Tungsten–niobium–sulfur composite nanotubes†

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Novel W–Nb–S composite inorganic nanotubes have been generated by replacing W in the S–W–S sandwich layers of WS_2 by Nb. The tubes are uniform, with the Nb concentration 10 atom%. Raman spectral features of the tubes are described.

Inorganic fullerene (IF) nanotubes, *e.g.* MX_2 (M = W, Mo; X = S, Se), first reported by Tenne *et al.*,[1] have engendered considerable scientific interest because they are good semiconductors and display excellent wear-resistant properties. To date, various approaches to the synthesis of these materials have been developed, such as chemical transport,[2] gas–solid reactions[3] and *in situ* heating,[4] leading to pure MX_2 nanoparticles, short and long tubes, bundles, and even microtubes. The structural features, lubricating properties and electronic behaviour of the IF nanotubes have been widely investigated.[5–8] For example, a single WS_2 nanotube has been used successfully as a microscope probe.[3,9] Recently, Levy and coworkers showed that small amounts of noble metals (Au and Ag) could be intercalated between WS_2 tube walls.[10,11] Akin to their bulk crystals, IF nanotube band gaps are dependent upon tube diameter.[12] It is therefore interesting to prepare doped nanotubes and to assess their electronic and mechanical performance. Here, we describe the generation of a novel $W_xNb_yS_2$ IF nanotube containing *ca.* 10 atom% Nb.

We prepared needle-like WO_x (mainly $W_{18}O_{49}$) nanotubes by the previously described procedure.[13] The needles were then covered with a suspension of Nb_2O_5 (Aldrich, 99.9% pure, particle size < 2 μm) in acetone, and the acetone was allowed to evaporate leaving Nb_2O_5 uniformly distributed over the needles. The sample was then reheated to *ca.* 1100 °C under 200 Torr H_2S. Using a scalpel, the grey needle-like deposit was removed from the quartz surface, subjected to high resolution transmission electron microscopy (HRTEM, JEOL-4000) and to energy dispersive X-ray (EDX, element > B) and Raman spectroscopic (Renishaw system 1000, $\lambda_0 = 514.5$ and 632.8 nm) analysis.

Previously, we had refined the oxide–sulfide conversion method[7] and successfully created very long pure WS_2 nanotubes by forming WO_x nanorods prior to oxide–sulfide conversion.[4] We have now found that the constituent atoms of Nb_2O_5-coated WO_x nanorods easily diffuse at high temperature (*ca.* 1100 °C), particularly through materials possessing substantial vacancies. Thus Nb probably occupies some of the W positions within $W_{18}O_{49}$, leading to $W_xNb_yO_z$. This replacement process is reminiscent of the behaviour of the bulk oxides, but in this case the nanorod templates and the suboxide features were retained. The presence of gaseous H_2S in the chamber facilitated oxide-to-sulfide conversion in an identical manner to that found for the synthesis of pure WS_2 or MoS_2 nanotubes,[1,3,4] resulting in homogeneous W–Nb–S composite nanotubes. These tubes are straight, *ca.* 5–10 μm long and *ca.* 20–100 nm in diameter. HRTEM images of the tubes are not different from those of WS_2 nanotubes. The majority have hollow cores, less than 30% of them being fully or partly filled with elongated WO_x crystals. Concentric nanotubes (layer separation *ca.* 0.62 nm) are observed. The outer layers are smooth and appear to be free of lattice defects. All the tubes are closed, *ca.* 20% by flat caps, forming a *ca.* 90-degree connection with the cylinders. Dislocations at the cap–cylinder junctions are apparent [Fig. 1(a), arrowed]. EDX revealed the presence of Nb [Fig. 1(b)] within the nanotubes. Measurements on ten isolated hollow nanotubes revealed a *ca.* 9 : 1 W to Nb atomic ratio, the metal : sulfur ratio being *ca.* 1 : 2. The overall stoichiometry of the nanotubes is $W_xNb_yS_2$ ($x = 0.9$, $y = 0.1$, 5% uncertainty). The flat tip feature (*ca.* 90-degree angle with the body) of the nanorods is determined by their intrinsic crystalline nature.[13] Hence, the flat nanotube tips probably form as a result of oxide–sulfide template conversion. This conjecture is supported by supplementary experiments, which showed that NbS_2 nanotubes could not be prepared directly from Nb_2O_5 powder alone. These results confirm that the suboxide plays a key role in the IF nanotube formation, and the process can be written in terms of eqns. (1) and (2):

$$WO_{x\,(\text{nanorod})} + Nb_2O_{5\,(\text{particle})} \rightarrow W_{0.9}Nb_{0.1}O_{x\,(\text{nanorod})} \qquad (1)$$

$$W_{0.9}Nb_{0.1}O_{x\,(\text{nanorod})} + H_2S_{\,(\text{gas})} \rightarrow W_{0.9}Nb_{0.1}S_{2\,(\text{nanotube})} + H_2O_{\,(\text{gas})} \qquad (2)$$

In order to ascertain whether or not Nb was present as an intercalate within the WS_2 tube walls, or as a dopant in the WS_2 structure, we undertook additional EDX analyses. The results showed that the W : Nb : S ratio remained nearly constant, independent of nanotube diameter and position. This behaviour is consistent with the EDX mapping, and implies that the nanotubes are fairly uniform. When intercalated Au and Ag are present, the nanotubes are heterogeneous, irrespective of their diameter and length.[10,11] Heterogeneous intercalation is likely to lead to internal stresses owing to the different atomic diameters of W and Nb, resulting in significant defects. In fact,

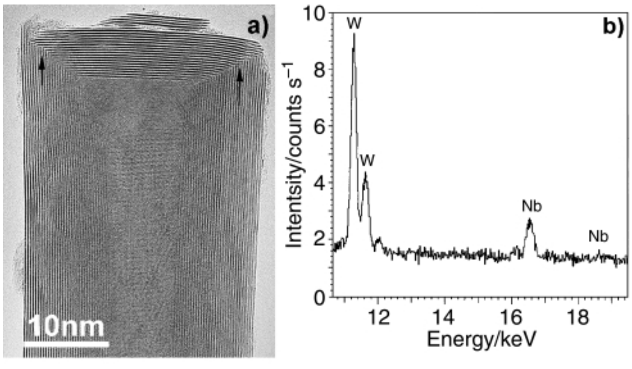

Fig. 1 (a) HRTEM image showing a *ca.* 90-degree flat cap, layer separation = 0.62 nm. Dislocations at the cap-cylinder junctions are apparent (arrowed); (b) EDX of an isolated hollow tube, revealing the presence of W and Nb. S signals are omitted from this profile.

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† Electronic supplementary information (ESI) available: HRTEM image of a typical 10-layered $W_{0.9}Nb_{0.1}S_2$ nanotube, layer separation = 0.62 nm and Raman bands of $W_{0.9}Nb_{0.1}S_2$ and WS_2 nanotubes and their assignments. See http://www.rsc.org/suppdata/cc/b0/b007074m/

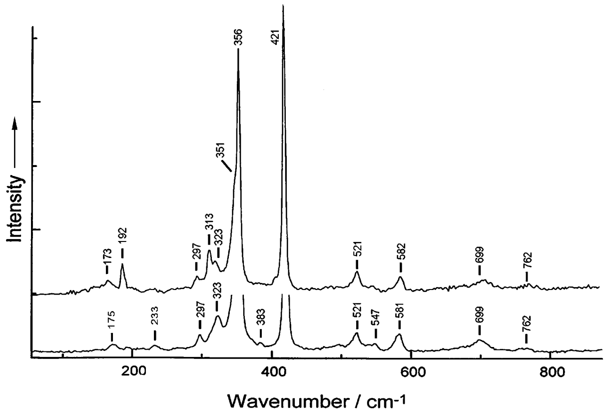


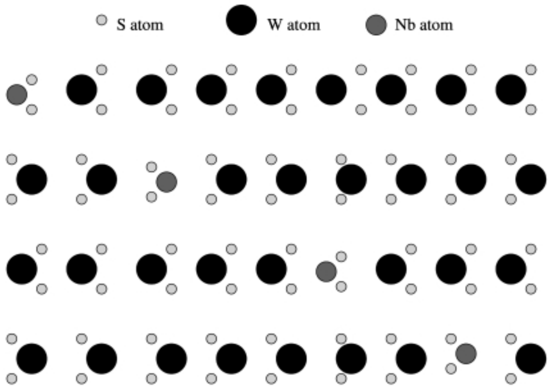
Fig. 2 Raman spectra ($\lambda_0 = 514.5$ nm) of $W_{0.9}Nb_{0.1}S_2$ (upper) and WS_2 (lower) nanotubes.

our HRTEM observations show that the distance between layer fringes is *ca.* 0.62 nm [Fig. 1(a)], identical with that in pure WS_2; only a few defects are present. Furthermore, expanded layer separations, *i.e.* > 0.62 nm, would be expected if Nb were to be intercalated between the WS_2 layers. However, very few crystals were found with expanded layer separations. Thus our nanotubes are Nb-doped and not intercalated.

Additional experiments have revealed that the W : Nb ratio can be altered by applying various amounts of Nb_2O_5 coating to the WO_x nanorods, prior to passage of H_2S during heating. The Nb concentration (*ca.* 10% atom%) can be doubled in the nanotubes; however, our results showed that Nb-dominated W–Nb–S tubes are difficult to construct.

The Raman spectrum of $W_{0.9}Nb_{0.1}S_2$ nanotubes taken with 632.8 nm excitation is identical to that of WS_2 nanotubes. The 514.5 nm spectrum of the Nb-doped tubes, however, does show some differences from that of WS_2 (Fig. 2), notably the appearance of a medium intensity band at 313 cm^{-1}, a shoulder on the low wavenumber side of the $e_{2g}{}^1$ band at 356 cm^{-1} and an increase in the relative intensity of the 192 cm^{-1} band. The intensity of the 192 cm^{-1} band is *ca.* half that of the disorder-induced zone-edge phonon [LA(M)] band at 173 cm^{-1} for WS_2, whereas its intensity for the Nb-doped tubes is *ca.* 5 times that of the 173 cm^{-1} band. The 192 cm^{-1} band has been observed in the Raman spectra of 2H-bulk and nanotubes of WS_2, but has not been assigned.[14] Its increase in relative intensity on going from pure WS_2 nanotubes to Nb-doped WS_2 nanotubes implies that it is caused by scattering from a disorder-induced zone-edge phonon. The band at 313 cm^{-1} has not previously been seen in the Raman spectra of any form of WS_2, and is also probably due to the increased disorder in the lattice owing to the presence of Nb. The shoulder at 351 cm^{-1} is the first overtone of the LA(M) band, with its apparent intensity enhanced by its proximity to the strong band at 365 cm^{-1}. The Raman bands and their assignments are summarised in Table 1 of ESI.†

The formation of $W_{0.9}Nb_{0.1}S_2$ nanotubes can be accounted for by considering the layered structure of the $W_{0.9}Nb_{0.1}S_2$ crystals. According to our EDX analysis, only *ca.* 10% of the W atoms are replaced by Nb. Therefore, we suggest that the Nb-doped material remains as the $2H_b$-type WS_2 structure, rather than becoming the $2H_a$-type NbS_2 structure. We propose a model for layered $W_{0.9}Nb_{0.1}S_2$ (Fig. 3). In this structure, the doped Nb atoms (medium circles) should not cause severe lattice defects and can easily be stabilised by neighbouring atoms. This suggestion is supported by our Raman spectra; the spectra of the Nb-doped and pure WS_2 tubes are identical using 632.8 nm excitation, whereas new bands attributable to increased lattice disorder are seen using 514.5 nm excitation. The crystal lattice spacing, particularly *c*/2, remains almost unchanged when compared with that of pure WS_2 layers. If a nanotube is to be formed by rolling up such composite layers, one would not expect a significant *c*/2 change. This conjecture is also supported by the facts that the composition of our nanotubes is uniform and that we did not observe severe defects on the tube walls.



(110) section of the $W_{0.9}Nb_{0.1}S_2$, based on $2H_b$-WS_2 structure

Fig. 3 Proposed model for the layered $W_{0.9}Nb_{0.1}S_2$ structure.

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