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Rhenium(IV) Sulfide Nanotubes

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Nanotube materials possess unique physical and chemical properties, which currently are the focus of intense scientific studies and which have made nanotubes attractive for, for example, (nano)-electronics, chemical sensing, electron field emission, and battery applications. Since the initial discovery of carbon nanotubes (CNT),[1] a number of similiar materials have been prepared. These include CNT analogues (BN[2] and $B_xC_yN_z$ [3]) but also inorganic compounds that in their nontubular polymorphic forms crystallize in pseudo-graphitic, layered structures (WS_2,[4] MoS_2,[5,6] MSe_2 (M = Mo, W),[7] $NiCl_2$,[8] MS_2 (M = Nb, Ta),[9] Bi,[10] InS[11]). Each of the van der Waals interacting layers in these pseudographitic compounds are several atoms thick; a layer in the WS_2 structure contains, for example, a single layer of tungsten atoms sandwiched between two layers of sulfur atoms. Vanadium oxide tubes have been prepared as inorganic−organic composites in which VO_x layers are intercalated by α,ω-diamines.[12] Very recently, NbS_2[13] and WS_2[14,15] nanotubes grown around (or templated by) multiwalled carbon nanotubes (MWCNTs) were described. By adopting this MWCNT-templating approach, we are here able to report the preparation of a new, layered, metal sulfide material with nanotubular morphology, rhenium(IV) sulfide, ReS_2.[16] Contrary to other layered MS_2 compounds, ReS_2 contains in its ordinary (nontubular polymorphic) form metal−metal bonded clusters (Re_4) and metal atoms that are *octahedrally* rather than trigonal prismatically coordinated with sulfur.[17]

ReS_2 nanotube samples were prepared by Re impregnation of 20 mmol C in the form of MWCNTs (Hyperion Catalysis International, Graphite FIBRIL type CC, consisting of >90% MWCNT-material according to low magnification TEM). Impregnation was made with 5 mmol Re either as $ReCl_5$ dissolved in ethanol or as NH_4ReO_4 dissolved in water. After ultrasonic treatment of the slurry for 2 h, the solvent was removed by rotary evaporation at reduced pressure. The resulting dry powder was transferred to a quartz boat, which was placed inside a horizontal quartz tube and treated with H_2S at 1000 °C for 3 h.

For transmission electron microscopy (TEM) imaging, the samples were mechanically crushed with a mortar and pestle. The powder was then dispersed on a copper grid coated with a holey carbon film. This type of grid makes it possible to image the nanotubes on areas not overlapping the carbon film. Electron micrographs were recorded with a Philips CM-200 FEG transmission electron microscope. The microscope is equipped with an UltraTwin lens giving a resolution of ~0.12 nm. Figure 1 shows the high-resolution TEM (HRTEM) image of a straight part of an MWCNT covered with several intensely dark, strongly scattering, layers. The distance between the layers (0.62 nm) matches the Re−Re interlayer distance in ordinary ReS_2[17] where each Re atom layer is sandwiched between two S atom layers.

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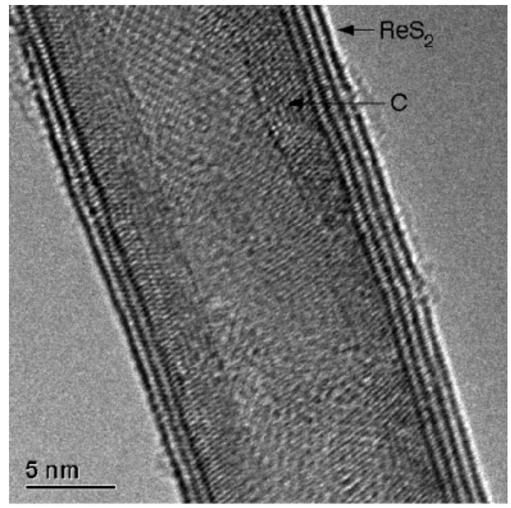

Figure 1. High-resolution transmission electron microscopy (HRTEM) image of a ReS_2 nanotube templated on a multiwalled carbon nanotube (MWCNT). The individual ReS_2 tube walls are seen as intensely dark, relatively widely spaced, parallel lines. The C walls of the underlying MWCNT are much less intense and more closely spaced.

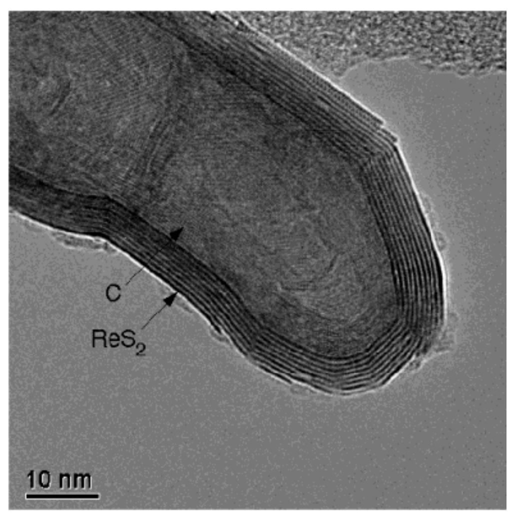

Figure 2. HRTEM image showing how the ReS_2 overlayers closely follow the shape of the closed end of an underlying MWCNT. The closed end of the ReS_2 material rules out a scroll-like structure of the tubes and makes it likely that closed, ball-like ReS_2 structures may exist.

EDX analyses of selected areas of the ReS_2/MWCNT sample revealed the presence of only Re, S, and C. Figure 2 shows how the ReS_2 overlayers closely follow the MWCNT substrate around the closed end of the carbon tube.

No distinct differences were observed by TEM between the samples prepared by means of $ReCl_5$ or NH_4ReO_4. In both cases templating was not perfect; some MWCNTs were not or only partly

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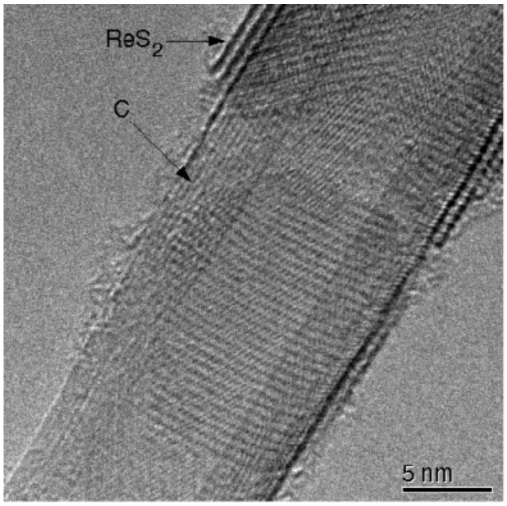

Figure 3. Fourier-enhanced HRTEM image of the open end of a ReS_2 nanotube templated on an MWCNT. By simultaneously considering the number of ReS_2 walls seen on the sides of the MWCNT and the amount of ReS_2 on top and underneath the MWCNT, i.e., the image intensity, the mental picture of an unevenly truncated ReS_2 tube emerges.

covered with ReS_2, and regularly shaped crystals of ordinary (nontubular) ReS_2 were also found. The X-ray powder diffraction diagrams of the ReS_2/MWCNT samples were very similar to that of ordinary ReS_2 prepared by sulfiding NH_4ReO_4 at 1000 °C. It is thus likely (cf. ref 14) that ordinary ReS_2 dominates the diagrams of our ReS_2/MWCNT samples. All X-ray diffraction patterns matched that calculated on the basis of the triclinic single-crystal structure of ReS_2 [JCPDS 82-1379].[17]

The impregnation procedure employed for preparing MWCNT-templated MS_2 nanotubes makes the distribution of metal on the template surfaces somewhat uneven. The number of ReS_2 walls formed on a particular MWCNT segment was presumably determined by the local concentration of the rhenium precursor. Nanotube structures in which a gradual change in the number of ReS_2 walls occurred were frequently found by HRTEM. Figure 3 shows the open end of a triple-walled ReS_2 tube; as the rhenium concentration along the direction of the MWCNT template presumably decreased, the amount of rhenium was insufficient for a triple-walled structure. Consequently, the ReS_2 tube fades away through intermediate double-walled and single-walled stages. Generally it should thus be possible to influence the average number of walls in the nanotubes through the synthesis conditions, thereby allowing control of the structural characteristics of the individual nanotubes.

Figure 3 shows that a particular ReS_2 nanotube is truncated not by a clean cut but in an irregular fashion. The types of irregular structures that may occur are schematically illustrated in Figure 4. The structure of the open end of the ReS_2 nanotube may be inferred by simultaneously considering the number of ReS_2 walls seen on the MWCNT sides and the TEM image intensity, which reflects the thickness of the ReS_2 material on top and underneath the MWCNT. The presence of incomplete walls with a quasi-hemi-cylindrical shape suggests that it may be possible to intergrow different nanotube materials to create junctions without rotational symmetry around the MWCNT axis. Several distinctly different groups of lattice fringes are observed in Figure 3. These groups have different orientations with respect to the tube axis, and a careful analysis of such data (see ref 15) may reveal information about the degree of chiral twist of the individual ReS_2 nanotube walls.

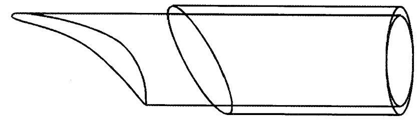

Figure 4. Schematic illustration of how the open-end termination of a double-walled MS_2 nanotube need not be a clean cut perpendicular to the tube axis.

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