Supporting Information

Evidence and Model for Strain-driven Release of Metal Nano-catalysts from Perovskites during Exsolution

Tae-Sik Oh,[†] Ehsan K. Rahani,[‡] Dragos Neagu,[§] John T. S. Irvine,[§] Vivek B. Shenoy,*,[‡] Raymond J. Gorte,[†] and John M. Vohs*,[†]

[†]Department of Chemical and Biomolecular Engineering, University of Pennsylvania, 311A Towne Building, 220 S. 33rd Street, Philadelphia, Pennsylvania 19104, United States
[‡]Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut Street, Philadelphia, Pennsylvania 19104, United States
[§]School of Chemistry, University of St. Andrews, Fife KY16 9ST, Scotland, United Kingdom

Calculation of expected pit volumes and exsolved metal particle sizes

The maximum radius, R (nm), of a particle forming sub-surface composed of Ni exsolved from a rectangular parallelepiped perovskite of area A_e (nm^2) and depth d_e (nm), under the constraint that $d_e/2 < 3\ R$ (required for the particle to escape the bulk; see modeling section) can be calculated using the following equation:

$$R \leq \sqrt{\frac{9 \cdot A_e \cdot x_e \cdot A_{\mathrm{Ni}}}{2 \cdot \pi \cdot a_{\mathrm{O}}^3 \cdot \rho_{\mathrm{Ni}} \cdot N_A \cdot 10^{-21}}}$$

The volume of a pit, V_P (nm^3), can be estimated by considering the perovskite volume change before and after reduction and the newly generated volume of the exsolved metal particle, while preserving the total number of cations, as follows:

$$V_P = 6\sqrt{6} \cdot A_e \cdot \sqrt{\frac{3 \cdot A_{\mathrm{Ni}} \cdot A_e \cdot x_e}{4 \cdot \pi \cdot a_{\mathrm{O}}^3 \cdot \rho_{\mathrm{Ni}} \cdot N_A \cdot 10^{-21}}} \cdot \left(1 - \frac{a_{\mathrm{R}}^3 \cdot (1 - x_e)}{a_{\mathrm{O}}^3} - \frac{A_{\mathrm{Ni}} \cdot x_e}{a_{\mathrm{O}}^3 \cdot \rho_{\mathrm{Ni}} \cdot N_A \cdot 10^{-21}}\right)$$

Where:

- x_e is the extent of exsolution ($x_e < 0.03$; $La_{0.4}Sr_{0.4}Ni_{0.03}Ti_{0.97}O_3$)
- A_{Ni} is the atomic weight of Ni metal (g/mol)

- ρ_{Ni} is the density of Ni metal (g/cm^3)
- $a_O{}^3$ is the perovskite unit cell before reduction (nm)
- $a_R{}^3$ is the perovskite unit cell after reduction (nm)
- N_A is Avogadro's constant (6.023 × 10^{23}/mol).

Predictions based on these two equations are presented in the Figure S1 below.

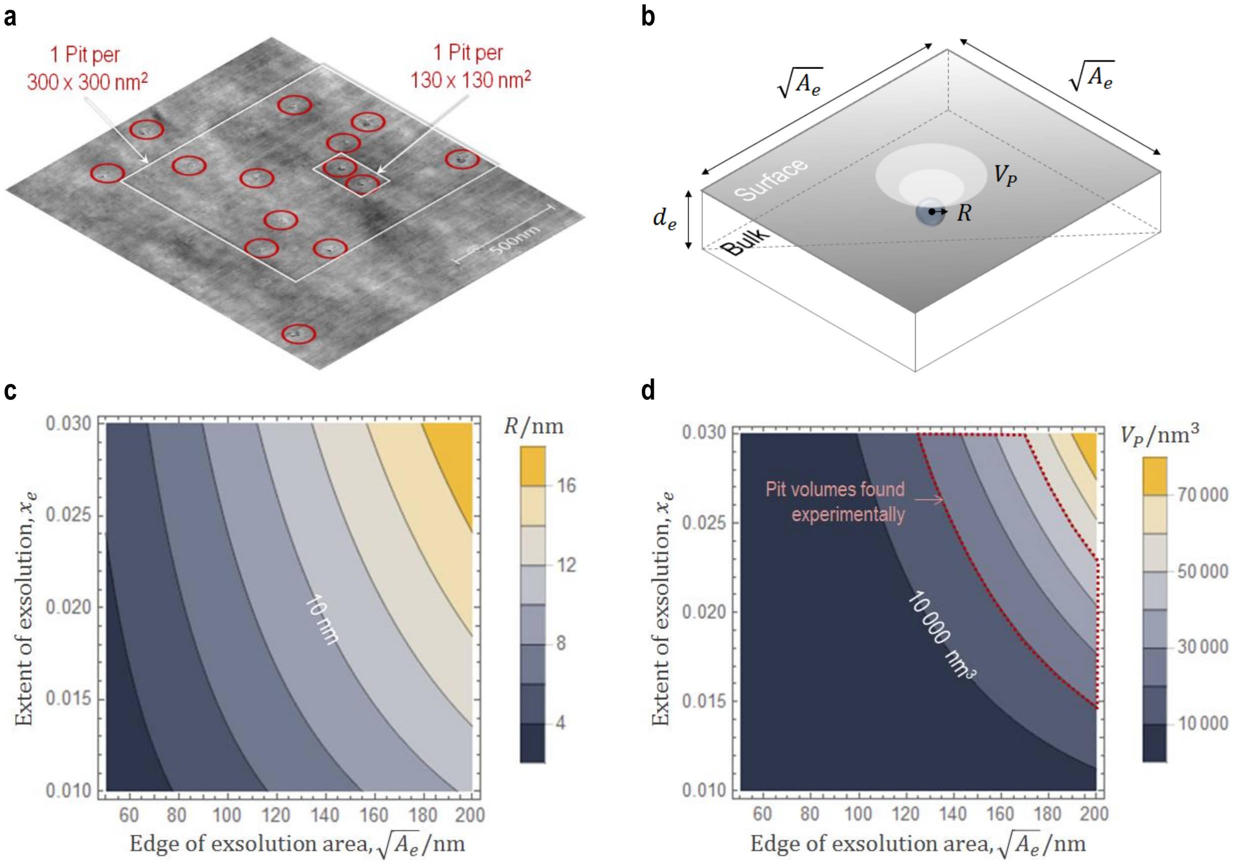

Figure S 1. Insights into the early stages of exsolution from pit volume and population. (a) Perspective view of the AFM scan in Fig. 1b highlighting average and local pit populations. According to this, exsolution from an area of 130 x 130 nm^2 is sufficient to form one sub-surface particle and corresponding pit. (b) Schematic of a rectangular parallelepiped of area A_e and depth d_e containing sufficient exsolvable ions to form one sub-surface metal particle of radius R and corresponding pit volume V_P. (c) Contour plot of R as a function of exsolution area A_e and extent of exsolution x_e., under the constraint that $d_e/2 < 3\ R$ (required for the particle to escape the bulk; see modelling section). The plot shows that particles with R = 9-12 nm are expected to form for area values of 130 x 130 nm^2, depending on the extent of exsolution. (d) Contour plot of expected pit volumes over the same A_e and x_e domains and in (c) and under the same constraint. The plot shows that in order to account for the pit volumes observed experimentally, particles of R = 10-14 nm would have to form sub-surface over areas of 130 x 130 to 170 x 170 nm^2, in reasonable agreement with (a) and (c).