Nanoscale Confined Template Synthesis of Fiber-like LiCoO$_2$ in Carbon Nanotubes: Synthesis and Characterization

Wen-Lou Wang and Xiao-Yuan Li*

Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

The preparation and characterization of various low dimensional nanomaterials have attracted extensive interest in recent years [1-4] due to their widely believed potential applications. We report here the synthesis and characterization of LiCoO$_2$ nanofibers at a relatively low temperature ($400{\, ^\circ\text{C}}$) in air by using carbon nanotube as the confinement template (Figure 1). Our synthesized LiCoO$_2$ nanofibers have diameters ranging from $\sim 5$ to $\sim 13$ nm, and this parameter is expected to be dependent on the property of the carbon nanotubes used. Some smaller nanofibers are found to bundle together as indicated by the arrow in Figure 1a. The spacing of the adjacent layers in the synthesized LiCoO$_2$ nanofibers is $\sim 4.6$ Å. It can be envisioned that the template role of carbon nanotubes can be realized in two ways, namely, the exterior coating or/and interior filling. As a coating template, the exterior surface of carbon nanotube or the surrounding of the belt-like graphitic sheets (which were produced by the reaction between carbon nanotube and the oxidizer) serve as the substrate for the direct formation of LiCoO$_2$. As a filling template, the nanopore (or the cavity) of a carbon nanotube serves as the confined nanoreactor or nanomold in which the fiber-like LiCoO$_2$ is formed. The study of the synthesized LiCoO$_2$ by X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and microRaman scattering ($\mu$RS) indicates that they can be formed in either or a mixture of two crystalline structures. The phase structure of LT-LiCoO$_2$ was observed in the nanofibers appearing in a more straight fiber shape, whereas the phase structure of HT-LiCoO$_2$ was observed in the nanofibers with somewhat distorted fiber shape. Both phases of LiCoO$_2$ nanofibers can be synthesized at a relatively low temperature ($\sim 400{\, ^\circ\text{C}}$), and be identified unambiguously by their characteristic XRD patterns, namely, the resolvability of 018, 110, 006 and 012 XRD lines. The LT-LiCoO$_2$ phase is formed more favorably at the initial stage of the reaction, whereas the HT-LiCoO$_2$ phase dominates the products after a certain prolonged heating time. The phase transition from LT-LiCoO$_2$ to HT-LiCoO$_2$ is likely to be a kinetic process under the present conditions, as suggested by their XRD and $\mu$RS. In addition, $\mu$RS indicates that there exist two different environments around the octahedral Co$^{3+}$O$_6$ in the LT-LiCoO$_2$ phase, but only one in the HT-LiCoO$_2$ phase. This work demonstrated the feasibility of using carbon nanotubes as the synthetic template or nanoscale confined reactors for the synthesis of nanomaterials.


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Fig. 1: HRTEM images of the synthesized nanofiber-like LiCoO$_2$ with diameters of ~ 13 nm (a) and ~ 5 nm (b), respectively. The layer spacing: ~ 0.46 nm.

Fig. 2: XRD patterns of the LiCoO$_2$ samples obtained by the precipitation in a solution containing carbon nanotubes, LiNO$_3$ and Co(NO$_3$)$_2$ (65% HNO$_3$) after refluxing for 8 hrs, and then heated at 400 °C for 2 (a), 5 (b), 20 (c), and 50 (d) hrs, respectively.

Raman Shift (cm$^{-1}$)

Fig. 3: microRaman spectra of the LiCoO$_2$ samples, each corresponding to the sample of the same label in Fig. 2. Trace e is from the Co$_3$O$_4$ sample obtained by the thermal decomposition of Co(NO$_3$)$_2$ at 900°C.