WS₂ layer formation on multi-walled carbon nanotubes

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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 then 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 $d$ spacing along the $c$ axis for WS$_2$ and a $\sim 4.4$-Å separation between the innermost WS$_2$ layer and the outermost carbon layer [7].

XRD analysis of the WO$_3$-coated MWCNs annealed at 350 $^\circ$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 $\sim \theta = 26.5^\circ$ (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 $^\circ$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 $\sim \theta = 26.5^\circ$ (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
The annealed WO₃-coated MWCNs were heated at 900 °C in the presence of H₂S/N₂ (flow rate 100 cm³ min⁻¹; H₂S : N₂ ratio ~ 1 : 4), with intervals up to a total H₂S exposure time of 6 min. The XRD graphs of 0-, 2-, 4- and 6-min sulphidisation periods are displayed in Fig. 3, in which the major reflections due to WO₃, WS₂ and MWCN are labelled.

3.3.1 2-min sulphidisation (Fig. 3). As a result of 2-min sulphidisation, the intensities of all WO₃ reflections are reduced by ~ 20%. A small peak, corresponding to 002 reflections of WS₂, is present at this stage, indicating that H₂S has begun to replace O atoms by S in the WO₃ coating and particles. Surface substitution of O by S will result in the presence of partial oxygen vacancies in the lattice arrays, and hence to maintenance of a monoclinic system with low-intensity peaks [6]. This outcome is consistent with the concept that the type of crystal lattice determines the peak distribution and that the atomic arrangement determines the reflection intensity [12].

3.3.2 4-min sulphidisation (Fig. 3). The WO₃ reflections 002, 020, 200 and 222 decreased to ~ 20% of their original intensity, whereas the WS₂ 002 reflection intensities were ~ 10 times stronger than those associated with 2-min sulphidisation (blue). Due to overlap with the 100 and 101 WS₂ peaks, the extent of the intensity decrease in the 220 and 022 WO₃ peaks is unclear. A similar situation occurs for the 112 WO₃ peak. Other WS₂ peaks, including 103, 110 and 112, have become visible. The 002 MWCN peak remains unchanged.

3.3.3 6-min sulphidisation (Fig. 3). The WO₃ reflections are reduced to ~ 5% of their original intensity. The thin defective WO₃ coating allows H₂S diffusion and would therefore facilitate transformation into WS₂. The peaks corresponding to the remaining WO₃ could also arise from separate WO₃ structures in the sample, which can still be detected after 10-min sulphidisation. However, the XRD reflections are now predominantly WS₂, which exhibits a well-defined crystal structure. The WS₂ peak intensities and positions are strong and consistent with those of pure WS₂ nanotubes [2]. According to HRTEM investigations, ~ 1–5 WS₂ layers coat the MWCNs (i.e., Lc is ~ 3–4 nm), which is smaller than the number found in separate WS₂ particles (> 7). Therefore, the XRD reflections to WS₂, which exhibits a well-defined crystal structure. The WS₂ peak intensities and positions are strong and consistent with those of pure WS₂ nanotubes [2]. 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ture. Meanwhile, as WS₂ forms, the oxidation state for W in WO₃ [M⁶⁺ (d⁰)] is reduced to M⁴⁺ (d²) [13]. A previous study demonstrated that WO₃ was reduced in the initial stages of the reaction [5]. Intermediate WO₃−ₓ species represent partial movement of W atoms (leading to the final structure), which have been identified by XRD and HRTEM [5, 6]. Meanwhile, W centres have been detected in pure WS₂ nanostructures, where reduction is complete [14].

Replacement of O by S in WO₃ requires a 63% lattice expansion (~0.24 nm) along the O–W–O (011) plane, and a 15% contraction along the (002) plane in monoclinic WO₃ (P₁₂₁/n1) respectively [11], in order to achieve the 0.62-nm (002) S–W–S basal plane spacing in WS₂ (P₆₃/mmc) (Fig. 4, right) [15]. The lattice expansion implies that a 1.5-nm-thick WO₃ coating may generate up to four WS₂ layers. The ‘inward-growth’ model means that the WO₃ monoclinic lattices can only expand inwards, leading to compression of the remaining inner core. This inner core compression may result in the crystallographic shear planes, reported previously by Sloan et al. [6]. In our sample, the WO₃ shear planes are not visible on the MWCN surfaces. Due to the thin defective WO₃ coating, the H₂S diffusion into the WO₃ lattice, which leads to WO₃ → WS₂ conversion on the MWCN surface, most probably occurs simultaneously along the radial (Fig. 5, c) and axial directions (Fig. 5, a). The simultaneous WS₂ layer formation of WS₂ layers along both axes means that the inward compression can be minimised along the axial direction, and the need for crystallographic WO₃ shear plane formation obviated. In a previous study, we found that the WS₂ coating layers exhibited helical structures and that the WS₂ tube helicity did not correlate with MWCN lattices [7]. The absence of lattice correlation between the WS₂ coating and the MWCN surface is possibly due to the large 0.44-nm separation [7]. The WS₂ helicity is unique throughout the tube structure, as revealed by electron diffraction [7], which supports the simultaneous WS₂ layer formation along the radial and axial directions on MWCNs. If the WS₂ layer formation were achieved via the melding of localised WS₂ layered domains, the WS₂ helicity is less likely to be uniform and one might expect various sections of the WS₂ shells to exhibit a range of helicities. In order to determine the extent of WS₂ formation on MWCN surfaces, time-dependent XRD analyses were carried out on sulphidised WO₃-coated MWCNs in 30-s intervals (Fig. 6). The extent of WS₂ layer growth along the c axis versus reaction time is also shown (Fig. 6, inset), which was obtained from the full width at half maximum (FWHM) of the WS₂ 002 peak [10]. The graph of WS₂ layer growth along the c axis can be divided into four regions, i.e. a (grey), b (blue), c (red) and d (green). No WS₂ was detected between 0 s and 50 s (region a), which is consistent with the real-time XRD data; i.e. no WS₂ in-plane Lₐ (e.g. 110, 100) and along the c axis Lₖ (e.g. 002, 103) reflections are present (Fig. 6). However, all WO₃ reflection intensities, e.g. 200, 020, 002, 022, 220, 222 and 112, decreased within the first 50 s. The WS₂ layer begins to form after 50 s, supported by the presence of a small WS₂ (002) peak (Fig. 6). Between 50 s and 120 s (i.e. region b), the intensity of WO₃ reflections continuously decreases and other WS₂ reflections are still absent. It is noteworthy that the XRD analysis shows only a slight increase

**FIGURE 5** Simultaneous growth model of WS₂ layers along the carbon nanotube radial (c) and axial (a) directions

**FIGURE 6** Time-dependent XRD profiles of sulphidisation in 25-s intervals (inset: WS₂ layer extent versus time)
in WS₂ (002) peak intensity (50–120 s, Fig. 6); however the number of WS₂ layers has already reached 10 (region b, inset). The WS₂ (002) peak intensity increases significantly in the 120–200-s range, and other WS₂ peaks, e.g. 103, 110, 100 and 112 (Fig. 6), become visible. The number of WS₂ layers within region c increases by two (inset). The intensity of all WO₃ peaks decreases significantly in region c. The peak intensity and number of WS₂ layers in region d are similar to c. Figure 6 provides useful information regarding WO₃ transformation into WS₂ on MWCN surfaces. First, region (a) corresponds to the diffusion of H₂S into defective WO₃ coating layers. In previous reports, Feldman et al. pointed out that the 1–2 WS₂ layers formed rapidly on the oxide particle surface within a few seconds, inhibiting particle aggregation [5, 16]. In our experiments, the absence of WS₂ layer formation between 0 s and 50 s (i.e. region a) is possibly due to insufficient hydrogen, i.e. the reducing agent arises only from H₂S (see Sect. 2), which slows the rate of reduction of the oxide coating. The role of H₂ during WO₃ → WS₂ conversion has been described previously; it was found that an excess of H₂ is required in order to rapidly reduce WO₃ to WS₂ or WO₂.₇ (i.e. the intermediate phase) [16]. The presence of suboxides probably facilitates WS₂ formation, because the suboxides possess octahedral structures (similar to the WS₂ structure) enabling ready replacement of O by S [16]. In our experiments, region a shows no WS₂ layer formation, but provides a longer time for H₂S diffusion into the coating WO₃, prior to WO₃ → WS₂ conversion, which assists simultaneous WS₂ layer growth along the c (radial) and a (axial) directions (Fig. 5). Between 50 s and 120 s (i.e. region b), the rapid increase in the number of WS₂ layers (Fig. 6, inset) is consistent with the simultaneous WS₂ layer formation model along the c and a axes. Nevertheless, the WS₂ (002) peak intensity in region b shows only a small increase, as compared with region c (i.e. 120–200 s, Fig. 6). Meanwhile, it is noteworthy that the WS₂ 002 peak width in region b remains the same as that in region c, indicating that the number of WS₂ layers on the MWCN surfaces is the same for both regions. In other words, WS₂ growth on MWCN surfaces has already ceased in region b. Previous XRD profiles, based on the inward growth model of WS₂ particles, showed that the WS₂ peak intensity increases with WS₂ peak intensity, which decreases with time [5, 16]. The increase/decrease in WS₂ and WO₃ peak intensities respectively is due to the fact that more WO₃ is converted into WS₂ layers. In our experiments, WS₂ layer formation on MWCN surfaces is rapid, which means that region b should exhibit a rapid increase/decrease in WS₂ (002) and WO₃ peak intensities respectively. However, this phenomenon is not observed. According to XRD data, the monoclinic WO₃ structure dominates in the overall sample between 50 s and 120 s (i.e. region b), mainly arising from the unreacted WO₃. The question therefore arises as to what is the actual WS₂ structure in regions b and c, because the WS₂ 002 reflection exhibits the same peak width, with different intensities. The XRD intensity is determined by the type and position of the atoms within the unit cell; the larger the crystal lattice, the sharper the peak [12]. A small increase in WS₂ peak intensity (region b) implies that the S atoms have not yet fully occupied O vacancies, but that the host structure (monoclinic phase) has already been transformed into the hexagonal cell. Accordingly, the XRD peaks of region b mainly arise from W atoms. As time progresses, more S atoms can occupy the lattice vacancies and the XRD peak intensity increases. Previous workers [16] proposed a structure consisting of two W-centred octahedral units connected via an O atom, with O atoms missing at the upper and lower sites of a prismatic cell. This structure provides a preferential pathway for O–S substitution about the W centres via the O–W–O planes along the b axis towards the WS₂ 002 planes [13]. However, the proposed structure is based on the inward growth process. The simultaneous formation of WS₂ on MWCN surfaces provides no preferential pathway for O–S substitution, and all W atoms need to be relocated within the cell. The structure of the W/O/S in region a is complex and remains to be established. Figure 7 shows the corresponding structures of WS₂ in region b, in which adjacent W atoms are connected via O atoms, similar to the O–W–O plane along the c axis (Fig. 4, right). When O atoms are released from the lattices, the S atoms immediately occupy the vacancies. In region b, the O population is greater than that of S; more S atoms are present in the lattice as the reaction time is extended (region c). The presence of a slight increase in the WS₂ layer number in regions c and d possibly arises from other WS₂ particles, not WS₂-coated MWCNs, because the H₂S diffusion and O–S substitution can still proceed on other larger WO₃ particles.

In summary, the XRD study shows that the conversion of WO₃ into WS₂ is a one-step process. The WS₂ layers grow simultaneously along radial as well as axial directions and no intermediate phases are involved. Time-dependent XRD profiles show that the WS₂ growth on the MWCN surfaces ceases before 120 s have elapsed.

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