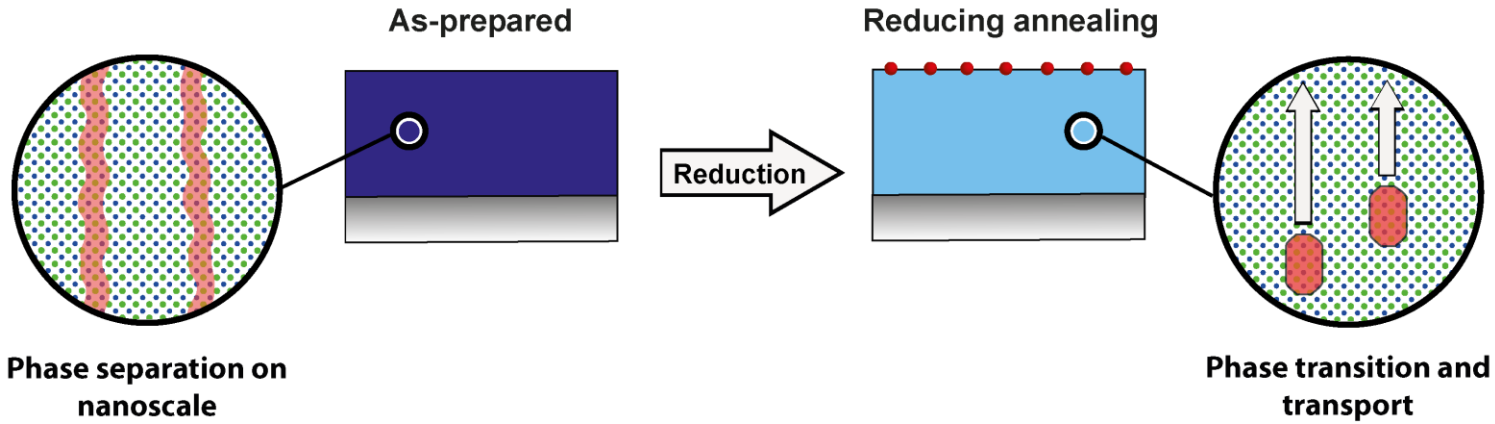
Metal exsolution

Conclusion & outlook

1) Alternative exsolution pathway via pre-formed nuclei



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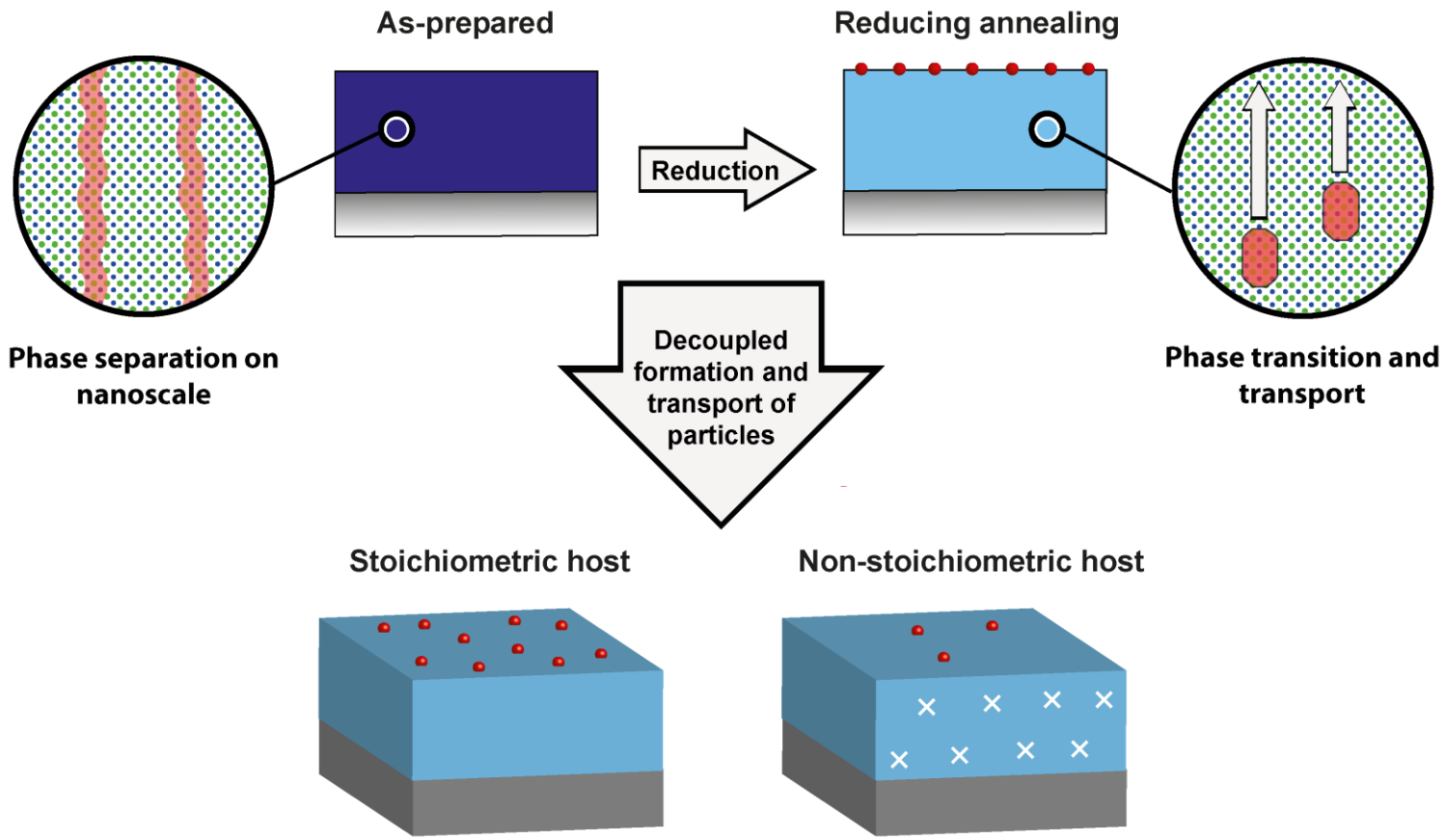

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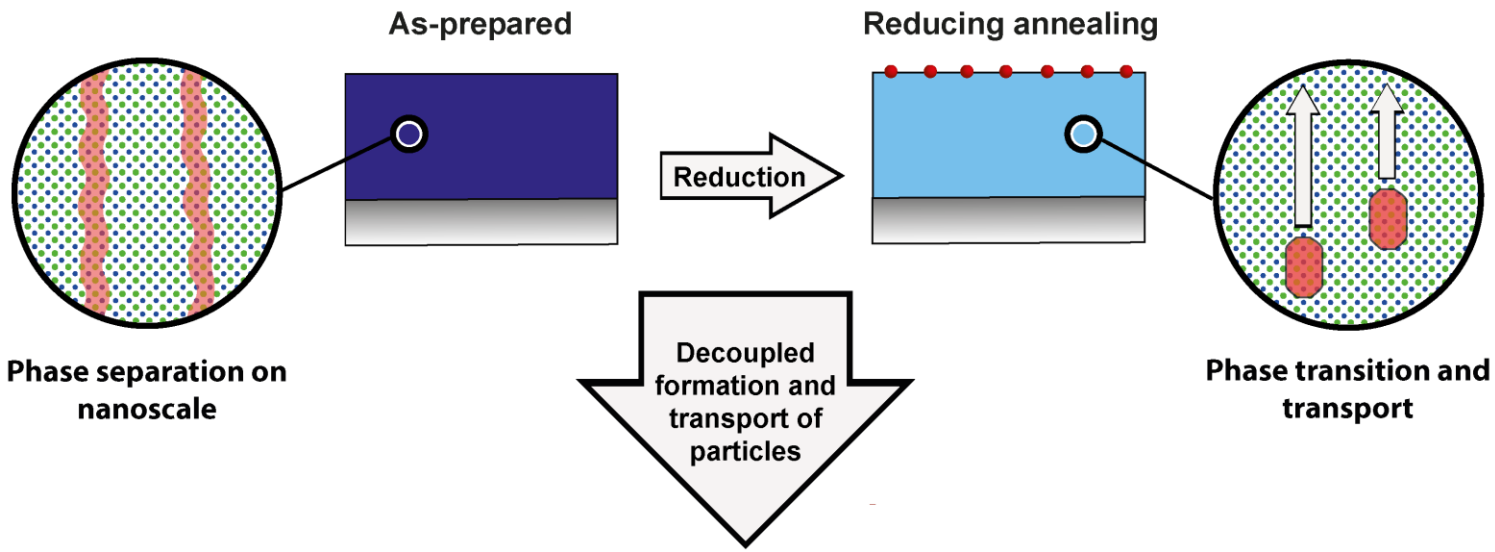
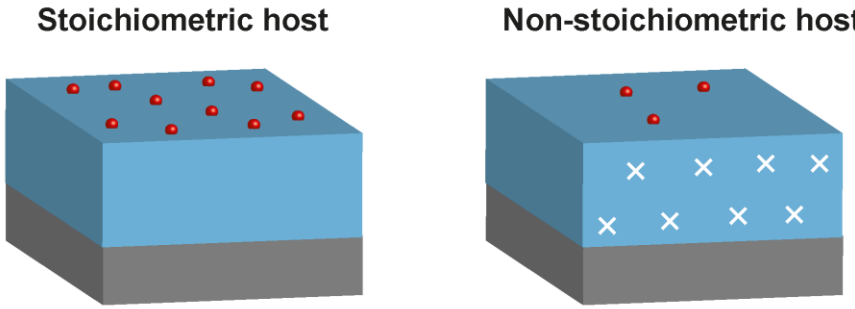


2) Defect structures influence nanoparticle transport to the perovskite surface



Metal exsolution

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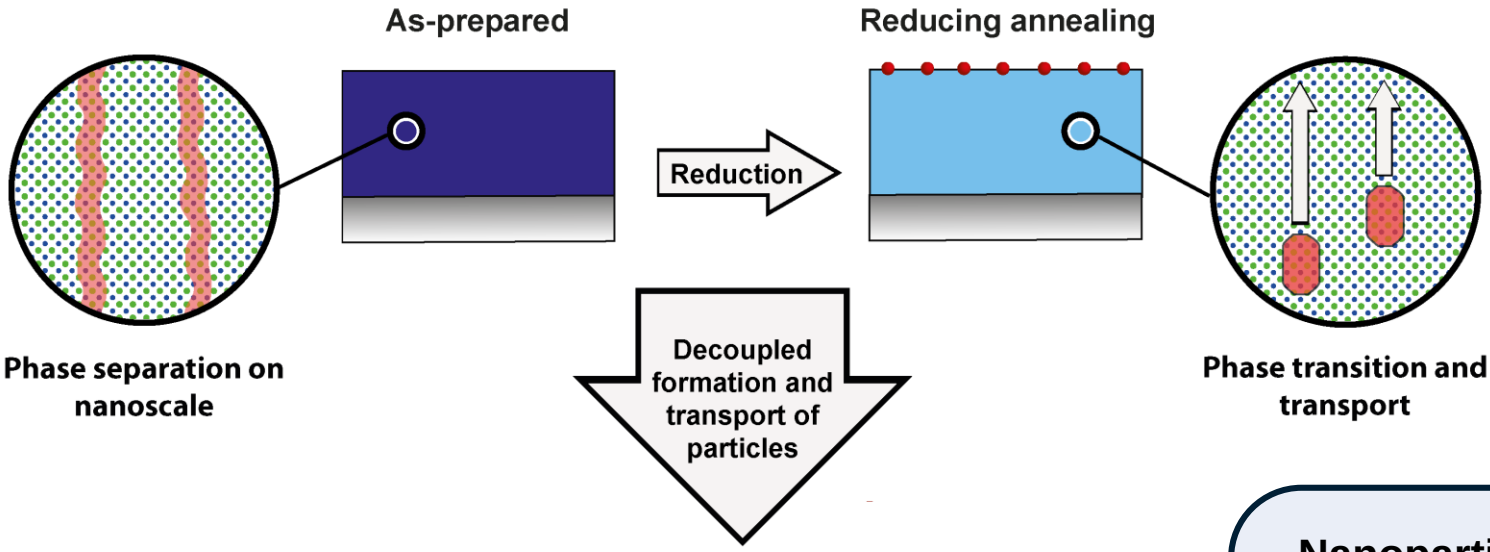
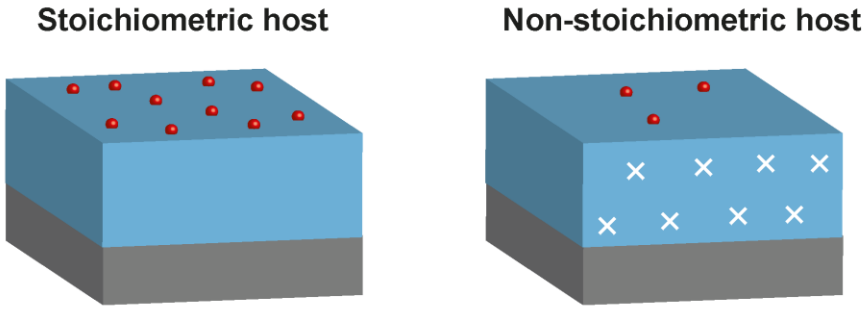
1) Alternative exsolution pathway via pre-formed nuclei



2) Defect structures influence nanoparticle transport to the perovskite surface



Nanoparticle-host interaction

- **Strain?**
- **Nanoparticle-host interface?**
- **Dislocation mobility?**