New Metal Disulfide Nanotubes

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Fullerene-like polyhedra and nanotubes of the layered metal disulfides, MoS_2 and WS_2, first described by Tenne and co-workers,[1,2] have aroused considerable interest. Formation of these disulfide nanotubes appears to involve the amorphous trisulfides as intermediates. Accordingly, we have found that heating MoS_3 or WS_3 in a stream of H_2 around 900−1100 °C directly yields the disulfide nanotubes.[3] This observation prompted us to consider the possibility of preparing nanotubes of layered disulfides of transition metals of Group 5 by using the trisulfides as the starting materials. Unlike MoS_3 and WS_3 which are amorphous, trisulfides of Nb and Ta are crystalline.[4] Despite this limitation, we carried out the hydrogen reduction of NbS_3 and TaS_3, prepared by the reaction of the elements in evacuated sealed tubes heated to 700 and 850 °C, respectively. To our surprise, we were able to obtain the disulfide nanotubes by the simple reaction,

$$MS_3 + H_2 \rightarrow MS_2 + H_2S \text{ (M = Nb, Ta)}$$

These are the first examples of nanotubes of layered metal disulfides other than MoS_2 and WS_2.

In a typical reaction, NbS_3 was heated in a stream of H_2 (100 sccm) at 1000 °C for 30−60 min. By this procedure, good yields of the disulfide nanostructures were obtained. By carrying out the reduction of TaS_3 similarly in H_2 (100 sccm) at 1000 °C for 30−60 min, TaS_2 nanostructures were obtained. The SEM images of the nanostructures of NbS_2 and TaS_2 in Figure 1 reveal the presence of bundles. We have examined the nanostructures by transmission electron microscopy (TEM) to unravel their structures.

In Figure 2, we show the TEM images of the NbS_2 nanotubes obtained by the reduction of NbS_3. The image in Figure 2a shows the presence of several nanotubes and nanorods while the image in Figure 2b shows individual nanotubes with hollow cores. The diameters of the hollow tubule is in the range ∼4−15 nm. The closed end of the nanotube in Figure 2b is noteworthy. The tip is nonspherical and almost polygonal unlike in the carbon nanotubes. We have also obtained TEM images of nanotube bundles with the nanotubes lying side by side along the length. Figure 2c shows high-resolution image of a nanotube with an interlayer spacing of ∼0.6 nm corresponding to the (002) plane. Electron diffraction (ED) patterns of some of the nanotubes showed the nanotubes to be single-crystalline with Bragg spots corresponding to known *d* values [JCPDS file card no. 41-0980]. Some of the diffraction patterns showed diffuse scattering or streaking due to bent layers or disorder. The X-ray diffraction pattern of the nanotubes was similar to that of bulk NbS_2. We have, however noticed a *c*-axis expansion of ∼3% in the nanotubes. Preliminary measurements did not reveal superconductivity down to 2 K. Theoretical calculations predict a high density of states at the Fermi level in NbS_2 nanotubes.[5]

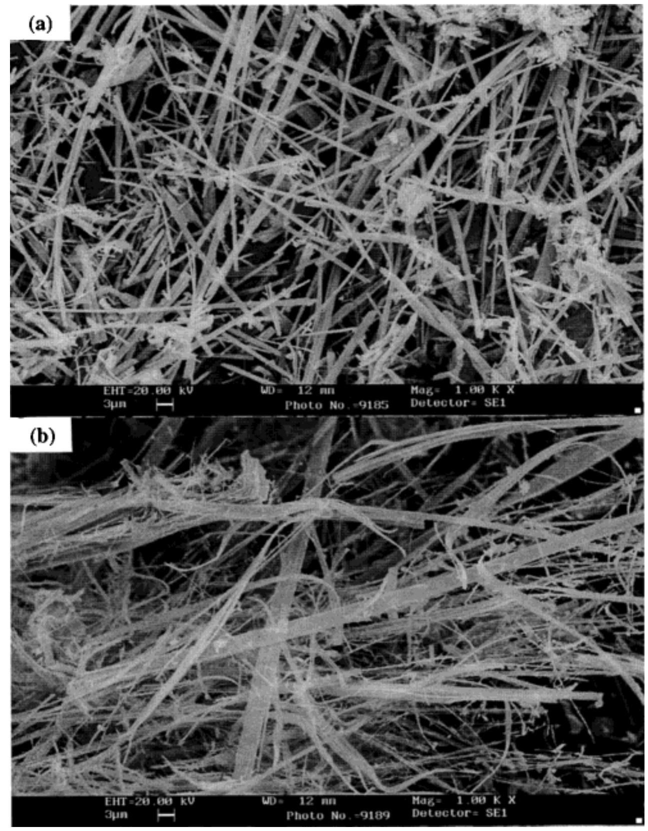

Figure 1. SEM image of the nanotubes of (a) NbS_2 and (b) TaS_2, obtained by the hydrogen reduction of the trisulfides.

In Figure 3, we show the TEM images of TaS_2 nanotubes obtained by the hydrogen reduction of TaS_3. The image in Figure 3a shows a nanotube with a hollow core of diameter ∼20−40 nm. Figure 3b shows the image of a nanotube with a nearly rectangular tip. Such tips have been observed in the nanotubes of MoS_2 and WS_2.[6] ED patterns of the nanotubes revealed Bragg spots with *d*-values in agreement with the literature [JCPDS file card no. 02-0137]. The X-ray diffraction pattern of the TaS_2 nanotubes was similar to that of bulk TaS_2, but with ∼3% expansion along the *c*-axis. The chemical composition of the nanotubes as obtained by EDAX gave a Ta:S ratio of 1:2. The TaS_2 nanotubes were also sensitive to electron beam heating and we have not yet been able to obtain high-resolution images.

We are optimizing the conditions for the synthesis of better nanotubes of NbS_2 and TaS_2. In the meantime, encouraged by

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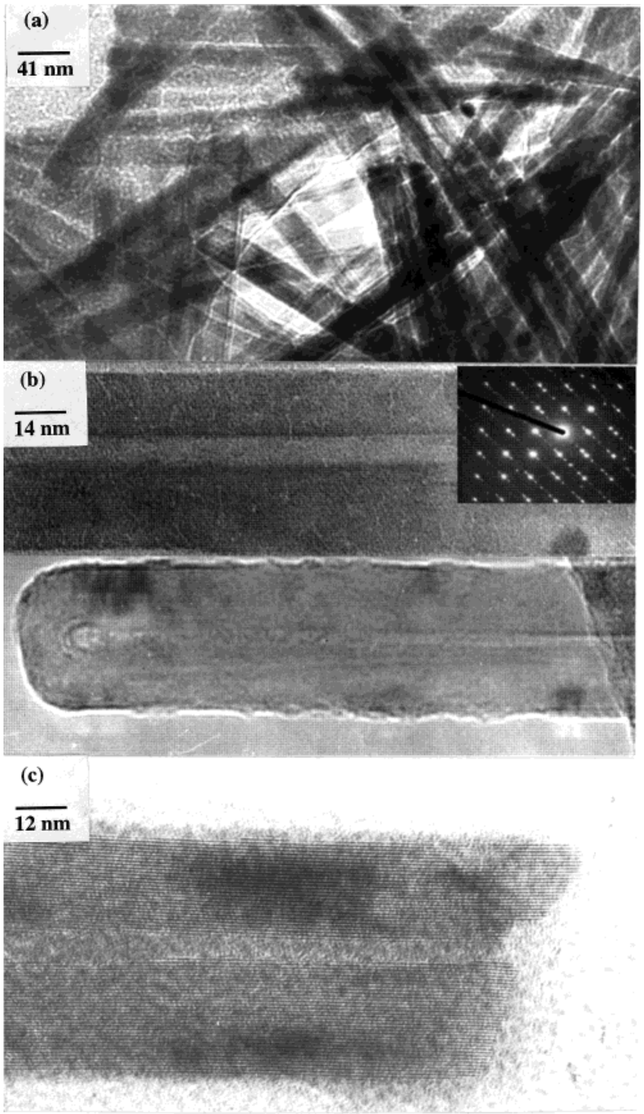

Figure 2. (a and b) TEM images of NbS_2 nanotubes obtained by the reduction of NbS_3 in a stream of H_2. The nanotube in part b shows a closed nonspherical tip. (c) HREM image of a nanotube showing an interlayer spacing of ∼0.6 nm.

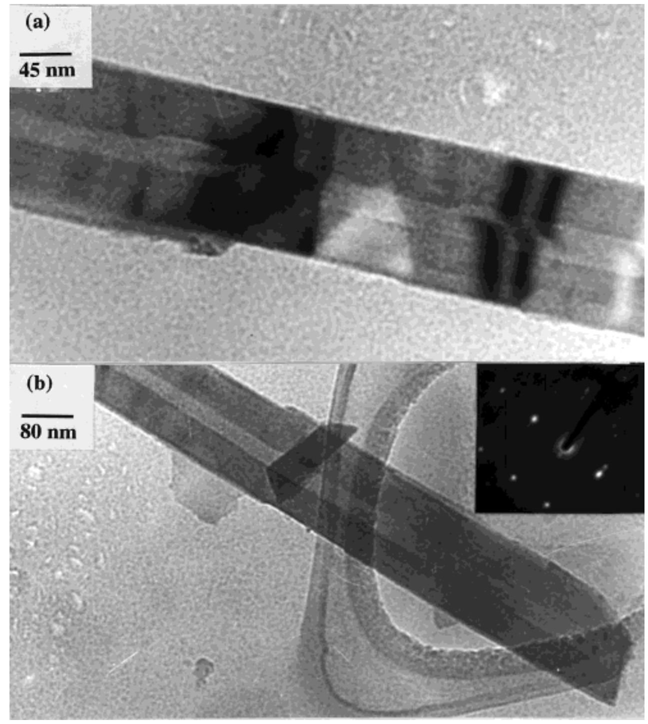

Figure 3. (a and b) TEM images of TaS_2 nanotubes obtained by the hydrogen reduction of TaS_3.

the results reported here, we are exploring the synthesis of nanotubes of the layered disulfides of Group 4 metals, by the trisulfide route. Preliminary studies have shown that nanotubes of TiS_2, ZrS_2, and HfS_2 are indeed formed by the hydrogen reduction of the corresponding crystalline trisulfides. It appears likely that triselenides of Nb and Ta would yield nanotubes of the diselenides on hydrogen reduction. $NbSe_2$ nanotubes are reported to be formed under high doses of electron irradiation,[7] but a chemical method of synthesis would be preferable. The present study enlarges the family of nanotubes significantly, encompassing the dichalcogenides of several metals of Groups 4 and 5.

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