

Structural Integrity of SnO₂ Nanotubes During Sodiation Examined by *in Situ* TEM Observation with Graphene Liquid Cell

Jun Young Cheong¹, Joon Ha Chang^{1,2}, Jeong Yong Lee^{1,2} and Il-Doo Kim¹

¹. Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea

². Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Daejeon, Korea

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 SnO₂ 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 SnO₂-based materials, either in lithiation or sodiation [2-4]. The previous works rooted in observing *in situ* transmission electron microscopy (TEM) observation on SnO₂ 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 SnO₂ 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 SnO₂ nanotubes was capped inside the two graphene sheets. Using SnO₂ 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 SnO₂ nanotubes is shown in Figure 1a, where it clearly has a void space, with SnO₂ nanograins. TEM image and diffraction pattern of SnO₂ nanotubes are also shown in Figure 1b and 1c, where it demonstrates polycrystalline nature of the nanotube. With void spaces in the center and SnO₂ 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 SnO₂ 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 SnO₂ nanotubes, having SnO₂ 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:

- [1] J. M. Yuk *et al*, *Science* **336** (2012), p. 61-64.
 [2] C.-M. Wang *et al*, *Nano Lett.* **11** (2011), p. 1874-1880.
 [3] A. Nie *et al*, *ACS Nano* **7** (2013), p. 6203-6211.
 [4] M. Gu *et al*, *Nano Lett.* **13** (2013), p. 5203-5211.
 [5] J. M. Yuk *et al*, *ACS Nano* **8** (2014), p. 7478-7485.
 [6] The authors acknowledge the funding from Korea CCS R&D Center (KCRC) grant by the Korea government (Ministry of Science, ICT & Future Planning) (No. NRF-2014M1A8A1049303), End-Run grant from KAIST by the Korea government in 2015 (Ministry of Science, ICT & Future Planning) (N01150615), and Institute for Basic Science (IBS) (IBS-R004-G3).

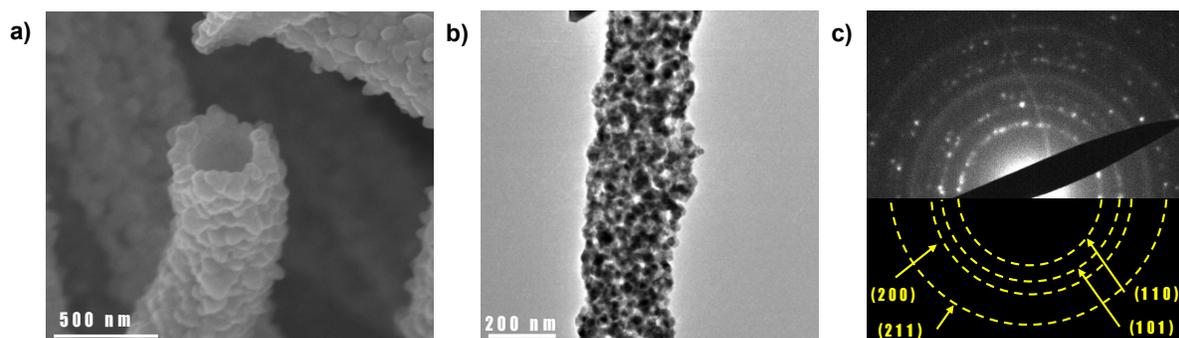


Figure 1. (a) SEM image of SnO₂ nanotubes showing the SnO₂ nanograins, (b) TEM image of SnO₂ nanotube, and (c) diffraction pattern of SnO₂ nanotube showing polycrystalline nature.

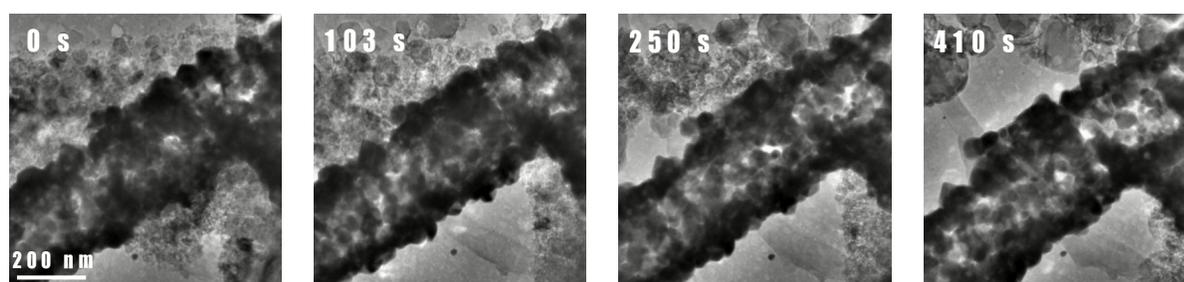


Figure 2. Time-series TEM observation images showing the morphological evolution of SnO₂ nanotubes during sodiation. Although minor differences are observed in terms of the shapes and sizes of some nanograins, SnO₂ nanotubes, in general, do not go severe volume expansion.