**Synthesis and characterization of WS$_2$/SiO$_2$ microfibers**

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**ABSTRACT**

Tungsten disulfide polycrystalline microfibers were successfully synthesized by a process involving electrospinning, calcination, and sulfidation steps. We used an aqueous solution of silicotungstic acid (H$_4$SiW$_{12}$O$_{40}$) and polyvinyl alcohol as precursors for the synthesis of composite fibers by the needle-less electrospinning technique. The obtained green composite fibers (av. diam. 460 nm) were converted by calcination in air to tungsten oxide WO$_3$ fibers with traces of SiO$_2$ and a smaller diameter (av. diam. 335 nm). The heat treatment of the WO$_3$ fibers under flowing H$_2$/H$_2$S/N$_2$ stream led to conversion to tungsten sulfide WS$_2$ with retention of the fibrous morphology (av. diam. 196 nm). Characterization of the intermediate and final fibers was performed by the XRD, SEM, TEM, HAADF STEM EDS, elemental analyses ICP-OES, and IR spectroscopy methods.

**GRAPHICAL ABSTRACT**

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Introduction

Electrospinning is a well-established method for the preparation of many types of materials with general nanofibrous morphologies [1]. An electrode, in the form of a syringe needle or free surface of a polymer solution, is electrically charged and a Taylor cone is formed from the droplet or surface. A jet of the evaporating solution is drawn toward a grounded or negatively charged counter electrode which serves simultaneously as a collector of solidified polymer fibers. This technique, closely resembling electro-spraying, is exploited for obtaining various fibrous morphologies: micro- and submicron fibers, nanofibers, hollow fibers, Janus-type fibers, porous structures, interconnected fibrous membranes, branched fibers and many other shapes [1–3]. The process is controllable by many variables, where the composition of the spinning solution is a dominant factor next to the applied voltage, electrode distance, feed rate, and several others [3]. Electrostatic spinning is used for the preparation of purely organic fibers where almost all regular and even modified polymers were successfully electrospun to form ultrafine or at least submicrometric fibers. However, not only these classical systems could be processed, and nowadays, we can witness intensive research on the fabrication of inorganic, purely ceramic, and mixed composite fibers by this technique [4, 5]. Many oxides, carbides, nitrides, and multimetallic compounds, such as perovskites and spinels, have been reported [1]. Inorganic nanofibers could be used in many already existing applications including energy storage, battery cathodes or anodes, catalysts, fillers in composite materials, gas sensors, and as precursors of fine ceramics [6]. Following the electrospinning process, green composites of inorganic precursors and organic polymers are formed. To obtain pure oxide ceramic fibers, it is necessary to remove the organic polymer matrix, in most cases, via high temperature burn up in an air atmosphere. Additional variables are thus involved, such as maximum firing temperature, time and rate of heating, and the used atmosphere. The ambient gas has a special importance during the annealing treatment after removal of the polymer in air atmosphere. By using various gaseous mixtures or pure gasses, it is possible to obtain diverse inorganic compounds in the form of ultrafine fibers. For example, reducing atmosphere could lead in some cases to purely metallic polycrystalline fibers or utilization of, e.g., ammonia, methane, and hydrogen sulfide, produces nitrides, carbides, or sulfides, respectively [7–9]. An advantage of the described method is the facile scale-up of micro- and nanofiber fabrication process via needle-less electrospinning from the solution surface, which potentially allows building an industrial-level production line with continuous operation [10–12].

Electrospinning of tungsten-containing fibers has to be based on a soluble inorganic precursor of this element. Simultaneously, it has to be transformed by after-spinning processes to a form, which is suitable for subsequent reactions without impurity elements, which could cause the formation of undesirable phases. In practical terms that dictates usage of water-soluble ammonium tungstates, tungstic acid, or other precursors forming tungsten trioxide by heat treatment in an oxygen atmosphere. Selection of the right precursor could be a challenging task due to the limited solubility of some precursors, such as the already mentioned tungstic acid or ammonium paratungstate. Much more soluble ammonium metatungstate, however, suffers from a high cost, which could be prohibitive for production on a multigram scale. Sodium tungstate, which is easily soluble in aqueous solvents, however, cannot be used due to the presence of unwanted sodium cations, which will remain embedded in the material even after a high-temperature treatment. Finding a proper precursor for industrial scale-up from laboratory conditions, therefore, is not straight forward.

Silicotungstic acid, H₄SiW₁₂O₄₀, is polyoxometalate acid consisting of 12 tungsten atoms and one silicon atom all compensated by oxides and four hydrogens forming a Keggin-type structure where silicon resides in the central tetrahedral cavity of a W₁₂ cage. This compound is mostly applied as a catalyst for a broad spectrum of reactions, even on an industrial scale. Production of ethyl acetate and acetic acid from ethylene via catalysis by silicotungstic acid was commercialized by Showa Denko [13]. Also, a significant application could be found as an additive to fuel cell membranes enhancing proton conductivity [14]. Silicotungstic acid is highly soluble in aqueous systems and we used it here as an inorganic precursor for the electrospinning process.

Tungsten disulfide W₅S₂ is a layered (2D) semiconducting material with many promising applications in electronics, optoelectronics, catalysis, gas
sensors, lubricants, biomedicine, and energy storage [15–21]. It has been prepared in the form of nanoplates, thin films, nanotubes, fullerene-like nanoparticles [22–24], quantum dots [25], rods, and fibers [26].

In the present work, the silicotungstic acid/polyvinyl alcohol (PVA) solution was electrospun via a scaled-up needle-less electrospinning procedure to green composite fibers that by calcination in air formed submicron polycrystalline fibers consisting of WO3/SiO2. Subsequently, H2S treatment of the annealed tungsten oxide fibers was undertaken, according to a procedure which was extensively used for sulfidation of pure WO3-x nanoparticles [27], providing tungsten disulfide WS2 microfibers.

Experimental

General

Polyvinyl alcohol (PVA, Mowiol 18–88, \(M = 130 \text{,000 g mol}^{-1}\)) and silicotungstic acid hydrate (purum) were obtained from Sigma-Aldrich and used as received. Deionized water was used as a solvent. For electrospinning, a Nanospider NS LAB500S (Elmarco, Czech Republic) system was used equipped with a cylindrical electrode with microblades for localization of electrical charge and solution droplets [10, 28] (Fig. 1).

The electrospinning process was performed under an ambient atmosphere in an air-conditioned room. The details of the electrospinning parameters are provided below. The prepared solutions were characterized before electrospinning by conductometry, viscosimetry, and surface tension measurements.

Preparation of electrospinning solution

PVA (150 g) was dissolved in deionized water (1150 g) by stirring and heating for several hours providing a 11.5 wt% solution. Silicotungstic acid hydrate (120 g) was dissolved in deionized water (200 g). Both solutions were combined at ambient temperature and homogenized by intensive stirring for several hours. A clear colorless viscous solution was formed and further characterized with respect to its physical properties (Table 1). The final polymer and tungsten precursor contents in the prepared solution were approx. 9.3 and 7.4 wt%, respectively.

Needle-less electrospinning

The prepared solution (approx. 800 cm\(^3\)) was transferred to the electrode vessel with a partially submerged electrode. A grounded counter electrode in the form of a stretched wire was covered with a large sheet of aluminum foil (approx. 0.8 × 0.4 m), and the electrode distance was set to 17.0 cm. The speed of the rotating electrode was set to 30 rpm. The applied voltage was set to 50 kV. The process was running for 4 h when half of the used solution was depleted, and the aluminum collector was covered by a thick layer of nonwoven felt of a green composite of PVA and silicotungstic acid. Electrospinning was interrupted due to a noticeable increase in viscosity of the solution. The increased viscosity was most probably caused by an increased rate of solvent evaporation from the relatively high surface area of the electrode and the solution. The solvent evaporation was exacerbated by ventilation of the chamber. The prepared fibrous material was peeled off, analyzed by SEM and TGA/DSC and used in further process.

Calcination and high-temperature treatment

Collected layers of electrospun fibers were treated in a muffle oven at 600 °C, which was set according to the TGA/DSC measurement. The oven was programmed to achieve the maximum temperature in 4 h followed by another 4 h at the constant temperature and finally spontaneous cool down to ambient temperature. After this heat treatment, the material was collected and analyzed.

High-temperature reaction with H2S

The high-temperature sulfidation was carried out in a reducing atmosphere. The conditions of the process were similar to those used for the synthesis of other sulfide nanostructures [27].

The powder was placed into a quartz boat and then inserted into a quartz reactor. The reactor was purged continuously with N2 in order to prevent traces of O2 and moisture that would otherwise interfere with the course of the reaction. Then, the reaction gases—forming gas (H2/N2 at a ratio of 10/90) and H2S—were added to the flow. Following this step, the reactor was inserted into a horizontal furnace, which was preheated to 840 °C and maintained at this temperature for 2 h. At this point, the boat was
moved out of the oven and left to cool spontaneously to room temperature.

During this entire series of steps, the reactor was purged with a continuous flow of reaction gases. Several experiments were run with various reaction conditions in order to study their possible influence on the result of the sulfidation process. The total flow rate was about 130–150 cm$^3$ min$^{-1}$. Composition of the gas flow was slightly varied between 5 and 10 cm$^3$ min$^{-1}$ H$_2$, 7–10 cm$^3$ min$^{-1}$ H$_2$S, and the rest was nitrogen carrier gas. The precursor powder was either placed directly into the quartz boat or into prefilled quartz crucibles, which were then placed in the boat.

**Characterization of the solutions and powders**

**Thermogravimetric analysis**

Thermogravimetric analysis and differential scanning calorimetry (TG/DSC) were performed using a Netzsch Jupiter STA 449 instrument with a heating rate of 10 K min$^{-1}$ and a maximum temperature of 1000 °C.

**Electrical conductivity, viscosity and surface tension of the solution**

The electrical conductivity of the solutions was measured with a Cond51 conductometer (XS Instruments). Viscosity measurement was performed on an Alpha Fungilab rotational viscosimeter. Surface tension was determined by a Sigma 700 tensiometer equipped with a Wilhelmy probe.

**Elemental analysis**

Samples for elemental analysis were mineralized by a heat-induced reaction between excess sodium peroxide, glycerine, and the analyzed material itself followed by quantitative dissolution in deionized water of known volume. A typical procedure was as follows: a precise amount of a material (e.g., 0.2012 g) was mixed with two droplets of glycerin in small pressure reactor and covered with sodium peroxide (approx. 3 g). The reactor was tightly sealed and heated with a burner until the slight snap-like sound was induced. After cooldown, the content of the reactor was quantitatively transferred to an analytical flask and filled with deionized water. The prepared solution was analyzed by the inductively coupled plasma method (ICP-OES) using a spectrometer.
iCAP 6500 Duo (Thermo, generator 27.12 MHz, amplitude 1.15 kW, plasma gas flow 12 dm$^3$ min$^{-1}$) emission lines 224.9 and 207.9 nm for W and 212.4 and 251.6 nm for Si.

**IR spectroscopy**

Infrared spectra were obtained on a Bruker Tensor 27 FTIR spectrometer with a Bruker Alpha-Platinum ATR system.

**Powder X-ray diffraction**

Powder X-ray diffraction (XRD) measurements were performed with a GNR Europe 600 diffractometer with a Co ($\lambda_{K\alpha} = 1.79030$ Å) lamp and using a TTRAX III (Rigaku, Tokyo, Japan) $\theta$–$\theta$ diffractometer. This set-up was equipped with a rotating copper anode X-ray tube operating at 50 kV/200 mA. A scintillation detector aligned at the diffracted beam was used after a bent Graphite monochromator. The samples were scanned in specular diffraction mode ($\theta$/2$\theta$ scans) from 10 to 80 degrees ($2\theta$) with a step size of 0.025 degrees and a scan rate of 0.5 degrees per minute. Phase identification and quantitative analysis were performed using the Jade 2010 software (MDI) and PDF-4 + (2016) database.

**Electron microscopy**

The nanofibrous materials were characterized by scanning electron microscopy (SEM) using model Versa 3D (FEI/Thermo Fischer Scientific, Czech Republic) and Zeiss Sigma 500 microscopes. Transmission electron microscopy (TEM) characterizations were performed on an FEI Tecnai G2 instrument at 200 kV equipped with a 4 k CCD camera FEI Eagle. The samples for the TEM measurements were dispersed in methanol and 4 $\mu$L of the suspension. The suspension was dripped on a Quantifoil copper grid and allowed to dry by evaporation at ambient temperature.

The TEM analysis and HAADF STEM EDS measurements of WS$_2$ fibers were performed with a Titan Themis Z at 200 kV, equipped with two Rose-Haider double-hexapole aberration correctors (probe and image), a Super-X large solid angle X-ray detector for EDS and a OneView high-speed CMOS camera for wide-field TEM imaging. The sample for the TEM measurements was dispersed in ethanol, then dripped on a copper grid and dried at ambient conditions.

SEM micrographs were analyzed by the ImageJ software for fiber diameter and size distribution.

**Results and discussion**

The composition of the electrospun solution was optimized for the maximal simplicity of the mixture. Silicotungstic acid was found as a precursor widely used in industry and satisfying demands for high water solubility and a high content of tungsten. Polyvinyl alcohol (PVA) was found to be suitable for electrospinning, being an inexpensive, easily accessible, and water-soluble material. It is available in a range of average chain lengths, different degrees of hydrolysis, and polydispersity [29, 30]. Mowiol 18–88 was chosen from all variants as the most common polymer from PVA families, which is also well soluble in comparison with fully hydrolyzed compounds [31].

Conductometric characterization of the starting solution provided an elevated value of 6.8 mS cm$^{-1}$ in comparison with 1 mS cm$^{-1}$ for the PVA solution. This is due to the dissociation of added silicotungstic acid. The surface tension (61.7 mN m$^{-1}$) was lower than the tabulated value for water 72.86 mN m$^{-1}$ [32] at approximately the same temperature. In general, lower surface tension means lower electrical force needed to initiate the electrospinning process because the Taylor cone is in a stable equilibrium between the electrical force field and surface tension [1]. Decrease in the surface tension also helps to prevent the formation of beaded structures on the fibers [1].

The electrospinning was performed via multi-jet spinning from free surface enhanced by blades on the electrode. The rotation speed of the electrode was set to ensure that the electrode is wetted by the solution during the entire cyclic movement. The transferred mass was collected on an aluminum foil electrode, where at first a thin layer of a white fabric formed, which turned to a thick 3D web of white material at the end of the electrospinning process. The fibrous mat was peeled off, collected, and analyzed by scanning electron microscopy (SEM) and thermal analysis (TGA/DSC).

The SEM measurements provided insight into the morphology of the prepared mats consisting of sub-micron fibers with a broad distribution and with an
average thickness of 460 nm (Fig. 2). These results correlate well with literature values of PVA electrospun fibers [33], which lay in a submicron range and typical hundred-nanometer thickness. It is possible to observe a few flat ribbon-like fibers, which are typical for PVA solutions with a relatively high concentration and viscosity [1]. Thinner fibers are present with a diameter around 200–300 nm (Fig. 3—black).

TG/DSC analysis (Fig. 4) was used to find a proper calcination temperature. Heating the sample causes steadily decreasing mass, followed by exothermic
burnout of the polymer matrix with an onset temperature of 437 °C. After exothermic removal of most of the organic material, a smaller decrease in mass is observed; however, the mass remains stable above 550 °C. Based on the results of the TG/DSC measurement, we have selected the calcination temperature of 600 °C.

The green composite fiber mat was transferred into an alumina crucible and calcined under air by steadily increasing the temperature up to 600 °C within 4 h followed by another 4 h at this temperature. Calcination was concluded by free cool-down to an ambient temperature. The white fibers were transformed into yellow-greenish brittle flakes, which were further analyzed by SEM, TEM, XRD, ICP-OES, and IR spectroscopy methods.

![Figure 4](image)

**Figure 4** TG/DSC traces measured in air of a green composite PVA and silicotungstic acid.

**Table 2** Elemental analysis of calcined (WO$_3$)$_{12}$/SiO$_2$ fibers by ICP-OES

|     | $w$  | $\sigma$ | $w_{\text{Nominal}}$ | $w_{\text{W/Si}}$ | $w_{\text{W/Si}}$ | Exp | Nominal |
|-----|------|----------|---------------------|-------------------|-------------------|-----|---------|
| Si  | 0.973| 0.010    | 0.988               | 76.98             | 78.55             |
| W   | 74.9 | 1.0      | 77.6                |                   |                   |

![Table 2](image)

**Figure 5** SEM images of the calcined composite of PVA and silicotungstic acid. (WO$_3$)$_{12}$/SiO$_2$ fibers with even surface (a), fibers with non-uniform surfaces (b), high-magnification of the annealed oxide fibers (c).
Quantitative elemental analysis of mineralized samples of calcined fibers by the ICP-OES method revealed concentrations of tungsten and silicon close to the theoretical values for a mixture of oxides (WO₃)₁₂/SiO₂ resulting from thermal decomposition of H₄SiW₁₂O₄₀ (Table 2). This stoichiometric ratio implies a complete conversion of the silicotungstic acid precursor to the bulk fibers.

From the electron microscopy analysis, it is evident that the calcined material has a polycrystalline fibrous structure in the submicron range of fiber thickness. The SEM images of the calcined material (Fig. 5a) show entangled array of fibers with a cylindrical cross section and fairly even surface morphology. On the other hand, Fig. 5b shows that in some other areas, many fibers exhibit rough surfaces with oxide bulges, indicating secondary precipitation of the oxide upon cooling of the specimen. Individual fibers are composed of crystallites (Fig. 5c). An average diameter has been measured with the ImageJ software from 50 individual fibers. Analysis of the size histogram (Fig. 3—gray) revealed an average diameter of 335 nm with a relatively broad distribution.

In comparison with the green fibers, it is observed that the average diameter of (WO₃)₁₂/SiO₂ fibers, i.e., following calcination, decreased; however, when the standard deviation is taken into account, both samples are comparable even from the mean thickness point of view. The slight shrinking of the fiber thickness can be attributed to the removal of the organic matrix from the green composite during calcination. Comparing both histograms provides identical size distribution; however, in the calcined sample also fibers with very thin diameters of 100 nm are present. It is also remarkable that the calcined fibers are curled compared to the green fibers, which are quite straight. Furthermore, many annealed fibers are broken into short sections, indicating lower fracture toughness of the annealed fibers.

Detailed SEM measurements, together with TEM analysis (Fig. 6), describe the (WO₃)₁₂/SiO₂ fibers as agglomerates of nanoparticles with crystalline structure analyzable by FFT to provide a complementary measurement to the XRD method. The result of this analysis is shown in the Supplementary material (Fig. 1S). The spacing of the crystal planes correlates well with the Miller indices from the XRD diffraction (Fig. 2S). The results of the FFT analysis and XRD are summarized in Table 3. Determination of the fine structure of thick fibers by TEM analysis was challenging (Fig. 6a). However, analysis of thinner fibers (less than 150 nm) permitted observing the crystal planes (Fig. 6b). XRD measurement (Fig. 7) provided diffractions of the WO₃ phase according to the COD database card [COD-1528915].

**Table 3** Summary of FFT and XRD analysis data on WO₃ fibers

| Spacing from FFT [nm/c] | d [Å] | Miller indices |
|-------------------------|-------|----------------|
| 0.26–0.27               | 2.6–2.7 | 202, 220 |
| 0.31                    | 3.1   | 112            |
| 0.365                   | 3.65  | 200            |
| 0.38                    | 3.8   | 002, 020       |

Figure 6 TEM image of a calcined (WO₃)₁₂/SiO₂ fiber (a) and its detailed structure (b).
Silica remains amorphous under these synthetic conditions and presents no diffractions. Several planes in the crystal lattice of WO₃ were recognized (Table 3), mainly (200), (020), (002) as the Miller indices of the corresponding planes.

The prepared material was analyzed also by infrared spectroscopy. The IR spectra are shown in the Supplementary material (Fig. 3S). The bands observed in the infrared spectra are consistent with the presence of W–O–W (400–1000 cm⁻¹) and Si–O–Si (1000–1200 cm⁻¹) deformation vibrations [34].

A high-temperature sulfidation reaction was carried out on the fibers in forming gas (H₂/N₂) and H₂S with the aim of converting WO₃ to WS₂ while maintaining the fiber morphology. The reaction converted the green-yellowish fibers into a black powder. The XRD diffractogram (Fig. 8) of the sulfided fibers shows that all the peaks can be indexed to the 2H-WS₂ phase COD-901291. This finding suggests that the silica islands in the fiber have not been affected and remain amorphous following this high-temperature (840 °C) reaction.

The SEM analysis (Fig. 9) of the sulfided samples revealed the average diameter of the fibers was 196 ± 54 nm. The images indicate that, in analogy to the oxide fibers, two kinds of morphologies are present: fibers with rough surfaces (a) and even surfaces (b). In the fibers with rough surfaces, the flakes are arranged as nanoflowers [35], which seem to emanate from a single bulge on the oxide fiber surface. In the fibers with even surfaces, the a-b plane of the flakes is presumably parallel to the fiber surface, i.e., their c-axis is perpendicular to the growth axis of the fiber. High-resolution TEM of a “rough” fiber shows clearly that the nanoflakes stand out of the fiber surface (<hk0> direction perpendicular to the fiber surface).

From the TEM images (Fig. 10), it can be seen that the fibers are made of small layered flakes arranged randomly with respect to the fiber axis. The measured interlayer spacing is 6.2 Å, which corresponds well to the WS₂ interlayer distance.

From the HAADF STEM EDS measurements (Fig. 11) and quantitative measurements of selected
areas (Table 4), it can be concluded that the fibers are composed of tungsten and sulfur with a 1:2 atomic ratio (WS₂) interspersed by SiO₂ islands. The analysis indicates that the amorphous silica serves as a binder for the WS₂ flakes in the fiber. Such a configuration imparts mechanical robustness for the WS₂ flakes, which are well-separated from each other in the fiber. Therefore, the present fiber morphology could serve as a highly reactive catalyst for different reactions or sensor for different gases.

**Conclusion**

We prepared tungsten disulfide WS₂ fibers by a three-step process. In the first step, we used the needle-less electrospinning technique with an aqueous solution of silicotungstic acid (H₄SiW₁₂O₄₀) and polyvinyl alcohol (PVA) as precursors for the preparation of composite green fibers. The obtained fibers (av. diam. 460 nm) were converted in the second step by calcination in air into tungsten...
oxide WO₃ fibers with traces of SiO₂ coming from the H₄SiW₁₂O₄₀ precursor and with smaller diameter (335 nm). In the final step, we heated the WO₃ fibers under flow of H₂/H₂S/N₂ and converted them to tungsten disulfide WS₂ fibers (av. diam. 196 nm). Based on that experience, we can presume that silicotungstic acid could be a fruitful candidate for water-based scaled up electrospinning followed by after treatment toward WO₃-based materials and other structures.

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**Declarations**

**Conflict of interest** The authors declare no conflicting financial interest.

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