

# Supporting Information for Electron tomography analysis of reaction path during formation of nanoporous NiO by solid state decomposition

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## 1 S.1. In-situ experiments

2 The decomposition of  $\text{Ni}(\text{OH})_2$  crystals was studied in-situ by exposing them  
3 to the electron beam in both broad beam (TEM) and scanning probe (STEM)  
4 modes. Figures S1a and S1b show bright field images for two different  $\text{Ni}(\text{OH})_2$   
5 plates at the beginning of transformation. The transformation results in lateral  
6 contraction, but negligible change in the thickness of the plate, as shown in  
7 Figures S1c and S1d.

8 By rastering the beam in STEM mode over a small selected area of a  $\text{Ni}(\text{OH})_2$   
9 crystal it was possible to induce the transformation in a localized segment (see  
10 Figure S3). In this experiment, a crystal was transformed by scanning the  
11 electron beam over a small area in the center of the plate, and changes were  
12 observed in this crystal and an adjacent crystal, which was only heated indirectly  
13 via contact with the first crystal and the substrate. This allowed the observation  
14 of slow transformation on the second crystal, which was not exposed to electron  
15 beam except for image acquisition. Figure S3a shows both crystals 1 and 2, at  
16 the beginning of the experiment. Figure 3b shows the region in the center of  
17 crystal 1 that was scanned. Continuous scanning of this small region caused  
18 complete transformation of crystal 1 and partial transformation of crystal 2 and  
19 other adjacent crystals, principally near the perimeter of the plate as shown in  
20 Figure S3c. Figure S3d, which was taken after tilting crystal 1 to  $[1\ 1\ 1]_{\text{NiO}}$  zone  
21 axis, shows that both crystals formed densified rims. This experiment confirms  
22 that the transformation under the electron beam was mainly thermal, unlike  
23 the observations made by Su et al [1] in  $\text{Mg}(\text{OH})_2$ . Also, although crystal 1 was  
24 exposed to localized electron dose and heating, the transformation of crystal 2  
25 clearly shows that under uniform heating, the transformation begins at the edges  
26 of the crystal. It should be noted that for image acquisition, low-dose, short  
27 termed STEM scans were used for recording the images that did not induce any

noticeable transformation. This is also evident from the intermediate stages of the experiment performed under a broad, parallel beam (TEM mode) shown in Figure S2.

In another in-situ STEM experiment, a slightly tilted  $\text{Ni}(\text{OH})_2$  crystal was scanned using an electron beam to study the initial stages of transformation. Figure S4, indicates, from the mottled contrast on one of the sides of the hexagonal crystal that the transformation begins with pores running parallel to the plate at the periphery of the crystal (Figure S4a corresponding to the schematic drawing in Figure 6a, followed by densification of the rim, closing the path parallel to the plate and resulting in pores normal to the plate. Note the increased porosity near the rim of the crystal in Figure S4b as also described in Figure 6b.

## S.2. STEM tomography porosity calculations

The reconstructed volume was segmented manually with the help of some interpolating and segmenting tools using the software Avizo[2]. In order to estimate the percentage porosity, the exterior of the crystal was cropped (the hexagonal outline) so that the porosity is not overestimated due to the voxels outside the edge of the crystal.

## S.3. STEM tomography error analysis

Electron tomography is a complex technique requiring numerous processing steps to ensure quantitative results. Errors can be introduced due to imperfect alignment of tilt-series, missing information at high tilts, and segmentation. Figure S5 shows representative sections of the reconstructed volume and the corresponding segmented volume in three orthogonal directions. To quantify all significant errors simultaneously, the error analysis was performed using the final segmented data and the original STEM projection near the  $0^\circ$  tilt angle. The original STEM projections can be considered “ideal” projections and used as a reference for the processed 3D reconstruction. The segmented data is represented digitally by a 3D cube of data with  $(0.34 \text{ nm})^3$  voxels (three-dimensional pixels) of either pure NiO (digital 1) or pores (digital 0). The voxels were summed normal to the NiO plate to produce a 2D projection with intensity proportional to NiO thickness. Figure S6 shows the summation of the segmented data compared to the original  $0^\circ$  STEM projection. The two images clearly exhibit similar features, thus providing a good qualitative check of the accuracy of the alignment, reconstruction and segmentation. For a quantitative check, these data sets can be compared pixel-by-pixel to estimate the compound error. First, the two images were registered with one another with respect to magnification, position and rotation. Then each pixel in Figure S6a shows the measured local mass thickness, which can be directly compared to the actual local mass thickness seen in the HAADF intensity in the corresponding pixel of the original STEM projection in Figure S6b. Due to the compound processing

error, each pixel intensity in Figure S6 corresponds to a range of pixel intensities in Figure S6b. Figure S7a plots the average STEM intensity for each measured local mass thickness. The standard deviation of each data point was then calculated, and the average error of 4.6% for all thicknesses is shown as a single error bar in the lower right of Figure S7a. The ratio between the standard deviation and the mean intensity for each thickness is also shown in Figure S7b which range from 4% - 6%.

## S.4. Videos

The following are the details of the movies available online.

### S.4.1. Movie 1: STEM tomography

This movie shows the surface rendering of the 3D tomogram, followed by orthogonal slices taken in two directions. Note that the pores in the center of the plate go from top to bottom in a zig zag manner, while the pore distribution across the plane of the plate is isotropic in nature. It can be also noted that the plate is denser in the center. The video also shows the pore network of a section of the plate, followed by the skeletonized tomogram showing the interconnectivity of these pores. The diameter of the sections in the skeleton correspond to the size of the pore (scaled down five times). This is also shown by using a color code (red = thick, blue = thin).

### S.4.2. Movie 2: In-situ transformation using STEM

This video shows the STEM experiment described in S.1. The STEM probe was scanned in the central region of crystal 1 and the changes in crystal 2 and other neighboring crystals were observed.

## References

- [S1] Su, D.; Jiang, N.; Spence, J. C. H.; He, F.; Petuskey, W. T. *J. Appl. Phys.* **2008**, *104*, 063514–1–063514–4.
- [S2] Avizo, version 7. <http://www.vsg3d.com/>.

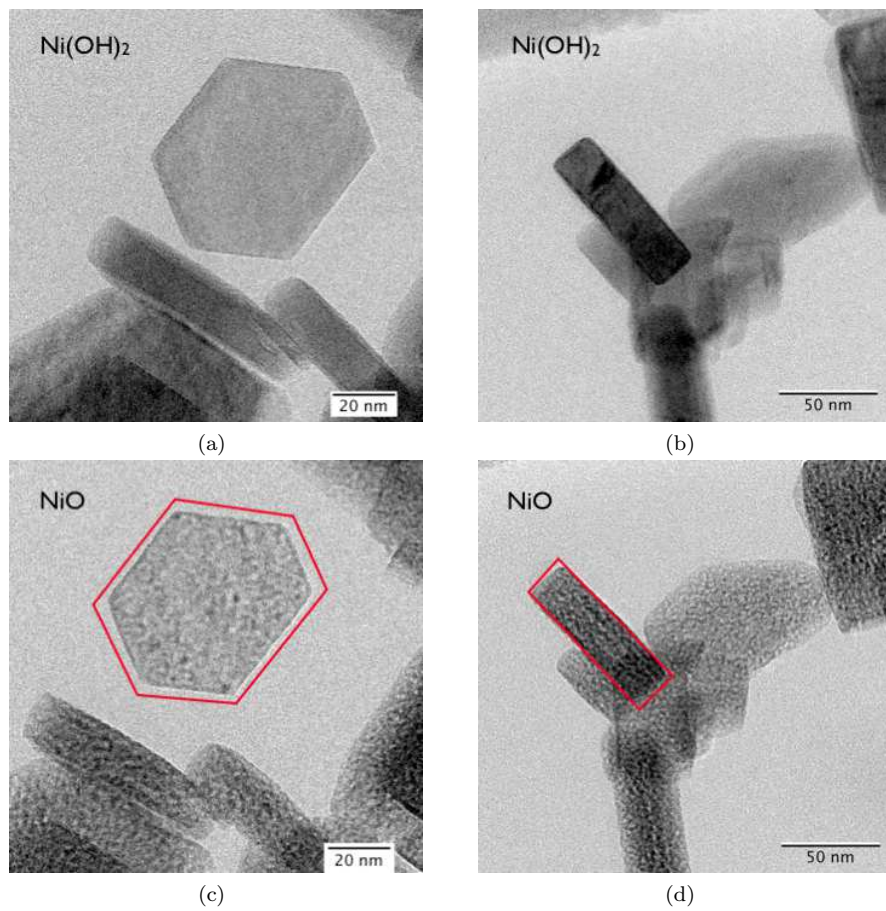


Figure S1: TEM BF images from in-situ experiment showing transformation sequence; a), b)  $\text{Ni(OH)}_2$  crystals at the beginning of transformation; b), c)  $\text{NiO}$  crystals after transformation under the electron beam. The outline of the plate shape before the transformation shows the lateral contraction and constant plate thickness.

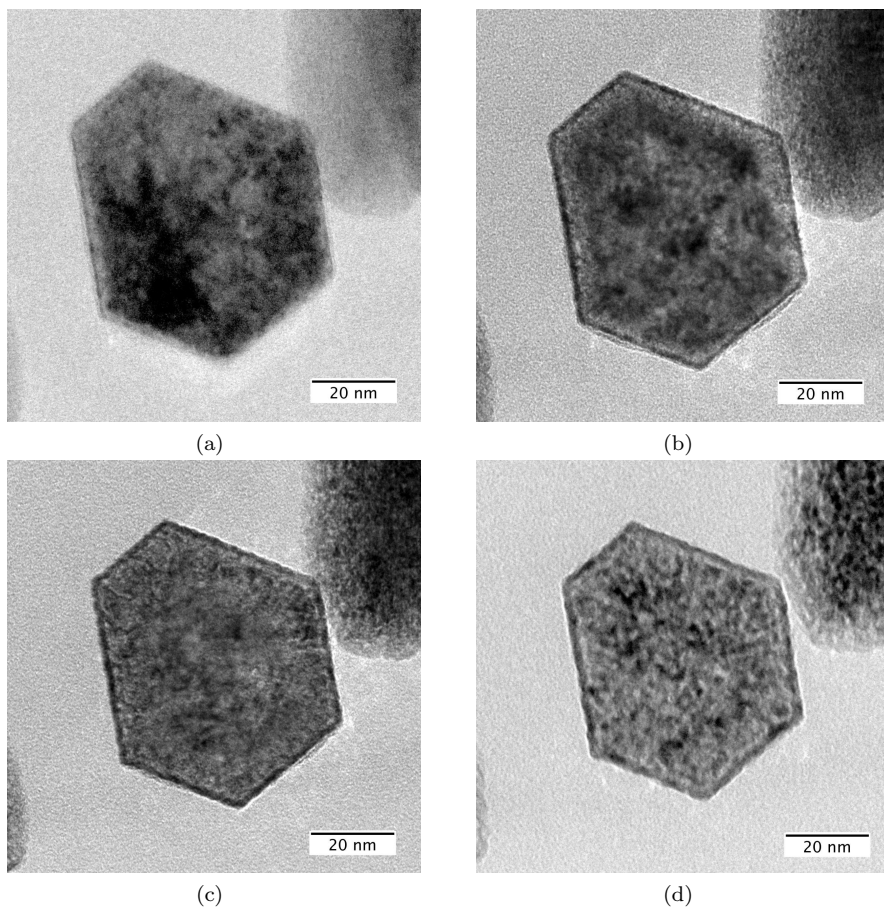


Figure S2: TEM BF images from Figure 1 in the paper reproduced with intermediate stages of transformation; a)  $\text{Ni}(\text{OH})_2$  crystals at the beginning of transformation; b) and c) intermediate stages showing transformation to porous NiO on the edges of the crystal, d) NiO crystal after complete transformation under the electron beam.

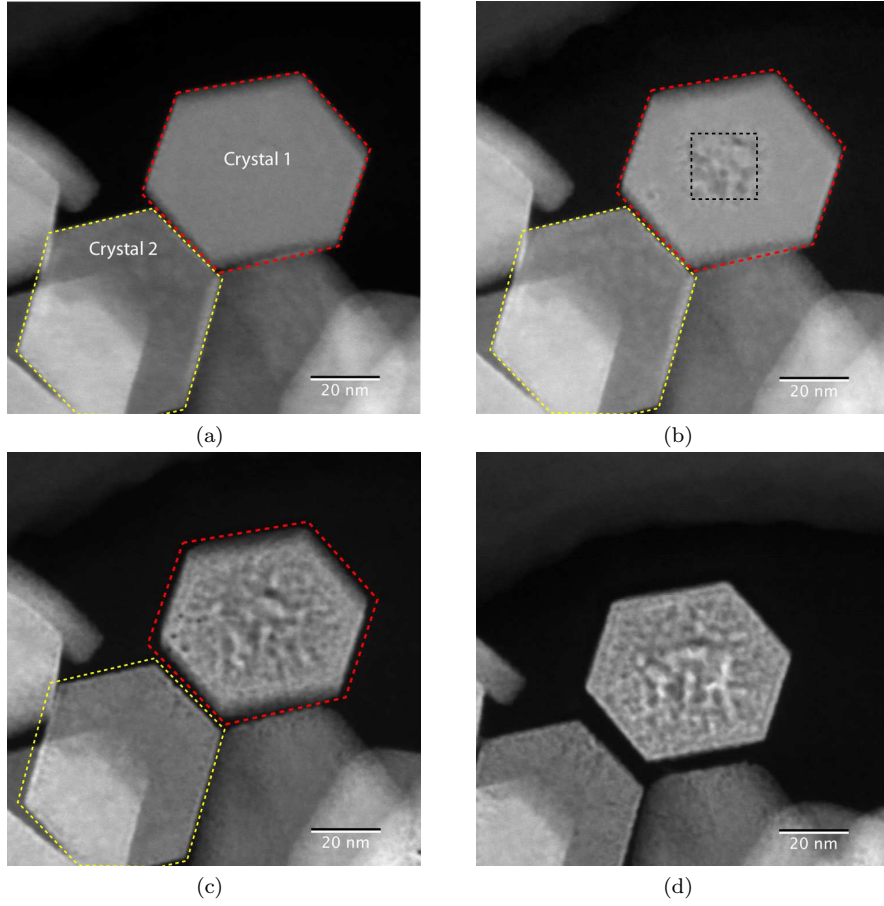


Figure S3: HAADF STEM images from in-situ experiment showing (a)  $\text{Ni}(\text{OH})_2$  crystals 1 and 2 at the beginning of transformation, (b) partial transformation in the center of the crystal 1 (c) partial transformation near the edges of the crystal 2 and (d) fully transformed crystal 1, tilted to zone axis. Note that during the entire experiment, only the square area shown in (b) was scanned, which indicates that the transformation was due to thermal decomposition by specimen heating.

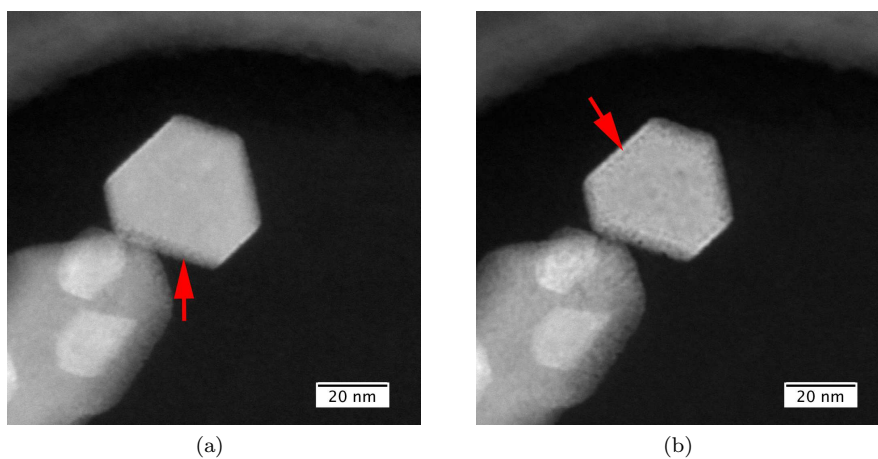


Figure S4: HAADF STEM images from in-situ experiment showing (a) mottled contrast on the side shown with a red-colored arrow indicating the early stage of transformation where the porous channels parallel to the plate are formed on the faces normal to the plate and (b) densification of the rim resulting in transport of  $\text{H}_2\text{O}$  normal to the plate as shown by the formation of porosity next to the rim indicated with a red-colored arrow.

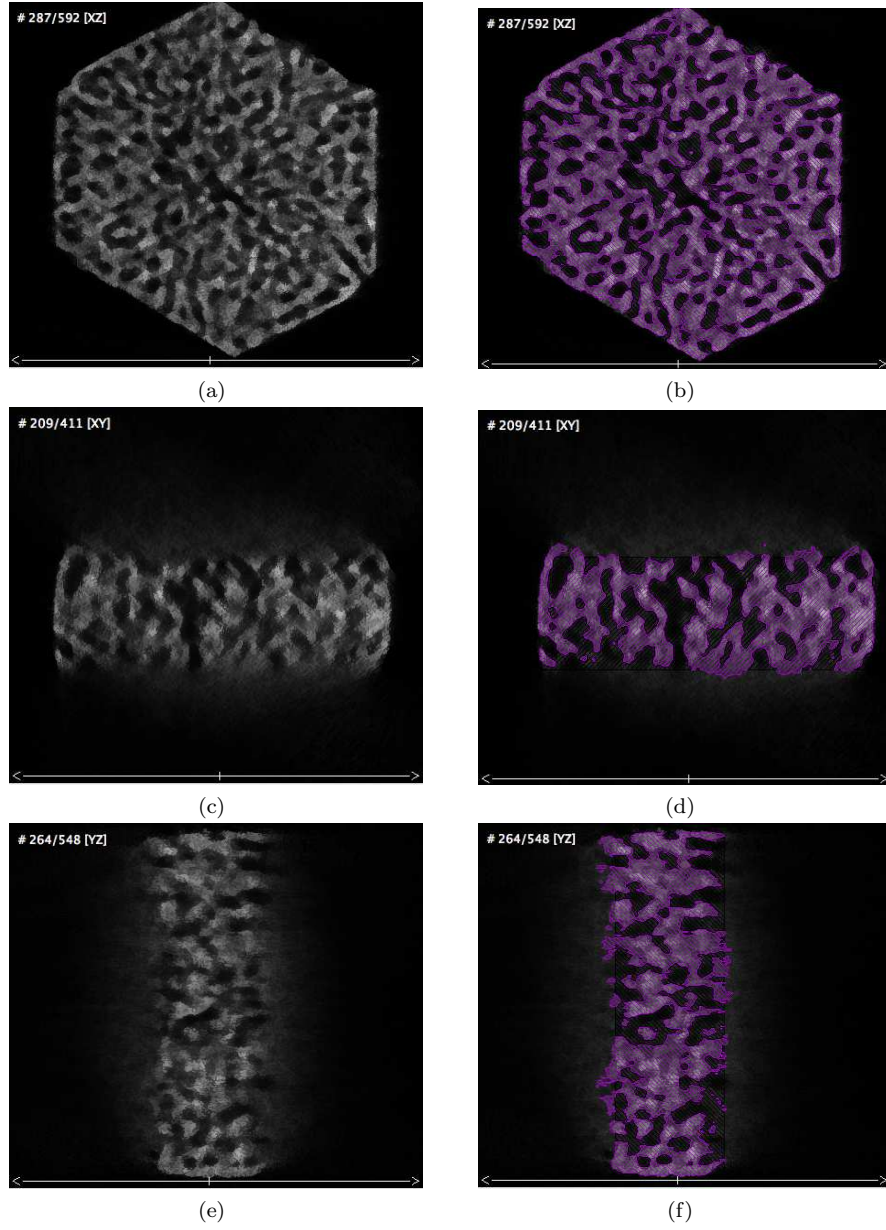


Figure S5: Slices from the reconstructed tomogram compared with those from the segmented volume.



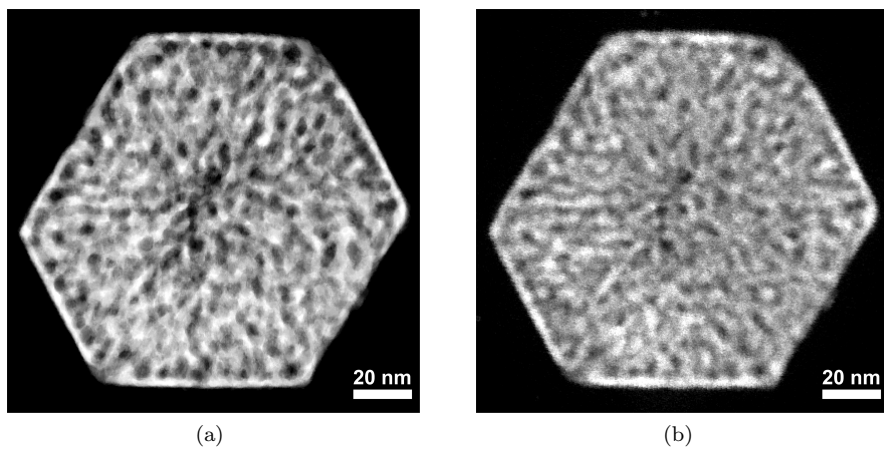


Figure S6: Images showing a) summation of the segmented data and b) original STEM image corresponding to  $0^\circ$  tilt.

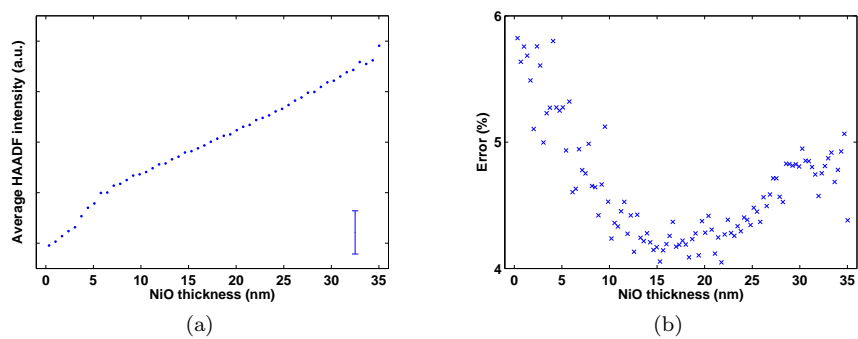


Figure S7: Error analysis showing: a) a plot of average HAADF intensity obtained from STEM image vs. equivalent thickness calculated from the segmented volume and b) distribution of error.

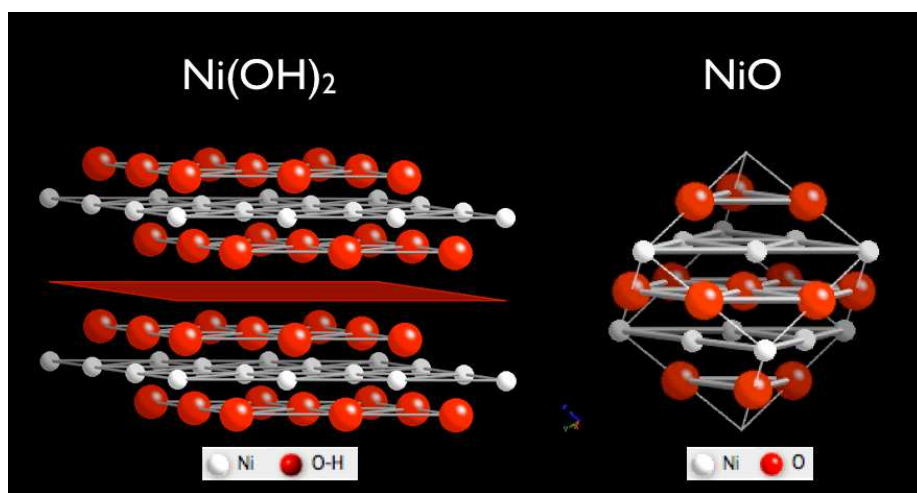


Figure S8: Comparative arrangement of close-packed planes in  $\text{Ni(OH)}_2$  and  $\text{NiO}$ .