WS$_2$/C Nanocomposites Reviewed

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Whilst generating nanotubes with modified material properties, multiwalled carbon nanotubes (MWCNs) were found to be capable of acting as templates for WS$_2$ nanotube growth. The MWCNs, coated with WO$_3$, by heating a mixture of MWCNs and a tungsten oxide precursor, i.e., H$_2$WO$_4$, were then sulphidised at 900°C in order to convert the WO$_3$ into WS$_2$ layers.

1. Introduction

The properties of carbon nanotubes hold considerable promise for their potential use in nanoelectronics.¹ Analogous inorganic nanotubes² have also been prepared and exhibit potentially useful properties.³⁻⁵ Studies on the combination of organic and inorganic nanotubes, generating heterojunction composites, have increased in number with a view to optimising the electronic effects (e.g., Schottky diode). Given the current state of electron beam lithographic technology, exploitation of the electrical properties of nanotube heterojunctions has now become possible.

The production of nanotube heterojunctions by arc-discharge experiments⁶⁻⁷ has resulted in the complete encapsulation of the heterojunction interface; this has now been extended to pyrolysis⁸ and to laser ablation.⁹ Recently, efforts have been focused on controlling the formation of the heterojunctions. Using carbon nanotubes as a template, various materials have been deposited onto their surfaces, including metals,¹⁰ metal oxides,¹¹,¹² nonmetal oxides,¹³,¹⁴ proteins,¹⁵ and organic polymers.¹⁶ One approach, developed at Sussex,¹⁷ has led to the production of a number of intriguing

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WS₂/C composites. The experimental details for preparing WS₂-coated MWCNs and WS₂-
coated single-walled carbon nanotube (SWCN) bundles are described elsewhere.\textsuperscript{(18,19)}

2. Discussion

An HRTEM study shows that ca. 70\% of the MWCNs exhibited WS₂ coatings, with the
degree of coverage varying between 25 and 100\%. The coating consisted typically of 1–4
layers, separated by ca. 0.62 nm, consistent with the expected separation of WS₂.\textsuperscript{19} Carbon
nanoparticles were also coated with WS₂ layers (Fig. 1). The WS₂ coatings are easily
distinguishable from the MWCN layers due to the stronger electron scattering nature of W
and S, and appear as darker, thicker basal plane lattice fringes (Fig. 2). The separation

Fig. 1. TEM image revealing WS₂-coated MWCNs and a WS₂-coated polyhedral carbon particle.

Fig. 2. HRTEM image of a WS₂-coated MWCN and its EDX profile (insert).
between the innermost WS$_2$ layer and the outermost MWCN layer is ca. 0.44 nm, a value which is maintained along the length of the coated area. The carbon layers remain intact, with a 0.34 nm basal plane d-spacing consistent with that of MWCNs$^{20}$.

EDX analysis was performed on uncoated, partly coated and fully coated MWCNs. The uncoated MWCNs showed only a C signal, whereas the fully coated MWCNs revealed the presence of W, S and C. A small O peak was occasionally detected. When the EDX probe was focused on an uncoated area of a part WS$_2$-coated MWCN, only C and a small O signal intensity was detected. When the probe was positioned over a coated area, W, S, C and a small quantity of O were recorded (Fig. 2 insert). Electron microscopic characterisation of the samples revealed that the WS$_2$ coats remain adhered to the MWCN surface. Even when the WS$_2$ layer does not completely enclose the circumference of the MWCN, the WS$_2$ layer remains in position after sonicating the samples for TEM investigations.

The XRD of a powder sample containing WS$_2$-coated MWCNs shows a well-defined crystalline pattern of reflections (Fig. 3). The peak positions and intensities match those of planar hexagonal WS$_2$ $^{21}$ indicating that the sample is composed of discrete WS$_2$.
nanostructures, due to the high reflection intensity, with a smaller contribution arising from WS₂-coated MWCNs. XRD analyses were carried out for a series of sulphidised samples, starting from annealed WO₃-coated MWCNs to WS₂-coated MWCNs. For such thin layers of WO₃/WS₂, it was found that the crystalline phase transformation from monoclinic WO₃ into hexagonal WS₂ occurs almost simultaneously, without involving intermediate reduced tungsten oxide species, i.e., WO₂⁺, as previously observed for the WO₃ to fullerene-like WS₂ conversion experiments.²²,²³

The hexagonal conformation of WS₂ was also realised from the HRTEM analysis of single-layered WS₂-coated MWCNs. Thicker WS₂-coated MWCNs result in destructive fringe interference, which makes the probing of WS₂ chirality difficult.²⁴ Figure 4(a) shows

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Fig. 4. (a) HRTEM image of a WS₂-coated MWCN. The highlighted box shows the striations consisting of discrete diffraction spots. Arrow A indicates the direction of 100 MWCN fringes. (b) A model of the discrete diffraction spots. (c) A model of hexagonal WS₂. (d) An enhanced TEM image of a WS₂-coated MWCN central core correlating the relative positions of W and S to the diffraction spots.
the details attained from a single-walled WS$_2$ layer coating an 8-walled MWCN. The MWCN lattice fringes terminate at the striations that originate from the WS$_2$ coat, consistent with the stronger diffraction arising from the heavier elements. Each striation comprises a series of discrete spots, separated by ca. 0.31 nm, which can be connected in order to delineate a hexagonal pattern (Fig. 4(b)). These spots are comparable to the structure of hexagonal WS$_2$, where the W atoms (separated by 0.31 nm) can be connected to form similar hexagonal patterns. By matching the models with the helicity of the tube (8.5°), we observed that the dark spots arise from the electron diffraction by W atoms in the WS$_2$ hexagonal lattice (Fig. 4(d)). From TEM analysis and model simulation of single-layered WS$_2$-coated MWCNs, the WS$_2$ coats appear to form a complete tube rather than a series of discrete WS$_2$ patches (Fig. 5). A complete WS$_2$ cylinder eliminates the W-S dangling bonds. However, a number of 2–4-layered WS$_2$-coated MWCNs were found to exhibit several layer defects. We postulate that the growth direction of the WS$_2$ coating is not restricted to an “inward” growth model as was observed for pure WO$_3$ to WS$_2$ nanoparticle formation.$^{22}$ The thinness of the initial WO$_3$ coatings would allow the facile diffusion of H$_2$S throughout the entire oxide layer, resulting in the simultaneous formation of WS$_2$ layers. The competition of WS$_2$ layers for a limited volume of WO$_3$ increases the probability of forming incomplete cylinders around the MWCN template, leading to numerous layer defects.$^{26}$

Simulation of a single-layered WS$_2$-coated MWCN (Fig. 5(a)) was achieved using Cerius’ software. Calculations indicated that the WS$_2$ nanotube required a (90,–14) vector in order to satisfy the determined 8.5° helicity and 8.4 nm diameter (Fig. 5(b)). The simulations were simplified by bisecting the model along its axis into 2 half cylinders and by omitting the MWCN. The TEM simulations were performed on one half of the model (Fig. 5(c)), and revealed the nature of the striations leading to tadpole-like fringes at the edge of the tube, separated by ca. 2.7 nm. When TEM simulations were performed for a complete (90,–14) tube, a number of large hexagonal fringes appeared as a result of interference arising between the overlap of the front and rear parts of the tube (Fig. 5(d)), which is consistent with the complex hexagonal fringes observed within the actual TEM images of the (90,–14) WS$_2$ nanotube (Fig. 5(a)).

We recently reported that several factors might influence the formation of the WS$_2$ layers.$^{16}$ In particular, their formation would be limited by the MWCN morphology, the strain energy for forming small diameter WS$_2$ nanotubes,$^{27}$ and the thickness/coverage of the MWCNs initially covered with WO$_3$. We find that the axial flexibility of WS$_2$ is comparable to that of carbon in the 5–40 nm diameter range. Although no specific MWCN tip geometry is found to be favourable for WS$_2$ coating, the MWCN tips are frequently incompletely coated. Figure 6 shows a single-walled WS$_2$-coated MWCN, the partial coverage of which suggests that the tip was only partly covered with WO$_3$. In fact, a clean MWCN surface is observed in the image where no WO$_3$ remained (Arrow A). There are areas where the WO$_3$ coverage supported the formation of WS$_2$ (Arrow B), which appears, itself, to be covered by an amorphous material. EDX analysis confirmed the presence of W, S, C and small quantities of O. It is probable that this amorphous layer consists of unreacted WO$_3$, or a reduced form, i.e., WO$_2$–, which cannot support the generation of a complete WS$_2$ layer. Nevertheless, the WS$_2$ lattice fringes can be discerned in regions of the amorphous coating (Arrows B and C).
We found that the smallest MWCN diameter to be coated by a single layer of WS$_2$ was ca. 7 nm, which is consistent with current reports of small-diameter MX$_2$ nanotubes.\textsuperscript{22,28,29} However, the arc production of MWCN usually produces large-diameter tubes that lead to large-diameter WS$_2$ coatings, according to the template growth of WS$_2$ particles/tubes.\textsuperscript{18,23} In an attempt to generate smaller diameter WS$_2$ coatings, SWCN bundles, which often have diameters ca. 5–35 nm, were also used as templates. TEM revealed that the sample contained numerous multiwalled WS$_2$ nanotubes, WS$_2$ particles and SWCN bundles. The formation of long WS$_2$ nanotubes from the amorphous tungsten oxide precursors is unlikely.
Therefore, it is possible that WS\textsubscript{3} nanotubes grow via SWCN bundles as templates, similar to MWCNs. If SWCN bundles have acted as templates for WS\textsubscript{3} nanotube growth, WS\textsubscript{3} nanotubes should contain SWCN bundles.

HRTEM revealed that several of the multiwalled WS\textsubscript{3} nanotubes actually contain SWCN-like fringes (Fig. 7). These tube-like fringes are separated by ca. 1 nm and do not lie parallel to the basal plane fringes of WS\textsubscript{3}. We distinguish these fringes from WS\textsubscript{3} lattice interference, as the appearance of complex localised details of the WS\textsubscript{3} tube can be observed through the SWCN-like fringes. Figure 7 (insert) reveals that the W atom diffraction spots appear throughout the centre of the tube, even through the SWCN-like fringes without diminished details, reinforcing the concept that the heaviest elements scatter the electron beam more strongly in the order: W > S > C. Unfortunately, EDX only revealed the presence of W, S and a small quantity of C, when focused on a WS\textsubscript{3} nanotube containing these fringe-like details.

Interference from adjacent WS\textsubscript{3} layers, due to different chiralities, will produce lattice interference patterns throughout the length of the tube and not within a localised area (Fig. 8).\textsuperscript{,22} This result has also been demonstrated by TEM simulations of chiral WS\textsubscript{3} nanotubes,
Fig. 7. HRTEM image of a WS$_3$ nanotube that contains SWCN-like fringes. The insert reveals that the diffraction spots of WS$_3$ appear throughout the tube length and across the SWCN fringes.

Fig. 8. TEM image of a WS$_3$-coated SWCN bundle. Magnified area shows the SWCN models contained within the WS$_3$ nanotube.
where the complex patterns are not confined to a particular region within the nanotube core, but appear throughout the central region.\cite{26} Moreover, TEM defocusing indicated that these tube-like fringes were observable within a narrow range located near the centre of the tube. However, SWCNs were frequently observed lying outside the WS\textsubscript{2} nanotubes, their structures collapsing after 5 min exposure to intense electron irradiation. During this study, WS\textsubscript{2} nanotubes containing the SWCN-like fringes were observed for ca. 10 min, and did not affect the structure. We surmise that the WS\textsubscript{2} nanotube acts as a protective sheath for the SWCNs.

As the WS\textsubscript{2} nanotubes are generated by the deposition of WO\textsubscript{3} on the SWCN bundle template, it is reasonable to assume that the entire core of each WS\textsubscript{2} nanotube would be filled with SWCNs. We presume, therefore, that the SWCNs are oxidised when oxygen is released from WO\textsubscript{3} during the sulphidisation step; this would account for the small number of WS\textsubscript{2} nanotubes containing SWCN-like fringes.

The TEM study revealed the presence of numerous WS\textsubscript{2} structures exhibiting complex symmetry.\cite{25} Figure 9 shows a highly curved WS\textsubscript{2} nanotube, with an inner diameter of ca. 5 nm at its narrowest point, consistent with a small SWCN bundle diameter, although there are no discernible SWCN fringes. As few small-diameter WS\textsubscript{2} nanotubes have been observed previously, it is likely that these structures are stabilised by successive layers,\cite{25,26} and that numerous lattice defects and dislocations are observed in the layers. Other types of WS\textsubscript{2} structures were also observed. For example, several nanoflasks (Fig. 10) and nanocages (Fig. 11) were also present, both exhibiting open and closed ends. Although it is difficult to explore any relationship between the SWCN bundles and the WS\textsubscript{2} nanostructures, due to the small number of WS\textsubscript{2} tubes that exhibit SWCNs, we believe that the WS\textsubscript{2} forms in a similar fashion to WS\textsubscript{2}-coated MWCNs, through a template mechanism. However, the

![TEM image of a complex WS\textsubscript{2} nanostructure.](image)

Fig. 9. TEM image of a complex WS\textsubscript{2} nanostructure.
structure of WS$_2$ can be markedly different from that of pure WS$_2$ nanotubes, because the morphologies are highly irregular. This is attributed to the deposition of WO$_3$ on the initial shape of the SWCN, which is reflected in the final WS$_2$ structure.

3. Conclusions

The synthesis of WS$_2$ from WO$_3$ and the underlying formation mechanisms have been well established. We find subtle differences between the formation of pure WS$_2$ nanotubes and template-controlled WS$_2$ nanostructures, such as crystallographic phase transformation and directional growth. We note that the template controls the morphology of the coating structure and that the helicity of the WS$_2$ coating layers is not obviously related to the helicity of the MWCN outer layer.
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References