Binary Phase of Layered Nanotubes

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ABSTRACT

A binary phase of layered nanotubes, where MWCNs (Multi-walled carbon nanotubes) are coated by WS₂, are generated by pyrolysing WO₃-coated MWCNs in an H₂S/N₂ atmosphere at 900 °C. TGA and TEM show that WS₂ acts as an antioxidant to the MWCN core.

INTRODUCTION

It has been demonstrated that MWCNs can act as templates for the generation of other types of nanotubes,[1, 2] despite problems associated with their high surface tension.[3] Previous methods for coating MWCNs with WO₃ involved surface oxidation, which generated –COOH or –OH groups[2, 4] and the MWCNs were often found uncapped and peeled.[4] Here we describe a technique for depositing WO₃ onto the surface of MWCNs and conversion to WS₂ without affecting the carbon template.

EXPERIMENT

H₂WO₄ (250 mg) and MWCNs (50 mg) were mixed at −78 °C in liquid NH₃ (~20 cm³) and the mixture was set aside in order to attain room temperature. The solid residue was then heated at 350 °C for 15 min in an air flow (100 cm³ min⁻¹) to convert H₂WO₄ to WO₃ and then further heated at 900 °C for 15 min in a mixture of H₂S and N₂ (ca. 1:3 ratio, total 50 cm³ min⁻¹) to convert WO₃ into WS₂. The products were ultrasonically dispersed in acetone and mounted on lacey carbon films (Cu support grids) for TEM analysis. The following equipment was employed as appropriate: high-resolution transmission electron microscopy (HRTEM, JEOL 4000 EX II operated at 400 kV, Philips CM 200 operated at 200 kV) equipped with an energy dispersive X-ray probe and line mapping (EDX), and thermogravametric analysis (Perkin Elmer TGA-7, heating rate of 10 K min⁻¹).
DISCUSSION

HRTEM showed that 60% of the MWCNs were either partly or fully coated with dark material, typically with 1 to 3 layers (Figure 1). A number of features are distinguishable in the HRTEM images of the sample: 1) the d-spacing of MWCN layers is maintained after the experiment at ca. 3.4 Å; 2) the d-spacing of the dark layers is ca. 6.2 Å, consistent with separate WS$_2$ nanotubes; 3) the distance between the centres of the outermost C layer and the innermost WS$_2$ layer is ca. 4.4 Å; 4) the residual amorphous layer coating both the partly and fully coated MWCN is WO$_{3-x}$, resulting from the incomplete conversion of WO$_3$ to WS$_2$.

![HRTEM image of MWCNs and polyhedral carbon particle coated with WS$_2$.](image)

EDX analysis was carried out on both partly and fully coated MWCNs. Only a C signal was detected when the probe was focused on the uncoated sections of a partly coated MWCN. C, W and S, together with a trace of O, were detected when the EDX probe was focused on the coated section (Figure 2). Quantitative analysis showed the atomic ratio of W to S was 1:2 (± 0.1), implying a WS$_2$ structure.
Figure 2. EDX profile for a fully WS$_2$-coated MWCN.

Line mapping analysis was carried out on a fully WS$_2$-coated MWCN. The C, W and S mappings were taken from C-K$_{\alpha}$, W-M$_{4\alpha}$1 and S-K$_{\alpha}$ states respectively (from the EDX probing results). The mapping profile intensity was found to be $W > S > C$. The width of W and S profiles was greater than the C profile and indicates that the MWCNs are actually sheathed within WS$_2$ tubes.

A diffractogram (Figure 3b) was derived from Fourier Transform calculations on the WS$_2$-coated region of Figure 3a. Two sets of diffraction spots appear in hexagonal arrays, which match the diffraction pattern for the hexagonal WS$_2$ structure. Two hexagonal arrays result from the electron beam scattering by the front and rear coated sections of the MWCN, which are rotated from each other by ca. 17°. Therefore the WS$_2$ nanotube is helical and inclined at ca. 8.5°. Above the white arrows (Figure 3a) part of the WS$_2$ coat is extended away from the overlap of the front and rear coating sections. Striations, inclined at 8.5°, are observed extending from one side of the WS$_2$ coat to the other, which are comprised of spots separated by ca. 3.1 Å. This is represented in Figure 3c (upper), where the spots correspond to the positions of W atoms, in hexagonal WS$_2$, in which they are separated by 3.153 Å (3c, lower). By enhancing the HRTEM image (Figure 3a) by computer, the bonding structure of WS$_2$ can be clearly observed (Figure 3d).
Figure 3a) HRTEM image of a partly WS$_2$-coated MWCN (below white arrows), insert shows electron diffraction pattern from a WS$_2$-coated MWCN. b) diffractogram obtained from the lattice image of Figure 3a showing the tube helicity to be ca. 8.5°. c) a simulated dark spot array from the excess of WS$_2$ coating the rear of the tube; the W-W distance is ca. 3.1 Å. d) an enhanced HRTEM image of WS$_2$ coating the rear of the MWCN.

Previous reports showed that MWCNs are significantly damaged when heated at 700 –750 °C for 30 min and lose about 99 % mass. The remaining 1 % are significantly damaged and decapped.[5] For comparative purposes, TGA analyses were performed on MWCNs, WS$_2$-nanostructures and WS$_2$-coated MWCNs. In Figure 4, the TGA curve of MWCNs (red line)
shows that the onset of oxidation begins *ca.* 700 °C and drastic mass loss occurs between 700 and 900 °C. At ca. 910 °C their mass loss is ca. 99 %. The TGA curve of WS₂-nanostructures (green line) exhibits a 3.4 % mass loss at ca. 530 °C. This is attributed to the conversion of WS₂ into WO₃. No further mass loss is recorded towards the end of the experiment. The TGA of WS₂-coated MWCNs (blue line) shows a stepwise profile. The first mass loss is around 450 °C, attributed to the WS₂ converting to WO₃. This occurs at a slightly lower temperature than separate WS₂-nanostructures, possibly due to the thinner and more defective WS₂ layers coating the MWCN allowing easier diffusion of gases between the layers. The second mass loss occurs between 550 and 850 °C, attributed to the oxidation of MWCNs. The resulting dark-green powder (WO₃ is a light green powder, therefore the darker green colour arises from the presence of MWCNs mixed with WO₃) was subjected to TEM analysis and revealed the presence of MWCNs that are slightly thinned and decapped (Figure 5).

![TGA curve of MWCNs, WS₂-nanostructures and WS₂-coated MWCNs.](image)

**Figure 4.** TGA of MWCNs, WS₂-nanostructures and WS₂-coated MWCNs.
Figure 5. TEM image of WS$_2$-coated MWCNs after TGA. Selected MWCNs exhibit a reduction in the number of carbon layers towards the tip due to peeling (arrows).

CONCLUSIONS
We have demonstrated the facile way in which WO$_3$ can be deposited onto MWCN surfaces and converted to WS$_2$. Interestingly, this transformation converts disordered WO$_3$ into layered WS$_2$ nanotubular sheaths. Due to its composite nature, we have improved the ability of MWCNs to withstand oxidation, which may find application as fire-retardant strengthening additives.

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