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TEM Characterization of WS_2 Nanotubes

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WS_2 nanotubes and fullerene-like nanoparticles (IF) were first observed by reaction of H_2S with a thin film of tungsten [1]. Pure phases of hollow multi-walled WS_2 nanotubes were prepared from tungsten oxide precursor *via* a two-step reaction, and their growth mechanism has been studied [2].

Recently, large quantities (grams) of multi-walled WS_2 nanotubes were obtained in a one step synthesis, using a fluidized-bed reactor that was used for the synthesis of fullerene-like WS_2 nanoparticles, but under modified conditions [3]. In this process nanowhiskers of WO_{3-x} and subsequently WS_2 nanotubes were produced in a single process using commercially available WO_3 nanoparticles as precursors. Very long (hundreds of micrometers) open ended nanotubes appear either as bundles in the bulk of IF-WS_2 product, or as thin foils attached to the walls of the reactor. Transmission electron microscopy (TEM) analysis of a broken area in a ribbon, obtained during the detachment of a thin foil from the reactor wall, showed long and uniform nanotubes which are mostly 4 -7 layers thick (FIG. 1a). To further analyze the structure of the ribbons, one such ribbon was embedded in a polymer matrix and subsequently cross-sectioned by ultramicrotome. TEM of such section reveals clearly well aligned nanotubes. Lattice image of few cross-sectioned nanotubes is shown in the insert (FIG. 1b). The observed nanotubes are close packed and their circular cross section was somewhat distorted, probably during the microtomy. Isolated WS_2 nanotubes and bundles thereof, mixed with fullerene-like particles, were also found in the center of the reactor, consisting of 300µm long nanotubes of rather perfect shape. It is very likely that much longer nanotubes exist in the ribbons and bundles; however it was rather difficult to separate them for analysis without damaging their integrity. The flawless structure of a typical nanotube is appreciated from the high resolution TEM image showing WS_2 layers separated by 6.2Å in the nanotube side-walls (FIG. 2a). In contrast to the nanotubes in the foils, these isolated nanotubes have been shown to be of perfectly circular in cross-section, by tilting the sample along the tube axis. The nanotubes consist of coaxial-cylinders build up of hexagonal sheets. All nanotubes in this study were found to be chiral. The helicity angles of the nanotubes were determined from the electron diffration (ED) pattern [4].
In order to gain understanding of the nanotubes growth mechanism, partially reduced or sulfidized intermediates were also isolated from interrupted processes [5]. TEM image of such intermediate of a WS_2 nanowhisker encapsulating a reduced oxide core is shown in FIG.2b.

Refernces

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[5] Frey, G.L.; Rothschild, A.; Sloan, J.; Popovitz-Biro, R. Tenne, R. *J. Solid State Chem.***2001, *162***, 300.

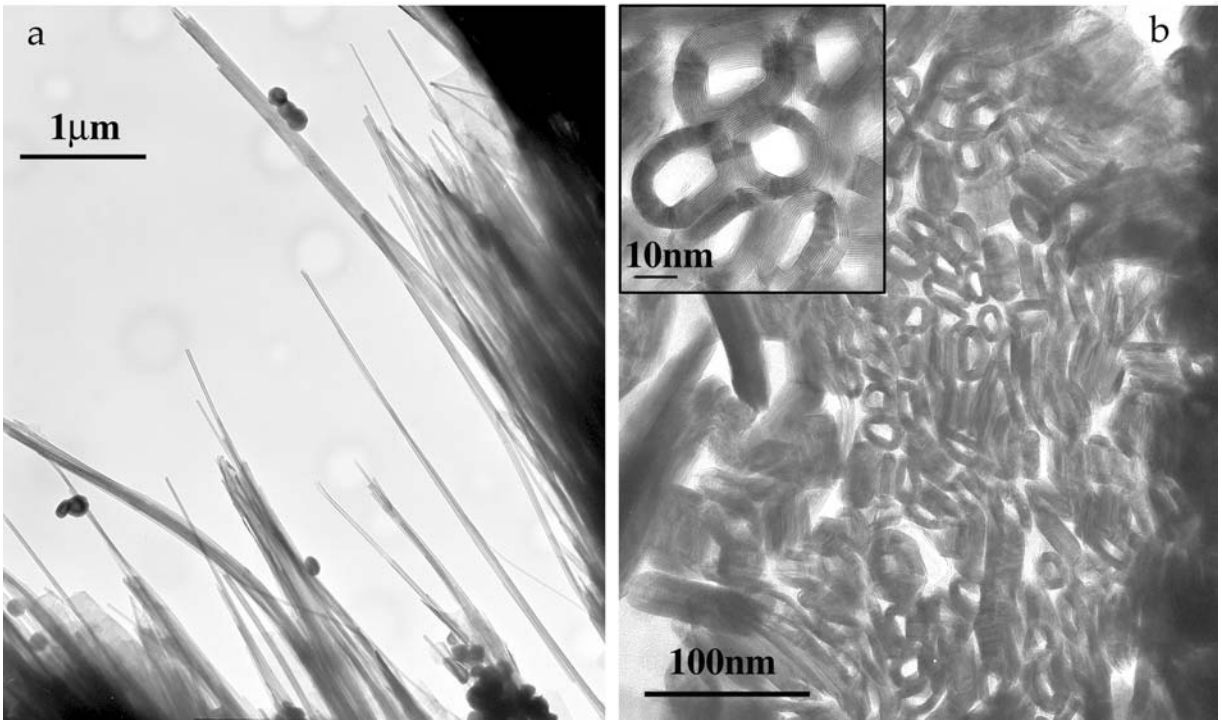

FIG. 1 (a) TEM micrograph of WS_2 nanotubes observed in a fissure of a ribbon detached from the reactor wall. (b) A cross-section of embedded ribbon of nanotubes.

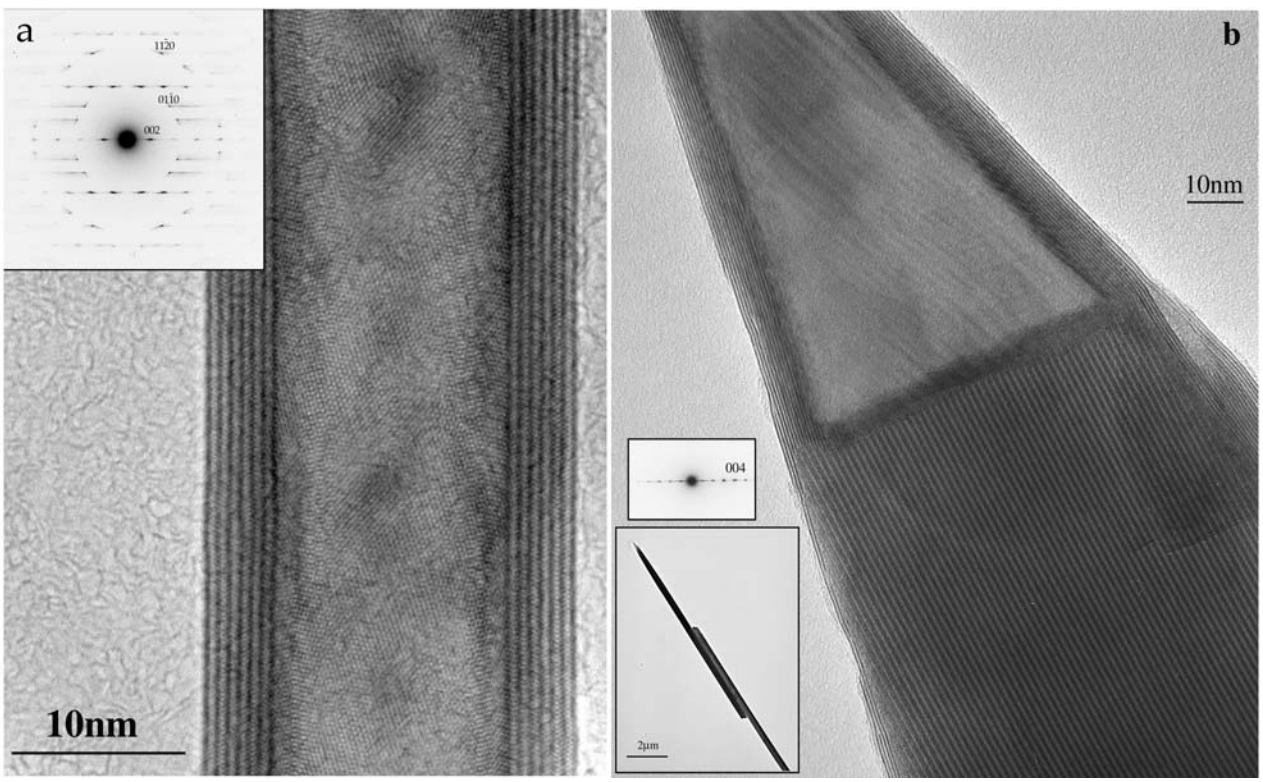

FIG. 2 (a) High-resolution image of a typical WS_2 nanotube and its electron diffraction in the inset. (b) A pencil-shaped oxide nanowhisker encapsulated by closed WS_2 layers. The oxide was assigned to be $W_{18}O_{49}$ phase from the ED pattern.