Nanostructures

WO_2Cl_2 Nanotubes and Nanowires**

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Since the discovery of carbon nanotubes,[1] there has been much interest in synthesizing nanotubes of greater chemical complexity such as, chalcogenides (e.g., MoS_2, WS_2),[2] oxides (e.g, TiO_2, VO_x)[3] and recently halides (e.g. $NiCl_2$).[4] Complex nanotubes can exhibit fascinating new optical, electrical, and magnetic properties due to their dimensional confinement.[5] In solid-state chemistry, the partial replacement of cations of one type by another is ubiquitous; yet partial replacement of the anions can often change the dimensionality of the compound. Partial replacement of O^{2-} ions in 3D oxides by the heavier halides can promote the formation of van der Waals bonded layered structures that in turn more readily form nanotubes and nanowires than the pure oxides do; yet such materials can maintain many properties of the oxides. Herein we report the synthesis of WO_2Cl_2 nanotubes and nanowires; this represents the first synthesis of a new class of nanotubes/nanowires based on mixed anion (oxyhalide) compounds.

It is no accident that, following the discovery of carbon nanotubes, the chalcogenides were one of the first classes of inorganic nanotubes to be synthesized. Their layered structures encourage the formation of nanotubes/nanowires (see for example reference [3a,b]). Similarly, it is not surprising that VO_x, TiO_2–B and other titanates have been prepared as nanotubes/nanowires. In the case of the titanium oxides, layered titanates form during the hydrothermal synthesis, which curve or scroll to form nanotubes/nanowires.[5] However, the majority of oxides form 3D structures and other approaches have been adopted to promote 1D growth. For example, it is difficult to grow nanotubes/nanowires of WO_3, however, the reduced phases, such as $W_{18}O_{49}$, contain shear planes that limit growth thus forming wire shaped structures.[6] Templates can also be used to promote crystal growth in certain directions.[3b]

Partial replacement of O atoms by F atoms results in oxyfluorides, which generally adopt 3D structures. However if the O atoms are replaced in part by atoms of the heavier halides, Cl, Br, I then the resulting oxyhalides are often layered structures due to the propensity of the more electron-rich halides to exhibit van der Waals bonding between adjacent layers. Several compounds of this type are known

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for example, FeOCl, VOCl, WO_2Cl_2, WO_2Br_2, and MoO_2Cl_2.[7] They should form nanotubes/nanowires relatively easily and without the need to promote 1D growth. We have investigated the formation of nanotubes/nanowires based on WO_2Cl_2.

WO_3 can adopt a number of distorted forms of the ReO_3 structure, Figure 1, in which WO_6 octahedra share common vertices, thus forming a 3D network. Replacing a layer of O^{2-} ions in WO_3 by two layers of Cl^- ions results in the formation of the van der Waal's bonded layered structure WO_2Cl_2. The structure of this compound is shown in Figure 1b and is composed of layers containing W^{6+} coordinated by 4 O^{2-} ions to form a slightly distorted square in which each WO_4 units share common vertices. The W^{6+} ions are coordinated by a total of six anions, with the coordination being completed by two Cl^- ions, one immediately above and the other immediately below the W–O plane. The complete structure of WO_2Cl_2 (orthorhombic space group *Immm*) consists of these trilayer blocks(Cl-WO_2-Cl) stacked in the *c* direction such that each trilayer block is displaced by a translation $x+{}^1/_2$, $y+{}^1/_2$ with respect to its neighbor. Because the WO_2 layers in WO_3 (Figure 1) are preserved in WO_2Cl_2, the band structure and electronic properties of WO_2Cl_2 are similar to WO_3 and may be derived from the latter, with a perturbation due to the presence of the Cl^- ions.[8]

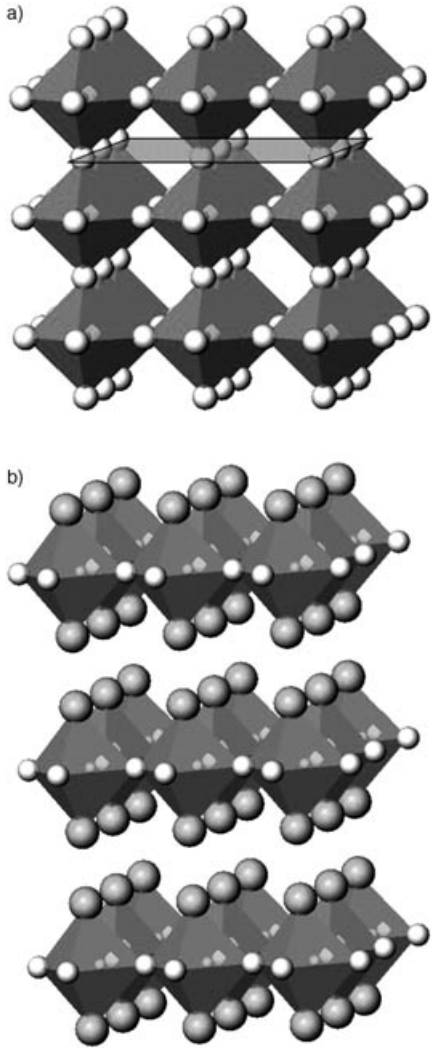

Figure 1. a) Ideal crystal structure of WO_3 showing vertex-sharing WO_6 octahedra. b) Crystal structure of WO_2Cl_2 showing the relationship to WO_3.

Nanotubes and nanowires of WO_2Cl_2 have been prepared by a simple process of exfoliation and restacking, the experimental details of which are described in the Expeimental Section. Transmission electron micrographs of the resulting materials are shown in Figure 2. In general, the nanotubes/nanowires exhibit diameters in the range 30–80 nm and can be up to 5 μm in length.

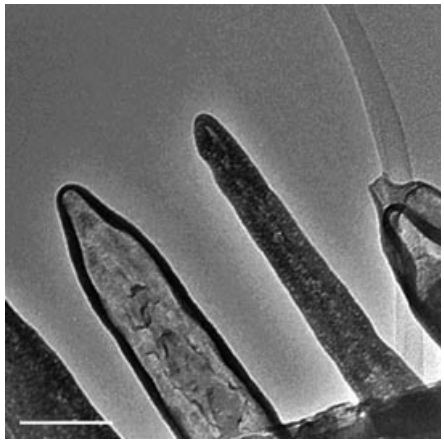

Figure 2. Transmission electron micrograph of WO_2Cl_2 nanotubes and nanowires. The bar on the image is 100 nm long.

There was no evidence of nanotubes/nanowires in the as-received WO_2Cl_2, despite the fact that these materials are made by a solid/gas reaction ($WO_3 + WCl_6$) that is known to promote nanotube growth in other layered materials such as the chalcogenides.[2,3a] Grinding the as-received WO_2Cl_2, reduced the particle size to around 0.1 μm (as observed by scanning electron microscopy), but did not induce nanotube formation. Stirring a mixture of ground WO_2Cl_2 for two weeks in polar solvents such as propylene carbonate or a 1:1 (*v*/*v*) mixture of ethylene carbonate/dimethyl carbonate also provided no evidence of nanotube formation. We had noted in our previous studies of bulk WO_2Cl_2 that when in contact with non-aqueous Li electrolytes the latter developed a colloidal appearance. Following this earlier observation, the ground solid was stirred in a 1 M solution of $LiPF_6$ in a 1:1 (*v*/*v*) mixture of ethylene carbonate and dimethyl carbonate resulting in a colloidal solution which, when filtered then centrifuged, washed in dimethyl carbonate then dried, gave rise to a fine powder. The powder contained in excess of 90% nanotubes/nanowires in equal proportions, based on TEM analysis. Figure 3 shows TEM images of nanotubes/nanowires taken from different regions of the sample from that of Figure 2, thus indicating the widespread nature of the nanotube and nanowire morphology. Although more detailed studies are necessary to elucidate the exact nature of the reaction, it seems clear that the electrolyte penetrates the van der Waals layers sufficiently to prize them apart and

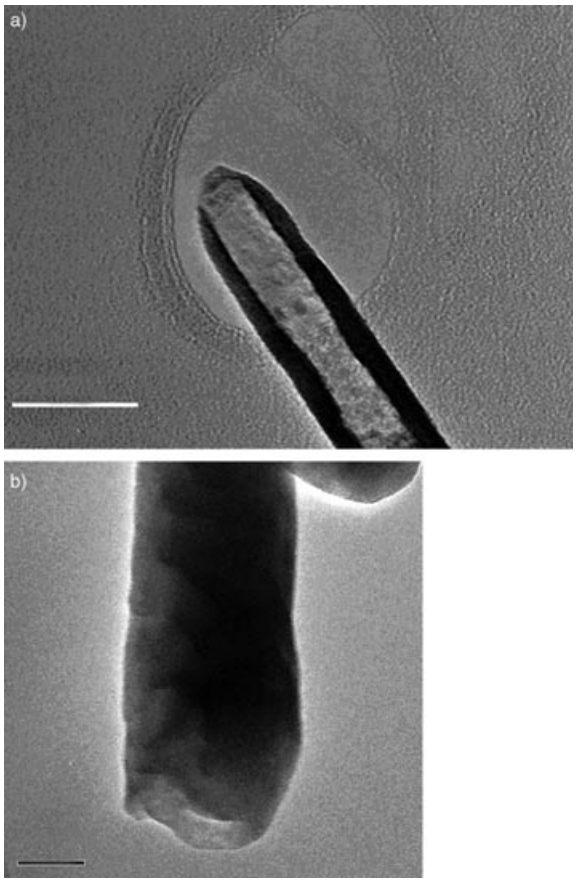

Figure 3. a) Transmission electron micrograph of a WO_2Cl_2 nanotube. b) Transmission electron micrograph of a WO_2Cl_2 nanowire. The bars are 50 nm long.

promote exfoliation. Subsequent repeated washing of the centrifuged material removes the electrolyte and restacks the layer but with the nanotube/nanowire morphology. This infers that while the layers are in solution they roll into tubes/wires. It is know from other studies that sheets in solution can roll into tubes or wires.[9] The use of other electrolytes, such as those based on propylene carbonate or acetonitrile, did not yield significant quantities of nanotubes/nanowires.

Although most of the material is composed of approximately a 1:1 ratio of nanotubes to nanowires, we have observed some examples of particles that are both nanotubes and nanowires, Figure 4. High-resolution transmission electron microscopy (HRTEM) has allowed a more detailed investigation of the structure of the walls of the tubes and the wires, Figure 5, which are identical. The measurement of the lattice images and electron-diffraction patterns confirm that the structure is that of WO_2Cl_2. The *c*-axis of the orthorhombic unit cell of WO_2Cl_2, along which the layers are stacked, lies along the radius of the tubes/wires with the *ab* plane coinciding with the plane of curvature of the tube walls. The *a* and *b* lattice parameters extracted from the electron microscopy are $a \approx b \approx 3.75$ Å (3.8414/3.8851 Å), with values obtained from the previous X-ray diffraction study given in brackets.[10] The HRTEM reveals that the tube walls consist of small domains, each of which adopts the WO_2Cl_2 structure with their *c* axis parallel to each other but with the structure of

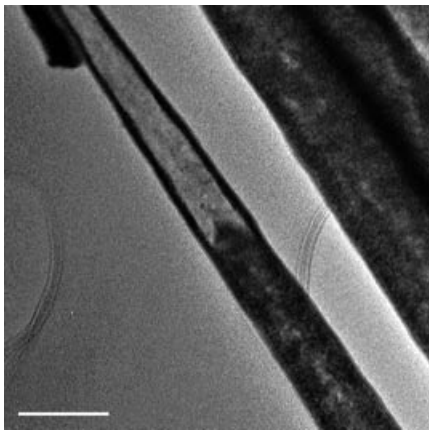

Figure 4. Transmission electron micrograph showing a combined tube and wire. The bar is 100 nm long.

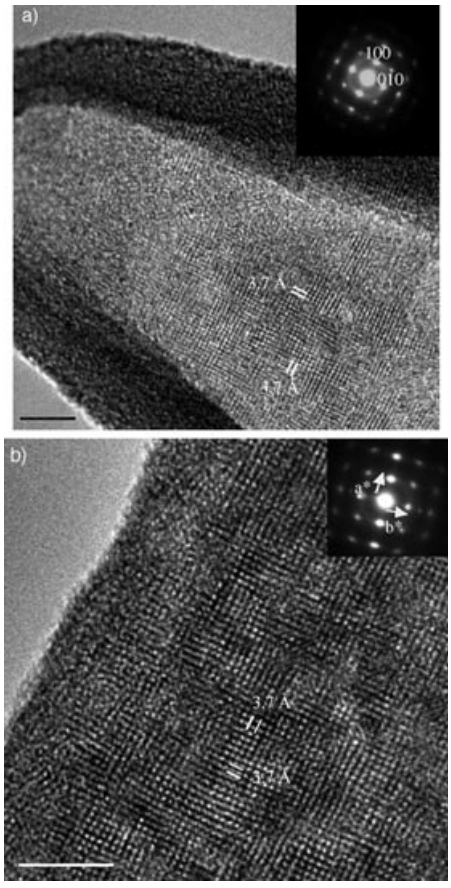

Figure 5. High-resolution transmission electron micrograph of a) a nanotube wall and b) a nanowire. In each case the lattice spacings are highlighted and selected area electron diffraction patterns down the [001] direction are shown as an inset. The bars are 5 nm long.

each domain being incoherent with it neighbors. It is interesting to note that the tubes are invariably capped as shown in Figure 2.

Layered structures in general favor the formation of nanotubes/wires. However the majority of examples are based on CdI_2, $CdCl_2$, or similar structure types, in which the MX_6 octahedra share common edges. In contrast, in WO_2Cl_2 the octahedra share common vertices. Although the

radius of curvature involved in bending a sheet into a scroll is relatively small compared with the average bond length, bending a sheet of edge-sharing octahedra is much more difficult than is the case of a sheet of corner-sharing octahedra; in the latter case this only requires a small deviation of the M-O-M angle from 180° in the direction of curvature of the tubes. Many oxides built from vertex-sharing polyhedra have M-O-M bond angles that are far from 180°.[11] This demonstrates that the lattice energies are relatively insensitive to variations in the bond angles, in keeping with the nature of the metal–oxygen bonding in such materials Therefore the vertex-sharing layered structures of materials such as WO_2Cl_2 are excellent candidates for nanotube formation. As a result, it is likely that other oxyhalides with similar structures for example, MoO_2Cl_2, will also readily form nanotubes/wires.

WO_2Cl_2 is an intercalation host. Both Li and Na atoms have been intercalated up to a maximum of $Li_2WO_2Cl_2$ and $Na_{1.5}WO_2Cl_2$ respectively. Such intercalated materials are layered tungsten bronzes that exhibit a mixture of electronic and ionic conductivity and display an intense blue color. The ability to switch color on and off with intercalation/deintercalation is the basis of electrochromic displays. The tubes/wires have the same structure and hence the potential to act as intercalation hosts with attendant changes in the electronic, ionic and optical properties. However the confined dimensions of the tubes/wires can lead to rapid switching on intercalation/deintercalation. The intercalation of Li and Na atoms into WO_2Cl_2 nanotubes/wires is under investigation and will be reported subsequently.

In conclusion we have succeeded in preparing, for the first time, mixed anion (oxyhalide) nanotubes and nanowires. Doubtless, further examples of this new class of nanotubes/nanowires will be synthesized in the future.

Experimental Section

WO_2Cl_2 (Aldrich, 99 %), was ballmilled for 1 to 1.5 h by using a SPEX Centri-Prep 8000M mixer/mill. All milling was carried out under an Ar atmosphere to prevent hydrolysis of the material. The milled solid was returned to the glove-box and stirred in a 1 M solution of $LiPF_6$ in a 1:1 (*v*/*v*) mixture of ethylene carbonate and dimethyl carbonate (Merck) for several days. The resulting colloidal solution was then centrifuged, washed in dimethyl carbonate and dried.

HRTEM imaging and selected-area electron diffraction (SAED) were carried out by using a JEOL-JEM 2011 electron microscope operating at 200 kV and equipped with a side-entry $\pm 20°$ double-tilt specimen holder. The specimens were prepared by making a suspension of powdered samples in organic solvent and depositing one drop onto a holey carbon-coated Cu grid. This was carried out in the glovebox. The specimen holder was loaded so as to minimize the sample exposure to the atmosphere.

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