Oxidation of Filled Carbon Nanotubes Inside a Transmission Electron Microscope

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Recently, it was demonstrated that nanocable-like materials such as turbostratic carbon nanotubes filled with Ga-doped ZnS (a.k.a. $Zn_{0.92}Ga_{0.08}S$@CNT) could be used as precursors for otherwise difficult-to-produce nanostructures [1]. In this communication, we show how an environmental transmission electron microscope can be used to follow the oxidation of an isolated filled carbon nanotube.

The synthesis of the sample examined here is described elsewhere [1]. Transmission electron microscopy (TEM) experiments were performed in an FEI TITAN 80-300 ETEM (where E stands for environmental). The instrument, which was operated at 300 kV, is fitted with an environmental cell, a monochromator, an objective lens aberration corrector and an energy dispersive X-ray (EDX) analyzer. The reaction temperature was varied from 500 to 600^{o}C using a double-tilt heating stage from Gatan. A controlled flow of pure oxygen gas was used at pressures ranging from 4 to 12 mbar. Various sample grids were used, with plasma-etched Au grids found to be the least intrusive under the conditions used.

Fig. 1 shows the nanocable-to-nanotube transition of a single isolated $Zn_{0.92}Ga_{0.08}S$@CNT structure. Initially, this CNT was filled and both the carbon shell and the semiconducting core were crystalline (Fig. 1a and inset). A few minutes after exposure to oxygen at 570^{o}C, the carbon shell was eliminated. The sulphide core was then gradually consumed (Figs. 1b and 1c). During this process, the diameter of the nanocable increased from 204 nm in (a) to 214 nm in (d). At t = 70 min, the core had been consumed and the temperature was raised to 590^{o}C, resulting in partial sintering of the oxide nanocrystals that defined the walls of the structure. As seen in Fig. 1e, these crystals were arranged in a faceted pattern and had an average thickness of 13 nm. Fig. 1f shows that the crystals have a spacing of 0.26 nm which is consistent with the spacing of wurtzite ZnO {0002} planes.

In conclusion, a single isolated carbon nanostructure was followed throughout an oxidation cycle in a TEM. The present results are consistent with the original ex situ experiments [1], which were carried out using bench laboratory techniques.

[1] U.K. Gautam et al., *Adv. Mater.* 20 (2008) 810.

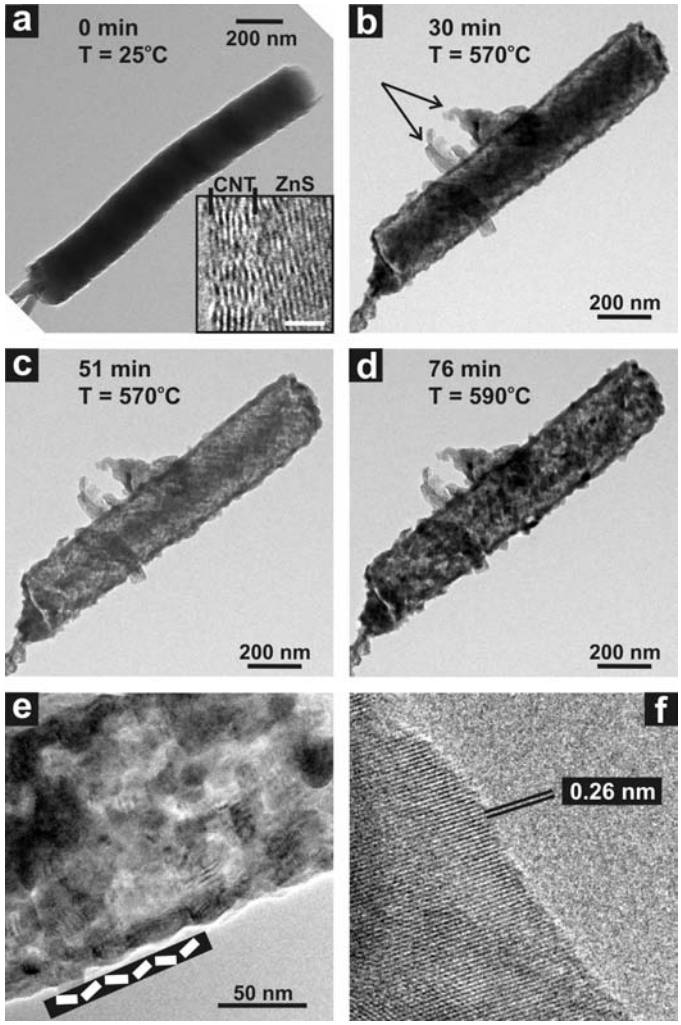

FIG. 1 (a) Bright-field TEM image of a thick, low-aspect-ratio Zn0.92Ga0.08S@CNT. Inset: detail of the sulphide core – carbon shell region. Scale bar: 2 nm. (b) to (d) Different stages of the structure during in-situ TEM oxidation. The arrows in (b) indicate unexpected foreign structures. (e) Detail of (d) highlighting the faceted nature of the thick external wall. (f) High-resolution image of an oxide grain on the external wall of (d).