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$MoSe_2$ and WSe_2 nanotubes and related structures

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$MoSe_2$ and WSe_2 nanotubes are obtained by the reduction of the corresponding triselenides in hydrogen or by the decomposition of the ammonium selenometallates in a hydrogen atmosphere.

Tenne and coworkers[1,2] have demonstrated that the layered metal disulfides, MoS_2 and WS_2, form fullerene-like nested polyhedra as well as nanotube structures. Nanotubes of these two sulfides have been prepared by treating the oxides, MoO_3 and WO_3, first with a mixture of 5% H_2 + 95% N_2 followed by H_2S around 900 °C.[1–3] It is likely that amorphous trisulfides are formed as intermediates in this process. Accordingly, by heating amorphous MoS_3 or WS_3 or the ammonium thiometallate precursors in hydrogen around 900 °C, we have been able to directly obtain good yields of MoS_2 and WS_2 nanotubes.[4] Fullerene-like structures of the layered Mo and W diselenides have been prepared by the reaction of the oxides with H_2Se and H_2 + N_2 at high temperatures.[2,5] In this communication, we describe our preliminary results on the synthesis of nanotubes and nanorods of $MoSe_2$ and WSe_2 by new routes. Considering that the Mo and W trisulfides are intermediates in the formation of the disulfide nanotubes, we conjectured that the corresponding amorphous triselenides could act as intermediates in the formation of the diselenide nanotubes. We have therefore, examined the hydrogen reduction of amorphous WSe_3 and $MoSe_3$, prepared by the standard procedures.[6] Equally importantly, we have carried out the decomposition of the ammonium selenometallates in a hydrogen atmosphere to obtain the diselenide nanostructures.

Reduction of $MoSe_3$ in a stream of hydrogen (100 sccm) at 850 °C yields nanotubes as evidenced by the low-resolution transmission electron microscope (TEM) images in Fig. 1(a) and (b). Fig. 1(c) shows a TEM image of a nanorod, with a layer separation of 0.64 nm. Hydrogen reduction of WSe_3 at 750 °C yields WSe_2 nanotubes. High-resolution TEM images of some of the nanotube-like structures are shown in Fig. 2(a), (b) and (c), with the lattice fringes corresponding to the expected layer spacing of 0.65 nm. The top image in Fig. 2(c) is that of a WSe_2 nanorod emanating from a precursor particle, while the bottom image in the figure appears to be due to a single-walled nanotube, but the separation between the layers is 0.65 nm. The nanorod shows lattice fringes corresponding to the (002) planes, but the nanoparticle at the tip does not show any lattice planes. Such nanoparticles can act as nucleation centres for the growth of the nanorods or nanotubes. The growth of the nanorod or nanotube starting from the inner core of a particle and proceeding towards the outer edge, is different from that of the carbon nanotubes where the layers grow from the outer edge of the catalyst particle, encapsulating the metal catalyst particle.

The formation of the diselenide nanostructures from the triselenides involves the simple reaction, $MSe_3 + H_2 \rightarrow MSe_2 + H_2Se$ (M = Mo or W). Since the triselenides are formed by the

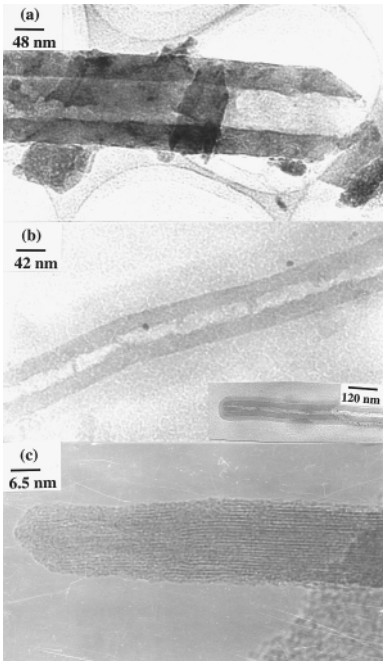

Fig. 1 (a) and (b) TEM images of a $MoSe_2$ nanotubes obtained from the decomposition of $MoSe_3$; (c) high-resolution TEM (HREM) image of a $MoSe_2$ nanorod.

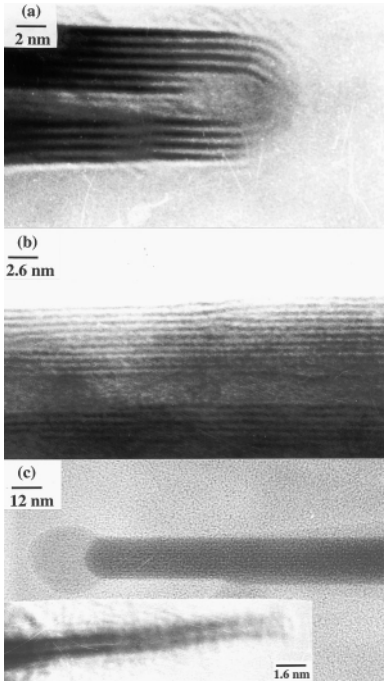

Fig. 2 (a), (b) HREM images of WSe_2 nanotubes obtained by decomposition of amorphous WSe_3 in a flow of H_2; (c) TEM images of a WSe_2 nanorod emanating from the precursor particle (top), and a single-walled WSe_2 nanotube (bottom).

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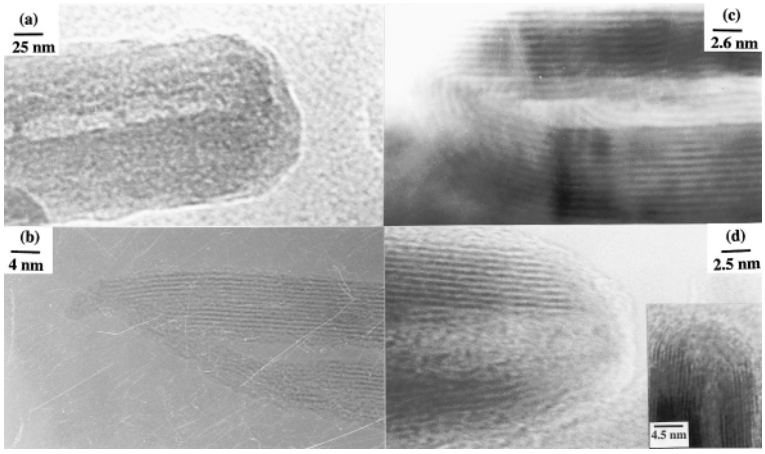

Fig. 3 (a) TEM image of a $MoSe_2$ nanotube obtained by the decomposition of $(NH_4)_2MoSe_4$; (b)–(d), HREM images of $MoSe_2$ nanotubes.

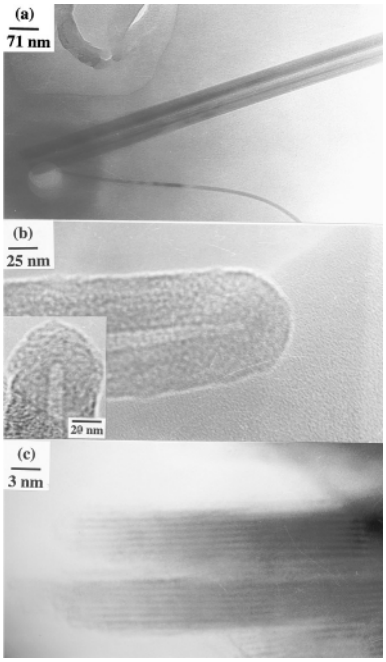

Fig. 4 (a), (b) TEM images of WSe_2 nanotubes obtained by the decomposition of $(NH_4)_2WSe_4$ in a flow of H_2. The nanotube in (a) shows a flat tip. (c) HREM image of a WSe_2 nanotube.

thermal decomposition of ammonium selenometallates, we have directly carried out the reduction of the selenometallates. Fig. 3 shows the TEM images of $MoSe_2$ nanotube structures obtained by heating $(NH_4)_2MoSe_4$ in a flow of H_2 (500 sccm) at 900 °C. The low-resolution image in Fig. 3(a) shows a nanotube closed at one end. The high-resolution images in Fig. 3(b), (c) and (d) show the $MoSe_2$ layers with a spacing of ~0.64 nm corresponding to the (002) planes. Although there is a core in the image in Fig. 3(b), the tube end has an unusual structure. The images in Fig. 3(c) and (d) appear to show closed tips, but the structure of the tip is not clearly evident. Fig. 4(a) and (b) show low-resolution images of WSe_2 nanotubes obtained by the decomposition of $(NH_4)_2WSe_4$ under a flow of H_2 (100 sccm) at 750 °C, the image in Fig. 4(b) showing closed tips. The image in Fig. 4(c) appears to be an open nanotube.

Powder X-ray diffraction (XRD) patterns of the nanotubes and nanorods of $MoSe_2$ and WSe_2 were characteristic of hexagonal structures with $a = 3.28$, $c = 12.82$ Å and $a = 3.29$ and $c = 12.99$ Å, respectively. EDAX analysis of the nanotubes showed the metal : selenium ratio to be close to 1 : 2. Selected area electron diffraction patterns commonly showed Bragg spots corresponding to the (002) and (100) planes, the (103) reflection appearing in only few of them.[7] Diffuse streaking was observed along the rows in some of the patterns.

The present study demonstrates that hydrogen reduction of the triselenides, and more significantly, of the ammonium selenometallates provides a useful route for the synthesis of the $MoSe_2$ and WSe_2 nanotubes. The reaction involved in the latter method is, $(NH_4)_2MSe_4 + H_2 \rightarrow MSe_2 + 2H_2Se + 2NH_3$ (M = Mo, W). In the decomposition of the ammonium selenometallates, the diselenide nanotubes are deposited a small distance away from the location of the starting material indicating that the amorphous triselenide may be acting as a vapor transport agent as well. In conclusion, we have been able to obtain nanotube-like structures of $MoSe_2$ and WSe_2 by the reduction of the amorphous triselenides as well as of the ammonium selenometallates. While we have been able to record a variety of nanotube and nanorod structures, with the former often exhibiting defective structures and variable wall thickness on either side of the core,[3] or loss of structure at the tip, we are presently continuing our studies in an attempt to obtain better images.

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