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In-situ TEM study of sodiation and failure mechanism of antimony

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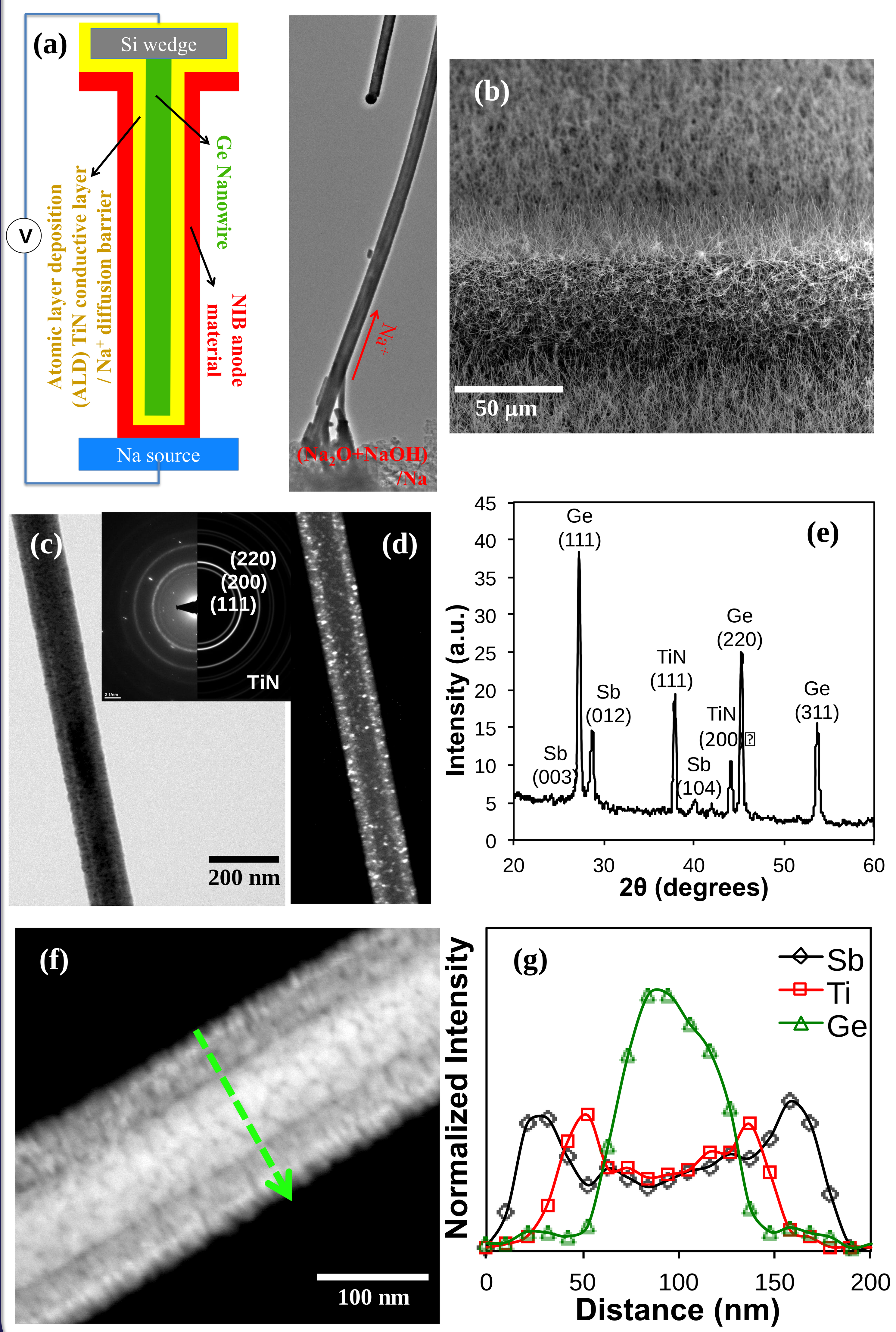
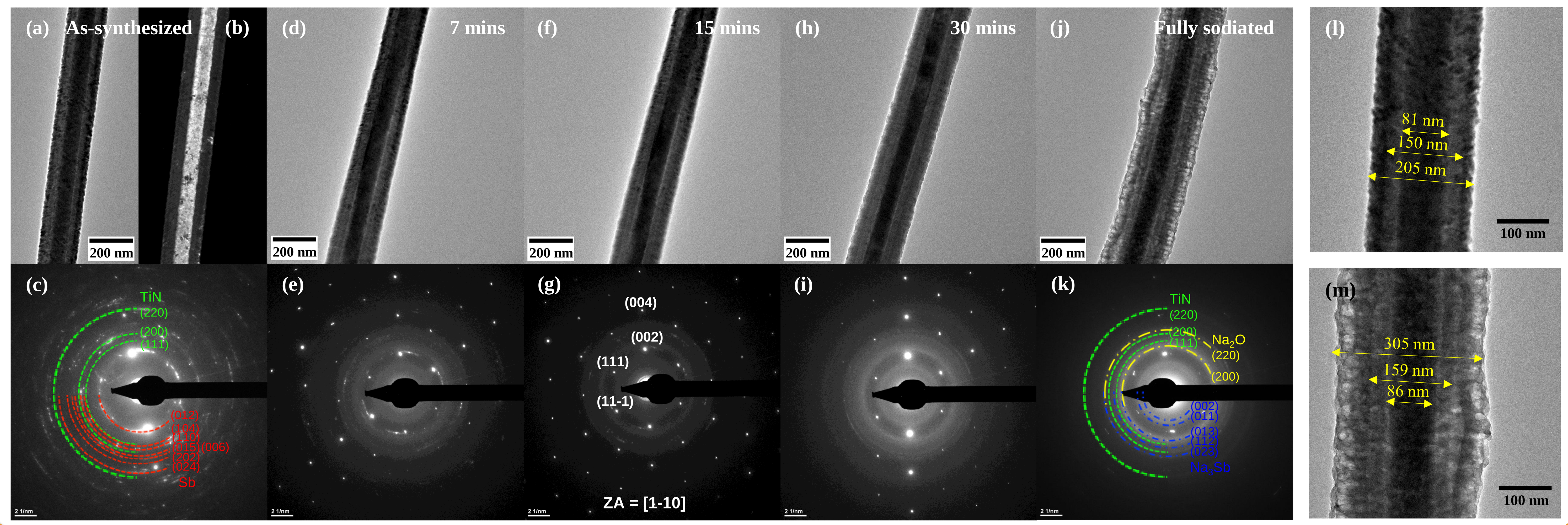
Experiment setup and microstructure

(a) Illustration for the setup of the in-situ transmission electron microscopy open-cell experiment. This setup could provide a universal platform for investigating a variety of electrode materials for Li^+, Na^+, Mg^{2+}, Ca^{2+} ion batteries. (b) Low magnification SEM micrograph of TiN@Ge nanowires grown on Si wedges. (c) BF-TEM micrograph of a single TiN@Ge nanowire, with its corresponding selected area diffraction pattern inserted. (d) DF-TEM micrograph of TiN, obtained using a portion of the (111) and (200) rings. (e) XRD pattern of Sb(50nm$_{geo}$)/TiN@Ge nanowires. (f) HAADF micrograph of Sb(50nm$_{geo}$)/TiN@Ge; the morphology of dewetted Sb nanoparticles can be observed. (g) The EDX analysis along the line shown HAADF micrograph.



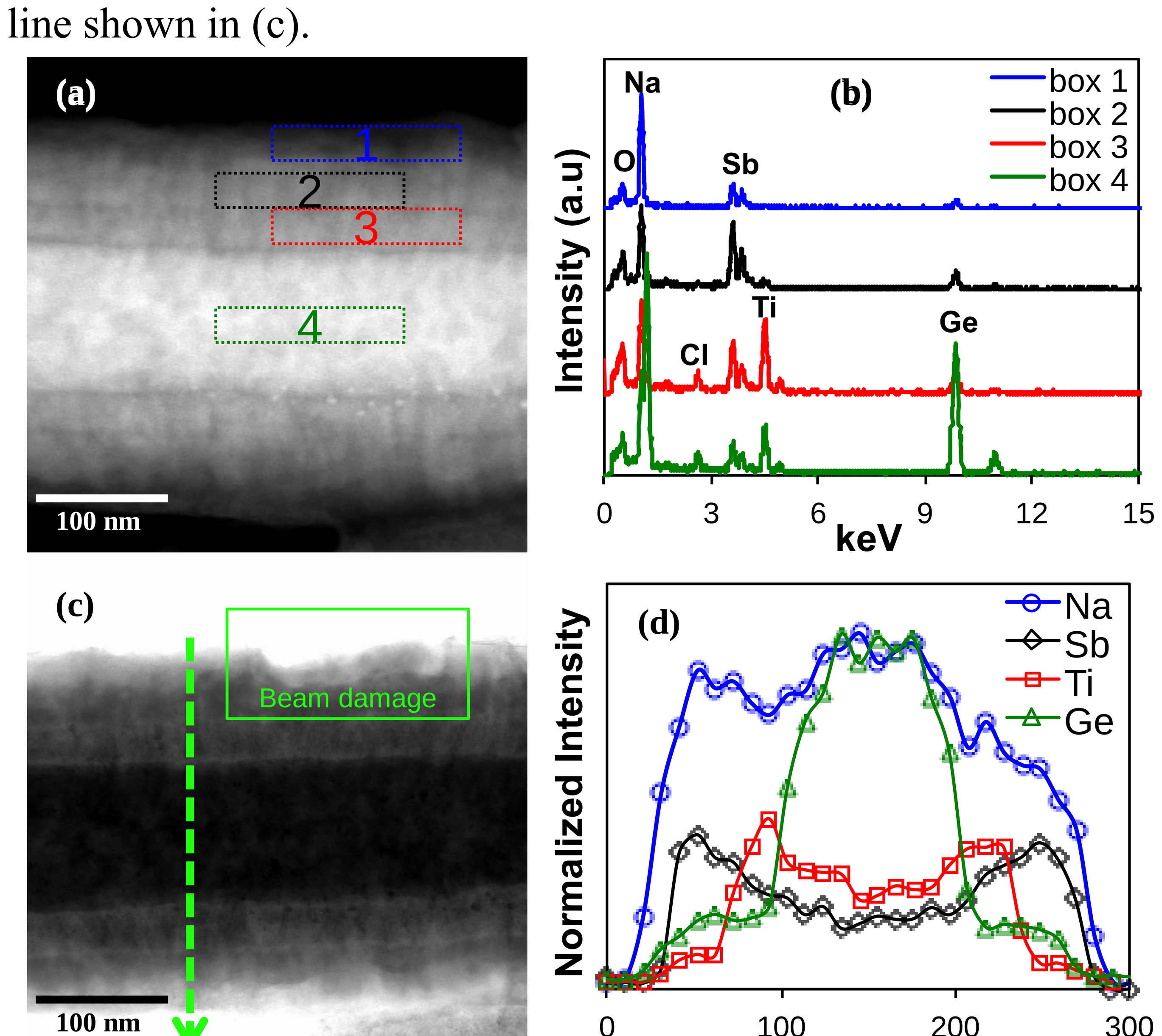
Sodiation mechanism of Sb: phase transformation and geometry change

TEM analysis of a single Sb(50nm$_{geo}$)/TiN@Ge nanowires during sodiation under a beam-blank condition. (a-c) as-synthesis; (d-e) after 7 minutes; (f-g) after 15minutes; (h-i) after 30 minutes; (j-k) in fully sodiated state. The indexed selected area diffraction patterns indicates that: The Ge core is oriented near the [1-10] symmetric zone axis. The forbidden {002} reflections are observed as a result of double diffraction. DF-TEM micrograph shown in (c) was obtained using g = (002)$_{Ge}$. (l-m) Comparison of wire diameters of (l) the as-synthesis and (m) the fully sodiated microstructures.



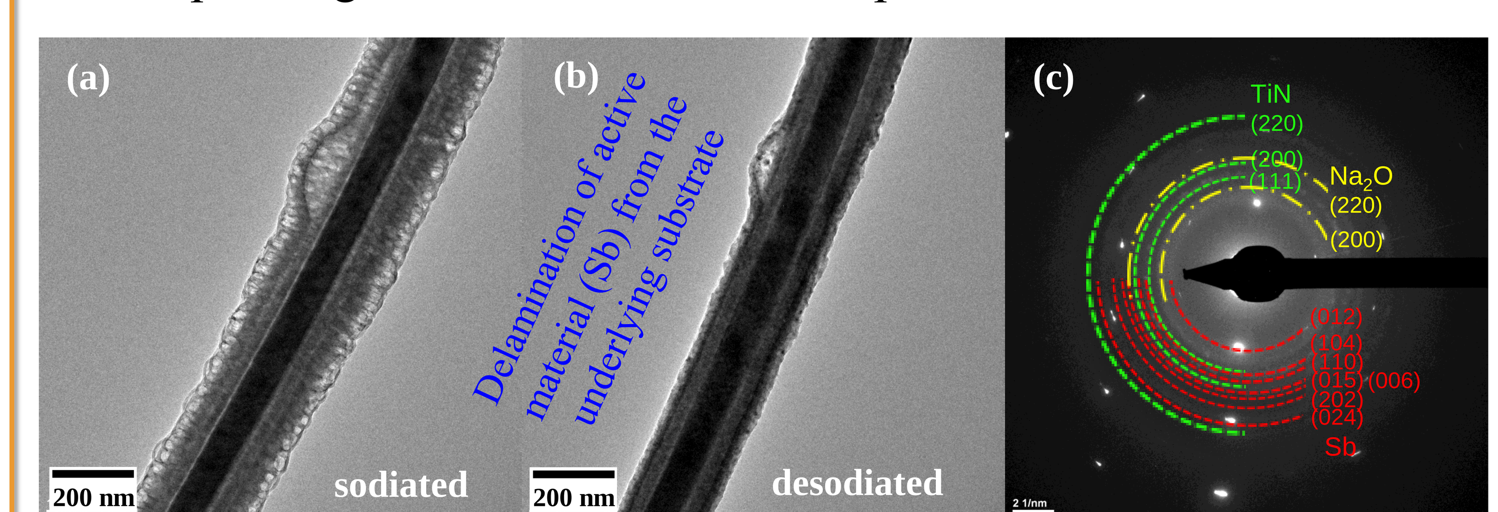
STEM analysis of sodiated microstructure

(a) HAADF micrograph of Sb(50nm$_{geo}$)/TiN@Ge in fully sodiated state. (b) EDX analysis of the region boxes marked in (a). (c) The corresponding BF-STEM micrograph highlights the beam damage after EDX analysis in region 1. (d) The EDX analysis along the line shown in (c).



Electrode failure mechanism

TEM analysis of a single Sb(50nm$_{geo}$)/TiN@Ge nanowires during desodiation. (a) in sodiated state; (b) in desodiated state; (c) the corresponding selected area diffraction pattern in desodiated state.



- A major failure mechanism for Sb anode is the delamination of active material from the underlying substrate.
- Sb film undergoes significant volume expansion upon sodiation. The stress buildup, especially at the Sb/TiN interface, would drive the delamination of the Sb film from the substrate.
- Another contributor to Sb film delamination is a possible Na segregation to Sb/TiN interface, weakening the mechanical bonding. Sodiation is known for elastic softening of materials.
- The delamination process is irreversible as shown in the desodiated microstructure.

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