Synthesis of carbon nanotubes filled with long continuous crystals of molybdenum oxides

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We report the synthesis of continuous and crystallographically aligned single crystals of molybdenum oxide based nanowires up to micrometres in length inside carbon nanotubes: opened tubes are filled using molten MoO_3 followed by controlled reduction under dilute hydrogen to MoO_2 material.

Recently, PbO, Bi_2O_3 and V_2O_5[1] in their molten states have been demonstrated to enter and fill into the nanotubes by capillary action.

Here we describe the filling of carbon nanotubes with continuous crystals of oxides of molybdenum.

Carbon nanotubes were prepared by the arc-evaporation technique and selectively opened by nitric acid oxidation.[2] The tubes were then filtered, washed with deionised water and dried in air. Carbon tubes filled with MoO_3 were prepared by mixing molten MoO_3 with open nanotubes. A mixture of solid MoO_3 (0.5 g) and open nanotubes (0.5 g) was placed in an evacuated sealed silica vessel which was heated from room temp. to 800 °C at a rate of 10 °C min^{-1} and was held at 800 °C for a further 3 h. The sample was allowed to cool at 1 °C min^{-1} to 400 °C and then rapidly cooled to room temperature.

The reduction of MoO_3-filled tubes was conducted by passage of a stream of 8% H_2 in 92% Ar composite gas. The furnace temperature was ramped from 150 to 450 °C at 10 °C min^{-1} and held at 450 °C for 2 days (also to 500 °C for 6 h) before cooling to room temperature.

Electron micrographs were obtained by using JEOL 4000EX and 2000FX high-resolution transmission electron microscopes.

Fig. 1 shows the TEM image of a typical MoO_3-filled open nanotubes. The sample contained a significant percentage (*ca.* 50%) of nanotubes filled with continuous single crystals. The fringe separation of the crystals inside the tube is 3.70 ± 0.05 Å corresponding to the (100) interplanar separation for MoO_3 (JCPDF file). We observed that in most cases the (010) plane of the MoO_3 single crystals adopts a preferred orientation with respect to the nanotubes and is perfectly parallel to the (0002) carbon layers of the nanotube. Crystalline MoO_3 belongs to the orthorhombic system and has a layered structure. The successive layers of MoO_6 which lie parallel to the (010) plane are held by van der Waals forces. In the orientation on the nanotubes these MoO_6 octahedra are parallel to the carbon layers. Preferred orientations of other materials in filled tubes have been noticed previously, including samples both from the *in situ* arcing method (epitaxial),[3] the solution method[2] and the molten filling method [(010) direction of V_2O_5 parallel to the tube axis)].[1]

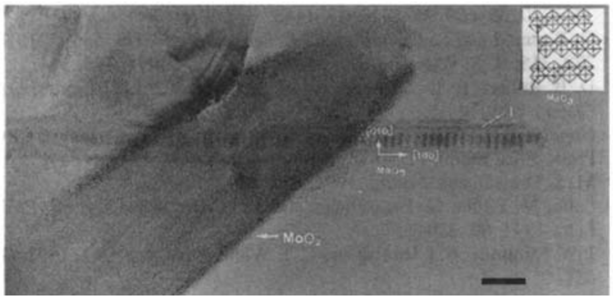

Fig. 1 Typical high-resolution TEM image of a tube filled with long single crystals of MoO_3. The fringe separation inside the tube is 3.70 ± 0.05 Å corresponding to the (100) interplanar separation of MoO_3. Preferred orientation of [010] direction perpendicular to the tube axis [parallel with respect to (010) plane] can be clearly seen. An ultra-thin coating of MoO_2 of uniform thickness (darker contrast) on the carbon structure is found. Intercalation of the MoO_3 is also seen in this tube (denoted as **I**). A schematic diagram of the layered MoO_3 structure is provided on the right hand corner. (Scale bar 100 Å.)

In some tubes the TEM data show intercalation of MoO_3 in the gaps left by partially missing carbon shells. There are also some extremely thin (one to a few atomic layers) coatings of molybdenum oxide (with darker contrast) on the carbon structures (Fig. 1). Similar features have been seen with V_2O_5 filled nanotubes.[1]

X-Ray powder diffraction (XRD) studies on bulk samples of the MoO_3-filled tubes show evidence for reduced MoO_x phases. Thus a number of tubes were found to be filled with reduced MoO_x (clear images cannot be obtained) and the internal diameters of the MoO_x-filled tubes were generally wider than those of MoO_3-filled tubes. The parameters of the reduced molybdenum oxide coatings match favourably with the MoO_2 parameters. However, the measurements on these extremely thin layers may have significant errors. We infer that during the molten oxide filling process some reduction of MoO_3 by carbon occurs at the carbon/metal oxide interface.

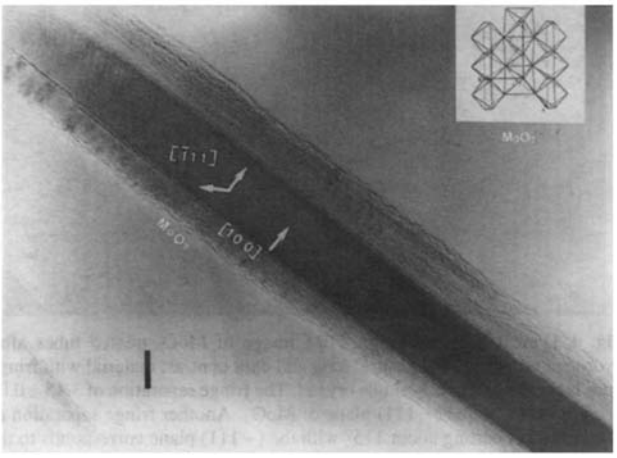

Fig. 2 Typical high-resolution TEM image of MoO_3-treated tubes after hydrogen reduction. The internal diameter of this filled tube is 18 nm compared with the typical internal diameters of 4–5 nm of unfilled tubes indicating some internal carbon layers may have been sacrificed as they are in contact with the molybdenum higher oxides. The central long and dark contrast material with fringe lines is a typical MoO_2 single crystal. The fringe separation of 3.45 ± 0.05 Å corresponds to the (−111) plane of MoO_2. Preferred orientation of [100] direction perpendicular to the tube axis and cutting 110 ± 5° with the [−111] direction can be clearly seen. A schematic diagram of the MoO_2 structure with the Mo–Mo bonding across the shared edges, is provided on the right hand corner. (Scale bar 100 Å.)

A study was made of the reduction of the MoO_3-filled tubes using hydrogen. It is well established that heating MoO_3 under hydrogen can give rise to stepwise reduction through a complex phase diagram of MoO_x systems[4] arriving eventually at MoO_2 (JCPDF file). The reduction was carried out with 8% H_2 in argon under a fast flow rate (60 ml min^{-1} over 0.5 g). Two temperature heating programmes were employed (10 °C min^{-1} to 450 °C and held for 2 days and at 10 °C min^{-1} to 500 °C and held for 6 h). The reduced samples gave identical XRD spectra. The XRD spectrum clearly shows that the reduced molybdenum oxide–tube sample contains exclusively MoO_2 and there was no indication of other phases. However, we note that the XRD data only arise from crystallites larger than *ca.* 5 nm (5 × 5 × 5 nm) and thus the nature of the encapsulated oxide cannot be inferred solely from the XRD spectra. Figs. 2 and 3 show typical HRTEM images of the samples of reduced molybdenum oxide inside the carbon nanotubes. The nanotubes appear to be completely filled with long single crystals (*ca.* 20 nm) and they have a darker contrast than the tubes filled with MoO_3. The lattice fringe separations and the interplanar angles match well with published data for MoO_2 but do not correspond to any known hydrogen molybdenum bronzes or intermediate oxide phases.[9] We therefore propose that the encapsulated reduced molybdenum oxide is pure MoO_2 although we cannot discard with certainty the remote possibilities of an intermediate non-stoichiometric oxide or an unknown molybdenum oxide phase.

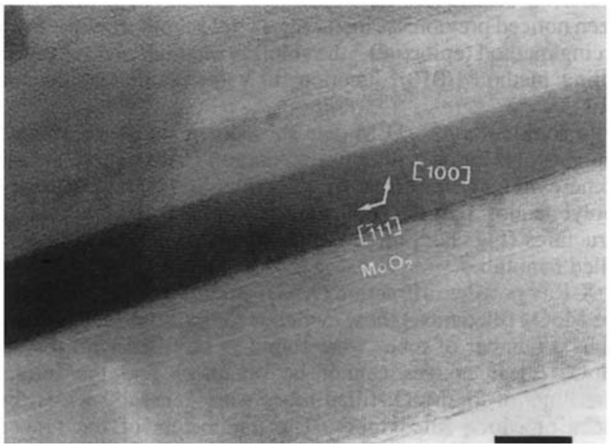

Fig. 3 Typical high-resolution TEM image of MoO_3-treated tubes after hydrogen reduction. Three layers of (100) MoO_2 coatings can be clearly seen. The interlayer distance is 5.60 ± 0.05 Å. (Scale bar 100 Å.)

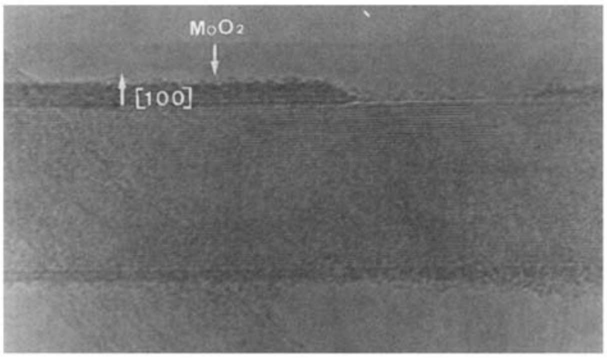

Fig. 4 Typical high-resolution TEM image of MoO_3-treated tubes after hydrogen reduction. The central long and dark contrast material with fringe lines is typical of a MoO_2 single crystal. The fringe separation of 3.45 ± 0.05 Å corresponds to the (−111) plane of MoO_2. Another fringe separation of 2.47 ± 0.05 Å cutting about 115° with the (−111) plane corresponds to the (200) plane. Preferred orientation of [100] direction with [−111] direction can be clearly seen. The [100] direction apparently creates 60° with respect to the tube axis because the (100) plane is in parallel to another (0002) carbon layers in the adjacent face of this polygon tube which cannot be directly visualised in the TEM image.

The MoO_2 crystals show a strong preferred orientation of the [100] plane direction perpendicular to the tube axis and cutting about 110 ± 5° with the [−111] direction. This suggests the (100) planes are parallel to the (0002) planes of the carbon layers of the nanotube. Fig. 4 also clearly shows there are coatings of molybdenum oxides on the external surfaces of the nanotubes. The coatings do not always evenly cover the tubes, however; MoO_2 with one to three layers of (100) planes parallel to the (0002) carbon layers are distinct (Fig. 4). Using selected area electron diffraction, Bertrand and Dufour[6] have demonstrated that isothermal reduction of crystals of MoO_3 in flowing H_2 under the controlled temperature range 996–1016 °C will yield MoO_2 with its [100] direction parallel to the parent [010] MoO_3. The same crystallographic relationships are found between the encapsulated MoO_3 and MoO_2. We also note that topotactic reduction should lead to a reduction in crystal size, however, we did not observe any voids between the crystal and the inner wall of the nanotubes. The loss of the water must be accompanied by shrinkage of the original dimensions of the MoO_3 crystal in which case there may be small undetectable and continuous gaps existing between the MoO_2 crystal and the inner carbon wall. Such a gap could provide a channel for the ingress of hydrogen and exit for water vapour.

Reduced molybdenum oxides such as the rutile-related structure of MoO_2 have metal–metal bonding along the edge-sharing octahedra (Fig. 2) with very short interatomic Mo–Mo contacts. Single crystals of MoO_2 have a resistivity of *ca.* 1×10^{-4} ohm cm at 0 °C,[7] similar to the value of pure bismuth metal, and have a higher conductivity at all temperatures than many metallic elements.[8]

These reduced molybdenum oxide filled tubes may be regarded as nanowires for which interesting properties have been predicted.[9–12]

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Received, 3rd July 1996; Com. 6/04662B