

Hierarchical ex-solution in vertically aligned heterostructures

Corresponding Author: Professor Vincenzo Esposito

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors present nanoparticle exsolution from vertically aligned nanostructure (VAN) thin films. The vertical nanostructures lead to the fast exsolution of Ni ions towards the surface with a slight change in the film lattice. This work is new and interesting. However, I cannot recommend publishing the current manuscript in Nature Communications due to the following reasons.

1. The authors claim that the exsolved nanoparticles from VAN are stable. However, the reduction time-dependent exsolution behavior shows that the particle population density decreases very quickly (You can compare 1 minute and 1 hour data). At the same time, the particle size increases quickly. Indeed, the particle size is too large compared to the reported papers. This means that the aggregation of exsolved nanoparticles on the surface is very fast compared to the conventional exsolved nanoparticles. The authors should correct the sentences regarding the stability of the exsolved nanoparticles from VAN and add sentences regarding the large size of nanoparticles compared to the conventional exsolved nanoparticles.
2. One of the reasons for the high thermal stability of exsolved nanoparticles is the "socketed" structure on the surface. However, the exsolved particles from VAN seem to be not embedded on the oxide support. The authors should add sentences regarding this. Or, can authors show the atomic scale TEM images of the exsolved nanoparticles on the surface?
3. Fig. 2 shows a thin layer on top of VAN. The authors need to explain this layer. Can this layer affect the particle migration/aggregation and the nanoparticle's shape?
4. The change in out-of-plane lattice parameters is tiny after exsolution. Can authors further provide reciprocal space mapping (RSM) after exsolution (to further check the change in in-plane lattice parameters)?
5. RMS needs to be changed to RSM.

Reviewer #2

(Remarks to the Author)

The paper 'Hierarchical ex-solution in vertically aligned heterostructures' by Zamudio-García et al. reports on exsolution behavior of Ni nanoparticles from vertically aligned nanostructures (VAN) of Ga-doped ceria and Pr-/Ni-codoped and A-site sub-stoichiometric SrTiO₃ in comparison to the exsolution active bulk thin films. The authors observe differences in particle size and particle dispersion between VAN and bulk thin film and argue that the high density of vertical interfaces induced in the VAN structures facilitates the cation / metal transport towards the surface.

Generally, the topic of metal exsolution is of general interest, while the mechanistic processes and relevant parameters for more/less rapid exsolution processes is an important scientific issue. Here, I fully acknowledge the high quality of materials control in VAN structure, which is obtained by the authors as well as the high quality and extensive compilation of microscopy data regarding the exsolution behavior.

However, for publication in Nat. comms. I would expect deeper mechanistic insights into the observed behavior which currently is lacking in the manuscript. Particularly, it remains blurry how and to what extent vertical interface can promote the exsolution process, limiting the scientific leap of the presented study. Moreover, it seems like the horizontal transport and coalescence behavior of the nanoparticles plays the dominant role here, while the transport towards the surface seems quite similar between the samples (i.e., either small but many particles, or fewer but larger particles; see comments below).

Therefore, while I appreciate the well-written manuscript, but I would rather see this study in a different journal, unless a

significant improvement of mechanistic understanding of the proposed process is provided.

Furthermore, I have a couple of questions and concerns that should be addressed (see list below).

1. Required film volume for large particles: The observed nanoparticles are quite large in volume, while the Ni-containing compound has only 10% of Ni on its B-site. Can the authors estimate if it is feasible that all the required Ni comes from the volume below the particle? Or is significant in-plane diffusion required? Can the depletion of Ni be determined? E.g. by SIMS analysis?
2. Total yield of Ni for the different samples: related to that, it seems that the total volume (i.e. number of particles times volume per particle) is quite similar for VAN and single layer? Can this be compared and estimated? If it is similar, the vertical diffusion of Ni to the surface will be similar? And it seems likely that also the surface diffusion might differ between the samples due to their different chemistry?
3. Size of Ni particle compared to spacing of vertical interfaces: It is also shown that the particle size is much larger than the typically spacing between vertical interfaces (much larger than shown in the sketch in Fig.4). Hence, if these interfaces are preferred routes for Ni exsolution (which they could) I would expect a high dispersion or even homogeneous distribution of Ni on the surface?
4. Mass transport mechanism: Provided that the vertical interfaces are preferred diffusion paths, the authors should discuss (and corroborate by modelling) what is causing enhanced mass transport? Is it a structural distortion or strain? Or is the presence of defects facilitating mass transport? Or is it electrostatic interaction?
Furthermore, to fully support the main claim of enhanced exsolution along the vertical interfaces, a systematic variation of the interface density should be provided, e.g. by varying the ratio of the VAN compounds.
5. Neither in the paper nor in the SI the authors report the morphology of the as-grown samples. It is required to add AFM and SEM data for some of the samples addressed in the paper or SI. Also, the coalescence kinetics study in Fig. 3 would be stronger if similar data was shown for the single layer sample.
Minor comments:
6. I would like to ask the author to comment on the extend of nanoparticle socketing at the thin film surface as this is a feature that is oftentimes shown for exsolved nanoparticles. It appears that no socketing can be observed for the present material system.
7. It is not really clear to me what the conductivity data adds to the study. Can the authors track the exsolution process via in-plane conductivity measurements? It is not clear to me how? In Fig. 5b,c, it is also unclear to the reader what specifically is defined as 'after electrochemical characterization'? Did the sample see H₂/Ar or O₂ or both? How many cycles, etc., should be defined more clearly.
8. As for the XRD analysis: All peaks should be labeled clearly. E.g. the peaks around 40 and 44 degs have no index? Some peaks are marked by an asterisk, but there seems to be no definition?
It is also not clear if these data refer to linear or log scales (I assume the latter), as there are no ticks or indications on the y-axis.
9. In the XPS study (Fig. S7), the fitting procedure should be explained in detail. E.g., were the peak parameters identical for as-grown and annealed samples? Were the peak width and spacing fixed?
More specifically, from the XPS spectra the nickel cations are identified to be present in oxidation state (II). It is not straightforward to determine the oxidation state on the basis of the Ni 2p core-level spectrum. I would like to ask the authors to comment how the analysis was performed.
10. Regarding the discussion in line 342 – 344 and line 358 – 360. There are many reports on the irreversibility of nanoparticle exsolution, i.e. stable nanoparticles during re-oxidation. The discussion needs to be updated.
11. There seems to be a typo between RSM and RMS in some places in the text.

Reviewer #3

(Remarks to the Author)

The authors present a novel approach to promote efficient nanoparticle exsolution from vertically aligned heterostructures at intermediate temperatures, proposing an exsolution mechanism based on diffusion through the numerous vertical interphases that characterise such nanocomposites. This results in a favourable surface diffusion, which is different from traditional epitaxial films where bulk diffusion prevails. The authors propose that vertical strain also plays a critical role in the retaining of the columnar microstructure integrity of the film during exsolution, showing improved redox stability. Moreover, the exsolved nanoparticles remain stable after oxidation in air and do not reincorporate into the film, which is crucial for energy applications to prevent performance degradation. This, combined to nanoparticle stability during redox cycles, provide new directions in tailoring the exsolution process of metal nanoparticles in vertically aligned nanocomposites at intermediate temperatures for potential application in energy- and catalysis-related scenarios.
However, I cannot recommend this work for publication in Nature Communications in its current form. Although original and potentially of significance to the field of exsolution and related fields, the work is not sufficient to support some of the

conclusions and claims, in my opinion, hence requiring additional evidence. Moreover, the potential significance of the results is not addressed with enough details to provide the breakthrough advance in the field that is required by Nature Communications standards, due to lack in advance in understanding of the phenomena described leaving too much room for interpretation. The following points are some examples detailing such criticism:

1. Lines 267-284: The mechanistic pathway proposed for the exsolution in the VAN structures reported in the work lacks sound proof. Modelling on the proposed mechanism would be appropriate to validate the authors interpretation of the ex situ data reported in the results section of the manuscript.
2. The discussion of the presumably secondary phase observed in Figure 3f, which is then again visible in Figure S13c, being NiO leaves too much room for interpretation, as no experimental evidence is presented in the work to validate such hypothesis (e.g., EDX, XPS). This could be a possibility for the sample reported in Figure S13 (after an oxidation cycle), however why would a NiO phase develop under reducing conditions?
3. From line 352: again, a possible explanation for the origin and nature of the formed smaller nanoparticles after a 2nd reduction cycle is presented, but no evidence for such claims is provided in the work. This needs to be addressed as, for now, the work does not support such conclusions (line 32: "One possible explanation for the presence of these nanoparticles is that they are originated from the secondary material that was no longer present on the VAN surface. Another possibility is that they came from the SPTNO bulk, which has a lower Ni concentration due to the previous exsolution, forming smaller nanoparticles.")

Some minor comments are:

- Details on the statistics used to calculate nanoparticle density are missing and should be provided, as well as further SEM images to prove homogeneous distribution overall and comparisons of particle densities (e.g., for what claimed in line 219).
- Some sentences appear to be incomplete and need revisions (e.g., line 210-211, line 218)
- The methods section should present more detailed information in order to ensure reproducibility of analysis
- After Van der Pauw measurements, the authors claim that no degradation or morphological changes are observed for the VAN samples, however the SEM image reported in Figure 5c clearly show additional secondary phase having formed on the surface of the material after electrical conductivity tests.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have properly addressed the comments raised by reviewers. The DFT calculations are added to further account for the lower migration energy along the interface compared to the bulk system. The NPs certainly do not show strong anchoring compared to the conventional exsolved NPs, implying the relatively smaller stability. However, the exsolution along the vertical interface is very fast and a new finding. This could potentially offer new applications. Thus, I suggest accepting the manuscript.

Reviewer #2

(Remarks to the Author)

The authors have carefully addressed the majority of my concerns. I think the inclusion of DFT as a supporting argument for facilitated Ni-diffusion along the VAN interface is a good improvement of the manuscript and supports the general story.

In my eyes, however, the overall conclusion still has room for speculation. This is particularly due to the involved dimensions of the nanoparticles vs. VAN structure, which was noted by various reviewers. It seems to be a remaining question if the experimental observations are proof enough to claim a 'facilitated ion diffusion along the internal interfaces of the VAN structure' or if the particle sizes are determined by a 'varied surface diffusion and coalescence behavior'. I acknowledge that it is experimentally very difficult to distinguish these two processes, as they are partially convoluted. Therefore, I would suggest to add a bit more of a comprehensive discussion of these two processes, i.e. mass transport to the surface and mass transport along the surface.

A systematic comparison of particle size, density, and particularly total volume would help to assess how the overall volume of Ni varies with and without VAN support. This was done e.g. in Weber et al., Nature Materials 23, 406–413 (2024), which also discusses a surface limitation of the exsolution process. Based on the discussion within the rebuttal, one should also note that the lack of reversibility of Ni exsolution/dissolution from SrTiO₃-based materials was discussed in 10.1039/D3TA02927A by the same authors which could be referred to in the discussion.

Overall, I think the manuscript has significantly improved, contains a rich amount of interesting data, and can be thus considered for publication in Nature Communication. However, I would like to see the author responses to the points mentioned below, as well as a more comprehensive discussion regarding exsolution dynamics vs. surface dynamics to guide the reader.

Comments to consider:

1. In my eyes, figure 3h is still misleading, as even in the initial state of the exsolution, the authors mention a particle size of

15nm which is larger than the spacing between the VANs (~5nm or so?). Also, fig. 3h indicates that there is also a network of connected interfaces in lateral dimensions (I can follow the boundary between red and green in-plane) while I understand the real structure more like a columnar enclosure of secondary phase which is fully surrounded by the parent compound. Can the authors clarify?

2. Furthermore, comparison of the EDS data in Fig 3d and 3f is very difficult as the color code applied for the two samples is different (i.e. reddish color for SPTNO is used in 3f, but not used in 3d...?). The authors may want to only display the Ni signal for both images (not only for d) so the reader can compare differences in the Ni distribution within the oxide bulk. E.g. in Fig. S5b Ni particle formation in bulk is also visible for the VAN sample.

3. In Fig. S18a, a TEM cross section image obtained from the single-phase sample after reduction is shown, where a columnar structure of reduced Ni (?) becomes visible. Can the authors exclude that there are dopant inhomogeneities present in the as-deposited sample? In the literature referenced in the manuscript it was shown that spontaneous formation of NiOx columns may occur already at a doping level of 5% while the authors discuss a system with a Ni doping level of 10%. This could also lead to differences in the exsolution behaviour (e.g. more pronounced trapping of Ni in bulk).

4. The assignment of XRD intensity in the SI needs some clarification. The authors index a 'relaxed' SPTNO peak at lower angles than the 'strained' SPTNO peak. Since the strained phase seems to have a larger lattice constant than the STO substrate, it seems to have a larger lattice constant than STO. In the strained case, it is hence expected to be in compressive strain and thus an enlarge out-of-plane lattice constant. Therefore, I would expect that 'strain relaxation' results in a shift towards larger angles (lower out of plane lattice constant). The nature of this peak should be discussed in detail – to me it appears that it might indicate a secondary phase forming? This may not impede the overall message of the paper, but it deserves a detailed discussion of the fundamental structural properties of the starting materials.

5. Moreover, I am still missing time/temperature-dependent evaluation of the nanoparticle density for the parent compound for comparison to Fig. 2. This can be used for direct comparison to the VAN-based data.

Reviewer #3

(Remarks to the Author)

The authors have included substantial extra work in the revised manuscript, and addressed most of the comments and remarks from the reviewers.

The work now supports most of the conclusions and claims, and can be considered for publication in Nature Communications, however the data analysis of the secondary phase still lacks sound proof.

The EDS maps reported in the response to the reviewers document (Figure S12) does not support the claims of the authors regarding the secondary phase being Ni-based. Either a STEM-/TEM-EDX map should be provided, due to the higher sensitivity of the technique, or a higher-resolution SEM-EDX map. The one provided does not show Ni-enrichment where the secondary phase is present from the image shown. Moreover, the other elemental maps should be included as well (O, C, Pr, Ce, Gd), not only the ones from Sr, Ti and Ni.

Once this is addressed and proven, I agree with its publication in Nature Communications.

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

The authors have added additional discussion to their manuscript, which now presents a high-standard data set as well as a clear and comprehensive discussion of all involved processes. I acknowledge the additional edits and clarifications in the figures which further improve readability.

From my side, the manuscript is now ready for publication and I will be happy to refer to this work once online.

Reviewer #3

(Remarks to the Author)

The authors have adequately addressed the comments from my previous revision by providing proper evidence to support the claims in the paper. Therefore, I recommend the manuscript for publication in its current form.

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RESPONSE TO REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

The authors present nanoparticle exsolution from vertically aligned nanostructure (VAN) thin films. The vertical nanostructures lead to the fast exsolution of Ni ions towards the surface with a slight change in the film lattice. This work is new and interesting. However, I cannot recommend publishing the current manuscript in Nature Communications due to the following reasons.

We thank the reviewer for the useful comments and revisions, which are considered constructive for improving the manuscript.

1. The authors claim that the exsolved nanoparticles from VAN are stable. However, the reduction time-dependent exsolution behavior shows that the particle population density decreases very quickly (You can compare 1 minute and 1 hour data). At the same time, the particle size increases quickly. Indeed, the particle size is too large compared to the reported papers. This means that the aggregation of exsolved nanoparticles on the surface is very fast compared to the conventional exsolved nanoparticles. The authors should correct the sentences regarding the stability of the exsolved nanoparticles from VAN and add sentences regarding the large size of nanoparticles compared to the conventional exsolved nanoparticles.

The time-dependent study conducted in this work aimed to investigate the Ni diffusion kinetics in a functional oxide film with columnar nanostructure. Our study demonstrates that the Ni particle size from the VAN is two times smaller compared to the conventional film, which is desirable for energy applications.

Size: However, as pointed out by the reviewer, the particle size obtained in this work is relatively larger than other reports in the literature. Nevertheless, since the composition of the film and preparation conditions are different, a direct comparison with the literature is not straightforward. For instance, factors such as the film orientation (*J. Am. Chem. Soc.* **2019**, 141, 7509) and lattice-strain (*Nat. Comm.* **2019**, 10, 1471) have been demonstrated to play a key role in the particle size after the exsolution process. In our study, the VAN was deposited on STO (001), resulting in a lattice misfit strain (ϵ) of +1.7 % (tensile-strained). Kim et al. observed that the Ni nanoparticle particle size was considerably higher for STO (001) oriented films (40 ± 17 nm) compared to STO (111) films (20 ± 7 nm). Additionally, Han et al. demonstrated that compressive-strained films lead to the formation of considerably smaller nanoparticles compared to tensile-strained films. These findings could explain the larger particle size observed in this work. Additionally, related compositions in the literature, such as $(\text{Sr}_{0.7}\text{Pr}_{0.3})_{0.9}\text{Ti}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$, have shown similar particle sizes of 50-100 nm (*Applied Catalysis B Environ.* **2020**, 272, 118973; *SN Applied Sciences* **2019**, 1, 322). In our case, the particle size of the nickel nanoparticles from VAN after a reduction at 550 °C for 6 h is around 17 nm, as observed in Fig. 2a. This value is hence comparable with the literature.

For clarity, we have added sentences and references in the discussion regarding the large size of nanoparticles, as suggested by the reviewer.

Stability: Regarding the stability of the nanoparticles, it is noteworthy that the Ni exsolved nanoparticles remain stable after different redox cycles, as shown in Fig. S20. It is important to emphasise that these particles do not redissolve into the VAN due to their distinctive columnar microstructure. As also pointed out by the reviewer, the kinetics study shows a rapid decline in

population density between 1 minute and 1-hour data. However, to our knowledge, such a short reduction time (1 minute) is not typically studied, and our data refer to the very early stage of the nucleation, which may be faster. Such first initial stages of the exsolution process before particle nucleation are normally not reported in the literature. Yet, the nucleation is favoured at high temperatures, i.e. at 650 °C, inducing an initial fast particle growth, which is slower at larger stages. This effect is observed in our work by the similar particle size and population density for the samples reduced at 650 °C for 1h, 6h and 12 h (Fig. 2). Furthermore, the enhanced Ni exsolution and stability features in vertically aligned nanostructures were also discussed by the atomistic insights obtained by DFT calculations addressed in the manuscript's revised version (Fig. 4 and Fig. S19). The calculations nicely confirm our experimental findings.

We have corrected and modified the sentences about the stability of the Ni nanoparticles from VAN on page 8 to clarify this point.

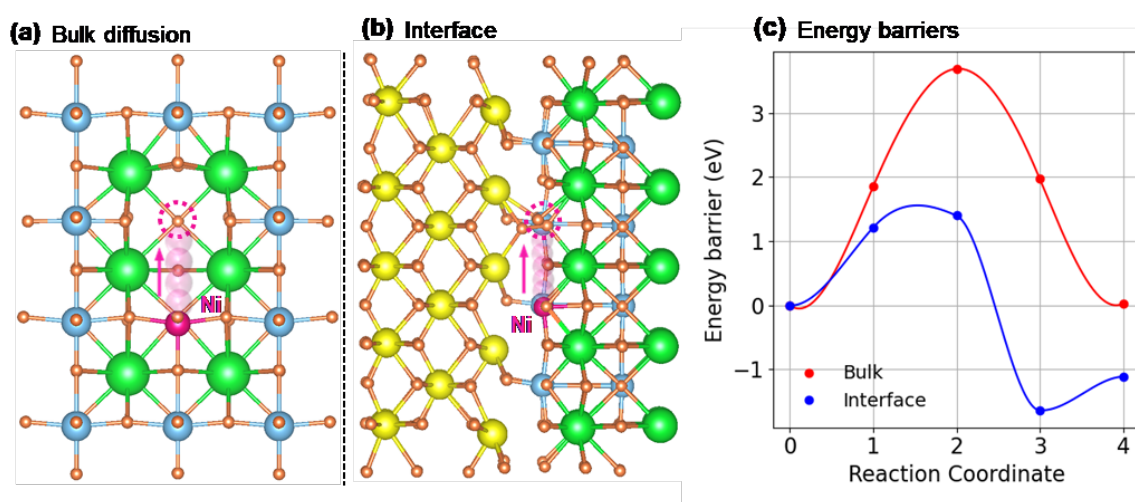


Fig. 4. DFT calculation for Ni migration within the bulk and interface. Schematics of Ni migration pathways across the (a) perovskite bulk and (b) perovskite-fluorite interface. (c) Calculated energy barriers for Ni migration for both scenarios, showing a lower migration energy for the diffusion through the interface.

2. One of the reasons for the high thermal stability of exsolved nanoparticles is the "socketed" structure on the surface. However, the exsolved particles from VAN seem to be not embedded on the oxide support. The authors should add sentences regarding this. Or, can authors show the atomic scale TEM images of the exsolved nanoparticles on the surface?

We thank the reviewer for this comment. We only partially agree with this comment. First, as observed by SEM and TEM analysis, the exsolved Ni nanoparticles from VAN showed a faceted shape, indicating a strong interaction between the metal and the oxide substrate (*ACS Nano* **2021**, 15, 81-110). In other words, the mass diffusion mechanism in Ni leads to the minimisation of individual particle surface energy via morphology change rather than particle-particle agglomeration. This effect indicates that the particles are socketed on the substrate. These findings also contradict those observed for the nanoparticles prepared by infiltration, in which a spherical shape is obtained due to the weak particle-support interaction.

Certainly, the unique microstructure architecture of VAN, composed of vertical columns, does not favour the usual anchoring mechanism of the particles on a single-phase substrate since the film is a composite composed of a heterostructure. However, although it is difficult to observe, a certain degree of interaction and anchoring with the exsolving phase must occur.

Moreover, the presence of embedded nanoparticles in the literature is consistent with the presence of a significant number of Ni nanoparticles trapped within the host perovskite film due to the restricted bulk mass diffusion in conventional films (*i.e.*, *Nat. Comm.* **2023**, 13, 6682; *Adv. Mat.* **2023**, 35, 2208984; *ACS Nano* **2021**, 15, 4546; *Nat. Comm.* **2019**, 10, 1471; *J. Am. Chem. Soc.* **2019**, 141, 7509) (Please see Fig. R1 as representative example). We have included new cross-sectional TEM images for SPTNO film (Fig. 2) after reduction for comparison to the VAN film. Contrary to the traditional films, we have demonstrated by experiments and modelling that long-range columnar architecture enhances the exsolution kinetics and overcomes the bottleneck of nanoparticle migration to the surface.

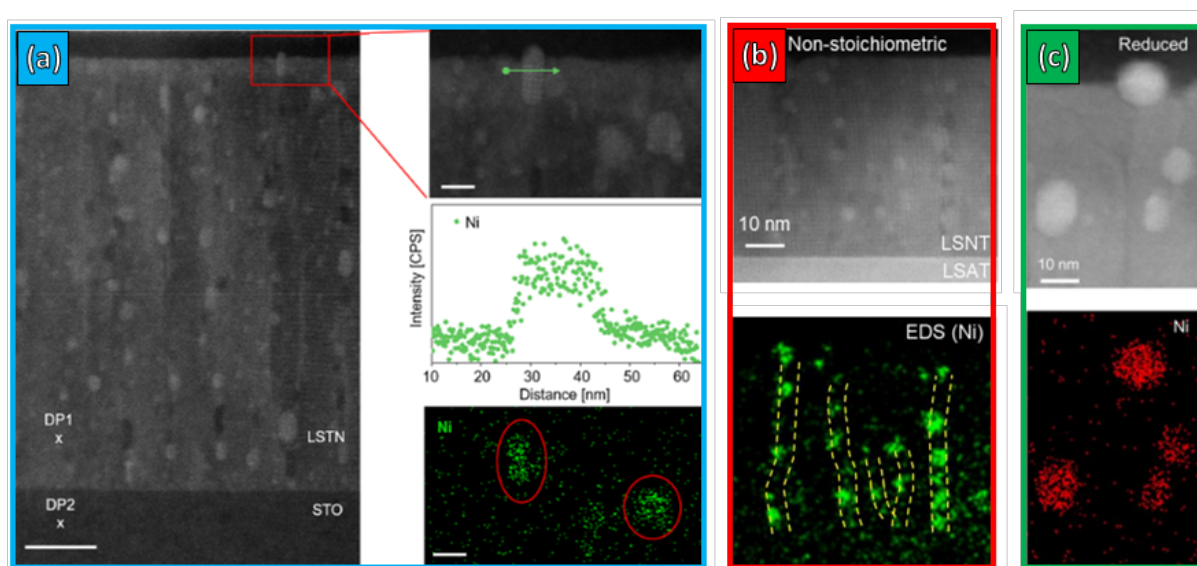


Figure R1. Cross-sectional TEM images and EDS analysis reported in the literature showing the presence of Ni nanoparticles trapped within the film. Blue: (a) *J. Am. Chem. Soc.* **2019**, 141, 7509 (Figure 2), Red: (b) *Nat. Comm.* **2023**, 13, 6682 (Figure S3) and Green (c) *Nat. Comm.* **2019**, 10, 1471 (Figure S4).

This discussion regarding the shape of the Ni nanoparticles and the absence of socketing in the VAN is surely relevant to the paper. Therefore, we have included it on page 14.

3. Fig. 2 shows a thin layer on top of VAN. The authors need to explain this layer. Can this layer affect the particle migration/aggregation and the nanoparticle's shape?

The bright, thin layer on top of the VAN is Iridium deposited by sputtering, necessary for preparing the lamella and SEM characterisation in the FIB-SEM. This layer ensures high electronic conductivity on the surface, which is crucial for the obtention of the lamellas. Please note that the same Ir layer is also discernible in the cross-sectional HAADF-STEM image of the as-prepared sample (Fig. 1a). Since this layer is deposited after the reduction process (by traditional sputtering

at room temperature), it does not influence particle migration or nanoparticle shape. Further clarification regarding lamella preparation has been provided in the experimental section, along with Fig. S22 showing the nature of this layer .

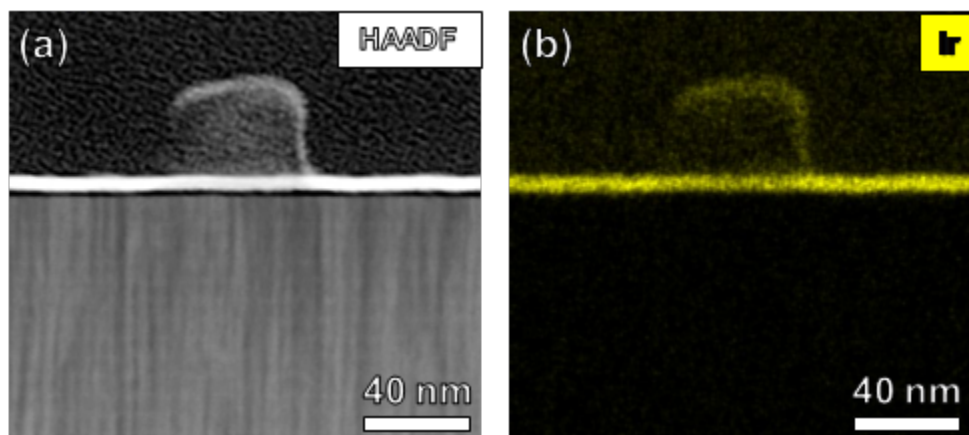


Fig. S22. (a) Cross-sectional HAADF-STEM image and (b) Ir EDS mapping of the VAN sample after reduction.

4. The change in out-of-plane lattice parameters is tiny after exsolution. Can authors further provide reciprocal space mapping (RSM) after exsolution (to further check the change in in-plane lattice parameters)?

We have performed RSM after exsolution (Fig. S9) and included a new discussion in Page 6.

5. RMS needs to be changed to RSM.

We apologise for this mistake. We have corrected this typo error in the manuscript.

Reviewer #2 (Remarks to the Author):

The paper ‘Hierarchical ex-solution in vertically aligned heterostructures’ by Zamudio-García et al. reports on exsolution behavior of Ni nanoparticles from vertically aligned nanostructures (VAN) of Ga-doped ceria and Pr-/Ni-codoped and A-site sub-stoichiometric SrTiO₃ in comparison to the exsolution active bulk thin films. The authors observe differences in particle size and particle dispersion between VAN and bulk thin film and argue that the high density of vertical interfaces induced in the VAN structures facilitates the cation / metal transport towards the surface. Generally, the topic of metal exsolution is of general interest, while the mechanistic processes and relevant parameters for more/less rapid exsolution processes is an important scientific issue. Here, I fully acknowledge the high quality of materials control in VAN structure, which is obtained by the authors as well as the high quality and extensive compilation of microscopy data regarding the exsolution behavior.

However, for publication in Nat. comms. I would expect deeper mechanistic insights into the observed behavior which currently is lacking in the manuscript. Particularly, it remains blurry how

and to what extent vertical interface can promote the exsolution process, limiting the scientific leap of the presented study. Moreover, it seems like the horizontal transport and coalescence behavior of the nanoparticles plays the dominant role here, while the transport towards the surface seems quite similar between the samples (i.e., either small but many particles, or fewer but larger particles; see comments below). Therefore, while I appreciate the well-written manuscript, but I would rather see this study in a different journal, unless a significant improvement of mechanistic understanding of the proposed process is provided. Furthermore, I have a couple of questions and concerns that should be addressed (see list below).

We thank the reviewer for recognising the quality of our work and for the valuable comments that helped improve the manuscript.

1. Required film volume for large particles: The observed nanoparticles are quite large in volume, while the Ni-containing compound has only 10% of Ni on its B-site. Can the authors estimate if it is feasible that all the required Ni comes from the volume below the particle? Or is significant in-plane diffusion required? Can the depletion of Ni be determined? E.g. by SIMS analysis?

As mentioned in the earlier response to the comment from reviewer #1, the particle size obtained in this work is relatively larger compared to other reports in the literature. Nevertheless, since the composition of the film and preparation conditions are different, a direct comparison with the literature is not straightforward. Factors such as film orientation (*J. Am. Chem. Soc.* **2019**, 141, 7509) and lattice-strain (*Nat. Comm.* **2019**, 10, 1471) have shown to significantly influence particle size after the exsolution process. In our study, the VAN was deposited on STO (001), obtaining a lattice misfit strain (ϵ) of +1.7 % (tensile-strained). Kim et al. observed that the Ni nanoparticle particle size was considerably higher for STO (001) oriented films (40 ± 17 nm) when compared to STO (111) films (20 ± 7 nm). Additionally, Han et al. demonstrated that compressive-strained films lead to the formation of considerably smaller nanoparticles compared to tensile-strained films. These findings likely account for the larger particle size obtained in this work. Additionally, related compositions in the literature, such as $(\text{Sr}_{0.7}\text{Pr}_{0.3})_{0.9}\text{Ti}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$, have shown particle size between 50-100 nm (*Applied Catalysis B Environ.* **2020**, 272, 118973; *SN Applied Sciences* **2019**, 1, 322). Nevertheless, the particle size of the Ni nanoparticles from VAN after a reduction at 550 °C for 6 h is around 17 nm, as observed in Fig 2a, which is comparable with the literature.

As discussed in line 12, the nanoparticle nucleation in the VAN sample predominantly takes place at the surface, and all the Ni does not come from the volume below since the column width is only 5nm and the particle size is higher. Fig. 3h shows the coalescence process of Ni ions to form Ni nanoparticles.

We have added sentences in the discussion section regarding the large size of the nanoparticles and the in-plane migration, as suggested by the reviewer. Further discussion can also be found in the subsequent responses (Question 2 and 3)

2. Total yield of Ni for the different samples: related to that, it seems that the total volume (i.e. number of particles times volume per particle) is quite similar for VAN and single layer? Can this be compared and estimated? If it is similar, the vertical diffusion of Ni to the surface will be similar? And it seems likely that also the surface diffusion might differ between the samples due to their different chemistry?

To investigate the vertical diffusion of Ni within the conventional film and compare it to the one observed for the VAN, electron transparent lamellas after reduction were prepared and

characterised by TEM, as suggested by the reviewer. As shown in the new Fig. 3c-f and Fig. S18, the particle size is different, as noted earlier, but the film microstructure after exsolution is also different.

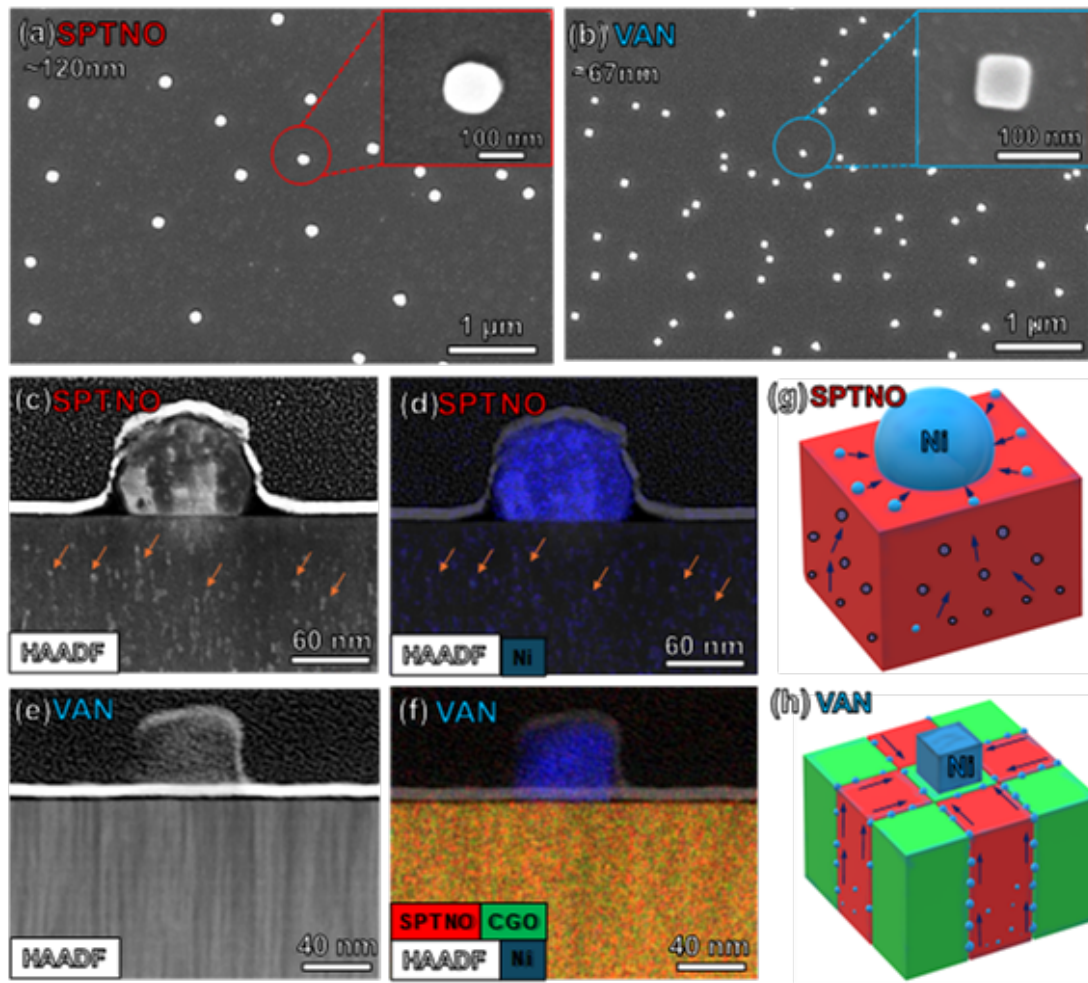


Fig. 3. Comparison between the Ni exsolution process and particle size in traditional epitaxial films and VAN. (See page 11 for more details).

A detailed observation of the conventional SPTNO film revealed the presence of Ni nanoparticles segregated within the bulk due to the hampered bulk mass diffusion, leading to "trapped" nanoparticles in the host perovskite oxide. On the contrary, this phenomenon is not observed in the VAN, which shows a clean columnar microstructure without Ni segregation within the film, thereby confirming the enhanced diffusion kinetics.

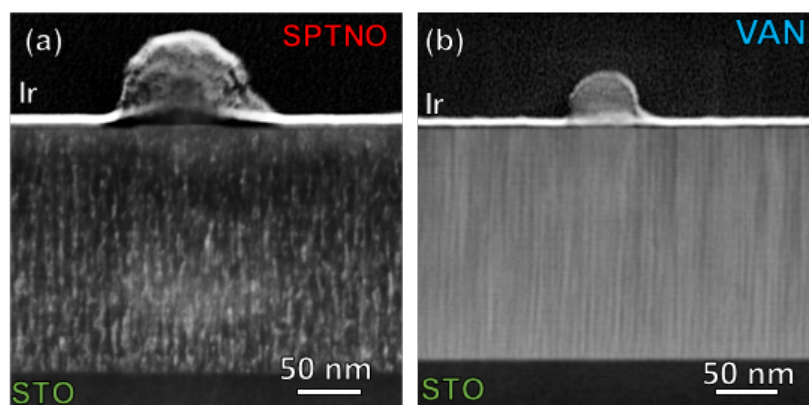


Fig. S18. Cross-sectional HAADF-STEM images for (a) SPTNO and (b) VAN after reduction at 650 °C for 12 h.

It is also worth mentioning that the presence of a large number of Ni nanoparticles trapped in the host perovskite in conventional films has been consistently observed in the literature (*i.e.*, *Nat. Comm.* **2023**, 13, 6682; *Adv. Mat.* **2023**, 35, 2208984; *ACS Nano* **2021**, 15, 4546; *Nat. Comm.* **2019**, 10, 1471; *J. Am. Chem. Soc.* **2019**, 141, 7509) (Please see Figure R1 as representative example).

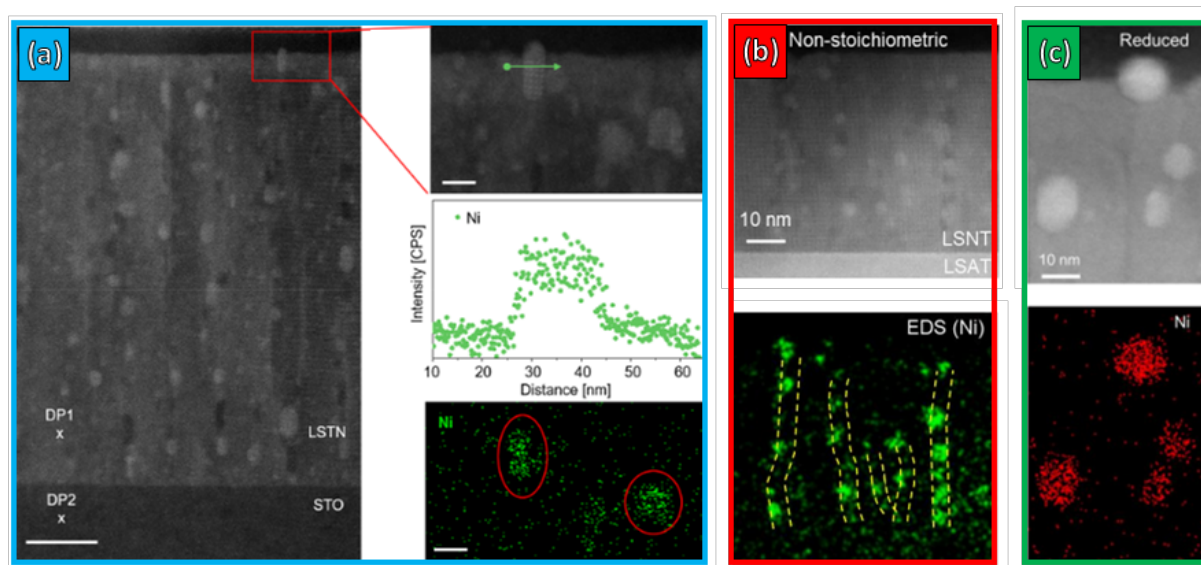


Fig. R1. Cross-sectional TEM images and EDS analysis showing the presence of Ni nanoparticles trapped within the film reported in the literature. Blue: (a) *J. Am. Chem. Soc.* **2019**, 141, 7509 (Figure 2), Red: (b) *Nat. Comm.* **2023**, 13, 6682 (Figure S3) and Green (c) *Nat. Comm.* **2019**, 10, 1471 (Figure S4).

DFT calculations are included in the revised manuscript to investigate the Ni migration in vertically aligned nanostructures (new Fig. 4, page 13). Unlike single-phase thin films, our research provides experimental evidence and modelling results that demonstrate the significant enhancement of exsolution kinetics facilitated by the long-range columnar architecture.

As mentioned in response to the first question, the surface diffusion is different for both samples due to numerous grain boundaries available on the surface, which serve as preferred paths for particle nucleation. In the case of conventional films, the particle growth is primarily governed by the nanoparticles emerging from the bulk film.

3. Size of Ni particle compared to spacing of vertical interfaces: It is also shown that the particle size is much larger than the typically spacing between vertical interfaces (much larger than shown in the sketch in Fig.4). Hence, if these interfaces are preferred routes for Ni exsolution (which they could) I would expect a high dispersion or even homogeneous distribution of Ni on the surface?

We sincerely appreciate the reviewer's attention to this question. In the initial stages of the exsolution process, we observed a high dispersion of Ni nanoparticles on the VAN surface, with individual particle sizes measuring approximately 15 nm (Fig. 1c and Fig. R2). These results demonstrate the enhanced Ni diffusion kinetics in the VAN without compromising the film microstructure, as the columnar architecture remains intact after the exsolution process. The low spacing between interfaces, owing to the narrow column width, promotes the coalescence process, ultimately forming larger Ni particles. This phenomenon is readily evident in the analysis of the cross-section presented in Fig. 1b, where the high population and proximity of the particles can induce further particle growth as the reduction time increases. To provide a more comprehensive understanding of this phenomenon, we have incorporated additional discussion in our manuscript concerning the relationship between Ni nanoparticle size and the spacing of vertical interfaces. Additionally, we have also pointed out that the sketch in Fig. 3h shows the proposed mechanism for Ni diffusion and initial particle growth, while the final particle size is bigger due to the coalescence process.

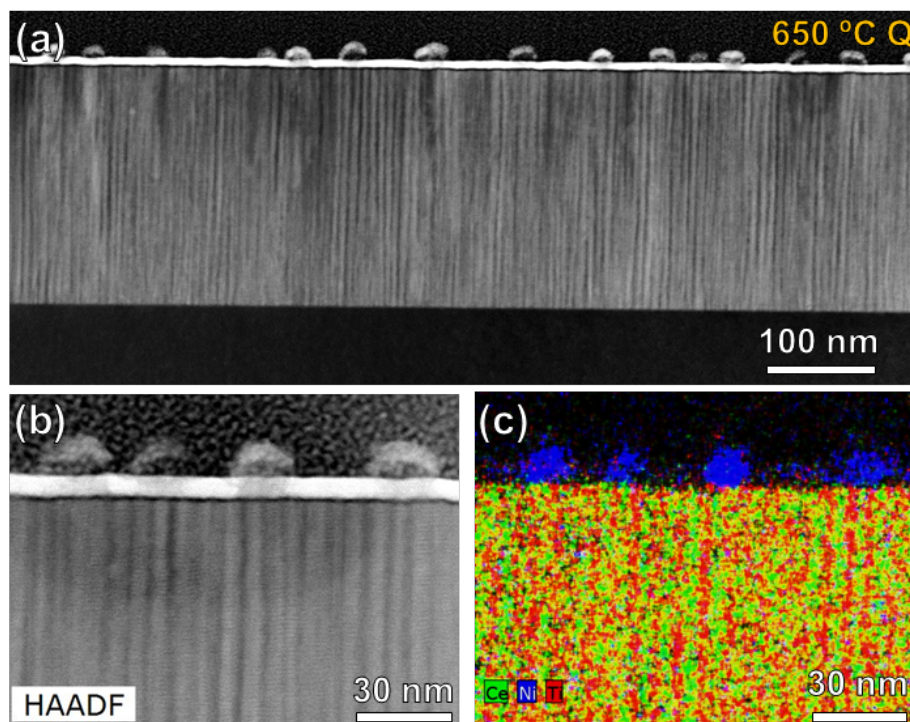


Fig. R2. (a,b) Cross-sectional HAADF-STEM image of the VAN film after reduction at 650 °C for 1 minutes and (c) EDS analysis of a selected area showing the Ni nanoparticle formation.

4. Mass transport mechanism: Provided that the vertical interfaces are preferred diffusion paths, the authors should discuss (and corroborate by modelling) what is causing enhanced mass transport? Is it a structural distortion or strain? Or is the presence of defects facilitating mass

transport? Or is it electrostatic interaction?

Furthermore, to fully support the main claim of enhanced exsolution along the vertical interfaces, a systematic variation of the interface density should be provided, e.g. by varying the ratio of the VAN compounds.

DFT calculations are now included in the revised manuscript to study the Ni migration in vertically aligned nanostructures (Fig. 4, Page 13), and the reason for enhanced mass transport is addressed. We appreciate the reviewer's suggestion to vary the perovskite/fluorite ratio in the VAN to explore its impact on interface density. It is indeed an interesting avenue for investigation (*ACS Appl. Electron. Mater.* **2021**, 3, 5278-5286). However, we acknowledge that conducting such experiments would need substantial efforts, including creating new targets with different phase ratios, the growth of epitaxial thin films, and comprehensive SEM and TEM characterisations in different atmospheres. Given the current study's practical challenges and scope, we have opted to leave this intriguing idea for future research. Our study is extensive enough to cover many new findings related to exsolution in VAN heterostructures.

However, to embrace the reviewer's comment, we have incorporated a discussion to highlight the potential for future work in which the ratio of VAN components can be systematically varied to gain further insights into interface density effects.

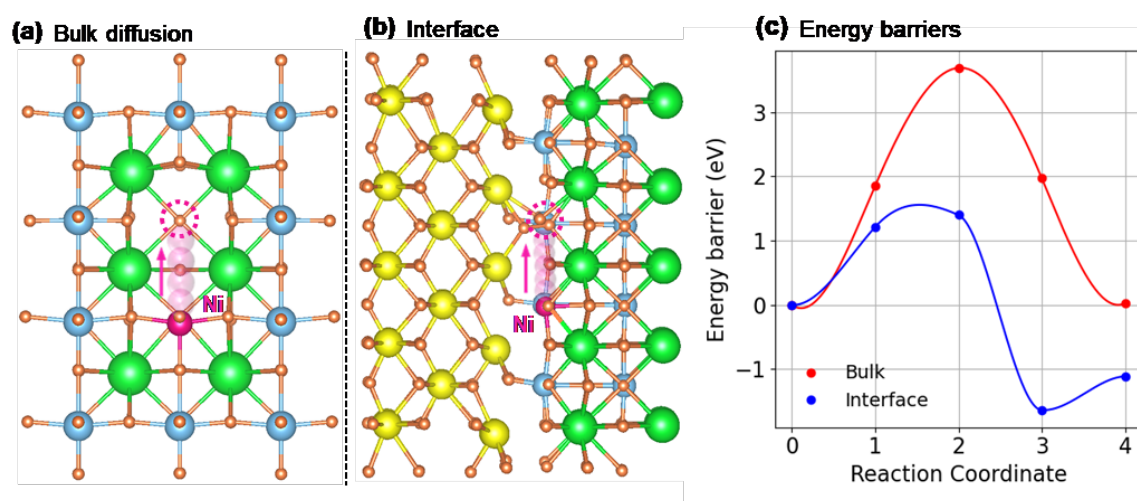


Fig. 4. DFT calculation for Ni migration within the bulk and interface. Schematics of Ni migration pathways across the (a) perovskite bulk and (b) perovskite-fluorite interface. (c) Calculated energy barriers for Ni migration for both scenarios, showing a lower migration energy for the diffusion through the interface.

5. Neither in the paper nor in the SI the authors report the morphology of the as-grown samples. It is required to add AFM and SEM data for some of the samples addressed in the paper or SI. Also, the coalescence kinetics study in Fig. 3 would be stronger if similar data was shown for the single layer sample.

The morphology of both as-grown conventional SPTNO and VAN films was thoroughly characterised by AFM (Fig. S4), revealing comparable roughness levels below 1 nm and a dense microstructure. We also have included new SEM data at different magnifications to provide further insights into the as-grown VAN film (Fig. S3). AFM and SEM characterisations of the as-grown

VAN film show a highly homogenous and dense surface morphology, consistent with TEM findings.

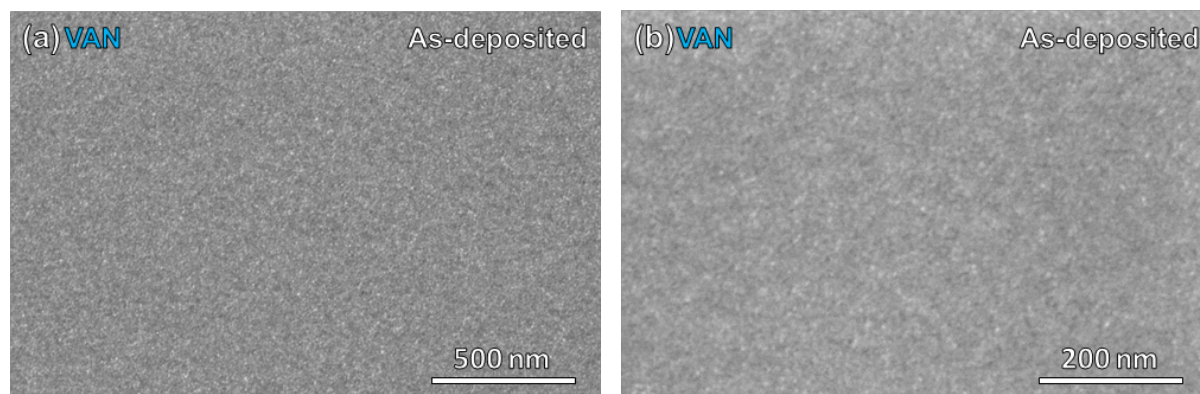


Fig. S3. (a,b) Top-view SEM images at different magnifications of the as-grown VAN film.

Minor comments:

6. I would like to ask the author to comment on the extend of nanoparticle socketing at the thin film surface as this is a feature that is oftentimes shown for exsolved nanoparticles. It appears that no socketing can be observed for the present material system.

SEM and TEM analysis revealed that the exsolved Ni nanoparticles derived from VAN showed a faceted shape, indicating a strong interaction between the metal and the oxide support (*ACS Nano* **2021**, 15, 81-110). These findings contradict those observed for the nanoparticles prepared by infiltration, in which a spherical shape typically prevails due to weaker particle-support interaction. In our study, we thoroughly investigated these nanoparticles' thermal and redox stability under various reduction times and redox cycles. It is worth noting that the unique microstructure architecture of VAN, composed of vertical columns, does not seem to favour the socket of the particles as the film is composed of a heterostructure, unlike conventional single-phase films. To address these findings, we have included further discussion in page 14. Nevertheless, as previously highlighted, many Ni nanoparticles trapped in the host perovskite film are associated with limited bulk mass diffusion in conventional films. This phenomenon is consistent with the evidence presented in previous research (*i.e.*, *Nat. Comm.* **2023**, 13, 6682; *Adv. Mat.* **2023**, 35, 2208984; *ACS Nano* **2021**, 15, 4546; *Nat. Comm.* **2019**, 10, 1471; *J. Am. Chem. Soc.* **2019**, 141, 7509).

7. It is not really clear to me what the conductivity data adds to the study. Can the authors track the exsolution process via in-plane conductivity measurements? It is not clear to me how? In Fig. 5b,c, it is also unclear to the reader what specifically is defined as 'after electrochemical characterization'? Did the sample see H₂/Ar or O₂ or both? How many cycles, etc., should be defined more clearly.

The in-plane conductivity was determined through ex-situ measurements using the Van der Pauw method in both oxidising and reducing conditions to confirm the redox stability of the samples further. While the primary focus of this study revolves around the experimental and modeling demonstration of hierarchical exsolution in VANs, the conductivity measurements provide valuable insights into the potential application of these films in functional-oxide electrochemical devices. The conductivity of the samples was measured in two cycles of Air/5% H₂-Ar to confirm the

reproducibility of the data and redox stability of the samples. The cooling down was performed under a reducing atmosphere. We have included further experimental details on the electrochemical characterisation in the Method section of the manuscript.

8. As for the XRD analysis: All peaks should be labeled clearly. E.g. the peaks around 40 and 44 degs have no index? Some peaks are marked by an asterisk, but there seems to be no definition? It is also not clear if these data refer to linear or log scales (I assume the latter), as there are no ticks or indications on the y-axis.

We have labelled all the peaks in the XRD patterns. The y-axis in the XRD data is presented in log scales. We have included this information in the discussion and the y-axis in the XRD figures.

9. In the XPS study (Fig. S7), the fitting procedure should be explained in detail. E.g., were the peak parameters identical for as-grown and annealed samples? Were the peak width and spacing fixed?

More specifically, from the XPS spectra the nickel cations are identified to be present in oxidation state (II). It is not straightforward to determine the oxidation state on the basis of the Ni 2p core-level spectrum. I would like to ask the authors to comment how the analysis was performed.

We have included detailed information about the fitting procedure of the XPS data in Methods. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Physical Electronics PHI-5700 using a Mg K α source (1253.6 eV). Each spectral region was scanned several times to obtain a good signal-to-noise ratio. A Multipak-V9.3 software package was used for data analysis. Binding energies were determined concerning the position of the adventitious C 1s peak at 285.0 eV (accurate $\pm$ 0.1 eV). A Shirley-type background was subtracted from the signals, and the recorded spectra were always fitted using Gaussian–Lorentzian curves to accurately determine the binding energy of the different element core levels. The full width at half maximum (FWHM) and spacing between the peak splitting were fixed for as-deposited and reduced samples to lead to a comparison of the data.

Ni 2p core-level was selected instead of 3p due to the significant overlapping of Ti⁴⁺ 3s with Ni⁰ 3p in the binding energy range 62–67 eV. The Ni 2p core-level has been employed before to study Ni-nanoparticles by XPS (*Nat. Comm.* **2018**, 9, 4829; *Nat. Comm.* **2016**, 7, 10667). In our study, a single band centred at 854.8 eV attributed to Ni²⁺ can be observed in the Ni 2p_{3/2} for the as-deposited sample. After reduction, a new band raised at a lower binding energy of 852.4 eV, attributed to Ni⁰, confirming the presence of Ni metal on surface. We have included new sentences regarding the fitting of Ni 2p core-level.

10. Regarding the discussion in line 342 – 344 and line 358 – 360. There are many reports on the irreversibility of nanoparticle exsolution, i.e. stable nanoparticles during re-oxidation. The discussion needs to be updated.

We have revised the discussion regarding nanoparticle stability during reoxidation in the literature.

11. There seems to be a typo between RSM and RMS in some places in the text.

We apologise for this mistake. We have corrected this typo error in the manuscript.

Reviewer #3 (Remarks to the Author):

The authors present a novel approach to promote efficient nanoparticle exsolution from vertically aligned heterostructures at intermediate temperatures, proposing an exsolution mechanism based on diffusion through the numerous vertical interphases that characterise such nanocomposites. This results in a favourable surface diffusion, which is different from traditional epitaxial films where bulk diffusion prevails. The authors propose that vertical strain also plays a critical role in the retaining of the columnar microstructure integrity of the film during exsolution, showing improved redox stability. Moreover, the exsolved nanoparticles remain stable after oxidation in air and do not reincorporate into the film, which is crucial for energy applications to prevent performance degradation. This, combined to nanoparticle stability during redox cycles, provide new directions in tailoring the exsolution process of metal nanoparticles in vertically aligned nanocomposites at intermediate temperatures for potential application in energy- and catalysis-related scenarios. However, I cannot recommend this work for publication in Nature Communications in its current form. Although original and potentially of significance to the field of exsolution and related fields, the work is not sufficient to support some of the conclusions and claims, in my opinion, hence requiring additional evidence. Moreover, the potential significance of the results is not addressed with enough details to provide the breakthrough advance in the field that is required by Nature Communications standards, due to lack in advance in understanding of the phenomena described leaving too much room for interpretation. The following points are some examples detailing such criticism:

We thank the reviewer for their valuable comments and suggestions, all of which have been carefully considered to enhance the quality of the manuscript

1. Lines 267-284: The mechanistic pathway proposed for the exsolution in the VAN structures reported in the work lacks sound proof. Modelling on the proposed mechanism would be appropriate to validate the authors interpretation of the ex situ data reported in the results section of the manuscript.

The revised manuscript now includes new mechanistic insights obtained through DFT calculations. These insights are extensively discussed to evaluate the influence of vertical interphases on the Ni migration process in a VAN compared to traditional bulk diffusion (Fig. 4 and Fig. S19, Page 13)

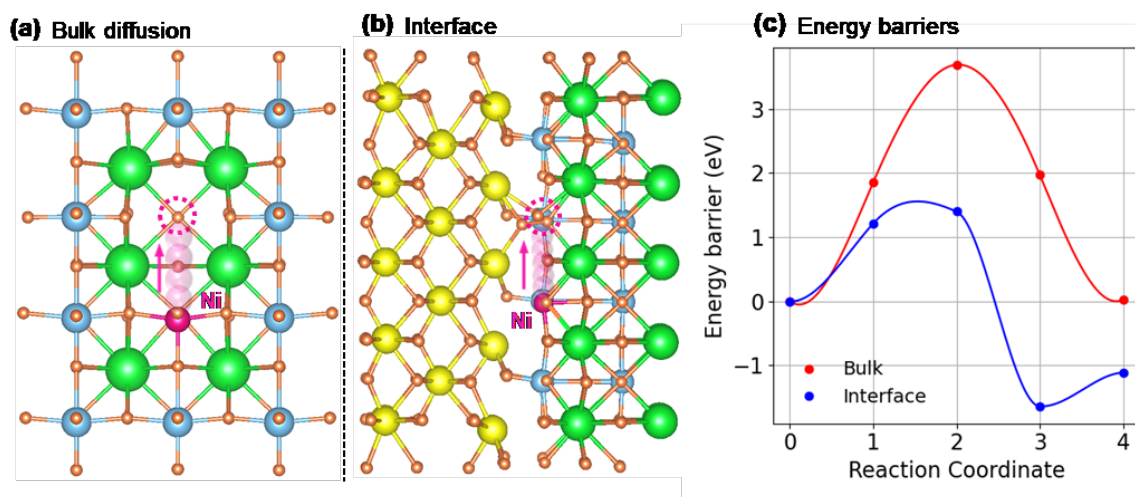


Fig. 4. DFT calculation for Ni migration within the bulk and interface. Schematics of Ni migration pathways across the (a) perovskite bulk and (b) perovskite-fluorite interface. (c) Calculated energy barriers for Ni migration for both scenarios, showing a lower migration energy for the diffusion through the interface.

2. The discussion of the presumably secondary phase observed in Figure 3f, which is then again visible in Figure S13c, being NiO leaves too much room for interpretation, as no experimental evidence is presented in the work to validate such hypothesis (e.g., EDX, XPS). This could be a possibility for the sample reported in Figure S13 (after an oxidation cycle), however why would a NiO phase develop under reducing conditions?

We thank the reviewer for raising this question and apologise for any confusion in the explanation of this secondary phase. In reducing conditions, it is widely reported in the literature that the diffusion species that form metal clusters are Ni ions and not oxide (*Nat. Comm.* **2023**, 13, 6682; *Nat. Comm.* **2019**, 10, 1471; *J. Am. Chem. Soc.* **2019**, 141, 7509). Upon increasing the reduction time from 1 h to 6 h (Fig. 2), this secondary phase decreases considerably, leading to particle size growth and confirming the coalescence process. Subsequently, after increasing the reduction time from 6 h to 12 h, the particle size remains almost unchanged, confirming that the nucleation of the secondary phase, attributed to Ni ions, within the metal nanoparticles has finished.

The presence of this secondary phase in reducing conditions surrounding a larger metal particle has been observed previously in the literature (*Small* **2020**, 16, 2003224; *Chem. Mat.* **2018**, 30, 2838; *Chem. Mat.* **2018**, 30, 2515; *Nat. Comm.* **2017**, 8, 1855). Additional EDS analyses were performed to study this intermediate stage in the nucleation process (Fig. S12). As can be seen, the EDS mappings confirmed the presence of exsolved Ni nanoparticles from the VAN while maintaining the cation homogeneity. This result further confirms the negligible degradation of the film during the exsolution process.

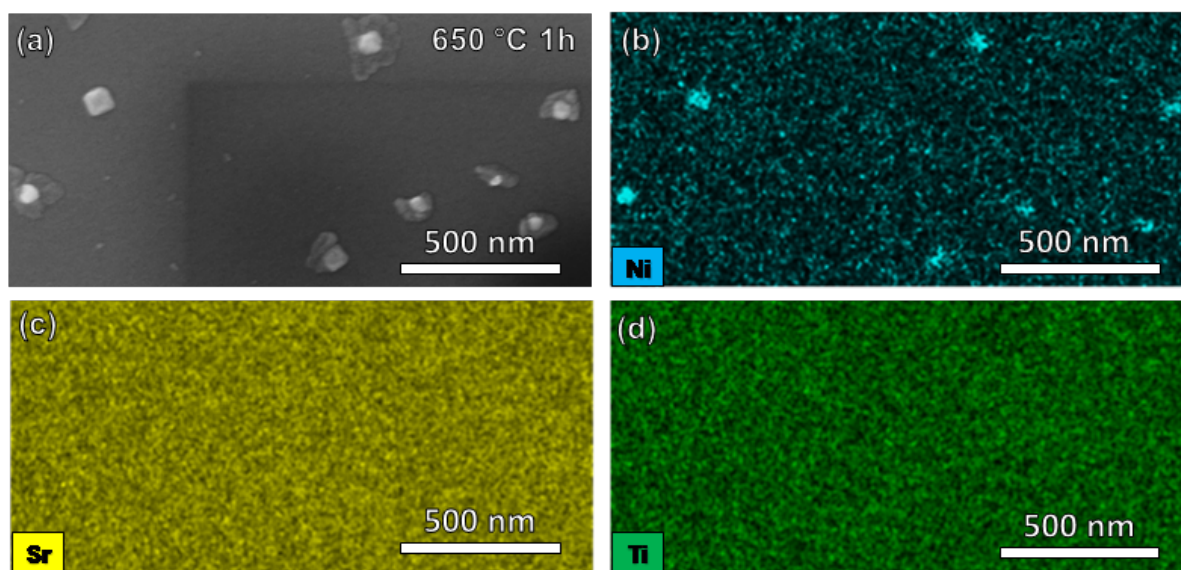


Fig. S12. (a) SEM image and (b-d) EDS mappings of the VAN sample after reduction at 650 °C for 1h

After an oxidation cycle, Irvine's group observed the transition metal oxide phase during the reoxidation process at an intermediate temperature (*Nat. Comm.* **2017**, 8, 1855). Similar irregularly shaped nanoparticles were also observed by Lai et al. after redox cycles, ascribed to the metal oxide phase (*Chem. Mat.* **2018**, 30, 2838; *Chem. Mat.* **2018**, 30, 2515). These findings agree with the presence of NiO after reoxidation in Fig. S20. We have included new sentences, literature, and Fig S20 to clarify this issue.

3. From line 352: again, a possible explanation for the origin and nature of the formed smaller nanoparticles after a 2nd reduction cycle is presented, but no evidence for such claims is provided in the work. This needs to be addressed as, for now, the work does not support such conclusions (line 32: "One possible explanation for the presence of these nanoparticles is that they are originated from the secondary material that was no longer present on the VAN surface. Another possibility is that they came from the SPTNO bulk, which has a lower Ni concentration due to the previous exsolution, forming smaller nanoparticles.").

The redox stability of the exsolved metal nanoparticles from VAN was studied under redox cycles in oxidising/reducing conditions. Prolonged treatment in an air atmosphere resulted in the formation of a secondary phase, which has been attributed to NiO, consistent with previous reports in the literature (*Nat. Comm.* **2017**, 8, 1855; *Chem. Mat.* **2018**, 30, 2838; *Chem. Mat.* **2018**, 30, 2515) as discussed in the previous question. A subsequent reduction treatment led to the disappearance of the NiO phase, accompanied by the presence of new smaller nanoparticles formed after reduction: $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$. Similar findings were previously observed by Lai *et al.*, who demonstrated that metal oxide particles with irregular shapes formed under oxidation conditions can be disintegrated into several smaller nanoparticles in reducing conditions (*Chem. Mat.* **2018**, 30, 2838). We have included new sentences in the manuscript to clarify the origin of the smaller nanoparticles further.

Some minor comments are:

- Details on the statistics used to calculate nanoparticle density are missing and should be provided, as well as further SEM images to prove homogeneous distribution overall and comparisons of particle densities (e.g., for what claimed in line 219).

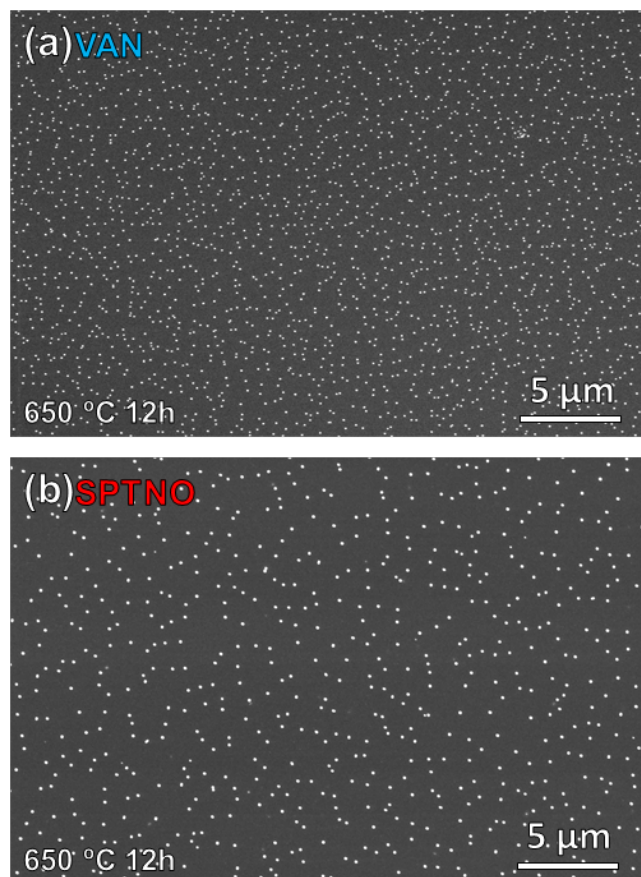


Fig. S13. Low magnification SEM images of (a) VAN and (b) SPTNO samples showing homogenous nanoparticle distribution.

The particle size and distribution were calculated from different areas of the sample surface using ImageJ software. Additionally, as suggested by the reviewer, we have included new SEM images to prove further the homogenous distribution in both SPTNO and VAN samples. As can be seen in the new Fig. S13, the Ni exsolution from VAN leads to higher nanoparticle density with lower particle size compared to the conventional film. We have included new sentences in the discussion to include these results.

- Some sentences appear to be incomplete and need revisions (e.g., line 210-211, line 218)

We have revised and corrected the sentences in lines 210-211 and 218 to improve the readability.

- The methods section should present more detailed information in order to ensure reproducibility of analysis

Further details about the preparation and characterisation of the samples have been included, as suggested by the reviewer. We have revised and corrected the sentences in lines 210-211 and 218 to improve the readability for the reader.

- After Van der Pauw measurements, the authors claim that no degradation or morphological changes are observed for the VAN samples, however the SEM image reported in Figure 5c clearly show additional secondary phase having formed on the surface of the material after electrical conductivity tests.

A microstructural characterisation was conducted for both samples after the electrochemical tests to check the stability of the films (Fig. S11). In both cases, the Ni-exsolved nanoparticles remained stable after the electrochemical measurements in both oxidising and reducing conditions. The conventional SPTNO exhibited a lower population density and particle size than the VAN. Some small cracks were also observed in reducing conditions in the single films. In contrast, the VAN film showed no signs of degradation, and some particles were surrounded by the secondary phase, as previously observed in reducing conditions. This secondary phase was attributed to Ni ions because the cooling was conducted in a reducing atmosphere. Following the reviewer's suggestion, we modified the discussion of the microstructural characterisation after electrochemical tests, including the presence of the secondary phase.

Dear Editor and Reviewers,

We would like to thank the reviewers once more for the insightful comments and suggestions. We also appreciate the overall positive evaluation of the paper with the addition on the atomistic model.

In the text below, you will find the point-by-point answers to the latest comments. We recognized the importance of some of the question risen and we have collected new data to make our analysis and hypothesis more robust. We hope that the revised version of the paper and the updated supplementary data will encounter the favor of the referees so that the paper can be accepted for publication on NatComm.

RESPONSE TO REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have properly addressed the comments raised by reviewers. The DFT calculations are added to further account for the lower migration energy along the interface compared to the bulk system. The NPs certainly do not show strong anchoring compared to the conventional exsolved NPs, implying the relatively smaller stability. However, the exsolution along the vertical interface is very fast and a new finding. This could potentially offer new applications. Thus, I suggest accepting the manuscript.

Answer: We thank the reviewer for appreciating our work and for carefully evaluating the manuscript.

Reviewer #2 (Remarks to the Author):

The authors have carefully addressed the majority of my concerns. I think the inclusion of DFT as a supporting argument for facilitated Ni-diffusion along the VAN interface is a good improvement of the manuscript and supports the general story.

We thank the reviewer for taking the time to read our work and for the positive feedback. We appreciate the careful review of our manuscript.

In my eyes, however, the overall conclusion still has room for speculation. This is particularly due to the involved dimensions of the nanoparticles vs. VAN structure, which was noted by various reviewers. It seems to be a remaining question if the experimental observations are proof enough to claim a 'facilitated ion diffusion along the internal interfaces of the VAN structure' or if the particle sizes are determined by a 'varied surface diffusion and coalescence behavior'. I acknowledge that it is experimentally very difficult to distinguish these two processes, as they are partially convoluted. Therefore, I would suggest to add a bit more of a comprehensive discussion of these two processes, i.e. mass transport to the surface and mass transport along the surface. A systematic comparison of particle size, density, and particularly total volume would help to assess how the overall volume of Ni varies with and without VAN support. This was done e.g. in Weber et al., Nature Materials 23, 406–413 (2024), which also discusses a surface limitation of the exsolution process. Based on the discussion within the

rebuttal, one should also note that the lack of reversibility of Ni exsolution/dissolution from SrTiO₃-based materials was discussed in 10.1039/D3TA02927A by the same authors which could be referred to in the discussion.

Answer: Following the reviewer's recommendation, we have expanded the discussion on the growth process of Ni particles by referencing previous studies and including the works suggested by the reviewer. Additionally, we have included results comparing particle sizes between the bulk film and the VAN.

Overall, I think the manuscript has significantly improved, contains a rich amount of interesting data, and can be thus considered for publication in Nature Communication. However, I would like to see the author responses to the points mentioned below, as well as a more comprehensive discussion regarding exsolution dynamics vs. surface dynamics to guide the reader.

Answer: We thank the reviewer for this comment. Our work presents substantial experimental data corroborated by DFT calculations, demonstrating improved exsolution in vertically aligned nanostructures (VAN). This enhancement is attributed to the hierarchical columnar microstructure, which provides faster diffusion pathways for Ni migration with lower migration energy than traditional films. It is also worth mentioning that other authors have previously reported improved ion transport in VANs (*Adv. Mat.* **2019** 31 1803241; *Nat. Comm.* **2015** 6 8588). As suggested by the reviewer, we have incorporated new comments and relevant literature to provide a more comprehensive discussion on the exsolution and surface dynamics in the VAN structure on pages 2, 14 and 15.

Comments to consider:

1. In my eyes, figure 3h is still misleading, as even in the initial state of the exsolution, the authors mention a particle size of 15nm which is larger than the spacing between the VANs (~5nm or so?). Also, fig. 3h indicates that there is also a network of connected interfaces in lateral dimensions (I can follow the boundary between red and green in-plane) while I understand the real structure more like a columnar enclosure of secondary phase which is fully surrounded by the parent compound. Can the authors clarify?

Answer: We agree with the reviewer that the original Fig. 3h may not represent the initial stage of exsolution. Therefore, we have replaced this figure. Please note that studying the very initial stage of the exsolution process using ex-situ measurements is quite challenging.

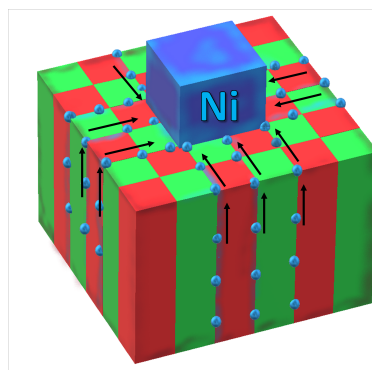


Figure 3h. Illustration of early stages of the nanoparticle nucleation process in VAN under reducing conditions.

Regarding the VAN structure, various microstructures have been reported in the literature, including "nanopillars-in-matrix" or "nano-checkerboard", as described by Sun *et al.* and Chen *et al.* (*Annu. Rev. Mater. Res.* **2020** 50 229-253; *Adv. Mater.* **2019** 31 1803241). The SPTNO-CGO VAN (50 wt. % of SPTNO) studied in this work exhibits a long-range columnar microstructure with a column width of approximately 5nm for both SPTNO and CGO components. A columnar enclosure of one phase surrounded by the parent compound would likely require a considerably higher weight percentage of the parent compound or exhibit significantly different column widths for each phase, contrary to our observations. We have included new comments on page 5 to address this issue better.

2. Furthermore, comparison of the EDS data in Fig 3d and 3f is very difficult as the color code applied for the two samples is different (i.e. reddish color for SPTNO is used in 3f, but not used in 3d...?). The authors may want to only display the Ni signal for both images (not only for d) so the reader can compare differences in the Ni distribution within the oxide bulk. E.g. in Fig. S5b Ni particle formation in bulk is also visible for the VAN sample.

Answer: Following the reviewer's recommendation, the new Fig. 3f displays only the Ni signal to facilitate a better comparison with the traditional epitaxial film. For Fig S5b, the sample was reduced at 650 °C for only 1 min and rapidly cooled down by quenching. This short reduction time was studied to gain better insights into the initial stages of the exsolution process. EDS analysis reveals that a certain amount of Ni is still migrating towards the surface while maintaining the long-range columnar ordering of the VAN. In the sample reduced for 12 h, HAADF-STEM and EDS analysis confirmed the enhanced Ni exsolution kinetics in the VAN, as supported by DFT modelling, without Ni particles trapped within the film. This effect contradicts the findings observed for the traditional films in this work and the literature (Please see Figure R2). We have included new comments on pages 9 and 13 to address this issue better.

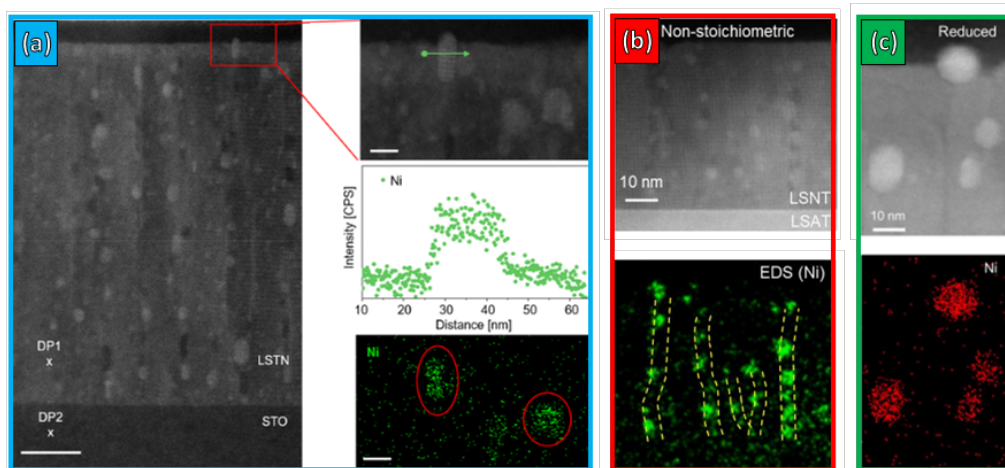


Figure R2. Cross-sectional TEM images and EDS analysis reported in the literature showing the presence of Ni nanoparticles trapped within the film. Blue: (a) *J. Am. Chem. Soc.* **2019**, 141, 7509 (Figure 2), Red: (b) *Nat. Comm.* **2023**, 13, 6682 (Figure S3) and Green (c) *Nat. Comm.* **2019**, 10, 1471 (Figure S4).

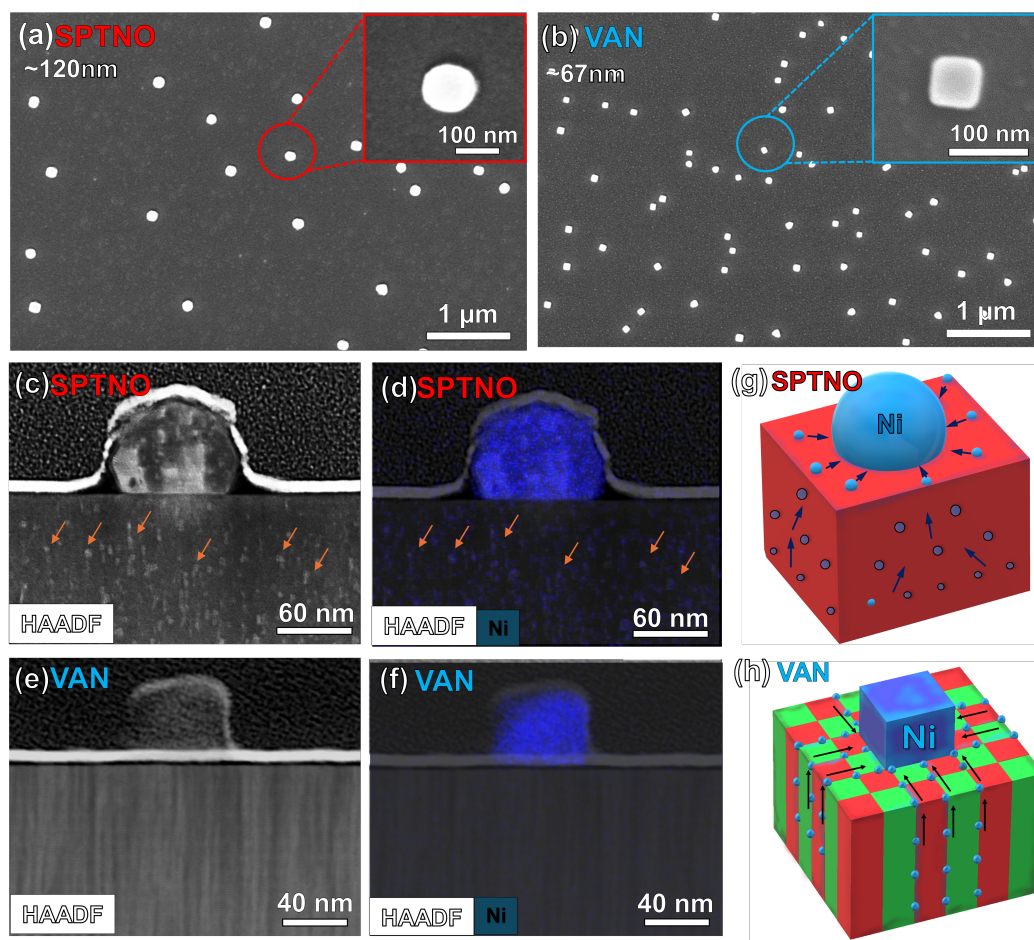


Figure 3. Comparison between the Ni exsolution process and particle size in traditional epitaxial films and VAN

3. In Fig. S18a, a TEM cross section image obtained from the single-phase sample after reduction is shown, where a columnar structure of reduced Ni (?) becomes visible. Can the

authors exclude that there are dopant inhomogeneities present in the as-deposited sample? In the literature referenced in the manuscript it was shown that spontaneous formation of NiO_x columns may occur already at a doping level of 5% while the authors discuss a system with a Ni doping level of 10%. This could also lead to differences in the exsolution behaviour (e.g. more pronounced trapping of Ni in bulk).

Answer: We thank the reviewer for this comment. Fig S18a shows Ni nanoparticles trapped within the host perovskite of the traditional film. Fig. 3c presents a higher magnification HAADF-STEM image of this sample, confirming the presence of discrete Ni particles after reduction, as highlighted by orange arrows and verified by EDS analysis. This phenomenon is commonly observed in traditional films due to the hindered bulk mass diffusion towards the surface compared to the VAN structure (Please see Fig. R2).

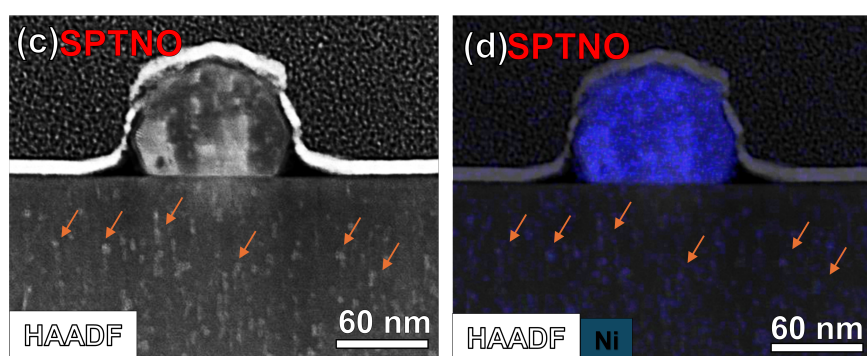


Figure 3c,d. Cross-sectional HAADF-STEM images of the traditional SPTNO showing Ni particles trapped within the host oxide after reduction.

In the literature mentioned by the reviewer and cited in our work (*ACS Nano* **2021** 15 4546-4560), interesting findings on the exsolution of embedded Ni nanoparticles from epitaxial SrTi_{0.9}Nb_{0.05}Ni_{0.05}O₃ are reported. As mentioned by the reviewer, this work observed the spontaneous formation of NiO_x within the host oxide of the as-deposited material using a stoichiometric target of SrTi_{0.9}Nb_{0.05}Ni_{0.05}O₃ and tailored deposition conditions. In our study, we used a different perovskite composition, (Sr_{0.9}Pr_{0.1})_{0.9}Ti_{0.9}Ni_{0.1}O_{3-δ}, featuring A-site deficiency. Traditionally, A-site deficient perovskites promote the exsolution of reducible cations from the host lattice. Many recent studies exploring the exsolution process in epitaxial films incorporate a 10% deficiency in the A-site (*Nat. Comm.* **2022** 13 6682; *Nat. Comm* **2019** 10 1471; *Small* **2020** 16 2003224; *J. Am. Chem. Soc.* **2019** 141 7509-7517), which has been shown not to promote phase separation between NiO_x and the host perovskite oxide for the as-deposited material.

Additionally, regarding the doping level, 10% Ni was the doping content used in all the works mentioned above, *i.e.*, La_{0.2}Sr_{0.7}Ti_{0.9}Ni_{0.1}O_{3-δ}. The exciting findings of NiO_x formation in SrTi_{0.9}Nb_{0.05}Ni_{0.05}O₃ observed by Weber *et al.* may be attributed to the carefully

nanoengineered control of films by tailoring the laser fluence and the different Ni solubility levels in the parent compound, which may induce this phase separation during growth. We have included new comments on page 6 to highlight these results and better address this issue.

4. The assignment of XRD intensity in the SI needs some clarification. The authors index a 'relaxed' SPTNO peak at lower angles than the 'strained' SPTNO peak. Since the strained phase seems to have a larger lattice constant than the STO substrate, it seems to have a larger lattice constant than STO. In the strained case, it is hence expected to be in compressive strain and thus an enlarge out-of-plane lattice constant. Therefore, I would expect that 'strain relaxation' results in a shift towards larger angles (lower out of plane lattice constant). The nature of this peak should be discussed in detail – to me it appears that it might indicate a secondary phase forming? This may not impede the overall message of the paper, but it deserves a detailed discussion of the fundamental structural properties of the starting materials.

Answer: We agree with the reviewer and apologize for this oversight. A minor reflection can be observed at around $2\theta = 44^\circ$ in both the as-prepared and reduced sample (Fig S6d). This effect may be attributed to a minor, unidentified impurity formed during self-assembling. It is important to note that the intensity of this impurity is three orders of magnitude lower than the SPTNO peak, as shown in Fig. S5, with a logarithmic y-axis scale confirming its minor presence. Under reducing conditions, this small reflection shifts slightly to higher angles and does not change in intensity, much like the strained SPTNO. This suggests that the impurity may be a perovskite-type phase similar to SPTNO but with a slightly higher lattice cell parameter. We have added new comments on page 7 to clarify this issue in the discussion of the XRD data.

5. Moreover, I am still missing time/temperature-dependent evaluation of the nanoparticle density for the parent compound for comparison to Fig. 2. This can be used for direct comparison to the VAN-based data.

Answer: We thank the reviewer for this comment. Our study demonstrates enhanced exsolution kinetics for the VAN with hierarchical columnar microstructural compared to traditional films, as shown and discussed for the samples reduced at 650 °C for 12 h (Fig 3a,b). Different reduction times and temperatures were explored for the VAN sample to study the exsolution and nucleation process, as described in Fig. 2. Moreover, as suggested by the reviewer in the first comment, we have improved the discussion of the exsolution and surface dynamics for the VAN in the new version of the manuscript. Following the reviewer's recommendation, we have added new SEM images at different temperatures and times for the parent compound to compare with the VAN results (new Fig S15). Additionally, we have included new comments on page 11.

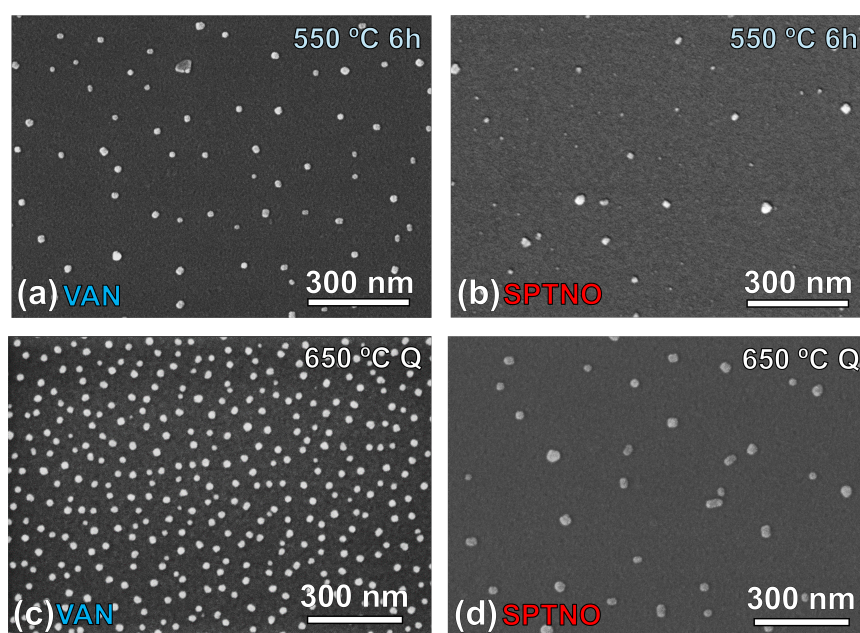


Fig. S15. SEM images of the samples reduced at 550 °C for 6 h for (a) VAN and (b) SPTNO. SEM images of the samples reduced at 650 °C for 1 min for (c) VAN and (d) SPTNO.

Reviewer #3 (Remarks to the Author):

The authors have included substantial extra work in the revised manuscript, and addressed most of the comments and remarks from the reviewers. The work now supports most of the conclusions and claims, and can be considered for publication in Nature Communications, however the data analysis of the secondary phase still lacks sound proof. The EDS maps reported in the response to the reviewers document (Figure S12) does not support the claims of the authors regarding the secondary phase being Ni-based. Either a STEM-/TEM-EDX map should be provided, due to the higher sensitivity of the technique, or a higher-resolution SEM-EDX map. The one provided does not show Ni-enrichment where the secondary phase is present from the image shown. Moreover, the other elemental maps should be included as well (O, C, Pr, Ce, Gd), not only the ones from Sr, Ti and Ni. Once this is addressed and proven, I agree with its publication in Nature Communications.

Answer: We thank the reviewer for appreciating our efforts to improve the quality of the manuscript.

As suggested by the reviewer, we have included a higher-resolution EDS mapping with all the elemental maps (Fig. S12). This new figure suggests that Ni atoms may form the secondary phase without the presence of any other elements. We want to remark that a similar secondary phase in reducing conditions surrounding large metal particles has been previously observed in the literature. This phenomenon has been associated with flat metal particles (*Small* **2020**, 16, 2003224; *Chem. Mat.* **2018**, 30, 2838; *Chem. Mat.* **2018**, 30, 2515; *Nat. Comm.* **2017**, 8, 1855).

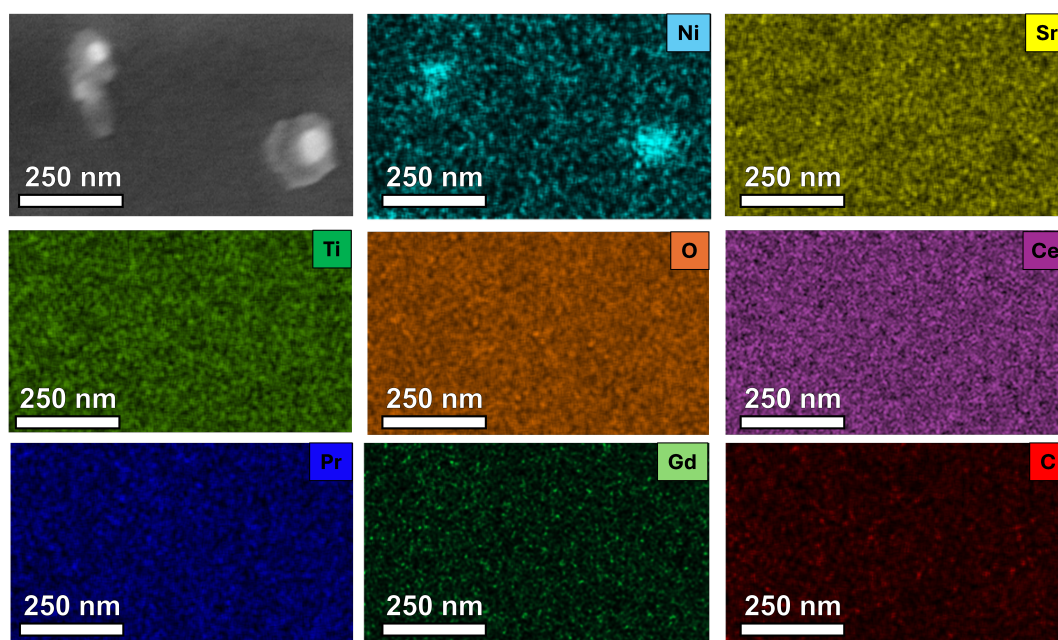


Fig. S12. SEM image and EDS mappings of the VAN sample after reduction at 650 °C for 1 h. This minor phase is only observed in the sample reduced at 650 °C 1h. Particle migration and coalescence and Ostwald Ripening are the proposed mechanisms in the literature for particle growth at the first stages of the exsolution process. It is widely reported that Ni ions are the diffusion species that form metal clusters in reducing conditions (*Nat. Comm.* **2023**, 13, 6682; *Nat. Comm.* **2019**, 10, 1471; *J. Am. Chem. Soc.* **2019**, 141, 7509). This hypothesis aligns with the considerable increase in particle size for the sample reduced for 1 h (Fig 2e) compared to only 1 min (Fig 2d). Ni is migrating on the surface at this stage, and Ni ions merge to form bigger particles. Interestingly, after increasing the reduction time to 6 h (Fig. 2c), the particle size has increased, and this phase is not present, similar to that observed for the reduction for 12 h. We have incorporated new comments to better address this issue on page 10.