Microwave-assisted synthesis of WS$_2$ nanowires through tetrathiotungstate precursors

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Abstract

Tungsten disulfide (WS$_2$) nanowires have been synthesized through a microwave-assisted chemical route that uses tungstic acid, elemental sulfur and monoethanolamine as starting reagents for obtaining a precursor solution of tetrathiotungstate ions. Acidification of the precursor solution yields amorphous precipitates, which lead to the formation of nanowires of WS$_2$ with thickness of about 5–10 nm when heated at 750 $^\circ$C under argon atmosphere for 1.5 h. Phase and the microstructure of the prepared powders have been investigated through x-ray powder diffraction and high-resolution transmission electron microscopy, respectively. Optical absorption of the WS$_2$ powders reveals a red shift of the exciton bands compared to bulk WS$_2$.

Keywords: tungsten disulfide, monoethanolamine, microwave heating, nanowires

1. Introduction

One-dimensional (1D) nanostructures of layered WS$_2$, such as nanorods, nanotubes, nanowires and nanofibers, have drawn substantial research interest from different fields of technology ever since Iijima reported the formation of carbon nanotubes from graphite in 1991 [1]. Nanostructured WS$_2$ finds application as hydrogen and lithium storage material [2, 3]; as material for solid-state secondary lithium battery cathodes [4]; in inorganic–organic nanocomposites for application in batteries and other electrochemical devices [5]; as catalyst in hydrodesulfurization of crude oil [6, 7] and as solid lubricants [8–10].

Tenne et al carried out extensive studies on various layered materials and have been pioneers in the preparation of concentric polyhedra and/or nanotubes of MS$_2$(M = Mo and W) layered materials through gas-phase reaction of H$_2$S with the respective metal-oxides at elevated temperatures and under reducing atmosphere [11–15]. Production of macroscopic quantities of WS$_2$ nanotubes had later been reported through modification of the gas-phase reaction, where W/WO$_3$ was heated under a mixture of Ar and H$_2$S gases [16]. Beside the gas-phase reaction processes, there are various solution-based and a few alternative methods that have gained recognition for the preparation of 1D nanostructures of WS$_2$. Hydrothermal method [17–19] is one of the most widely reported solution-based routes. Nanotubes of WS$_2$ have been synthesized by autoclaving a solution mixture of ammonium tungstate, citric acid and hexadecylamine at 180 $^\circ$C for 7 days followed by heat treatment of the precursors under H$_2$S flow [18]. Shang et al adopted a two-step hydrothermal process using tungstic acid, sodium sulfate and thiourea as the starting reagents to obtain quasi-1D WS$_2$ nanocrystals with width and thickness of around 140 nm and 30 nm, respectively [19]. Another well-established solution-based method of the preparation of WS$_2$ nanotubes is thermal decomposition of ammonium tetrathiotungstate at $\sim$1300 $^\circ$C in a flow of hydrogen gas [20] or direct decomposition of various tetraalkylammonium tetrathiotungstate precursors under nitrogen atmosphere [21]. Later, Li et al modified the thermal decomposition route of tetrathiotungstate ion to prepare WS$_2$ nanotubes (with diameters of 5–37 nm and lengths between 0.2 and 5 $\mu$m) through pyrolysis of co-condensed self-assemblies of anionic
tungstates (WS$_2^-$) and cationic surfactant molecules at 850 °C under argon atmosphere [22]. WS$_2$ microtubes, microribbons and ropes have also been grown through alternative methods, such as the iodine-transport reaction close to equilibrium [23] at 1060 K, when heated in an evacuated silica ampoule for 22 days at a pressure of 10$^{-3}$ Pa. Most of these synthesis strategies are constrained either by their prolonged and tedious processing at high temperature or by pressure conditions or by the technical skill required for the preparation of the precursor material. Recently, Gedanken and co-workers [24] have reported an alternative and technically proficient method of growing WS$_2$ nanorods through sonochemical reaction between W(CO)$_6$ and sulfur in diphenylmethane at 90 °C under argon atmosphere, followed by heat treatment of the precursors at 800 °C under argon flow. Microwave-assisted method is another significant alternative that has gained attention in recent years as a simple, rapid and efficient process for growth of nanostructured oxides [25, 26] and sulfides [27–29]. Despite the recognition of the microwave-assisted method for the preparation of various sulfides, we are unaware of reports on the preparation of nanostructured WS$_2$ through this method. Motivated by this observation, we have attempted to synthesize 1D nanostructures of WS$_2$ through microwave irradiation induced reaction between tungstic acid and elemental sulfur in dilute monoethanolamine (MEA). The process leads to the formation of tetrathiotungstate ions in-situ, which on acidification results in precipitates that are separated and heat-treated at 750 °C for 1.5 h under argon atmosphere. Microwave irradiation facilitates instantaneous generation of the tetrathiotungstate precursors in solution, which in consequence makes the process of preparation of nanostructured WS$_2$ much faster and less cumbersome compared to the other reported chemical routes [30]. The developed process is technically simple and makes use of a domestic microwave oven.

2. Experimental

2.1. Preparation method

All the chemicals were used as received without further purification. In the preparation, tungstic acid was chosen as the source of the tungsten, instead of sodium tungstate, in order to avoid sodium ion contamination in the final product. Tungstic acid was freshly prepared by acidification of an aqueous solution of 1 g of sodium tungstate (Na$_2$WO$_4$•2H$_2$O, Merck India, 98%) with concentrated HCl. The prepared precipitate of tungstic acid was mixed with 10 ml of MEA (HOC$_2$H$_2$CH$_2$NH$_2$, Merck India, 98%) in presence of 1 ml of distilled water to obtain a whitish colloid, which transformed to a clear solution on stirring through formation of MEA chelated complex of tungstate [(MEA – H$^+$)$_2$WO$_4$]. In a separate container, 0.8 g of elemental sulfur (Merck India, 99.6%) was solubilized in 10 ml of MEA under microwave irradiation through formation of monoethanolamineium sulfides, bisulfides and polysulfides (i.e. S$_{\text{dissolved}}$) [31, 32]. The clear solutions of tungstic acid and sulfur (in MEA) were then mixed together, and the resultant homogenous red color precursor solution was subjected to microwave irradiation for 5–6 min in cycles of 30 at 800 W. The precursor solution was then acidified with concentrated HCl to obtain a brown colored precipitate. The brown precipitate, on filtration and washing with water for several times, transformed to a yellowish-brown colored precursor mass when dried in a vacuum desiccator. Annealing the dried mass at 750 °C for 1.5 h in argon atmosphere resulted in the black colored powders of WS$_2$. A domestic microwave oven (LG MG-396WA/397WB, 800 W, 2.45 GHz) was used for the microwave irradiation.

In the developed process, the amount of sulfur (and MEA) in the starting solution was always taken in excess to the stoichiometric requirement of W:S mole ratio of 1:2. This ensured adequate concentration of S$^{2—}$ ions in the microwave irradiated precursor solution.

2.2. Characterization

The optical absorption spectra of the microwave irradiated precursor solution as well as the annealed powders (dispersed in ethanol) were recorded at room temperature using Shimadzu UV-1601 UV-vis spectrophotometer. The phase analysis of the prepared powders was carried out using X’pert Pro 3040/60 high-resolution x-ray diffractometer with CuK$\alpha$ radiation (\(\lambda = 1.5418 \text{ Å}\)) at a rate of 5 ° per min. The simultaneously recorded thermogravimetry (TG) and differential thermal analysis (DTA) of the precipitate obtained through acidification of the microwave irradiated precursor solution, was carried out on NETZSCH STA 409 PC instrument at a heating rate of 10 °C min$^{-1}$ under argon atmosphere using alumina crucible. Composition of the as-prepared precipitate as well as the heat-treated (at 750 °C for 1.5 h) powders obtained through acidification of the microwave irradiated precursor solution, was analyzed through Fourier transform infra-red (FTIR) spectroscopy using KBr pellets and Perkin–Elmer Spectrum RXI instrument. The chemical composition of the final powders was confirmed through energy dispersive x-ray (EDX) analysis using OXFORD ISIS-300 electron microprobe. JEOL JEM-2100 high-resolution transmission electron microscope (HRTEM) was used to obtain the detailed microstructure of the annealed powders. The sample for the HRTEM studies was prepared by dispersing the powders in ethanol through ultra-sonication and drop casting the dispersion onto a carbon coated copper grid.

3. Results and discussion

UV-vis spectra of the microwave irradiated, red colored precursor solution of MEA chelated complex of tungstate and sulfur in MEA revealed absorption bands centered at 217, 278, 394 and 335 nm, as shown in figure 1(a). The first three absorption bands matched with those of the tetrathiotungstate ions (WS$_2^-$) [30, 33], which might have formed in the precursor solution through microwave-induced exchange reaction. This reaction may involve the successive
The alkaline solution of sulfide, ions required for the reaction were provided by water impurity in the transformation of WO$_4^{2-}$ ion at 335 nm. This ion possibly forms as the intermediate using solution of sulfur powders in organic diamines [34]. Similar arguments describing the synthesis of CdS nanowires could be summarized by the following reaction:

$$\text{(MEA - H}^+)_2\text{WO}_4 + S^{2-} \xrightarrow{\text{microwave}} \text{(MEA - H}^+)_2\text{WS}_4$$

$$+ (\text{MEA + H}^+)\text{SOS}_(\text{trace}) + \text{OH}^-.$$  \hspace{1cm} (1)

The S$^{2-}$ ions (or H$_2$S) required for the above reaction were probably generated through disproportionation of sulfur in the alkaline solution [35, 36] of MEA. The hydroxyl (OH$^-$) ions required for the reaction were provided by water impurity in the alkaline solution of tungstic acid present in the reaction mixture. The alkaline solution of sulfide, bisulfide, or polysulfide is thermodynamically unstable, and the dissolved sulfur (S$_\text{dissolved}$) probably decomposed (at temperatures higher than 85°C) to thiosulfate (S$_2$O$_3^{2-}$) and HS$^-$, in accord with the net consumption of dissolved sulfur [35]. Consequently, microwave irradiation should have accelerated the decomposition of dissolved sulfur in MEA and, hence, augmented the generation of HS$^-$ ion in the solution. The generated HS$^-$ ions remained in equilibrium with the S$^{2-}$ ions in solution. Drawing similarities with the available literature [35, 36], the probable chemical reactions for the generation of S$^{2-}$ ions through microwave-induced disproportionation of sulfur (S$_\text{dissolved}$) in alkaline solution of MEA, in presence of OH$^-$ ions in the reaction medium, can be summarized by the following set of equations:

$$\text{MEA} + S \xrightarrow{\Delta} S_{\text{dissolved}},$$  \hspace{1cm} (2)

$$S_{\text{dissolved}} + \text{OH}^- \xrightarrow{\Delta} \frac{1}{4} \text{S}_2\text{O}_3^{2-} + \frac{1}{2}\text{HS}^- + \frac{1}{4}\text{H}_2\text{O}.$$  \hspace{1cm} (3)

$$\text{HS}^- \rightleftharpoons \text{H}^+ + \text{S}^{2-}.$$  \hspace{1cm} (4)

The formation of S$^{2-}$ in the microwave heated alkaline solution of MEA and sulfur (i.e. S$_\text{dissolved}$) was tested through blackening of lead acetate soaked paper. The presence of S$_2$O$_3^{2-}$ ions in the solution was tested through formation of white precipitate with aqueous solution of BaCl$_2$. The formation of S$_2$O$_3^{2-}$, HS$^-$ and S$^{2-}$ ions in the microwave irradiated solution of MEA and sulfur (i.e. S$_\text{dissolved}$) was also validated through UV-vis spectroscopy. The absorbance bands at 232, 360 and 305 nm in the UV-vis spectra may be respectively assigned to HS$^-$, S$^{2-}$ ions [37, 38] and zero-oxidation sulfur (S$^0$) in soluble state [36, 39]. The band at 232 nm can be ascribed to S$_2$O$_3^{2-}$ ions. This assignment was confirmed by comparing the observed band with those for a known solution of MEA and sodium thiosulphate. It could thus be inferred that the microwave irradiated solution of sulfur and MEA was composed of S$_2$O$_3^{2-}$, HS$^-$, S$^{2-}$ ions and neutral sulfur species in the soluble state (S$^0$).

Acidification of the microwave irradiated, red colored precursor solution, containing thiotungstate ions and sulfur dissolved in MEA with concentrated HCl, generated brown precipitates, which turned to yellowish brown on drying in vacuum. Formation of brown amorphous precipitates of WS$_3$ through acidification of thiotungstate precursors is well documented [40] and is given by the following equation:

$$\text{WS}_4^{2-} + \text{H}^+ \xrightarrow{\text{acidification}} \text{WS}_3 + \text{H}_2\text{S}.$$  \hspace{1cm} (5)

Corroborating with the literature and also from the fact that WS$_3$ and WS$_2$ are the only two known sulfides of tungsten, the obtained precipitate was identified as WS$_3$. However, to gain more credence, the precipitate was characterized by FTIR spectroscopy and its solubility was qualitatively tested in concentrated nitric acid and MEA. In contrast to WS$_2$, the yellowish brown precipitate dissolved in concentrated nitric acid leaving a minor yellow residue. The yellowish brown precipitate was, however, completely soluble in MEA without any residue. The yellow solid, that was obtained as...
a residue when the yellowish brown precipitate was treated with nitric acid but did not appear when treated with MEA, was possibly of sulfur. Sulfur is insoluble in concentrated nitric acid but is soluble in MEA. Thus, the yellowish brown precipitate, obtained on acidification of the microwave irradiated precursor solution, was possibly a mixture of WS$_3$ and sulfur.

FTIR spectroscopy studies of the yellowish brown precipitate showed a medium and broad absorption band centered around 515 cm$^{-1}$, which could be assigned to the doubly degenerate W–S bond stretching mode for WS$_3$ [41]. In addition, a weak but distinct absorption band was observed at 468 cm$^{-1}$. This band matched with the characteristic S–S stretching mode for elemental sulfur (S$_8$) [42], thereby, confirming the presence of sulfur in the obtained precipitate. Furthermore, the absence of the characteristic absorption bands corresponding to the symmetric and asymmetric S–W–S stretching modes for WS$_2$ molecule at 533 cm$^{-1}$ and 528 cm$^{-1}$ [41], respectively, confirms that the precipitate is a mixture of WS$_3$ and S. The above observation was further corroborated by EDX studies of the precipitate, which revealed the higher W : S atomic ratio than the expected ratio of 1 : 3.

It can therefore be ascertained that apart from WS$_3$, elemental sulfur also precipitates out of the microwave irradiated precursor solution of MEA chelated complex of tungstate and S$_{\text{dissolved}}$ on acidification, through decomposition of S$_2$O$_5^-$ ions in the solution. The simultaneous precipitation of WS$_3$ and elemental sulfur, through acidification of microwave irradiated precursor solution, can be represented by the following equations:

$$S_2O_5^- (\text{microwave irradiated precursor solution}) \xrightarrow{\text{HCl}} SO_2 \uparrow + S \downarrow + H_2O.$$

$$\text{(MEA} - H^+)_2WS_4 \rightarrow (\text{MEA} - H^+)_2WO_3(\text{trace}) \xrightarrow{\text{HCl}} WS_3 \downarrow + [(\text{MEA} - H^-)^+Cl^-] + H_2O + H_2S.$$

The dried yellowish brown precipitate, containing WS$_3$ and elemental sulfur, when annealed at 750$^\circ$C yields black powder of WS$_2$ with volatilization of sulfur. The generation of WS$_2$ can thus be given as follows:

$$\text{WS}_3 \xrightarrow{\Delta \text{annealing at 750$^\circ$C}} \text{WS}_2 \text{ (nanostructured)} + S \uparrow. \hspace{1cm} (8)$$

Solubility tests were carried out for the black annealed powders, to qualitatively assess the composition of the final product. Unlike the as-prepared yellowish brown precipitates, the annealed powder was insoluble in nitric acid and MEA. As expected for WS$_2$, the black powders dissolved in HF-aqua regia mixture. This qualitatively established the absence of WS$_3$ and elemental sulfur in the annealed black powders. The observation was corroborated by the FTIR spectra for the powders, which was also marked by the absence of the characteristic absorption bands for S and WS$_3$. Furthermore, EDX studies of the annealed powders revealed the atomic percentage of S and W in the final sample as $\sim$64.8% and 35.1% (within the instrumental error of $\pm$5%), respectively, and the S : W elemental ratio of 1.84. EDX measurements, therefore, indicated that the sulfur content and the W : S atomic ratio in the annealed powders was within the acceptable range of the WS$_2$ stoichiometry [19].

Thermal decomposition behavior of the yellowish brown precursors, obtained after acidification of precursor solution, is shown in figure 2. The TG curve showed a gradual weight loss of $\sim$71% up to 500$^\circ$C corresponding to two endothermic heat effects observed in the DTA and a broad peak in the DTG curve in the same temperature range.

The first endothermic peak observed below 200$^\circ$C in the DTA curve, which was manifested by a weight loss of $\sim$2.5% in the TG curve, was assigned to the loss of adsorbed moisture and the escape of trapped gases (such as, H$_2$S, SO$_2$, and HCl) from the powder matrix. Since the composition of the precursor was inferred as a mixture of WS$_3$ and S, the major weight loss of $\sim$68.5% (as reflected in the TG curve) occurring between 200 and 500$^\circ$C could be cumulatively assigned to the loss of interlayer water molecules, the conversion of WS$_3$ to WS$_2$ through loss of sulfur and the volatilization of free elemental sulfur contained in the sample. The entire heat loss process was manifested by a small endothermic effect in the DTA curve in the corresponding temperature range. However, according to [43, 44], WS$_2$ is stable up to $\sim$340$^\circ$C and it decomposes exothermally to S and WS$_2$ (as indicated by equation (8)) above 340$^\circ$C with W$^{6+}$ reduced to W$^{4+}$ and S$^2-$ oxidized to S$^0$, simultaneously. In figure 2, the DTA plot for the present sample showed a small endothermic peak instead of the expected exothermic event in the corresponding temperature range. This was possibly because the expected exothermal event in the conversion of WS$_3$ to WS$_2$ got overly compensated by endothermic heat effect generated through vaporization of the sulfur contained in the sample. The exothermic peak at about 630$^\circ$C in the DTA curve, which shows no significant weight loss in TG,
Figure 3. XRD pattern of the nanostructured WS$_2$ powders obtained through heat treatment of the precursors at 750 °C for 1.5 h under argon atmosphere.

can be attributed to the phase change from amorphous to crystalline WS$_2$.

X-ray powder diffraction (XRD) of the as-prepared, yellowish brown precipitate showed broad modulations without any peak formation, indicating the material to be amorphous. XRD pattern of the powders obtained on subsequent annealing of the precursors at 750 °C for 1.5 h revealed broad peaks (as shown in figure 3), which were indexed to the 2H WS$_2$ phase according to JCPDS card no. 08-0237. The XRD pattern of the powders showed hexagonal unit cell dimensions in agreement with the literature values. However, the major diffraction peak at $2\theta \approx 14.04^\circ$, corresponding to the 002 reflection, slightly shifted towards lower angles in comparison to the bulk 2H WS$_2$ system ($2\theta \approx 14.32^\circ$). The shift may be attributed to the strain relaxation in the 2H WS$_2$ crystal lattice due to the formation of curved nanostructures [13, 14]. This observation was supported by the calculated cell parameters of the same $a$ (0.31 nm) and somewhat longer $c$ (1.26 nm) compared with those of the 2H WS$_2$ system ($a = 0.31$ and $c = 1.236$ nm; JCPDS card no. 08-0237).

Room temperature UV-vis spectrum of the annealed (at 750 °C for 1.5 h) precursors is depicted in figure 1(b). It shows two weak absorption bands centered at 646 and 533 nm, which can be assigned to the excitons A and B of WS$_2$, respectively. The observed positions of the excitonic bands are shifted to higher wavelength in comparison to the respective excitons at 635.8 and 525.3 nm, reported for the bulk 2H WS$_2$ system [45]. The shift is however lower than reported for the 1F-WS$_2$ nanostructures (i.e. at 649.1 and 551 nm, respectively) [14, 45]. Our spectra thus indicate formation of WS$_2$ nanostructures with intermediate exciton wavelength between the bulk 2H WS$_2$ and 1F-like WS$_2$ nanostructures.

Bright-field TEM micrographs for the annealed powders of WS$_2$ are shown in figures 4(a) and (b). The figures show the formation of WS$_2$ nanowire-like structures, with thickness $\sim$5–10 nm. Li et al reported similar morphology for hydrothermally synthesized MoS$_2$ nanowires [46]. HRTEM image of the same sample clearly identifies a single nanowire of WS$_2$ with well-defined lattice fringes (figure 4(b)). Figure 4(c) illustrates the selected area electron diffraction (SAED) patterns for the sample. It shows distinct rings, characteristic of an assembly of nanocrystallites, which can be indexed to the 002, 103, 105 and 112 reflections of the 2H WS$_2$ phase.

The inter-planar distance along the c-axis, corresponding to the $d_{002}$ plane, was measured from the average distance between two adjacent lattice fringes and was found to be approximately 0.64 nm, which is consistent with the XRD
result. The value of the corresponding d_{002} spacing for the bulk 2H-WS₂ is 0.618 nm (from JCPDS file), which is slightly smaller than the measured value, supporting our inference on the formation of folded nanostructures of WS₂. The exact mechanism of formation of WS₂ nanowires through microwave-induced localized temperature and pressure effects at the reaction sites requires further investigations.

4. Summary

A simple and rapid method has been developed for the synthesis of WS₂ nanowires, with thickness ∼5–10 nm, through microwave irradiation induced reaction of tungstic acid with elemental sulfur in a medium of dilute monoethanolamine (MEA) via formation of tetrathiotungstate ions as intermediates. Amorphous precipitates, obtained on acidification of the precursor solution of tetrathiotungstate ions, when annealed at 750 °C, yield the WS₂ nanowires. In the process, microwave induced reactions facilitate the solubilization of tungstic acid in MEA through formation of MEA chelated complex of tungstate and also aid in the in-situ formation of tetrathiotungstate ions via the generation of S²⁻ ions from monoethanolammonium polysulfide complex. Thus, MEA not only acts as a solvent but also as a coordinating agent. Structural studies indicate strain relaxation in 2H-WS₂ crystal lattices along the c-axis, suggesting the formation of curved nanostructures. Optical absorption studies support the findings through the red shift of the exciton bands.

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