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To cite this article: Youhu Chen, Yunpeng Li, Yuanfei Wang, Tian Tian & Lu-Chang Qin (2017) Thin WS₂ nanotubes from W₁₈O₄₉ nanowires, Materials Research Letters, 5:7, 508-515, DOI: 10.1080/21663831.2017.1337050

To link to this article: <https://doi.org/10.1080/21663831.2017.1337050>



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Published online: 13 Jun 2017.



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ORIGINAL REPORT



Thin WS₂ nanotubes from W₁₈O₄₉ nanowires

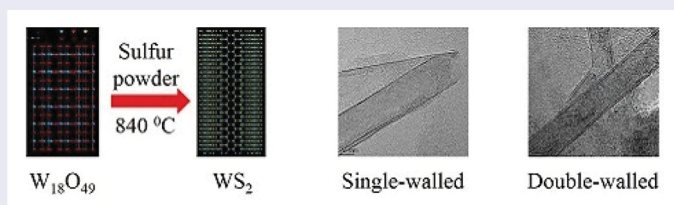
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ABSTRACT

Single- and double-walled WS₂ nanotubes of small diameter (< 10 nm) and few layers (< 4) have been synthesized by heating ultrathin W₁₈O₄₉ nanowires and S powders in an H₂/Ar atmosphere at 840°C. In the process of formation and growth of a WS₂ nanotube, the W₁₈O₄₉ phase transformed first into an amorphous WS₃ structure via the absorption and diffusion of the sulfur atoms to substitute the oxygen atoms, and followed by a phase transition from amorphous WS₃ to 2H-WS₂ by losing sulfur atoms to form the shell of the WS₂ nanotube.



IMPACT STATEMENT

Synthesis of thin WS₂ nanotubes with single- and doubled-walled structure from ultrathin W₁₈O₄₉ nanowires is developed and their structure and growth are studied using electron diffraction and microscopy.

ARTICLE HISTORY

Received 13 April 2017

KEYWORDS

WS₂; nanotube; electron diffraction; growth mechanism

1. Introduction

Following the discovery of fullerenes [1] and carbon nanotubes [2], it was soon realized that other inorganic compounds, having layered structures similar to that of graphite, could also form fullerene-like and nanotube structures. Metal dichalcogenides (MX₂, M = Mo, W, Nb, Hf; X = S, Se) are the typical example materials. Fullerene-like WS₂ nanoparticles and WS₂ nanotubes were first reported by Tenne et al. in 1992 [3]. Attention has also been drawn to other inorganic nanotubes since then owing to their interesting properties. Substantial progress has been made and demonstrated that MoS₂ and WS₂ nanotubes have great potential for applications in scanning probe microscopy [4,5], lubrication [6], catalysis [7,8], field-effect transistors [9], nanocomposites [10], and energy storage [11,12].

Several experimental methods have been explored to synthesize WS₂ nanotubes, including gas–solid reactions

[3,13–20], chemical transport [21,22], irradiation activation [23–25], sulphurization of tungsten film [26], and the solution route [27]. Most of the synthetic methods are based on high-temperature gas–solid reactions, where hydrogen and hydrogen sulfide or sulfur and metal oxide precursors were used as the reactants [20]. However, a common feature of these WS₂ nanotubes is that they all have relatively large diameters and always have more than five layers, resulting in a low-specific surface area.

Theoretical calculations using the density functional tight-binding theory have shown that MoS₂ nanotubes with an outer diameter larger than about 6 nm are more stable than nanostrips of comparable width [28]. Therefore, the threshold for the outer diameter of single- to four-walled nanotubes is 6.45, 7.13, 7.61, and 8.59 nm, respectively. WS₂ nanotubes are structurally analogous to MoS₂ nanotubes. Hence, the synthesis of WS₂ nanotubes of small diameter (< 10 nm) and few shells (< 4) has been

considered a great experimental challenge. Whitby et al. [29] reported use of multi-walled carbon nanotubes as templates for synthesis of single-walled WS₂ nanotubes. As for template-free methods, it was concluded that the generation of such thin nanotubes requires highly exergonic conditions to drive the reactions into windows of stability far enough from equilibrium, such as using laser ablation [25]. However, it was also suggested that these thin nanotubes were not obtainable by the conventional thermally driven process (< 1000°C), which is not sufficiently exergonic.

In this work, we use ultrathin W₁₈O₄₉ nanowires as the precursor to grow thin WS₂ nanotubes. The major advantage of our method is that the ultrathin W₁₈O₄₉ nanowires would serve directly as the templates for the formation and growth of WS₂ nanotubes. Since the W₁₈O₄₉ phase is non-volatile, the produced WS₂ nanotubes would retain the morphology of their template and a diameter below 10 nm would be reachable. As a result, both single- and few-walled WS₂ nanotubes have been obtained successfully using this method, where the W₁₈O₄₉ nanowires were reduced by sulfur powders in the reducing H₂/Ar atmosphere at about 840°C. It is therefore demonstrated that thin WS₂ nanotubes are obtainable by the conventional thermally driven process of synthesis. The structure of and growth mechanism for the thin WS₂ thin nanotubes are also studied.

2. Experimental

We obtained WS₂ nanotubes in a two-step process. In the first step, ultrathin W₁₈O₄₉ nanowires were prepared. In a typical procedure [30], 25 mg of WCl₆ was dissolved in 20 ml of ethanol and subsequently transferred to a Teflon-lined stainless steel autoclave heated to 180°C for 24 h. The obtained solution was then centrifuged and purified with ethanol for five times before the precipitates were collected. In the second step, 2 mg of W₁₈O₄₉ nanowires were first dispersed in 10 ml of ethanol. A quartz burette was then dipped into the ethanol solution to collect the W₁₈O₄₉ nanowires for reactions with sulfur powders at 840°C in a furnace for 3 h to allow the formation and growth of WS₂ nanotubes.

Transmission electron microscopy (TEM) images and electron diffraction patterns (EDPs) were obtained with Tecnai F20 operated at an accelerating voltage of 200 kV. Nano-beam electron diffraction (NBED) patterns were obtained by using a nearly-parallel nano-probe, which was generated under the microprobe mode with the usage of a smallest 30 μm condenser aperture. The diameter of a typical nano-beam electron probe is ~ 50 nm.

3. Results and discussion

Figure 1(a) shows a powder X-ray diffraction (XRD) pattern of the tungsten oxide nanowires which are in the monoclinic W₁₈O₄₉ structure (PDF#05-0392). The broadened reflections are attributed to the small crystallites. The low-magnification TEM image (Figure 1(b)) revealed that the nanowires had large aspect ratios and lengths of up to several microns. A low precursor concentration ($C_{\text{WCl}_6} \leq 5$ mg/ml) resulted in ultrathin and well-dispersed nanowires [30]. Selected-area electron diffraction (SAED) patterns showed the (010) and (020) reflections of W₁₈O₄₉ in agreement with the XRD analysis. The high-resolution transmission electron microscopy (HRTEM) images of individual nanowires demonstrated that the nanowires were single-crystalline and always grown in the [010] direction (Figure 1(c)). The *d*-spacing of the (010) lattice planes is 0.38 nm. Figure 1(d) shows the crystal structure of W₁₈O₄₉ and its [100] projection.

Figure 2(a) shows a HRTEM image of a single-walled WS₂ nanotube with a diameter of about 12 nm, which is larger than the threshold diameter of 6.45 nm. The additional wall (indicated with black arrow) is due to the folded edge of a nano-platelet, which was confirmed by comparing the power spectra of the two different regions (I and II). Careful examinations of the power spectra of the image reveal that this single-walled nanotube has a structure close to the zigzag configuration, which renders smaller folding energy in comparison with chiral nanotubes. Double-walled WS₂ nanotubes were also often observed in the samples. Figure 2(b) shows an HRTEM image of two double-walled WS₂ nanotubes. The outer and inner diameters of the smaller nanotube are 7.29 and 5.89 nm, respectively. The outer diameter is also beyond the threshold value of 7.13 nm for double-walled nanotube. It should be noted that the interlayer separation of this nanotube is different at the two sides with one side being 0.64 nm and the other 0.76 nm, suggesting that this nanotube has two nonconcentric shells. The interlayer separation of bulk 2H-WS₂ crystals is 0.62 nm and the interlayer separation multi-walled WS₂ nanotubes varied between 0.63 and 0.65 nm [25]. Since the outer diameter is 1.4 nm larger than the inner diameter, the closer contact of one side would lead to a larger separation of the other side. The NBED pattern (Figure 2(c)) and the power spectrum (inset of Figure 2(b)) obtained from this small nanotube reveal that both shells exhibited an arm-chair structure. The thicker double-walled nanotube has outer and inner diameter of 11.04 and 9.67 nm, respectively. The interlayer distance of one side is 0.64 nm, while the other is 0.73 nm.

Figure 3(a) shows an HRTEM image of a triple-walled WS₂ nanotube and the inset is an EDP revealing three

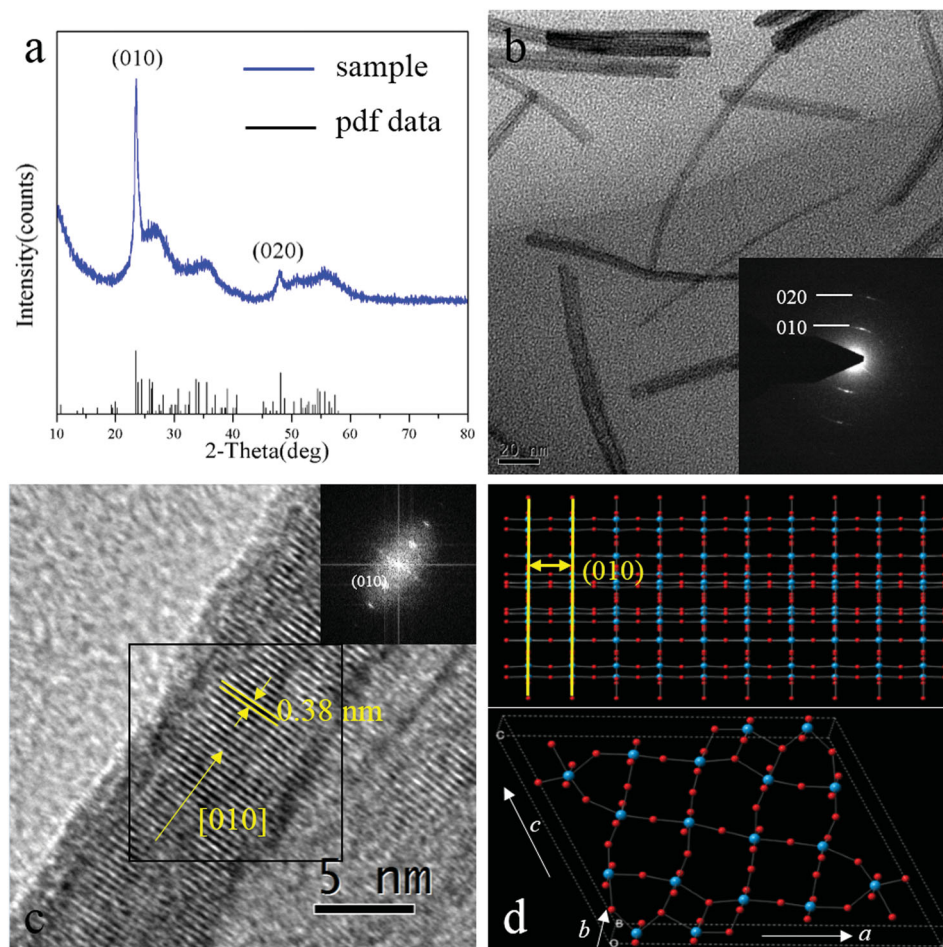


Figure 1. (a) XRD pattern of prepared $W_{18}O_{49}$ nanowires (blue line) is plotted against the crystal data (PDF#05-0392), which showed an excellent agreement. (b) Low-magnification TEM image of the $W_{18}O_{49}$ nanowires. Inset: SAED pattern of $W_{18}O_{49}$ nanowires. (c) High-resolution TEM image of individual nanowires displaying the (010) lattice spacing of 0.38 nm. Inset: Corresponding power spectrum of the selected area. (d) Structural model of the $W_{18}O_{49}$ phase: viewed in the [100] direction (top) and a unit cell (bottom).

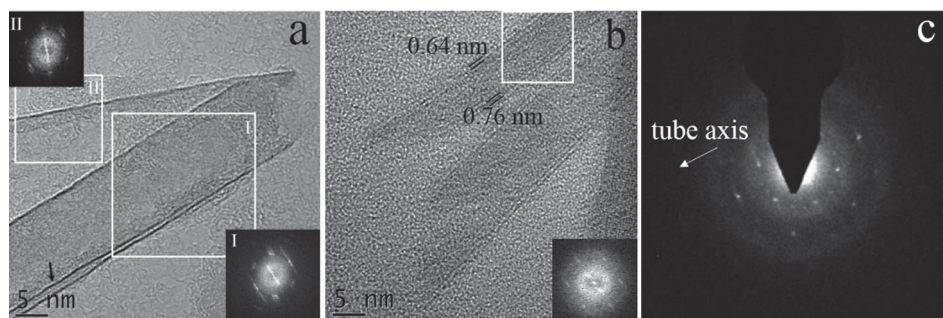


Figure 2. (a) HRTEM image of a single-walled WS_2 nanotube. Insets: Power spectra of selected area marked with I and II in the image, respectively. (b) HRTEM image of two double-walled WS_2 nanotubes. Inset: Power spectrum of the selected area. (c) NBED pattern of the smaller nanotube in (b) revealing that the nanotube has an armchair structure.

different helical angles. It is noticed that the diameter of each shell varied at different locations. The diameter of the inner, middle, and outer shell was measured between 10.3–12.0, 12.5–13.8, and 14.8–16.6 nm, respectively. The interlayer separation varied between 0.64 and 1.6 nm. The morphology of this nanotube deviated from

the ideal cylindrical structure of multi-walled WS_2 nanotube, which would consist of concentric shells with a single interlayer distance of 0.62 nm. An extra dark line (indicated by arrow) is attributed to an incomplete shell, which did not grow fully to completion. The helical angles of this nanotube were determined accurately from

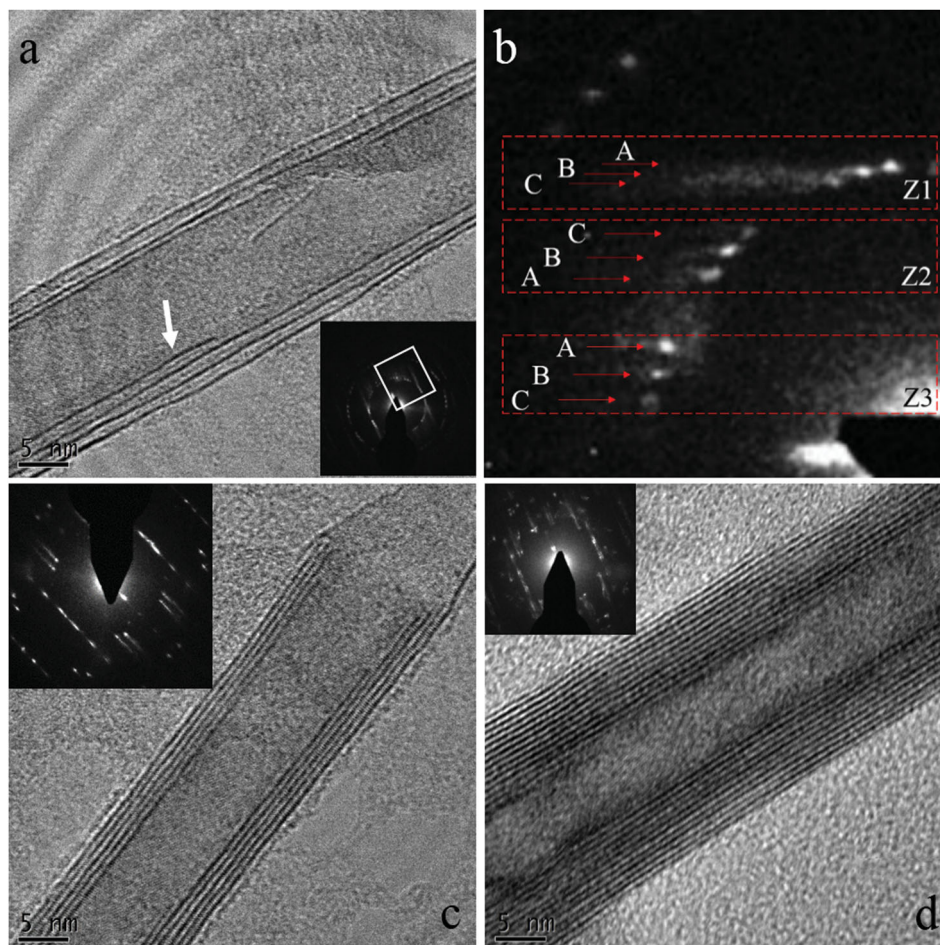


Figure 3. (a) HRTEM image of a triple-walled WS_2 nanotube. Inset: NBED pattern obtained from the nanotube. (b) Magnified portion of the enclosed region of the inset in (a). The diffraction space is divided into three zones labeled as Z1, Z2, and Z3, which are indicated by the dashed rectangles in the figure. The reflection layer line due to the same contributing shell of the nanotube is indicated by the same letter (A, B, or C) in different zones. (c) HRTEM image of a quintuple-walled WS_2 nanotube. Inset: NBED pattern of this nanotube. (d) HRTEM image of a multi-walled WS_2 nanotube with corresponding NBED pattern of the nanotube shown in the inset.

the NBED pattern [31–34]. Figure 3(b) displays a magnified portion of the diffraction layer lines where three groups of layer-lines are classified, from which the helical angles for these three shells are 19.9° (inner shell), 13.2° (middle shell), and 7.4° (outer shell), respectively, indicating that this nanotube consisted of three shells of different helicity. Since the electron scattering intensities due to each shell are proportional to the diameter of nanotube, the integrated intensities of each layer line can also be used for the identification of the contributing shell. As displayed in Figure 3(b), the layer lines in Group A have the highest reflection intensities and group C has the lowest. Hence, the final assignment of helical angle for outer, middle, and inner shell is 7.4° , 13.2° , and 19.9° , respectively. It is also noted that the helical angles have a wide distribution, indicating that there was no strong correlation in the growth of respective shells.

The sulphurization of thicker $\text{W}_{18}\text{O}_{49}$ nanowires would usually result in multi-walled WS_2 nanotubes of

more than five shells. Figure 3(c) shows an HRTEM image and NBED pattern (inset) of a quintuple-walled WS_2 nanotube. The outermost and innermost diameter is 13.72 and 8.34 nm, respectively. The helical angle of this nanotube is in 4.1° – 5.5° . Figure 3(d) shows an HRTEM image and NBED pattern of another thick WS_2 nanotube (> 10 shells), which has the outermost and innermost diameter of 20.39 and 7.93 nm, respectively, with an average inter-shell spacing of 0.62 nm. The helical angle is in a range of 15.9° and 20.5° . Similar features have also been observed in other multi-walled WS_2 nanotubes in this study. The inter-shell spacing varied between 0.62 and 0.65 nm and the smallest innermost diameter was even below 5 nm. Since the inter-shell spacing is close to the corresponding lattice spacing of the bulk 2H- WS_2 phase and the chiral angle has a relatively narrow range, it seems natural that the synthesized shell formed earlier would serve as a template for the formation and growth of fresh shells [35].

To gain insight into the growth mechanism for the WS₂ nanotubes, the morphology and structure of one incipient nanotube was studied. Figure 4 shows the TEM images of a nanotube with diameter of 40 nm, where the oxide was encapsulated by sulfide shells. The TEM images (Figure 4(a,c)) revealed that this nanotube had

one end open and the other closed and it was covered with two to three layers of WS₂ with *d*-spacing of 0.62 nm, in conformation with the (002) spacing of the 2H-WS₂ structure. The sulphurization should have started from outside and from the ends to the middle of the nanowhisker, which is different from the observations

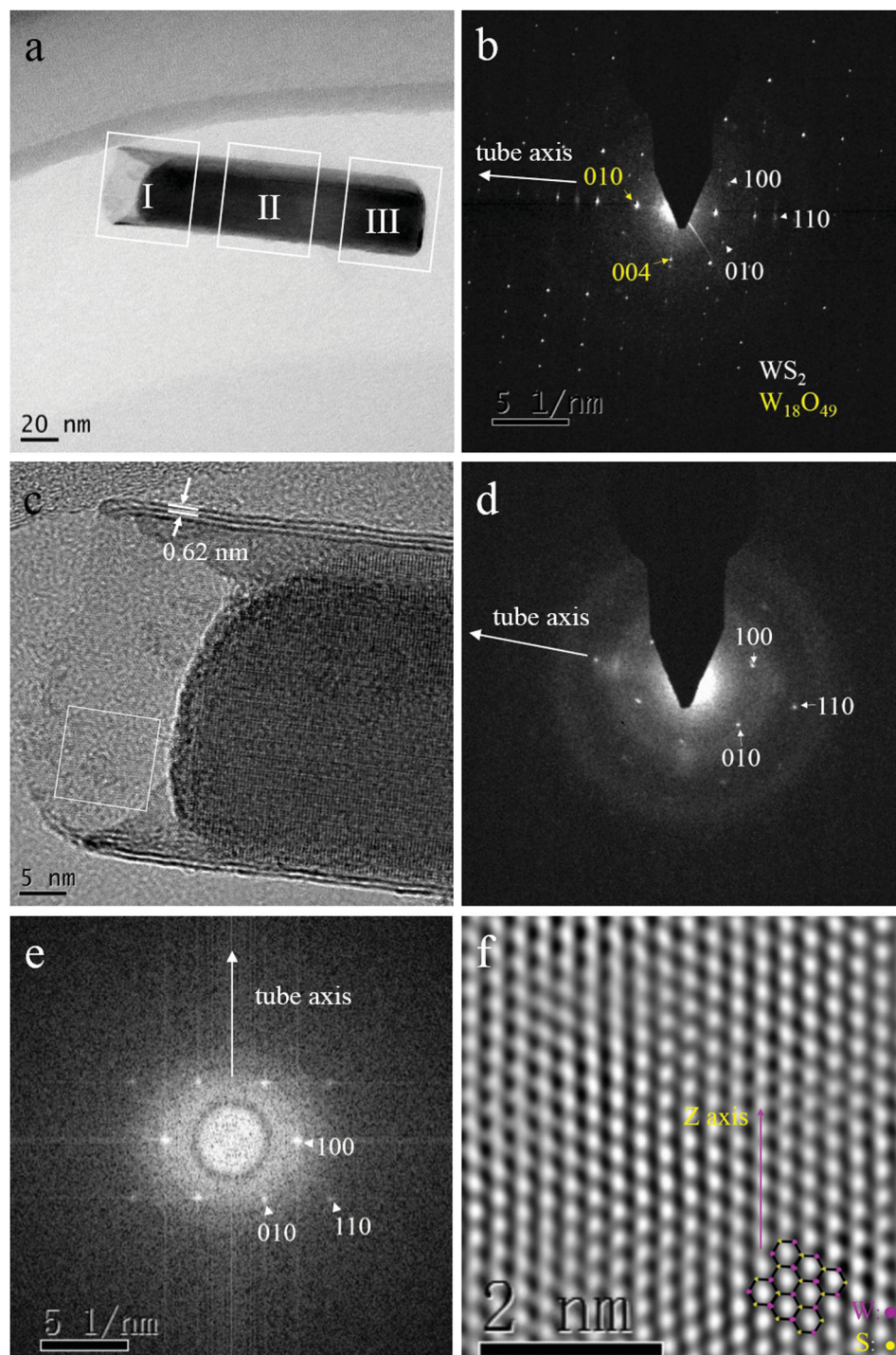


Figure 4. Characterization of a single WS₂ nanotube with crystalline oxide in the core. (a) Low-magnification TEM image. (b) SAED pattern of area II in (a). (c) HRTEM image of area I. (d) NBED pattern of thin area in (c). (e) Power spectrum of squared region in (c). (f) Fourier-filtered image.

of a previous report [20]. The space between the grown WS_2 shells provided a diffusion channel for S atoms for further sulphurization. The SAED pattern (Figure 4(b)) is a superposition of the Bragg reflections from both the sulfide shells and the oxide core. The (010) and (004) reflections (indexed yellow) are due to the $\text{W}_{18}\text{O}_{49}$ phase, while the (100) and (010) reflections (indexed white) pertain to the WS_2 phase. The diffraction pattern indicates that the oxide was single-crystalline. It should also be noted that electron diffraction analysis indicated that all shells have the same helical angle and are of an arm-chair structure. Figure 4(c) shows an HRTEM image of region I. The thin area shows only the WS_2 shells as indicated by the NBED pattern (Figure 4(d)). This result is also supported by an analysis of the Fourier-filtered images (Figure 4(e,f)). The Fourier-filtered image in Figure 4(f) reveals that the nanotube exhibited an arm-chair structure. The axial direction of the nanotube is also indicated in Figure 4(b,d–f).

The ultrathin $\text{W}_{18}\text{O}_{49}$ nanowires usually contained many oxygen vacancies—they provided reductive sites for the conversion of carbon dioxide into methane and isopropyl alcohol into propylene and also exhibited a ‘trapping’ effect to enhance the capture and adsorption of the substrate material [30,36]. In our study, the oxygen vacancies contained in the $\text{W}_{18}\text{O}_{49}$ nanowires also served as reductive sites and traps for catching S atoms from the atmosphere. Likewise, oxygen vacancies were not rich in the one-dimensional $\text{W}_{18}\text{O}_{49}$ nanostructures with relatively larger diameters [30]. These phenomena

give the explanations for why the reaction temperature required in our experiments was even below 840°C , while the needed temperature was above 1000°C in [15]. The energy for breaking the W–O bonds was also likely greater in the case when long and crystalline whiskers were used compared to the use of short semi-crystalline needle-like particles [16]. Based on these earlier studies, we believe that the reactions started from the oxygen vacancy sites and expanded into the remaining parts via the diffusion of S atoms. Since hydrogen does not reduce $\text{W}_{18}\text{O}_{49}$ further [20], its role is to prevent the further oxidation of $\text{W}_{18}\text{O}_{49}$ nanowires at the beginning and enhance the subsequent sulphurization.

In addition, the densities of $\text{W}_{18}\text{O}_{49}$ and 2H-WS_2 are 7.71 and 7.73 g/cm^3 , respectively, and the corresponding densities of W atoms in $\text{W}_{18}\text{O}_{49}$ and 2H-WS_2 are 6.23 and 5.73 g/cm^3 , respectively. If the mass of tungsten were to suffer no loss in the process of sulphurization, it cannot result in the formation of a hollow tubule with $\text{W}_{18}\text{O}_{49}$ converted directly into the 2H-WS_2 structure. Since the WS_2 nanotube always contained a hollow core, it suggests that a volume expansion must have occurred in the reactions. Furthermore, two-dimensional 2H-WS_2 platelets were also observed when the $\text{W}_{18}\text{O}_{49}$ nanowires were placed side by side on the substrate. Hence, we suggest that conversion of the W–O bonds into the W–S bonds would undergo initially the formation of amorphous WS_3 with inflated volume and followed by a phase transition to 2H-WS_2 with a loss of S atoms at a temperature close to 850°C according to the W–S phase diagram [37].

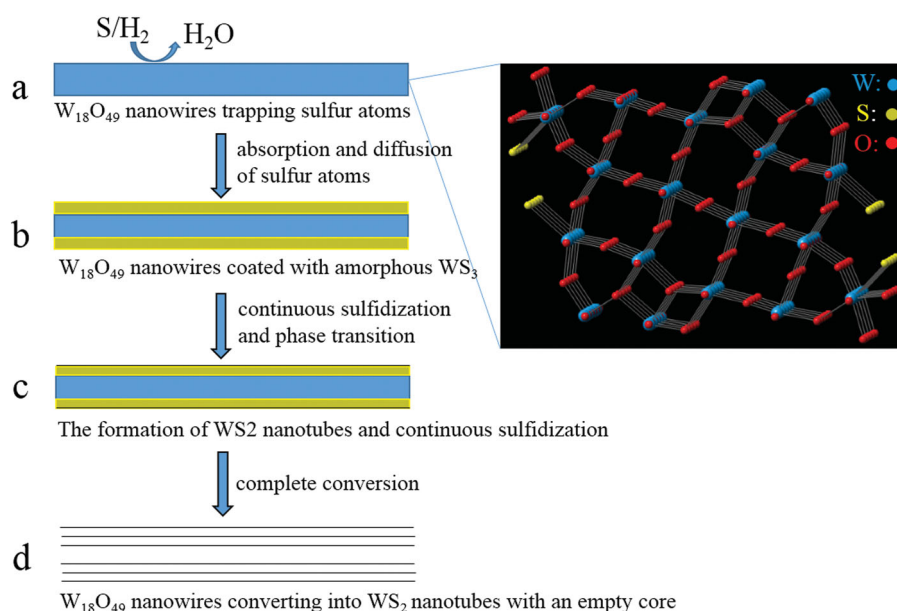


Figure 5. Illustration of the formation and growth of WS_2 nanotubes. (a) $\text{W}_{18}\text{O}_{49}$ nanowire precursor traps S atoms at oxygen vacancies. Inset shows O sites as traps for the absorption of S atoms, where the W, O, S atoms are indicated by color of blue, red, and yellow, respectively. (b) Formation of amorphous WS_3 leads to volume expansion. (c) $\text{W}_{18}\text{O}_{49}$ converts continuously to amorphous WS_3 , accompanied simultaneously by phase transition to 2H-WS_2 . (d) Complete conversion of a $\text{W}_{18}\text{O}_{49}$ nanowire to a WS_2 nanotube with a hollow core.

For ultrathin $W_{18}O_{49}$ nanowires, phase transition took place after the complete sulphurization. But for thicker $W_{18}O_{49}$ nanowires, sulphurization and phase transition could take place simultaneously. These are the reasons why the inner diameter of thinner nanotubes was always larger than that of thicker nanotubes. Figure 5 shows a schematic diagram illustrating the formation and growth of WS_2 nanotubes from $W_{18}O_{49}$ nanowires. It is remarkable that a good dispersion of $W_{18}O_{49}$ nanowires was essential to avoid tangling with each other in order to produce thin WS_2 nanotubes. Since the formation of thin WS_2 structure occurred locally, nanotubes consisting of single- to triple-walled would require ultrathin $W_{18}O_{49}$ nanowires as precursors. On the other hand, a precursor subject to starting temperature above 850°C would result in the formation of fullerene-like structures.

4. Conclusions

A route for synthesis of few-layer WS_2 nanotubes has been developed by heating ultrathin $W_{18}O_{49}$ nanowires together with S powders in an H_2/Ar atmosphere at 840°C to demonstrate that WS_2 nanotubes with fewer than three shells could be formed by conventional thermally driven synthesis below 1000°C . Single- and double-walled WS_2 nanotubes exhibited close to either zigzag or armchair structure, while multiple-walled WS_2 nanotubes showed a chiral structure with dispersed helical angles. The study of one incipient nanotube indicates that the conversion of a $W_{18}O_{49}$ nanowire into a WS_2 nanotube undergoes the following major steps: (i) S atoms are attracted preferentially to the O vacancies at the surface of the $W_{18}O_{49}$ nanowire, and subsequently diffuse to other sites to substitute O atoms; (ii) The $W_{18}O_{49}$ phase transforms gradually to amorphous WS_3 , accompanied by a volume expansion; and (iii) Phase transition from amorphous WS_3 to crystalline $2H-WS_2$ by losing S atoms, which forms the shells of the WS_2 nanotube.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This study was partially supported by National Natural Science Foundation of China [grant number 11474294], Zhejiang Provincial National Science Foundation [grant number LY14E020010], and Ningbo Innovative Team [grant number 2014B82004].

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