Enhancing Ni-Exsolution by Nonmetal B-site Substituents (Si and P) in SrTiO<sub>3</sub>-based Solid Oxide Fuel Cell Anodes

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## **Supplementary Information**

**Note S1**: The positive influence of A-site deficiency in exsolution is reported<sup>1</sup> with the following chemical reaction:

$$A_{1-x}B_{1-x}B'_{x}O_{3-\delta} \xrightarrow{\text{Exsolution}} (1-x)ABO_{3-\delta'} + xB'$$
(S1)

where reducing the non-stoichiometric composition  $A_{1-x}B_{1-x}B'_{x}O_{3-\delta}$  generates a stoichiometric composition of  $ABO_{3-\delta'}$  and produces a greater yield of exsolved B' (B-site substitutional defect). The reducibility of a cation can be determined from the Gibbs free energy change ( $\Delta G$ ) of the following reaction:

$$\frac{1}{x}M_{x}O_{y} + \frac{y}{x}H_{2}(g) \longrightarrow M + \frac{y}{x}H_{2}O(g)$$
(S2)

where M corresponds to A/B-site cations. The  $\Delta G$  of M from M<sup>n+</sup> to M<sup>0</sup> (where n is cation's oxidation number) qualitatively acts as the main driving force for exsolution.<sup>1,2</sup> Transition metals with relatively low reduction spontaneity, Fe<sup>3+</sup>, Ni<sup>2+</sup>, and Co<sup>2+/3+</sup> have  $\Delta G^{900 \,^{\circ}C}$  of - 16.54 kJ · mol<sup>-1</sup>, -49.54 kJ · mol<sup>-1</sup>, and -90.78 kJ · mol<sup>-1</sup>, respectively, but from an A-site deficient composition these metals exsolved with ease.<sup>1</sup>



**Figure S1**: Schematics illustrate the motivation for introducing Si/P-substitution. (a) The Bsite sublattice changes from octahedron to tetrahedron upon Si/P-substitution, forming oxygen vacancies in the process which can aid in reducing more reducible element in the material, Ni. (b) The short and distorted bonds between Si/P – 0 will cause the Ni – 0 to increase in bond length more than Ti – 0, as Ni – 0 is weaker in bond strength than Ti – 0. This will relatively weaken the elongated Ni – 0 bond.



**Figure S2**: Illustration of how the (100) orientation used in this work is equivalent to the (110) notation orientation used in Irvine and Gorte's work.<sup>3</sup>



**Figure S3**: Labelling for each of the five layers of the slab model demonstrated with the energetically preferred configuration of STO, (100) orientation and SrTiO termination.

Note S2: We relaxed the tetragonal (I4/mcm) STO unit cell (20 atoms,  $Sr_4Ti_4O_{12}$ , see Figure S2) and used this cell to construct the slab-model ( $Sr_{10}Ti_{10}O_{26}$ ) to compute bulk properties. The cations in the bottom two layers were fixed according to this precomputed bulk phase, see Figure S3. However, we allowed the O sites to change atomic coordinates during the relaxation because the additional B-site defects,  $Si_{Ti}^{\times}$  and  $P_{Ti}^{\bullet}$  inserted have a preference to alter the oxygen-sublattice.<sup>5-6</sup> In the previous relevant study by Gao *et al.*<sup>4</sup>, all the atoms in these layers (4 and 5) were fixed as that study did not include such B-site substitutional defects. These additional differences in atomic sites created a greater difference between  $E_{surf}$  and  $E_{bulk}$  (lower  $E_{seg}^{Ni}$  for STO slabs). Nevertheless, the difference was computed to be less than 0.4 eV. We kept this calculation setting consistent for the precomputed bulk phase in all the slab configurations in our theoretical study to obtain a reliable comparative analysis.

We introduced defects in the most energetically favorable configuration (smallest  $E_{seg}^{Ni}$ ), (100)oriented and SrTiO-terminated STO.<sup>3,4</sup> As shown in Figure S2, the (100) notation used for this orientation is identical to the (110) orientation reported by Irvine and Gorte groups.<sup>3</sup> Using (1) from the main text, we found (100)-SrTiO to have the smallest  $E_{seg}^{Ni}$  among six possible configurations studied: (100) SrTiO, (100) O<sub>2</sub>, (001) SrO, (001) TiO<sub>2</sub>, (101) SrO<sub>3</sub>, and (101) Ti, consistent with the literature<sup>4</sup>. Neagu *et al.*<sup>3</sup> explained the (100) orientation was experimentally found to be favored for cation-migration because the B-cation migration is likely to occur between adjacent B-sites along a curved trajectory in the (100) planes. There are two possible terminations in this (100) orientation, SrTiO-termination and O<sub>2</sub>-termination. The (100) SrTiO-terminated surface is favorable over the (100) O<sub>2</sub>-terminated surface. Gao *et al.*<sup>4</sup> explained this is because of the increased metal to oxygen atom ratio in the surface compared to the bulk. The (100) SrTiO-terminated configuration was used in slabs, Sr<sub>10</sub>Ti<sub>10-x-y</sub>Ni<sub>x</sub>(Si/ P)<sub>y</sub>O<sub>26</sub> for the calculations (Figure S4).



**Figure S4**: The slab models in (a-c) show the  $Si_{Ti}^{\times}$  or  $P_{Ti}^{\bullet}$  positions and configurations used for computing Ni-segregation energy,  $E_{seg}^{Ni}$  where  $Ni_{Ti}^{\prime\prime}$  is in layer 3 of slab used for  $E_{bulk}$  and  $Ni_{Ti}^{\prime\prime}$  is in layer 1 of slab used for  $E_{surf}$ . (a)  $Si_{Ti}^{\times}$  or  $P_{Ti}^{\bullet}$  in layer 1, (b)  $Si_{Ti}^{\times}$  or  $P_{Ti}^{\bullet}$  in layer 2, and (c)  $Si_{Ti}^{\times}$  or  $P_{Ti}^{\bullet}$  in layer 3.



**Figure S5**: CINEB supercells which show Ni transport path, indicated with arrows for (a) Sr-vacancy-oriented, (b) O-vacancy-oriented, and (c) direct transport routes. (d) Direct transport with Si\* in neighboring B-site. \*The same atomic position of Si is used in the case of P. (e) CINEB results of different Ni paths in (a) to (c).



**Layout S1**: The process of making composition supercells, shown with the example of ST85NS5 ( $Sr_{26}Ti_{27}Ni_3Si_2O_{87}$ ). Similarly, the bulk compositions, ST90N ( $Sr_{26}Ti_{29}Ni_3O_{87}$ ), ST80NS10 ( $Sr_{26}Ti_{26}Ni_3Si_3O_{87}$ ), ST85NP5 ( $Sr_{26}Ti_{27}Ni_3P_2O_{88}$ ), and ST80NP10 ( $Sr_{26}Ti_{26}Ni_3P_3O_{88}$ ) were made for DFT computations.

**Note S3:** We started our calculations from the relaxed  $2\times2\times2$  STO supercell, then included Asite deficiency, B-site substitutions, and O-site vacancies to obtain the materials, ST90N ( $Sr_{26}Ti_{29}Ni_3O_{87}$  approximating  $Sr_{0.8}Ti_{0.9}Ni_{0.1}O_{2.7}$ ), ST85NS5 ( $Sr_{0.8}Ti_{0.85}Ni_{0.1}Si_{0.05}O_{2.7}$ approximating  $Sr_{26}Ti_{27}Ni_3Si_2O_{87}$ ), ST80NS10 ( $Sr_{0.8}Ti_{0.8}Ni_{0.1}Si_{0.1}O_{2.7}$  approximating  $Sr_{26}Ti_{26}Ni_3Si_3O_{87}$ ), ST85NP5 ( $Sr_{0.8}Ti_{0.85}Ni_{0.1}P_{0.05}O_{2.725}$  approximating  $Sr_{26}Ti_{27}Ni_3P_2O_{88}$ ), and ST80NP10 ( $Sr_{0.8}Ti_{0.8}Ni_{0.1}P_{0.1}O_{2.725}$  approximating  $Sr_{26}Ti_{26}Ni_3P_3O_{88}$ ), as shown above in Layout S1. It should be noted that the Ni and nonmetal (Si/P) stoichiometries are 0.09375 (0.10) and 0.0625 (0.05), respectively. We determined the atomic positions of the defects ( $V_{Sr}^{"}$ ,  $V_{0}^{"}$ , and B-site substitutions) using Pymatgen,<sup>7</sup> from the electrostatic energy of (less than) 50,000 random unique structures. In the python script, we have defined the elements in their nominal charge states as, +2 for Sr, +4 for Ti, +2 for Ni, +4 for Si, +5 for P, and -2 for O. However, as the 2×2×2 supercell is relatively large (160 lattice positions), we selected the 10 configurations with the lowest Coulombic energies as initial values for each defect implementation. We relaxed the 10 structures after each of these defect implementations to obtain the most energetically stable configurations.



**Figure S6**: (a) The  $\Delta G$  of hydrogen reduction reaction spontaneity of the oxides of all the A and B site elements considered in compositions. (b) The  $\Delta G$  of decomposition of oxides NiO and TiO<sub>2</sub> comparing reducibility of Ni<sup>2+</sup> and Ti<sup>4+</sup>, respectively. The respective reactions are labeled with the connecting lines in the plot.



**Figure S7:** (a) The electrostatic interactions between  $Ni_{Ti}^{"}$  and  $Si/P_{Ti}^{z}$  in the 3 layers. The charge sign of defects is shown in same color of the atom as '+' for positive defect and '-' for negative defect. (b) The difference between bulk and surface sublattices, where 'P\*' means Si, Ti, and Ni also have similar sublattice changes but the image used to demonstrate it is of  $P_{Ti}^{z}$  defect. (c) Schematic of the Si/P accumulation favored by exsolved Ni could further Ni-segregation if thermodynamically greater content of Si/ $P_{Ti}^{z}$  is present.



**Figure S8**: Bader charges of the B-site ions (Ti, Ni, Si, and P) of the top three layers of slabs used for  $E_{surf}$ . Bader charges are labeled with a same colored arrow near the respective ions in, (a) slabs without any nonmetal atoms, Si or P (STN), (b) slabs with  $Si_{Ti}^{z}$  in layer 1, (c) slabs with  $P_{Ti}^{z}$  in layer 1, (d) slabs with  $Si_{Ti}^{z}$  in layer 2, (e) slabs with  $P_{Ti}^{z}$  in layer 2, (f) slabs with  $Si_{Ti}^{z}$  in layer 3, (g) slabs with  $P_{Ti}^{z}$  in layer 3. (h) The left vertical axis shows the change in Ni Bader charge between  $Ni_{Ti}^{"}$  in layer 1 (slab used for  $E_{surf}$ ) and  $Ni_{Ti}^{"}$  in layer 3 (slab used for  $E_{bulk}$ ) and the right vertical axis shows the Ni's Bader charge in layer 1 for the different Si/P positions.

**Note S4**: The missing terminal oxide bond (Figure S7 (b)) in layer 1 is associated with the energetically preferred configuration used, the SrTiO-termination in (100) orientation configuration. This termination incurred coordination unsaturation in slabs with Si or P in layer 1 gives smaller  $E_{seg}^{Ni}$  than that in layers 2 and 3, see Figure 1 (b). But in practice the orientations and terminations cannot be controlled. Therefore, it is not necessary for Si or P to undergo the degree of reduction we observed in Bader charge analysis for the slabs with Si/P<sub>Ti</sub><sup>z</sup> in layer 1. The larger electronegativity difference of Si – O bond (1.54) than P – O bond (1.25) suggests stronger (or more ionic) bond and more energy-intensive oxide bond of Si causing the  $E_{surf}^{Ni}$  value to be smaller and agrees with the smaller  $E_{seg}^{Ni}$  observed.

Si (2.09) and P (2.08) have similar Bader charges in layer 2 (Figures S8 (d-e)). However, in layer 3 P has a larger charge (2.20) than Si (2.15), which could be associated with the valence state, P<sup>5+</sup> vs Si<sup>4+</sup> Figures S8 (f-g). In addition, the smaller charge of layer 2 nonmetals compared to layer 3 could be due to charge redistribution incurred by higher charge<sup>4</sup> of Ni when Si<sup>Z</sup><sub>T1</sub> or P<sup>Z</sup><sub>T1</sub> are in layer 2 compared to that in layer 3. The Ni charge is about 1.48 in layer 2 for both Si<sup>Z</sup><sub>T1</sub> and P<sup>Z</sup><sub>T1</sub> configurations compared to 1.40 and 1.35 for Si<sup>Z</sup><sub>T1</sub> and P<sup>Z</sup><sub>T1</sub> in layer 3, respectively (Figures S8 (h)). We observe that the change in Ni valence ( $\Delta$ Ni Bader charge) follows the same trend as E<sup>Ni</sup><sub>Seg</sub>; greater  $\Delta$ Ni charge was observed for smaller E<sup>Ni</sup><sub>Seg</sub> and configurations underwent lower  $\Delta$ Ni charge for relatively large E<sup>Ni</sup><sub>Seg</sub>. This indicates that a greater reduction in Ni charge occurs when Ni segregation is favorable. In addition, we note that when the nonmetal substitutional defect is positively charged (such as Si/P<sup>Z</sup><sub>T1</sub> in layer 1) Ni have a lower charge than the Ni in STN. Conversely, when the nonmetal substitutional defect is negatively charged (such as Si/P<sup>Z</sup><sub>T1</sub> in layer 2 and 3) Ni have a higher charge than the Ni in STN. This is consistent with previous relevant studies and occurs due to charge redistribution.<sup>4</sup> **Note S5**: The smaller  $E_{seg}^{Si/P}$  value for configuration with  $Ni_{Ti}^{"}$  in layer 1 compared to  $Ni_{Ti}^{"}$  in layer 3, suggests that both  $Si_{Ti}^{z}$  and  $P_{Ti}^{z}$  have a relative energetic preference to be in the surface when  $Ni_{Ti}^{"}$  is in the surface compared to when  $Ni_{Ti}^{"}$  is in the bulk (Figure 1(d)). Therefore, after Ni-segregation we can expect slight accumulation of Si or P at the surface if excess nonmetals are substituted in the composition. This could be because  $SiO_4^{4-}$  or  $PO_4^{3-}$  prefer to adopt the tetrahedron sublattice at the surface because no terminal oxide bonds are present.<sup>5-6</sup> Adoption of tetrahedron geometry will lead to lattice distortion, which will lengthen the surrounding metal-oxygen bond. As Ni – O bond is weaker than Ti – O bond,<sup>4</sup> the Ni – O bond will be lengthened easily. However, too much Si or P at the surface will diminish the concentrations of  $Ni_{Ti}^{"}$ , retarding the Ni-segregation, see Figure S7 (c). If a greater amount of Si/P is present in the composition accumulation. The surface accumulation of Si/P can prevent Ni-segregation as, (i)  $Si_{Ti}^{z}$  or  $P_{Ti}^{z}$  could occupy probable  $Ni_{Ti}^{"}$  istes at the surface; and (ii) the  $Si_{Ti}^{z}$  or  $P_{Ti}^{z}$  defects in near-surface (layer 2) have a tendency to be negatively charged which would repel  $Ni_{Ti}^{"}$ , as illustrated in Figure S7 (c).



**Figure S9:** Section of images taken from configurations used in CINEB computation. (a) Influenced distortion in Ni sublattice, and (b) tetrahedral adoption from Ti-octahedron sublattice.

**Note S6**: (a) The  $P_{Ti}^{\bullet}$  in B-site will induce a greater reduction in B-site transition metals than  $Si_{Ti}^{\times}$ , as demonstrated using the following defect equations:<sup>5-6</sup>

$$SiO_2 + 3Ti_{Ti}^{\times} + O_0^{\times} \rightarrow Si_{Ti}^{\times} + 2Ti_{Ti}' + V_0^{\bullet \bullet} + \frac{1}{2}O_2 + TiO_2$$
 (S3a)

$$NH_{4}H_{2}PO_{4} + 4Ti_{Ti}^{\times} + O_{0}^{\times} \rightarrow P_{Ti}^{\bullet} + 3Ti_{Ti}' + V_{0}^{\bullet\bullet} + \frac{3}{4}O_{2} + NH_{3} + \frac{3}{2}H_{2}O + TiO_{2}$$
(S3b)

where upon 1 mole of  $\text{Si}_{\text{Ti}}^{\times}$  and  $P_{\text{Ti}}^{\bullet}$  defect formation there are 2 and 3 moles of  $\text{Ti}_{\text{Ti}}'$  (B-site reduction), respectively. This suggests that  $P_{\text{Ti}}^{\bullet}$  will induce a greater reduction in B-site than  $\text{Si}_{\text{Ti}}^{\times}$ , which is correlated to ease of  $V_0^{\bullet\bullet}$  formation by  $P_{\text{Ti}}^{\bullet}$  (forming  $\frac{3}{4}$  moles of  $O_2$ ) than  $\text{Si}_{\text{Ti}}^{\times}$  (forming  $\frac{1}{2}$  moles of  $O_2$ ).

Similar defect equations can be used to show the reduction induced in Ni,

$$\operatorname{SiO}_2 + 5\operatorname{Ni}_{\operatorname{Ni}}^{\times} + \operatorname{O}_0^{\times} \to \operatorname{Si}_{\operatorname{Ni}}^{\bullet\bullet} + 4\operatorname{Ni}_{\operatorname{Ni}}' + \operatorname{V}_0^{\bullet\bullet} + \operatorname{O}_2 + \operatorname{NiO}$$
(S4a)

$$NH_{4}H_{2}PO_{4} + 7Ni_{Ni}^{\times} + O_{0}^{\times} \to P_{Ni}^{\bullet\bullet\bullet} + 5Ni_{Ni}' + V_{0}^{\bullet\bullet} + \frac{3}{4}O_{2} + NH_{3} + \frac{3}{2}H_{2}O + 2NiO$$
 (S4b)

where reagents used in synthesis,  $SiO_2$  and  $NH_4H_2PO_4$  show that Si- and P-substitution creates  $V_0^{\bullet\bullet}$  and reduces Ni,  $Ni'_{Ni}$ .

(b) Using STO Liu *et al.*<sup>8</sup> reported that if  $E_{vac}$  is larger than 5 eV per  $V_0^{\bullet\bullet}$  formation, the concentration of  $V_0^{\bullet\bullet}$  will be less than 1 cm<sup>-3</sup> at 1200 K. Moreover, the pO<sub>2</sub> in a reducing atmosphere such as 97% H<sub>2</sub> and 3% H<sub>2</sub>O can be as low as 10<sup>-19</sup> atm according to thermodynamic equilibrium of H<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O.<sup>4</sup>

**Table S1:** The largest  $pO_2$  with  $E_{vac} \le 5$  eV.

	Highest pO <sub>2</sub> (atm)			
Temperature (°C)	ST90N	ST85NS5	ST85NP5	
700	$\leq 10^{-20}$	10 <sup>-20</sup>	10 <sup>-5</sup>	
800	10 <sup>-19</sup>	10 <sup>-17</sup>	10 <sup>-3</sup>	
900	10 <sup>-16</sup>	10 <sup>-14</sup>	10 <sup>-2</sup>	
1000	10 <sup>-14</sup>	10 <sup>-12</sup>	10 <sup>-1</sup>	



**Figure S10**: (a) The DOS of ST90N, ST85NS5, and ST85NP5. (b) The partial DOS of P 2p and O 2p of ST85NP5 indicate the states marked with stars are mostly attributed to these orbitals. (c) The partial DOS of the s, p, and d orbitals of the samples ST90N, ST85NS5, and ST85NP5. (d) The Ni-partial DOS of the samples ST90N, ST85NS5, and ST85NP5.

**Note S7**: We found one notable difference among the DOS spectra of ST90N, ST85NS5, and ST85NP5, in PDOS of ST85NP5 there are the two peaks at approximately -6 eV. After further examination, we found that these peaks refer to O 2p and P 2p peaks mostly (Figure S10 (b)) which could be due to the 1 extra O atom in the ST85NP5 system (compared to ST90N and ST85NS5). Moreover, we observed a spin-flip in Ni s-orbitals upon Si- and P-substitution, see Figures S10 (d). The partial DOS in ST90N-Ni s orbitals at around -4 eV mark flips from spin downstate (higher energy) to spin upstate (lower energy) in ST85NS5 and ST85NP5. This could be hypothesized as an increment of carrier mobility in Ni atoms upon Si- and P-substitution, which can aid Ni diffusion.<sup>9</sup> The CINEB result supports this with both Si- and P-substituents resulting in a lower Ni-migration barrier from the sample without nonmetal defect.



**Figure S11:** XRD measured lattice parameter changes upon different degree of Si and P substitution in the ST90N perovskite host lattice, ST90N (0%), ST85NS5, ST85NP5 (5%), and ST80NS10, ST80NP10 (10%). The solid lines represent Si-substituted samples and dashed lines represent P-substituted samples.



**Figure S12**: Schematics illustrate the lattice volume changes: (a) the lattice expansion due to 5% substitution of Si or P in Ti-site and (b) the contraction from 5% substituted unit cell upon 10% substitution of Si or P in Ti-site.

Note S8: (a) From experimental data, the analogous change of *c*-dimension ( $\Delta 0.02$  Å) and lattice volume, compared to the minor changes in *a*-dimension ( $\Delta 0.002$  Å) reflects the dominant impact of Si<sup>×</sup><sub>Ti</sub> and P<sup>•</sup><sub>Ti</sub> in B-site (as the ratio of other elements remains unchanged).<sup>1</sup> The unit cell's volume (from experimental data) expanded more in ST85NP5 than ST85NS5 (0.21% vs. 0.13%), and ST80NP10 contracted more than ST80NS10 (contraction by 0.17% vs. 0.12%), as shown in Figure S11. The ST85NP5's lattice expanded more than ST85NS5 forms V<sup>•</sup><sub>0</sub> with more ease than ST85NS5 (ST85NP5 has lower E<sub>vac</sub> than ST85NS5). Moreover, we observed a greater contraction in ST80NP10 than in ST80NS10 as the large Ti<sup>4+</sup> (0.605 Å) ion was replaced by smaller ionic radii of P<sup>5+</sup> (0.170 Å) than Si<sup>4+</sup> (0.260 Å).

(**b**) A similar trend was observed between XRD (Figure S11) and DFT (Figure S13 (a)). The slight variations in values between XRD and DFT results (Table 2 in main text) may be due to the minor compositional differences in the supercells. In general, we found tetrahedral sublattice shape is favorable among Si and P sublattices in the DFT computed cells (Figure S13 (b)). Ni-sublattice had 3 to 5 O atoms. The changes in polyhedral volumes of the sublattices can be determined from distortion index, D which is defined as<sup>10</sup>

$$D = \frac{1}{n} \sum_{i=1}^{n} \frac{|l_i - l_{av}|}{l_{av}}$$
(S5)

where n is the total number of bonds attached to the central atom of the sublattice;  $l_{av}$  is the average bond length; and  $l_i$  is the bond length of the i<sup>th</sup> bond in the summation. From the computed distortion index of Ni-sublattice (in Figure S13 (c)), we note that the Si and P substituted cells show greater distortion compared to the pristine ST90N. In addition, we observed that both Ni and Ti preferred having lower number of O atoms in their sublattices upon Si and P substitution, see Figures S13 (d-e).



**Figure S13:** (a) Lattice parameters of DFT computed cell, (b) 3- and 5- oxygen sublattices for Ni, and tetrahedral sublattices for Si and P, observed in the supercells, (c) Ni-sublattices' distortion index and (d) number of O atoms, and (e) Ti-sublattices' number of O atoms.



**Figure S14:** The high-temperature XRD of ST85NS5, from room temperature to 800 °C and back, (a) the changes in diffraction pattern upon heating and then cooling measured at 100 °C intervals, (b) the inset showing the selected range (70° to 90°) of HT-XRD patterns, and (c) the calculated lattice parameter changes.



**Figure S15:** The high-temperature XRD of ST85NP5, from room temperature to 800 °C and back, (a) the changes in diffraction pattern upon heating and then cooling measured at 100 °C intervals, (b) the inset showing the selected range (65° to 80°) of HT-XRD patterns, and (c) the calculated lattice parameter changes.

**Note S9**: (**a**) We examined the structural evolution of ST85NS5 during heating and cooling with HT-XRD. ST85NS5 did not show any significant structural changes and we observed reversible peak shifts at 2θ position of 77° (620) and 82° (622), see Figure S14 (b). We found the changes mostly occurred above 400 °C temperature. The lattice volumes changed reversibly, expanding upon heating, and contracting while cooling, see Figure S14 (c). We also studied the structural evolution of ST85NP5 during heating and cooling. It did not exhibit any significant structural changes. We observed reversible peak shifts at 68° (440) and 77° (620) for ST85NP5, see Figure S15 (b). These peaks shifted mostly above 400 °C. The lattice volume changes were also reversible, see Figure S15 (c).

(b) In operational conditions of 3%  $H_2O$  and 97%  $H_2$ , ST85NS5's powder samples were reduced for 15 and 30 hours. We used a ST85NS5 sample without any additive of SDC powder or activated carbon, as used in electrochemical testing or electron imaging, respectively. XRD measurements were taken after cooling the sample down to room temperature. After 30 hours of reduction, we observed no phase changes from the primary I4/mcm phase and a peak associated with metallic Ni (Fm $\overline{3}$ m) at 44.4° (111), see Figure S16.<sup>11</sup> This supports the notion that the host lattice maintains the structural integrity after the exsolution of Ni. We have furthered our investigation on exsolved Ni with XPS characterization.

(c) The 30-hours reduced sample's (ST85NS5) crystallinity was further confirmed by SAED evaluations on the TEM images, which corroborated the I4/mcm structure (Figures S17 (a) and (d)). Moreover, the TEM images (in Figures S17 (b) and (c)) showed crystalline arrays, with the magnified region associated with (220) planes of I4/mcm. This suggests that after reduction the material maintains it crystalline structure.



**Figure S16:** Thermal stability test results: (a) XRD results of 15 hours and 30 hours of reduced ST85NS5 sample at 800 °C in 3% humidified  $H_2$ , and (b) the corresponding lattice parameter changes during the 30 hours of reduction.



**Figure S17:** (a) The TEM image used for SAED of reduced ST85NS5 (in 3% humidified  $H_2$ ). (b) The TEM micrograph shows crystalline arrays with selected area magnified in (c) to demonstrate the (220) peak with d-spacing 2.76 Å. (d) The SAED show polycrystalline material with the primary phase's (I4/mcm) significant peaks (planes) labeled.

**Table S2:** Elemental compositions as measured by XPS and XRF compared with the

 theoretically expected values for all the synthesized samples.

Material	Nominal composition [%]	XRF composition (bulk) [%]	XPS composition (near-surface) [%]		
$Sr_{0.8}Ti_{0.9}Ni_{0.1}O_{3-\delta}$ (ST90N)					
Sr	44.4	41.8	46.2		
Ti	50.0	52.8	48.2		
Ni	5.6	5.4	5.6		
0	270.0	-	279.0		
$Sr_{0.8}Ti_{0.85}Ni_{0.1}Si_{0.05}O_{3-\delta}$ (ST85NS5)					
Sr	44.4	40.3	44.4		
Ti	47.2	46.7	46.3		
Ni	5.6	5.5	5.4		
Si	2.8	7.5	3.9		
0	270.0	-	287.0		
$Sr_{0.8}Ti_{0.8}Ni_{0.1}Si_{0.1}O_{3-\delta}$ (ST80NS10)					
Sr	44.4	43.3	43.9		
Ti	44.4	42.6	42.7		
Ni	5.6	4.8	5.8		
Si	5.6	9.3	7.6		
0	270.0	-	277.0		
$Sr_{0.8}Ti_{0.85}Ni_{0.1}P_{0.05}O_{3-\delta}$ (ST85NP5)					
Sr	44.4	43.8	48.0		
Ti	47.2	45.9	40.2		
Ni	5.6	4.2	5.1		
Р	2.8	6.1	6.7		
0	272.5	-	277.0		
$Sr_{0.8}Ti_{0.8}Ni_{0.1}P_{0.1}O_{3-\delta}$ (ST80NP10)					
Sr	44.4	41.4	42.3		
Ti	44.4	40.6	39.6		
Ni	5.6	4.7	5.5		
Р	5.6	13.3	12.6		
0	275.0	-	276.0		

**Note 10**: (a) In XRF characterizations, we observed an overestimation in Si and P valuation because of peak overlap with Sr at 2.0 keV and 1.7 keV in XRF for Si and P, respectively. Nevertheless, the Sr amount was unaffected as it was measured with its largest peak at 14.1 keV. In XPS characterizations, the Sr 3d peak overlapped with the P 2p peak which caused a slight overestimation in P content.<sup>12,13</sup>

(b) The fitted XPS spectra of Ni 2p orbitals shows the two spin-orbit components,  $2p_{1/2}$  and  $2p_{3/2}$  (Figure S18). The larger changes in binding energies observed in Ni 2p compared to the minor changes in Ti 2p is because of lower reducibility of Ti compared to Ni. This is suggested by  $\Delta G$  of (S2) in Figure S6 (a) and  $\Delta G$  for oxide decomposition of NiO and TiO<sub>2</sub> in Figure S6 (b). Furthermore, the oxygen vacancy formation energy data<sup>14</sup> gives a lower  $E_{vac}$  for Ni<sup>2+</sup> as B-site cation than Ti<sup>4+</sup>. This suggests the lattice contraction and expansion that was observed (mostly in the *c*-direction) in XRD and DFT is conveyed in the weaker Ni – O bond, rather than the stronger Ti – O bond.

(c) In previous works, similar lattice contraction was associated with decreased B - O interatomic distance and increased oxidation state of the B-site cation in perovskites.<sup>15,16</sup> Furthermore, Brown *et al.*<sup>17</sup> explained in their study on the relationship between bond strength and bond length, that the stronger bond (Ti – O in this case) will undergo smaller bond length changes compared to the weaker bond (Ni – O). This is reflected in large binding energy increase of Ni 2p by 0.3 eV (Figure 4 (a) of the main text) compared to minor changes in Ti 2p ( $\Delta B.E.$  is 0.03 eV) (Figure S19). In addition, both oxidation and reduction of surface Ni observed in the XPS characterization were analogous to the lattice volume changes observed in Section 3.2.1 of the main text.



**Figure S18:** The XPS spectra of Ni 2p orbitals for (a) ST90N, (b) ST85NS5, (c) ST80NS10, (d) ST85NP5, and (e) ST80NP10 illustrate the peaks for  $2p_{1/2}$  and  $2p_{3/2}$  spin orbital components.



**Figure S19:** The XPS spectra of Ti 2p  $2p_{1/2}$  and  $2p_{3/2}$  spin-orbital components for (a) ST90N, (b) ST85NS5, (c) ST80NS10, (d) ST85NP5, and (e) ST80NP10. The binding energy changes against substituent concentration for (f) Si- substituted and (g) P-substituted samples.

**Note S11:** For Si – O bonds (in Figures S20 (a) and (b)), 'nesosilicates' (major component,  $SiO_4^{4-}$ , blue) refers to islandic silicates where the corner O atoms are bonded with another element and the other component (green) is associated with silicates where the corner O atom is bonded with another Si atom. The tetrahedral silicates range in a wide binding energy spectrum, and with the increasing binding energy a shorter bond length is expected.<sup>18</sup> Therefore, we associate the larger binding energies to 'other silicates' where the silicate could possibly have Si in one of the corner O-sites, signifying improper or incomplete incorporation. Moreover, in the ST80NS10 material we found 1% of SiO<sub>2</sub> (Si<sup>4+</sup>) which is not present in the XRD of the material, this could be due (i) the closed-range peak binding energies of SiO<sub>2</sub> (Si<sup>4+</sup>) and other silicates components, and (ii) the minute amount of SiO<sub>2</sub> present. However, the unbonded Si, characterized at 99.4 ± 0.1 eV is not available in any of Si 2p spectra.<sup>13</sup> Please note that Si 2p<sub>1/2</sub> and 2p<sub>3/2</sub> are overlapping.

For P – 0 bonds (Figure S20 (c) and (d)), the major component is associated with the tetrahedral orthophosphate (purple),  $PO_4^{3-}$ . This refers to the substituent (P) incorporated in the perovskite structure. The other component (green) at higher binding energy, refers to  $P_2O_5$  and indicates poor B-site incorporation of P. We observed a third component in ST80NP10 sample, a hint of  $PO_3^-$  metaphosphate (orange) which has tetrahedral electron geometry and trigonal pyramidal molecular geometry. This component can also be attributed to improper incorporation. The unbonded P, which is typically characterized at 187.9 ± 0.1 eV is not available in both samples' P 2s spectra.<sup>13,19,20</sup>



**Figure S20:** The XPS spectra of Si 2p peaks for (a) ST85NS5 and (b) ST80NS10 deconvoluted to silicates (the major component) and other silicates (details in Note S11). P 2s XPS peaks for (c) ST85NP5 and (d) ST80NP10 samples deconvoluted to tetrahedral orthophosphates (the major component) and other components (details in Note S11). The pie charts represent the peak area percentages for each XPS data.



**Figure S21:** The XPS spectra of the nonmetals upon exsolution. The Si 2p peaks for ST85NS5 (a) before and (b) after exsolution. The P 2s peaks for ST85NP5 (c) before and (d) after exsolution. The pie charts represent the peak area percentages for each XPS data (details in Note S12). (e) The binding energy changes upon exsolution from the XPS spectra of core peaks, Si 2p of ST85NS5, and P 2s of ST85NP5.

Note S12: A higher concentration of  $V_0^{\bullet\bullet}$  upon Si- and P-substitution will make Ni more electron rich. Ni can better donate its electrons to H<sub>2</sub>, leading to the dissociative adsorption of H<sub>2</sub> while undergoing further reductive elimination to form H<sub>2</sub>O, which can facilitate Niexsolution. Furthermore, the reducing environment promotes  $V_0^{\bullet\bullet}$  formation, which in turn facilitates the Si- and P-tetrahedral adoption. This is because the higher concentration of  $V_0^{\bullet\bullet}$ can aid the transition of the oxygen sublattice from octahedral (6 metal-oxygen bonds) to tetrahedral (4 metal-oxygen bonds). The promoted  $SiO_4^{4-}$  and  $PO_4^{3-}$  tetrahedral configuration is supported by the slight increment of binding energies in Si 2p, and P 2s peaks upon exsolution (see Figure S21), implying improved B-site incorporation and bond strengths of Si - O and P -O bond strengths.<sup>18,21</sup> The small  $\Delta B.E.$  of about 0.1 eV could be due to the opposed reducing effect from the reducing environment. Moreover, this agrees with the computations which showed an increase in Si and P Bader charges upon Ni segregation. The Ni-exsolution drives the host lattice from its non-stoichiometric system (A:B  $\approx 0.8:1$ ) towards stoichiometry (A:B  $\approx$  1:1),<sup>1,11</sup> and the nonmetals can aid in stabilizing this latter phase. Si and P in B-site have stabilized perovskite phases in relevant reports.<sup>5,6</sup> Furthermore, we did not find the unbonded Si and  $P^{13}$  in the XPS spectra which agrees with the computations that Si or P will not be segregated.



**Figure S22:** The SEM image shows the electrode thickness of the symmetrical cell used in EIS measurements (picture taken after use from ST85NS5 sample) and the schematic of the symmetrical cell illustrates different components of the cell.



**Figure S23:** (a) The computed ASR from EIS for about 10 hours of reduction in 3% humidified  $H_2$  for ST90N, ST85NS5, ST80NS10, ST90NS5, ST85NP5, ST80NP10, and ST90NP5. (b) Schematic shows weakened Ni – 0 in 5% nonmetal substitution favors ASR and Ni-exsolution while strengthened Ni – 0 (in 10% substitution) favors near surface accumulation of Si/P and prevents further Ni-segregation.

**Note 13:** (a) The ST90NS5 and ST90NP5 demonstrated an increasing ASR. Whereas both 10% substituted samples (ST80NS10 and ST80NP10) showed an initial improved ASR compared to ST90N, but the ASR increased with the reduction time. In contrast, ST85NS5 and ST85NP5 showed an improved ASR, which stabilized over time.

(b) The strengthened Ni – O bonds upon 10% Si/P-substitution (as observed in Section 3.2.2.1 of the main text) makes Si/P adoption of tetrahedral sublattices near the surface more favorable (Figure S23 (b)). This near surface accumulation of Si/P could oppose the Ni-segregation and make Ni stay in the bulk, which is reflected in the increasing ASR of both ST80NS10 and ST80NP10, see Figure S23 (a). Furthermore, this agrees with computations suggesting that after Ni-segregation the Si/P have a slight energetic preference to be in the surface compared to before Ni-segregation, which in turn impedes Ni exsolution (Figure S7 (c)).

(c) We computed DRT using  $10^{-2}$  as regularization parameter and Gaussian discretization in inductance and ohmic resistance excluded EIS data. The low-frequency (0.15 Hz) component decreased from 0.199  $\Omega$ cm<sup>2</sup> to 0.050  $\Omega$ cm<sup>2</sup> for ST85NS5 and from 0.193  $\Omega$ cm<sup>2</sup> to 0.046  $\Omega$ cm<sup>2</sup> for ST85NP5. This was an expected behavior as the low-frequency corresponds to the rate-determining step on the surface, transferring electrons from the chemisorbed H atoms to the electrode, and releasing H<sup>+</sup> ions in the catalysis process.<sup>22-24</sup> Both medium (18 Hz) and high (800 Hz) frequencies have relatively minute impedances, ranging between 0.004  $\Omega$ cm<sup>2</sup> and 0.008  $\Omega$ cm<sup>2</sup> after 30 hours in both the samples, see Table S3. These high and medium frequencies can be roughly associated with ionic conduction or charge transfer processes.<sup>22-24</sup> Moreover, in the isothermal (800 °C) experiment we would expect smaller changes in the charge transfer processes, whereas the low-frequency component would decrease significantly as the electron transfer between H atoms and electrode in the interface surface would enhance with the growth of Ni nanoparticles as reduction time increases.<sup>4,22-24</sup>



**Figure S24:** The DRT for 100 hours of reduction in 3% humidified  $H_2$  at different time intervals and the fitted EIS of ST85NS5 at (a) 0h, (b) 1h, (c) 5h, (d) 10h, (e) 20h, (f) 30h, (g) 40h, (h) 50h, (i) 60h, and (j) 100h.



**Figure S25:** The DRT for 100 hours of reduction in 3% humidified  $H_2$  at different time intervals and the fitted EIS of ST85NP5 at (a) 0h, (b) 1h, (c) 5h, (d) 10h, (e) 20h, (f) 30h, (g) 40h, (h) 50h, (i) 60h, and (j) 100h.

Medium Total High Low High Medium Low Time Frequency Frequency Frequency R<sub>p</sub> Frequency Frequency Frequency [hrs.]  $R_p [\Omega cm^2]$  $R_p [\Omega cm^2] R_p [\Omega cm^2]$  $[\Omega cm^2]$ [Hz] [Hz] [Hz]  $Sr_{0.8}Ti_{0.85}Ni_{0.1}Si_{0.05}O_{3-\delta}~(ST85NS5)$ 0.020 0.199 0 0.029 0.248 844.065 18.415 0.159 1 0.018 0.025 0.198 0.241 784.685 18.311 0.142 5 0.011 0.014 0.115 0.140 783.937 18.305 0.142 10 0.008 0.011 0.092 771.762 0.111 18.263 0.142 20 0.006 0.009 0.071 0.086 774.867 18.252 0.142 30 0.006 0.008 0.065 0.079 779.632 18.284 0.142 40 0.006 0.008 0.063 0.077 770.525 18.227 0.142 50 0.005 0.007 0.056 0.068 763.034 18.169 0.142 0.005 0.006 0.050 0.061 771.324 18.218 0.142 60 0.006 0.050 769.800 100 0.005 0.061 18.233 0.142  $Sr_{0.8}Ti_{0.85}Ni_{0.1}P_{0.05}O_{3-\delta}~(ST85NP5)$ 0 0.018 0.025 0.193 0.236 801.183 18.637 0.145 1 0.0060.009 0.069 0.084 780.075 18.483 0.145 5 0.005 0.0070.056 0.068 794.092 18.593 0.145 10 0.005 0.006 0.050 0.061 771.324 18.218 0.142 20 0.005 0.006 0.049 0.060 795.515 18.581 0.145 30 0.004 0.006 0.049 0.059 781.316 18.811 0.137 40 0.004 0.046 768.516 18.201 0.142 0.006 0.056 0.004 0.006 785.907 18.439 50 0.046 0.056 0.142 0.006 776.476 60 0.004 0.046 0.056 18.281 0.159 100 0.004 0.006 0.046 0.056 772.246 18.219 0.142

**Table S3:** The DRT tool computed polarization resistance  $(R_p)$  associated with high, medium, and low frequency components and their respective frequencies.



**Figure S26:** The SEM images of the grain boundary regions indicated by blue lines, and bluefilled circles represent the Ni nanoparticles. (a) At 5 hours, a relatively smaller number of nanoparticles observed, and (b) after 35 hours of the reduction, the grain boundary is highly populated with nanoparticles, (c) an inset inscribes the observed nanoparticles. The high surface energy at the grain boundary is known to be preferred for nucleation of the exsolved nanoparticles.<sup>25,26</sup>

## References

- Neagu, D.; Tsekouras, G.; Miller, D. N.; Ménard, H.; Irvine, J. T. S. In situ Growth of Nanoparticles Through Control of Non-stoichiometry. *Nat. Chem.* 2013, 5 (11), 916– 923. DOI: 10.1038/nchem.1773.
- Gao, Y.; Chen, D.; Saccoccio, M.; Lu, Z.; Ciucci, F. From Material Design to Mechanism Study: Nanoscale Ni Exsolution on a Highly Active A-site Deficient Anode Material for Solid Oxide Fuel Cells. *Nano Energy* 2016, 27, 499–508. DOI: 10.1016/j.nanoen.2016.07.013.
- Neagu, D.; Oh, T.-S.; Miller, D.N.; Ménard, H.; Bukhari, S.M.; Gamble, S.R.; Gorte, R.J.; Vohs, J.M.; Irvine, J.T.S. Nano-socketed Nickel Particles with Enhanced Coking Resistance grown in situ by redox exsolution. *Nat. Commun.* 2015, 6 (1), 8120. DOI: 10.1038/ncomms9120.
- Gao, Y.; Lu, Z.; You, T. L.; Wang, J.; Xie, L.; He, J.; Ciucci, F. Energetics of Nanoparticle Exsolution from Perovskite Oxides. *J. Phys. Chem. Lett.* 2018, 9 (13), 3772–3778 (2018). DOI: 10.1021/acs.jpclett.8b01380.
- Hancock, C. A.; Slade, R. C. T.; Varcoe, J. R.; Slater, P. R. Synthesis, Structure and Conductivity of Sulfate and Phosphate Doped SrCoO<sub>3</sub>. *J. Solid State Chem.* 2011, *184* (11), 2972–2977. DOI: 10.1016/j.jssc.2011.08.040.
- Hancock, C. A.; Slater, P. R. Synthesis of Silicon Doped SrMO<sub>3</sub> (M = Mn, Co): Stabilization of the Cubic Perovskite and Enhancement in Conductivity. *Dalt. Trans.* 2011, 40 (20), 5599–5603. DOI: 10.1039/C1DT10253B.
- Ong, S.P.; Richards, W.D.; Jain, A.; Hautier, G.; Kocher, M.; Cholia, S.; Gunter, D.; Chevrier, V.L.; Persson, K.A.; Ceder, G. Python Materials Genomics (pymatgen): A Robust, Open-source Python Library for Materials Analysis. *Comput. Mater. Sci.* 2013, 68, 314-319. DOI: 10.1016/j.commatsci.2012.10.028.
- Liu, B.; Cooper, V. R.; Xu, H.; Xiao, H.; Zhang, Y.; Weber, W. J. Composition Dependent Intrinsic Defect Structures in SrTiO<sub>3</sub>. *Phys. Chem. Chem. Phys.* 2014, *16*, 15590-15596. DOI: 10.1039/c4cp01510j.

- Khaneja, N. Conservation of Energy, Density of States, and Spin Lattice Relaxation. Concepts Magn. Reson. A: Bridg. Educ. Res. 2017, 46A, e21457. DOI: 10.1002/cmr.a.21457.
- Hoppe, R.; Voigt, S.; Glaum, H.; Kissel, J.; Müller, H. P.; Bernet, K. A New Route to Charge Distributions in Ionic Solids, *J. Less Common Met.* **1989**, *156* (1-2), 105-122. DOI: 10.1016/0022-5088(89)90411-6.
- 11 Tsekouras, G.; Neagu, D.; Irvine, J. T. S. Step-change in High Temperature Steam Electrolysis Performance of Perovskite Oxide Cathodes with Exsolution of B-site Dopants. *Energy Environ. Sci.* **2013**, *6*, 256-266. DOI: 10.1039/c2ee22547f.
- Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. Handbook of X-ray Photoelectron Spectroscopy: a Reference Book of Standard Spectra for Identification and Interpretation of XPS data; Physical Electronics, PerkinElmer, Inc., United States, 1995.
- Naumkin, A. V.; Kraut-Vass, A.; Gaarenstroom, S. W. C. J. P. NIST X-ray Photoelectron Spectroscopy Database, NIST Standard Reference Database 20, Version 4.1. (2017), http://dx.doi.org/10.18434/T4T88K/ (accessed 2021-03-10)
- Emery, A. A.; Wolverton, C. High-Throughput DFT calculations of Formation
   Energy, Stability and Oxygen Vacancy Formation Energy of ABO<sub>3</sub> Perovskites. *Sci. Data* 2017, *4*, 170153. DOI: 10.1038/sdata.2017.153.
- Dabrowski, B.; Chmaissem, O.; Klamut, P. W.; Kolesnik, S.; Maxwell, M.; Mais, J.; Ito, Y.; Armstrong, B. D.; Jorgensen, J.D.; Short, S. Reduced Ferromagnetic Transition Temperatures in SrRu<sub>1-v</sub>O<sub>3</sub> perovskites from Ru-site vacancies. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2004, 70, 14423-29. DOI: 10.1103/PhysRevB.70.014423.
- Brakkee, R.; Williams, R. M. Minimizing Defect States in Lead Halide Perovskite Solar Cell Materials. *Appl. Sci.* 2020, *10* (9), 3061. DOI: 10.3390/app10093061.
- Brown, I. D.; Shannon, R. D. Empirical Bond-strength–bond-length Curves for Oxides. Acta Crystallogr., Sect. A: Found. Adv. 1973, 29, 266-282. DOI: 10.1107/S0567739473000689.
- Okada, K.; Kameshima, Y.; Yasumori, A. Chemical Shifts of Silicon X-ray Photoelectron Spectra by Polymerization Structures of Silicates. *J. Am. Ceram. Soc.* 1998, 81, 1970-1972. DOI: 10.1111/j.1151-2916.1998.tb02579.x.

- R. Franke, T. Chassé, P. Streubel, and A. Meisel, Auger Parameters and Relaxation Energies of Phosphorus in Solid Compounds. *J. Electron Spectrosc. Relat. Phenom.* 1991, 56 (4), 381-388. DOI: 10.1016/0368-2048(91)85035-R
- 20. Swift, P. Adventitious Carbon—the Panacea for Energy Referencing? *Surf. Interface Anal.* **1982**, *4*, 47-51. DOI: 10.1002/sia.740040204
- Furlan, A.; Gueorguiev, G. K.; Czigány, Z.; Darakchieva, V.; Braun, S.; Correia, M.R.; Högberg, H.; Hultman, L. Structure and Properties of Phosphorus-carbide Thin Solid Films. *Thin Solid Films* 2013, 548, 247-254. DOI: 10.1016/j.tsf.2013.10.010.
- 22. Escudero, M. J.; Aguadero, A.; Alonso, J. A.; Daza, L. A Kinetic Study of Oxygen Reduction Reaction on La<sub>2</sub>NiO<sub>4</sub> Cathodes by means of Impedance Spectroscopy. *J. Electroanal. Chem.* **2007**, *611*, 107-116. DOI: 10.1016/j.jelechem.2007.08.006.
- O'hayre, R.; Cha, S. -W.; Colella, W.; Prinz F. B. Fuel Cell Fundamentals, 3. Edition;
  Wiley, John Wiley & Sons, 2016
- Nielsen, J.; Hjelm, J. Impedance of SOFC Electrodes: A Review and a Comprehensive Case Study on the Impedance of LSM:YSZ Cathodes. *Electrochimica Acta* 2014, *115*, 31-45. DOI: 10.1016/j.electacta.2013.10.053.
- Duan, C.; Kee, R.J.; Zhu, H.; Karakaya, C.; Chen, Y.; Ricote, S.; Jarry, A.; Crumlin, E.J.; Hook, D.; Braun, R.; Sullivan, N.P.; O'Hayre, R. Highly Durable, Coking and Sulfur Tolerant, Fuel-flexible Protonic Ceramic Fuel Cells. *Nature*, 2018, 557, 217–222. DOI: 10.1038/s41586-018-0082-6.
- Liu, Y.; Zhu, X.; Li, M.; Ohayre, R.P.; Yang, W. Nanoparticles at Grain Boundaries Inhibit the Phase Transformation of Perovskite Membrane. *Nano Lett.*, 2015, *15*, 7678– 7683. DOI: 10.1021/acs.nanolett.5b03668.