WS₂ layer formation on multi-walled carbon nanotubes

1 School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, BN1 9QJ, UK
2 Department of Materials Science & Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ, UK

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ABSTRACT Time-dependent powder X-ray-diffraction analyses reveal that the conversion of WO₃ into WS₂ on carbon nanotube surfaces in the presence of H₂S is a one-step process. The WS₂ layers grow simultaneously along the tube in the radial and axial directions.

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1 Introduction

The production of WS₂ nanotubes and nanoparticles, first achieved by heating WO₃ nanoparticles at 800–1000 °C in the presence of H₂/H₂S (sulphidisation) [1], has recently been extended to WO₃–x and WC precursors [2–4]. X-ray-diffraction (XRD) studies, coupled with high-resolution transmission electron microscopy (HRTEM), have shown that the WO₃ particle surface is first reduced to WO₃–x (x = 1 and 2), followed by conversion into hexagonal layered WS₂ [3, 5]. The reactant gases (H₂ and H₂S) diffuse through the lattice defects in the outer WS₂ layers in order to continue the WO₃ → WO₃–x → WS₂ process. This ‘inward’ sequential layer growth process is terminated when the core is fully converted into WS₂. The morphology of the precursor essentially determines that of the product, i.e. a template effect operates [5]. The diffusion of H₂ and H₂O through defects in the formed WS₂ layer is a slow process, which requires extended periods of sulphidisation in order to complete the WO₃ → WS₂ conversion. Residual WO₃–x is always present in the product, as revealed by powder XRD analysis [2].

Sloan et al. showed that, by annealing WO₃–(2.5–2.9) nanorods in the presence of H₂/H₂S, other reduced tungsten oxide phases may also be generated and encapsulated within WS₂ particles [6]. HRTEM revealed that the tungsten oxide particle surfaces were converted into layered WS₂, and that WO₃–x crystalline lattice fringes were present within the core, together with numerous crystallographic shear planes and voids between the WO₃–x core and the outer WS₂ layers.

Recently, we produced WS₂-coated multi-walled carbon nanotubes (MWCNs) [7]. HRTEM analyses indicated that the ‘inward’ growth mechanism is in competition with an ‘outward’ growth mechanism on the MWCN surfaces. The ‘outward’ process is presumably facilitated by facile diffusion of H₂S through the thin and highly defective layers of WO₃ supported by the MWCNs [8]. In this paper, we probe this direct transformation of monoclinic WO₃ into hexagonal WS₂, without involving the intermediate species, i.e. WO₃–x.

2 Experimental

Tungstic acid (H₂WO₄, 250 mg) was mixed in liquid ammonia at −78 °C. Arc-generated MWCNs (50 mg) were added and the mixture was allowed to attain room temperature. The production of WS₂-coated MWCNs was carried out in three stages. Stage I: the solid residue, remaining after the excess of liquid ammonia had evaporated, was heated at 350 °C for 15 min in an air flow (100 cm³ min⁻¹), in order to convert the H₂WO₄ into WO₃. Stage II: the mixture was annealed at 900 °C under a N₂ flow (50 cm³ min⁻¹) for 15 min. Stage III: H₂S gas (10 cm³ min⁻¹) was introduced at 30-s intervals per min for a total of 6 min. The solid residue was then subjected to HRTEM (Philips CM200 and JEOL 4000EX-II) and powder XRD (Siemens Diffractometer D5000, Cu Kα = 1.5418 Å).

3 Results and discussion

3.1 Stage I – amorphous WO₃-coated MWCNs

The WO₃-coated MWCNs were heated at 350 °C in an air flow for 15 min, prior to sulphidisation. A typical example of the product is shown in Fig. 1a. The coating appears to be amorphous and is unevenly distributed over the surface of the MWCNs. Difficulties in distinguishing between the MWCN surface and the amorphous coating may have been exacerbated by the loss of the WO₃ coating during TEM operation. It is noteworthy that the arc-generated MWCNs are often coated with amorphous carbon. Our MWCN sample was annealed at 350 °C for 15 min in air, in order to remove the amorphous carbon coating [9]. Accordingly, the MWCN surface should be coated with WO₃, as confirmed by energy dispersive X-ray (EDX) spectra (see below). HRTEM showed that the WO₃ coating varies in thickness (from 0 to 2 nm) along the MWCN surface, and that the inner-core structure of coated MWCNs is still visible (Fig. 1a, arrow). Large
carbon particles also exhibited similar amorphous coatings. EDX analyses were conducted on both coated and uncoated MWCNs. The uncoated MWCNs showed only the C signal, whereas coated MWCNs showed C, W and O signals (Fig. 1b). The thickness of the WO$_3$ coating facilitates formation of up to two WS$_2$ layers on the MWCN surface, assuming a $\sim 6.2$-Å separation along the c axis for WS$_2$ and a $\sim 4.4$-Å separation between the WS$_2$ layer and the outermost carbon layer [7].

XRD analysis of the WO$_3$-coated MWCNs annealed at 350 °C revealed the presence of several small reflections (Fig. 2a), which makes the assignment of a crystal system to WO$_3$ difficult. However, the peaks which appear at low angles are correlated with monoclinic lattice arrays and are present in a predominantly amorphous sample; the 002 reflection, arising from MWCNs at $\sim 2\theta = 26.5^\circ$ (i.e. a value similar to that previously reported for pure MWCNs) [10], overlaps slightly with WO$_3$.

### 3.2 Stage II – annealed WO$_3$-coated MWCNs

Amorphous WO$_3$-coated MWCNs were annealed at 900 °C under N$_2$ for 15 min. At this stage the resulting solid contains WO$_3$-coated MWCNs, bare MWCNs and WO$_3$ particles. The XRD profile of annealed WO$_3$-coated MWCNs (Fig. 2b) shows that the WO$_3$ reflections mostly overlap with MWCNs. The only visible peak for MWCNs is the 002 reflection at $\sim 2\theta = 26.5^\circ$ (Fig. 2b, arrow). XRD indicates that the WO$_3$ structure has a well-defined monoclinic phase; reflection intensities are much stronger than those of stage I and match the computer-simulated powder XRD pattern of a WO$_3$ monoclinic crystal (Fig. 2c) [11]. However, HRTEM failed to reveal distinct lattice fringes for WO$_3$ coating the MWCNs (previously observed in pure WO$_3$ nanocrystals) [6], possibly for the following reasons. First, the MWCN lattice fringes interfere with WO$_3$. Secondly, the crystal growth on a planar substrate is linear with respect to the $x-y$ and $y-z$ planes. The MWCN surface is curved, implying that the stacking of W and O atoms to form crystal structures can only be achieved locally on the MWCN surface. If the localised WO$_3$ crystal domains are not well aligned to the incident beam, or are covered by amorphous WO$_3$, distinct WO$_3$ lattice fringes will not emerge. Meanwhile, determination by HRTEM of the