Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.


# Sub-Stoichiometric Germanium Sulfide Thin-Films as a High-Rate Lithium Storage Material

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ImageJ was used to determine the column diameter and size distribution from SEM images of films deposited at 70$^o$. The two images used for this analysis are shown in Figure S1. The columns identified by ImageJ are numbered in each image, and the diameter of each numbered column is given in Table S1. Both images indicate that the mean column diameter is just over 10 nm with a standard deviation of 2.46 nm for Figure S1a, and 0.86 nm for Figure S1b.

XRD was used to characterize the crystallinity of as-deposited and cycled $Ge_{0.95}S_{0.05}$ films. A blank stainless steel substrate exhibited three broad peaks between 43$^o$ and 51$^o$, and these peaks persisted through the deposited films. Crystalline germanium would give peaks at 27.4$^o$, and 45.5$^o$, and $Li_2S$ would give peaks at 26.9$^o$, 31.2$^o$, and 44.8$^o$, but no features are present for the as deposited of cycled films. The XRD patterns are shown in Figure S2.

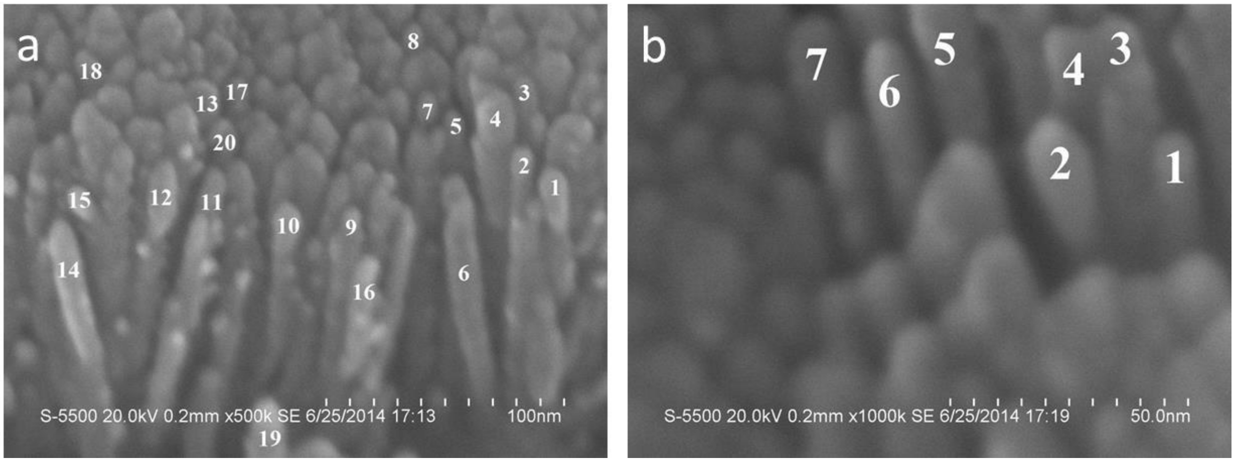


Figure S1. Analysis of two SEM images of $Ge_{0.95}S_{0.05}$ films deposited at 70$^{o}$ shows that the average column diameter is ~10nm. The numbered columns were identified and analyzed by ImageJ.[1] 20 columns are identified in a) while 7 are identified in b).

Table S1. Column diameters and statistical analysis of size distribution from two images analyzed by ImageJ.[1]

## Measurements from Figure S1a

| Column number | Diameter (nm) |
|---|---|
| 1 | 9.832 |
| 2 | 7.93 |
| 3 | 8.719 |
| 4 | 15.854 |
| 5 | 8.491 |
| 6 | 12.488 |
| 7 | 9.018 |
| 8 | 8.52 |
| 9 | 8.296 |
| 10 | 9.079 |
| 11 | 9.037 |
| 12 | 11.209 |
| 13 | 14.509 |
| 14 | 12.032 |
| 15 | 8.626 |
| 16 | 9.693 |
| 17 | 10.126 |
| 18 | 10.637 |
| 19 | 15.062 |
| 20 | 13.526 |
| Average | 10.63 |
| Std. Dev. | 2.46 |

## Measurements from Figure S1b

| Column number | Diameter (nm) |
|---|---|
| 1 | 8.269 |
| 2 | 10.685 |
| 3 | 9.756 |
| 4 | 10.43 |
| 5 | 10.779 |
| 6 | 10.175 |
| 7 | 10.331 |
| Average | 10.06 |
| Std. Dev. | 0.86 |

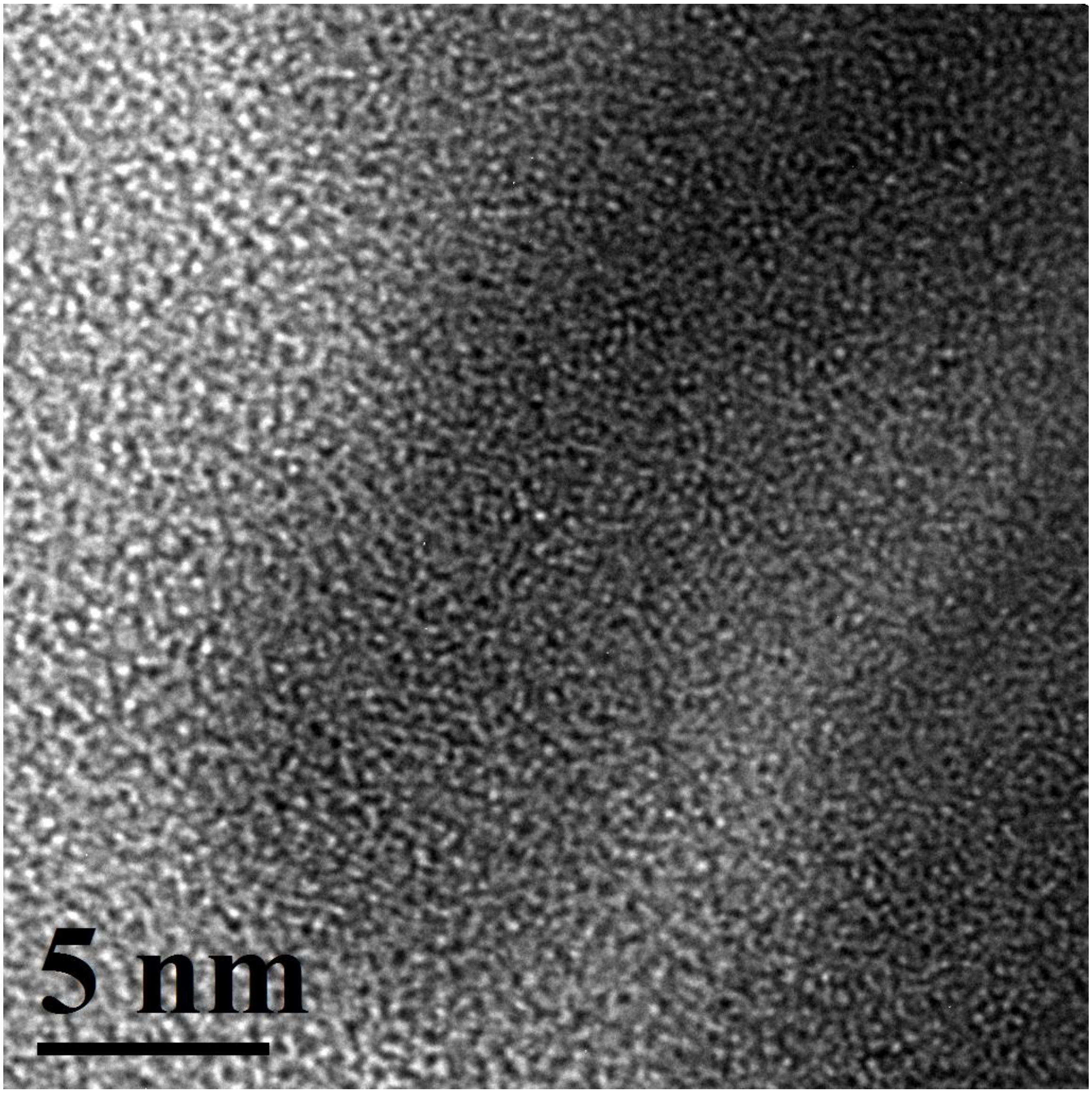


Figure S2. High resolution TEM image of uncycled $Ge_{0.95}S_{0.05}$ film deposited at 70$^{o}$ showing the tip region of a nanocolumn. The column shows uniform contrast indicating homogenous mixing of the germanium and sulfur in an amorphous structure.

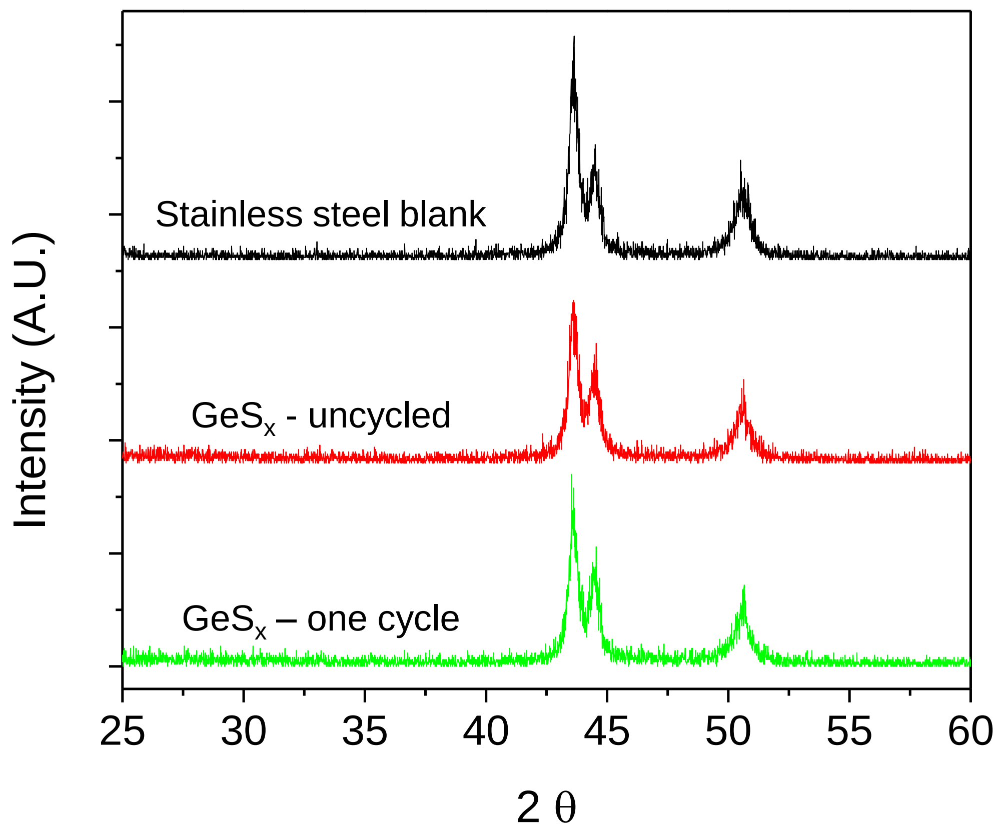


Figure S3. XRD patterns for a blank stainless steel substrate, an uncycled $Ge_{0.95}S_{0.05}$ film, and a $Ge_{0.95}S_{0.05}$ film after one cycle.

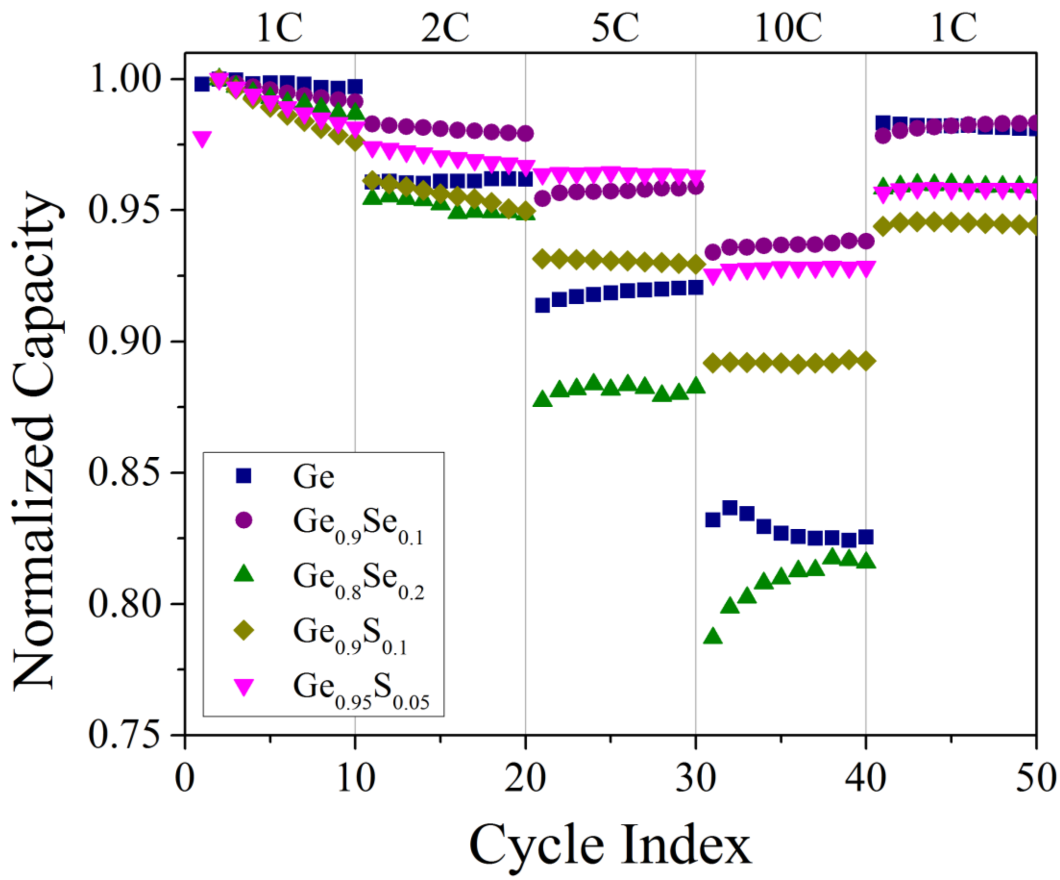


Figure S4. C-rate tests comparing nano-structured thin films composed of Ge, $Ge_{0.95}S_{0.05}$, $Ge_{0.9}S_{0.1}$, $Ge_{0.9}Se_{0.1}$, $Ge_{0.8}Se_{0.2}$ at rates up to 10C.

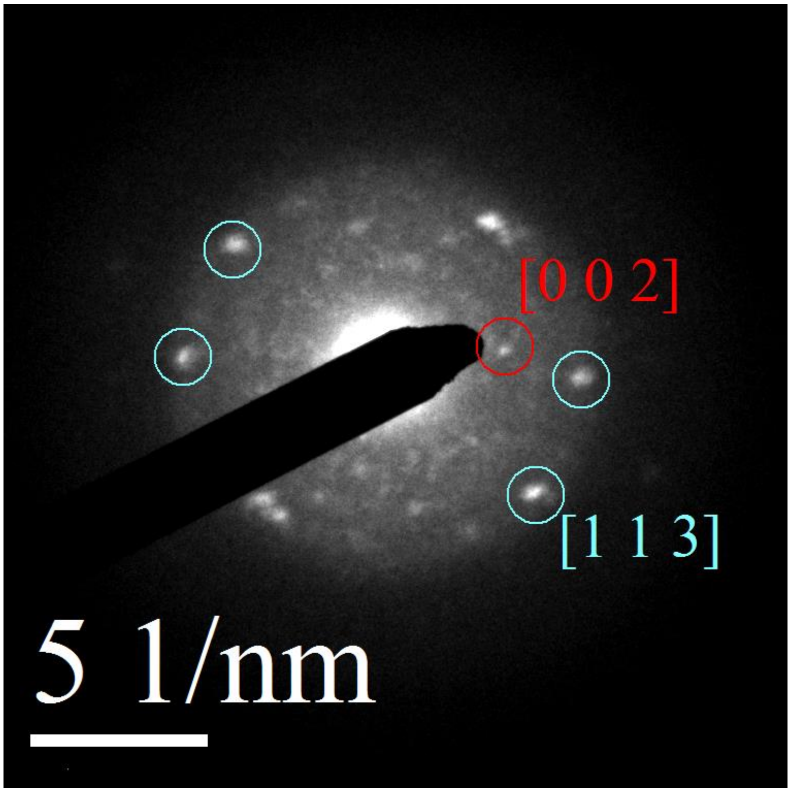


Figure S5. Electron diffraction pattern from a D-STEM beam of cycled $Ge_{0.95}S_{0.05}$ film deposited at 70$^{o}$ in fully discharged state with lattice spacings indicated. The observation of the [0 0 2] reflection indicates the presence of crystalline $Li_2S$. The pattern cannot otherwise be distinguished from Ge because the crystal structures for these materials share the same crystal system (cubic) and have similar cell parameters (a = 5.708 Å for Li2S and a = 5.658 Å for Ge) and space-groups (Fm-3m: 225 for Li2S and Fd-3m: 227-2 for Ge) with identic allowed lattice planes except the Ge [0 0 2] plane.

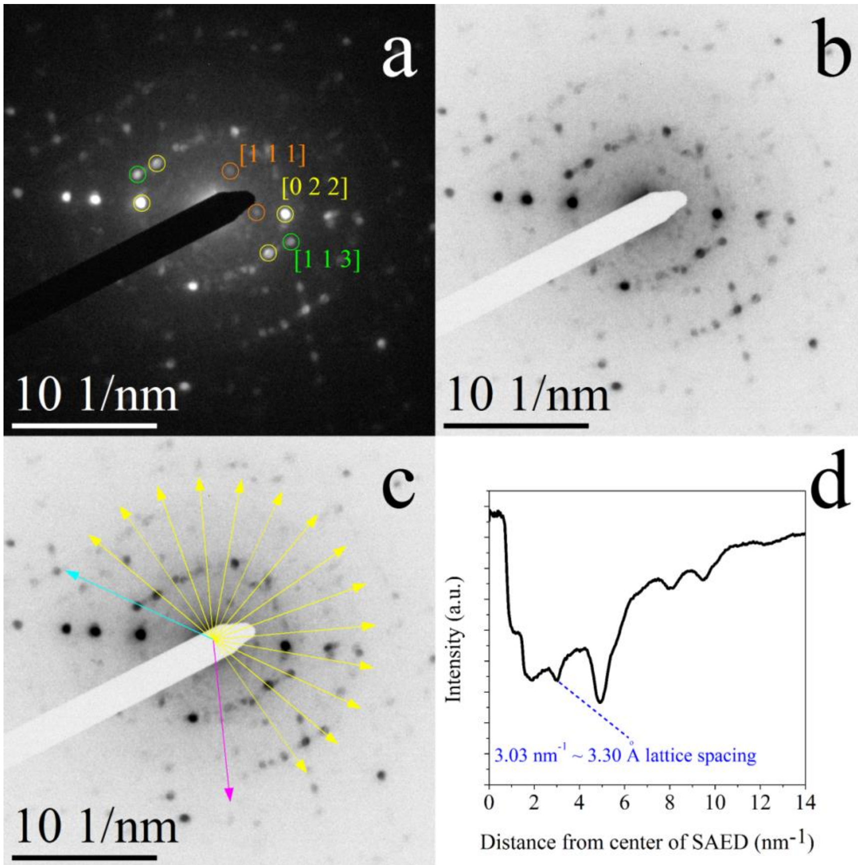


Figure S6. Electron diffraction pattern (a) from D-STEM beam of cycled $Ge_{0.95}S_{0.05}$ film deposited at 70$^{o}$ in fully discharged state. The diffraction pattern results from either crystalline Ge or $Li_2S$. Ge and $Li_2S$ share the same crystal system (cubic) and have similar cell parameters (a = 5.708 Å for Li2S and a = 5.658 Å for Ge) and space-groups (Fm-3m: 225 for Li2S and Fd-3m: 227-2 for Ge) with identic allowed lattice planes in the field of view except the [0 0 2] plane which is precluded by the structure factor for diamond-cubic germanium. However, the [0 0 2] reflection may be observed in germanium under special circumstances such as double diffraction. The most easily differentiated lattice planes would be the [1 1 1] planes: 3.27 Å for Ge and 3.30 for $Li_2S$ but the error associated with measurement of the corresponding spot patterns is larger than the difference in this spacing. Images (b) and (c) indicate the process by which fainter spots can be identified by inverting the grayscale image coloration and using the the Diff:Tool[2] add on to Gatan Digital Micrograph software to identify the extent of greyscale coloration as a function of distance on a radius from the diffraction pattern center. The plot in (d) shows how the local minima in intensity corresponds to the [1 1 1] lattice spacing marked in (a).

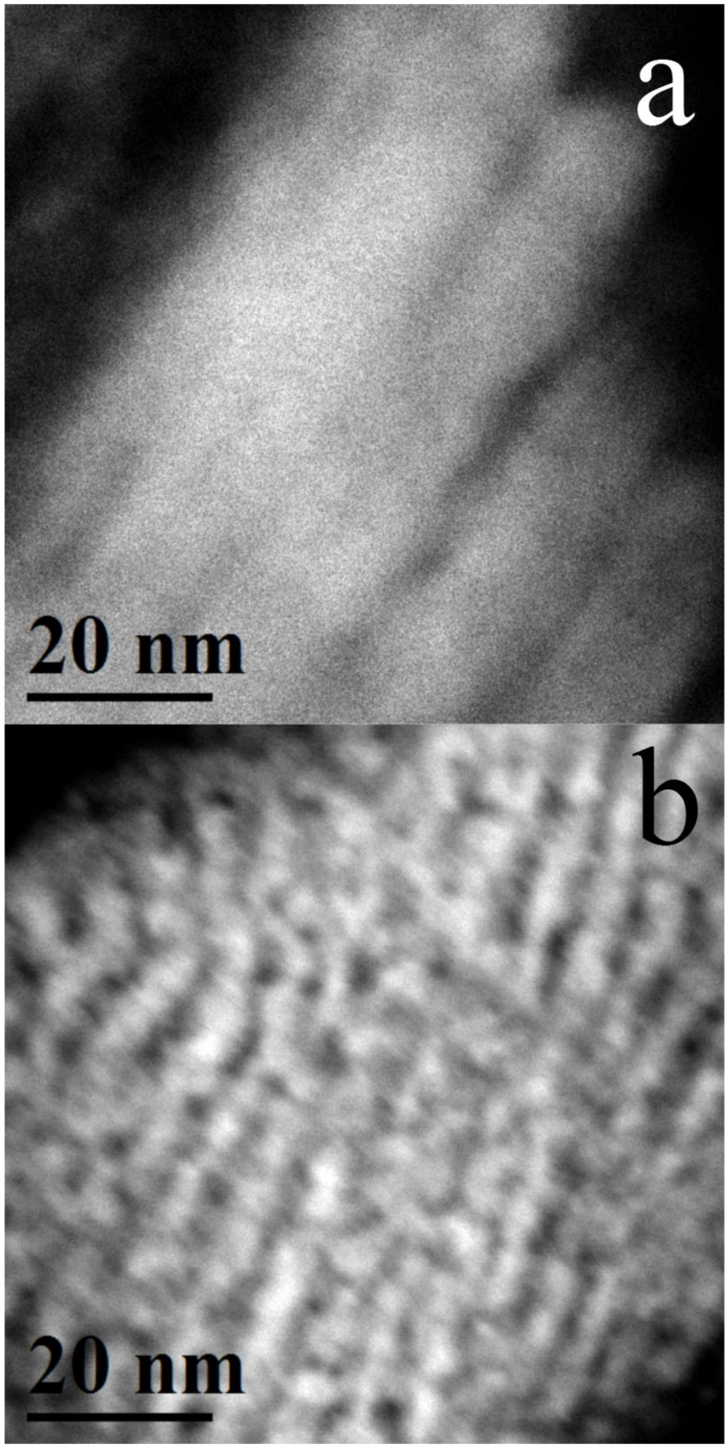


Figure S7. HAADF-STEM images from (a) uncycled and (b) once cycled $Ge_{0.95}S_{0.05}$ film deposited at 70$^{o}$ showing the phase segregation which occurs upon cycling. The nanocolumns are originally a uniform mixture of germanium and sulfur, indicated by the uniform intensity in (a). After charge and discharge, the variation in intensity of the nanocolumns show clear phase segregation into Ge-rich regions (bright contrast) and Ge-depleted regions (dark contrast).

**References**

1. Rasband, W. S. *ImageJ*, U. S. National Institutes of Health: Bethesda, Maryland, USA, http://imagej.nih.gov/ij/, 1997-2014.

2. D. R. G. Mitchell, *Microsc. Res. Techniq.,* 2008, **71**, 588-593.