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In-situ TEM Study on Electrochemical Behavior of α-MnO_2 Nanowire

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Manganese dioxide (MnO_2) is widely known to possess various allotropic forms such as α-, β- and γ-phases, which are constructed by combination of octahedral [MnO_6] building blocks to form different tunneled structures. These special structures are believed to account for the various characteristics of MnO_2 when it is employed as electrode material in lithium (ion) batteries [1-2]. There is, however, lack of direct proof demonstrating the role of tunneled structure during electrochemical lithiation/delithiation of MnO_2.

In this work, by applying high resolution transmission electron microscopy (HRTEM) to single α-MnO_2 nanowire along both axial and radial directions, the tunneled structure is clearly shown and characterized. The α-MnO_2 nanowire is proved to be single crystalline and grow along [001] direction. Cross-sectional HRTEM images have shown that the nanowire has a squared cross section and 2x2 tunnels align parallelly along its growth direction [001], matching very well with simulated crystal structure. An in-situ TEM setup for study of MnO_2's dynamic lithiation/delithiation process is also designed and demonstrated. This open-cell design inside TEM allows real time observation of electrode behavior during its charge and discharge process, enabling better understanding of electrochemical essentials of α-MnO_2 and possible modifications of its composition, morphology and structure to further improve its overall performance in battery application.

References:

[1] Chen K., Dong Noh Y., Li K., Komarneni S., Xue D., The Journal of Physical Chemistry C **117** (2013), p.10770.
[2] Xun Wang, Y. L., Journal of the American Chemical Society **124** (2002), p.2.

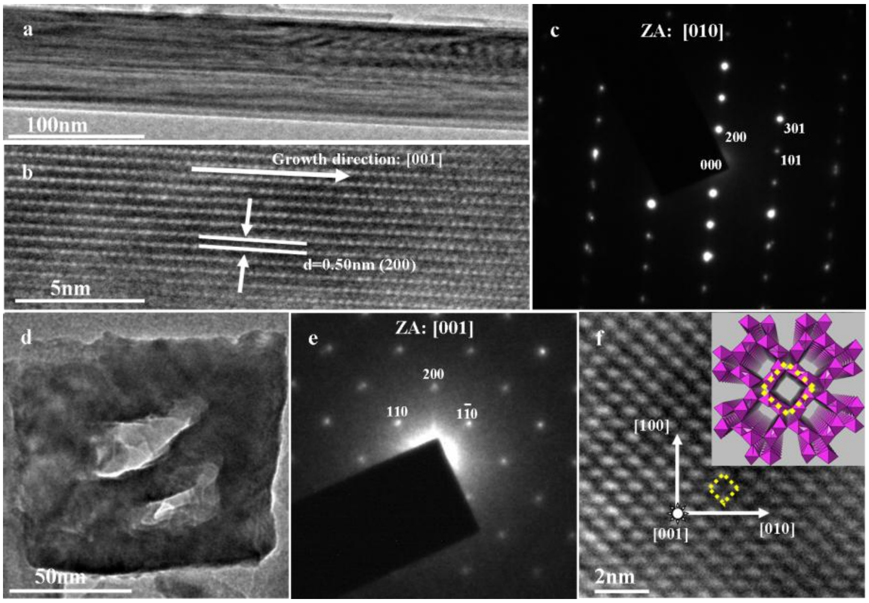

Figure 1 a: TEM image of single α-MnO_2 nanowire; b: HRTEM of α-MnO_2 nanowire along [010] direction; c: Electron diffraction pattern of α-MnO_2 nanowire along [010] zone axis; d: Cross-sectional image of α-MnO_2 nanowire; e: Electron diffraction pattern along [001] zone axis; f: Cross-sectional HRTEM and inserted simulation result along [001] direction showing 2X2 tunnels indicated by yellow dashed squares.

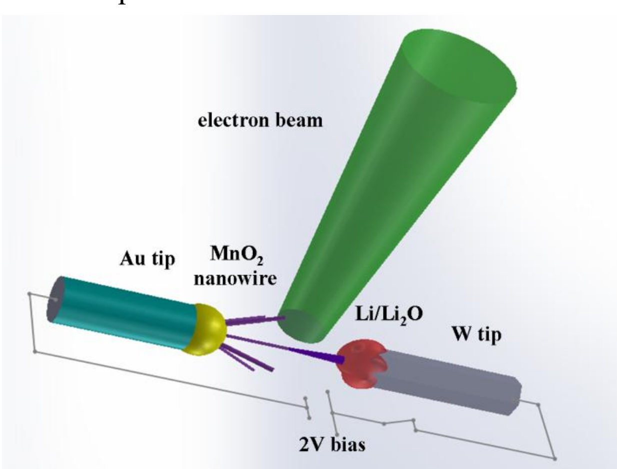

Figure 2 Cartoon for the in-situ TEM setup testing α-MnO_2 nanowire's lithiation/delithiation behavior. The nanowire is attached to a gold tip by conductive epoxy, while Li metal is attached to a tungsten tip and functions as the counter electrode. Lithiation starts when a constant potential of -2 V is applied to MnO_2 against Li counter electrode (+4 V for the delithiation process).

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