OXIDATION OF FILLED CARBON NANOTUBES INSIDE A TRANSMISSION ELECTRON MICROSCOPE

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Introduction

Filled (hybrid) carbon nanotubes (CNTs) have been studied intensively since 1993 [1], motivated by the prospect of using their inner chambers to synthesize novel crystals [2], to protect sensitive substances [3] or to tailor the properties of the host carbon shell or the guest material [4].

Recently, it was demonstrated that nanocable-like materials could be used as precursors for otherwise difficult-to-produce nanostructures [5]. An example of a transition from a nanocable to a nanotube is provided by the controlled oxidation of turbostratic carbon nanotubes filled with Ga-doped ZnS (a.k.a. $Zn_{0.92}Ga_{0.08}S$@CNT). Such studies of the reactivities of filled CNTs have usually been carried out using bench techniques. It is particularly challenging to characterize a single nanostructure throughout its life-cycle in a reactor. Even if such a study could be carried out, it may be affected by the transfer of the sample from a reactor to an analytical instrument (along with the danger of losing it). Thus, studies of the stability and reactivity of individual nanostructures should ideally be followed in analytical instruments that have in situ capabilities.

In this communication, we show how an environmental transmission electron microscope can be used to follow the oxidation of an isolated filled carbon nanotube.

Experimental

The synthesis of the sample examined here is described elsewhere [5]. 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°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.

Results and Discussion

The $Zn_{0.92}Ga_{0.08}S$@CNT studied here (Fig. 1a) have relatively large diameters of ~100 nm. However, they have several interesting properties: 1) more than 99% of the nanotubes are filled; 2) the encapsulated material is crystalline and a technologically relevant II-VI semiconductor; 3) the CNTs do not bundle; 4) the carbon shell is well-structured (turbostratic) and closes only one end of each nanotube.

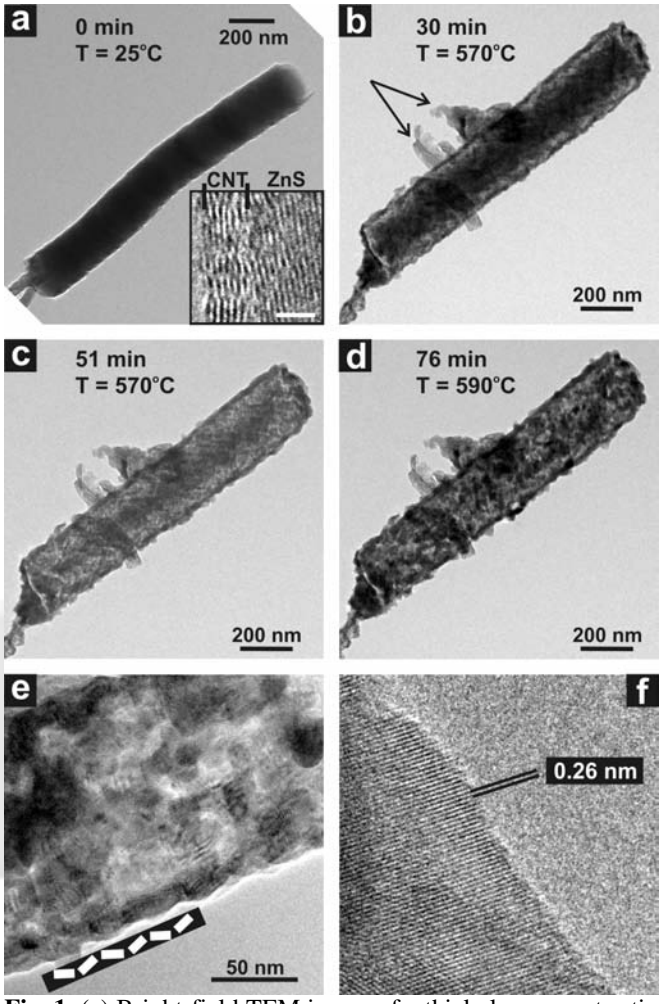

Fig. 1 (a) Bright-field TEM image of a thick, low-aspect-ratio $Zn_{0.92}Ga_{0.08}S$@CNT. Inset: detail of the sulphide core – carbon shell region. Scale bar: 2 nm. (b) to (d) Different stages of the structure during in-situ TEM oxidation. The arrows in (b) indicate unexpected foreign structures. (e) 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).

Fig. 1 shows the nanocable-to-nanotube transition of a single isolated $Zn_{0.92}Ga_{0.08}S$@CNT structure. This nanotube was not connected directly to the Au grid, but held in place on the elbow of another thinner structure (Fig. 1a). Initially, this CNT was filled and both the carbon shell and the semiconducting core were crystalline (inset of Fig. 1a). For practical reasons (time constraints) a slightly higher temperature than that in the original report [5] was used. A few minutes after exposure to

oxygen at 570°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°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. Several unexpected structures (indicated using arrows in Fig. 1b) were observed on the external walls. These may have been hidden behind the nanotube or migrated through the connecting thin wire due to thermal or chemical gradients.

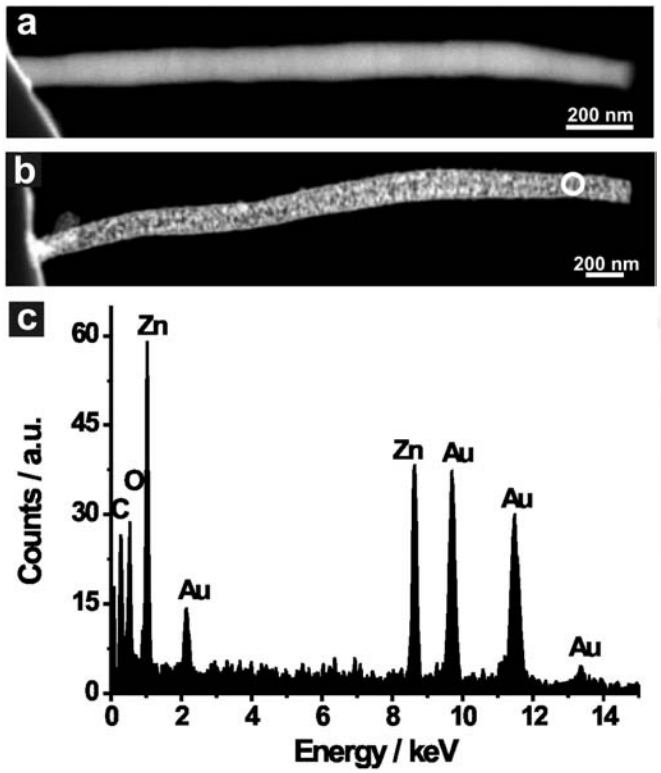

Fig. 2 (a) STEM HAADF image of a filled CNT before oxidation. (b) STEM HAADF image of the final reaction product. (c) EDX spectrum acquired from the region circled in (b).

The transformation of the solid cable-like structure into an open tube was confirmed using scanning TEM high-angle annular dark-field (STEM HAADF) imaging. This technique is sensitive to variations in thickness, atomic number and crystal orientation. The uniform contrast seen in the initial nanocables (Fig. 2a) was replaced by patchy contrast in the oxidised material (Fig. 2b), confirming the structural transition and the presence of the nanograins. Chemical analysis of the product (Fig. 2c) indicated the presence of Zn and O, with a noticeable absence of S. C contamination was also observed, originating from the unavoidable deposition of cracked gaseous carbon-containing species onto the probed area.

The ETEM procedure described above was visualized and recorded with sub-second time resolution. The reaction was paused when required to carry out detailed structural and analytical analyses.

Conclusions

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 [5], which were carried out using bench laboratory techniques.

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