Structural Integrity of SnO$_2$ Nanotubes During Sodiation Examined by *in Situ* TEM Observation with Graphene Liquid Cell

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Morphological evolutions and volume expansions of electrode materials that can be potentially applied for energy storage devices are critical issues as they trigger loss of electric contact and subsequent pulverization that lead to capacity decay and shorter cycle life. At the same time, understanding the morphological dynamics of electrode materials upon lithiation and sodiation is crucial to further suggest superior material designs that can best modify such structures.

Since the examination of morphological evolution of SnO$_2$ nanowires upon lithiation published in *Science* [1], much research has taken place to investigate more into the morphological evolution and grain dynamics and kinetics of SnO$_2$-based materials, either in lithiation or sodiation [2-4]. The previous works rooted in observing *in situ* transmission electron microscopy (TEM) observation on SnO$_2$ nanowire-based systems showed severe volume expansion, along with morphological changes, which suggested the need for designing the smarter materials that induce less volume expansion. At the same time, the previous works showed inherent limitations in two main points: 1) it used ionic electrolyte with multi-component (TEM) holder, instead of organic electrolytes, which are somewhat distant from the realistic cell condition and 2) the sodiation/lithiation were unidirectional, instead of multidirectional, which is somewhat distant from the actual sodiation/lithiation process in the battery where transport of Li/Na ions and electrons is happening in any random directions. To overcome some of these issues, a recent study on the growth orientation of Si nanoparticles was studied by *in Situ* TEM observation using graphene liquid cell (GLC) [5], where it demonstrated the possibility of utilizing GLC to observe electrochemical phenomena under more realistic cell condition. Here, we have expanded the study to the sodiation behaviour of SnO$_2$ nanotubes, where we were able to observe both the shell (tube part) and the core (hollow void center) by using GLC. For the assembly of GLC, monolayer graphene was firstly made by chemical vapor deposition (CVD) process and liquid electrolyte containing SnO$_2$ nanotubes was capped inside the two graphene sheets. Using SnO$_2$ nanotube for studying morphological evolution during sodiation is a significant progress because it can observe not only the interfacial parts of the material, but also the core part which will undergo morphological changes upon sodiation.

Scanning Electron Microscopy (SEM) image of SnO$_2$ nanotubes is shown in Figure 1a, where it clearly has a void space, with SnO$_2$ nanograins. TEM image and diffraction pattern of SnO$_2$ nanotubes are also shown in Figure 1b and 1c, where it demonstrates polycrystalline nature of the nanotube. With void spaces in the center and SnO$_2$ nanograins in the shell, it allows facile transport of Na ions while accompanying the volume expansion by filling the void spaces in the center upon sodiation. Unlike the previous study on SnO$_2$ nanowires upon sodiation [4], significant morphological changes were not observed in actual time series from 0 s to 410 s (Figure 2), although some changes in terms of grain sizes and shapes of the central regions (marked by yellow line) are observed.

To summarize, we have shown that SnO$_2$ nanotubes, having SnO$_2$ nanograin shells with void space...
in the core, do not undergo much volume expansion upon sodiation caused by the e-beam irradiation in GLC. Understanding and designing materials that can accompany volume expansion during electrochemical reaction are critical to overcome many challenges associated with volume expansion. [6]

References:


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![Figure 1.](image1.png)

(a) SEM image of SnO$_2$ nanotubes showing the SnO$_2$ nanograins, (b) TEM image of SnO$_2$ nanotube, and (c) diffraction pattern of SnO$_2$ nanotube showing polycrystalline nature.

![Figure 2.](image2.png)

Figure 2. Time-series TEM observation images showing the morphological evolution of SnO$_2$ nanotubes during sodiation. Although minor differences are observed in terms of the shapes and sizes of some nanograins, SnO$_2$ nanotubes, in general, do not go severe volume expansion.