

Thermal study on electrospun polyvinylpyrrolidone/ammonium metatungstate nanofibers: optimising the annealing conditions for obtaining WO₃ nanofibers

Imre Miklós Szilágyi · Eero Santala · Mikko Heikkilä ·
Marianna Kemell · Timur Nikitin · Leonid Khriachtchev ·
Markku Räsänen · Mikko Ritala · Markku Leskelä

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Abstract This article demonstrates how important it is to find the optimal heating conditions when electrospun organic/inorganic composite fibers are annealed to get ceramic nanofibers in appropriate quality (crystal structure, composition, and morphology) and to avoid their disintegration. Polyvinylpyrrolidone [PVP, (C₆H₉NO)_n] and ammonium metatungstate [AMT, (NH₄)₆[H₂W₁₂O₄₀·*n*H₂O] nanofibers were prepared by electrospinning aqueous solutions of PVP and AMT. The as-spun fibers and their annealing were characterized by TG/DTA-MS, XRD, SEM, Raman, and FTIR measurements. The 400–600 nm thick and tens of micrometer long PVP/AMT fibers decomposed thermally in air in four steps, and pure monoclinic WO₃ nanofibers formed between 500 and 600 °C. When a too high heating rate and heating temperature (10 °C min⁻¹, 600 °C) were used, the WO₃ nanofibers completely disintegrated. At lower heating rate but too high temperature (1 °C min⁻¹, 600 °C), the fibers broke into rods. If the heating rate was adequate, but the annealing temperature was too low (1 °C min⁻¹, 500 °C), the nanofiber morphology was excellent, but the sample was less crystalline. When the

optimal heating rate and temperature (1 °C min⁻¹, 550 °C) were applied, WO₃ nanofibers with excellent morphology (250 nm thick and tens of micrometer long nanofibers, which consisted of 20–80 nm particles) and crystallinity (monoclinic WO₃) were obtained. The FTIR and Raman measurements confirmed that with these heating parameters the organic matter was effectively removed from the nanofibers and monoclinic WO₃ was present in a highly crystalline and ordered form.

Keywords WO₃ · PVP · Annealing · TG/DTA-MS · XRD · SEM · Raman · FTIR

Introduction

One-dimensional (1D) nanomaterials, such as nanowires, nanofibers, nanorods, nanowhiskers, nanobelts, nanoribbons, and nanotubes have attracted great attention in recent years. They have already demonstrated outstanding electrical, magnetic, acoustic, optical, mechanical, thermal, sensing, and catalytic properties [1–4]. Various vapor phase (e.g., vapor–liquid–solid synthesis [5], laser ablation [6]), solution phase (e.g., hydrothermal, solvothermal, solution–liquid–solid syntheses [7]), and template directed (e.g., electrochemical anodization–reanodization and etching [8], atomic layer deposition [9]) techniques have been developed to obtain these materials.

Electrospinning is a recent method of choice to prepare 1D nanostructures. It offers a simple and convenient way for making polymer, inorganic, and composite fibers with both solid and hollow interiors. The produced fibers are usually extremely long (up to several hundreds of micrometers) and have uniform diameters ranging between tens of nanometers to several micrometers [10–13]. In

I. M. Szilágyi · E. Santala · M. Heikkilä · M. Kemell ·
T. Nikitin · L. Khriachtchev · M. Räsänen · M. Ritala ·
M. Leskelä
Department of Chemistry, University of Helsinki,
P.O. Box 55, 00014 Helsinki, Finland

I. M. Szilágyi (✉)
Materials Structure and Modeling Research Group
of the Hungarian Academy of Sciences, Department of Inorganic
and Analytical Chemistry, Budapest University of Technology
and Economics, Szt. Gellért tér. 4, 1111 Budapest, Hungary
e-mail: imre.szilagyi@mail.bme.hu

electrospinning, a high static voltage is applied to a polymer or polymer/inorganic solution. Under the strong electrostatic force, the solution is ejected from a nozzle. The charged jet is accelerated by the electric field, dries, and is deposited in the form of nanofibers onto a grounded substrate [14, 15].

When inorganic nanofibers are the target of electrospinning, the as-spun polymeric/inorganic composite fibers are calcined to remove the organic material. Proper calcination is a key step in obtaining high-quality inorganic nanofibers, as they are very brittle and can easily disintegrate to nanoparticles. Up to now, in annealings of electrospun fibers quite many different heating programs have been used, i.e., the heating temperature (300–1000 °C), the heating rate (0.5–5 °C min⁻¹), and the dwell time at the set temperature (1–12 h) varied in wide ranges [2, 10–21]. This shows that it is vital to find the appropriate annealing parameters for each polymer/inorganic composite. The annealing parameters depend mostly on the decomposition temperature of the polymer, the formation temperature of the targeted inorganic crystalline phase, and the mechanical stability of the inorganic nanofibers.

Though proper calcination is vital in getting high-quality electrospun ceramic nanofibers, only few studies have mentioned its importance [11, 13, 17]. Up to now, to the best of our knowledge, only TG and TG/DTA curves of electrospun polymer/inorganic nanofibers have been published [2, 11, 12, 14, 18–20], but these are not detailed thermoanalytical studies, and none of them used evolved gas analysis.

Here we present a model study on the heat treatment of electrospun polyvinylpyrrolidone [PVP, (C₆H₉NO)_n] and ammonium metatungstate [AMT, (NH₄)₆[H₂W₁₂O₄₀]·nH₂O] nanofibers. It clearly demonstrates the importance of finding the appropriate annealing conditions for polymer/inorganic nanofibers prepared by electrospinning. We use the PVP/AMT fibers as a model system, as we have recently developed a new electrospinning process for preparing WO₃ nanofibers (detailed results about the process will be published elsewhere). This process is unique because it is completely water-based, thus environmentally friendly and easy to handle, in contrast to the few previous reported WO₃ electrospinning methods, which used organic solvents to dissolve the polymer and the inorganic precursors [15–17]. As discussed previously, it was necessary to optimize the heating program of the as-spun PVP/AMT nanofibers.

In this study, the PVP/AMT nanofibers are prepared by electrospinning aqueous solutions of PVP and AMT. The annealing process of the PVP/AMT fibers and the product WO₃ nanofibers are characterized by thermal analysis (TG/DTA) and evolved gas analysis with a mass spectrometer

(TG/DTA-MS), X-ray diffraction (XRD), scanning electron microscopy (SEM), FTIR, and Raman spectroscopy.

Experimental section

The AMT/PVP nanofibers were prepared by electrospinning a 1:4 mixture of aqueous solutions of PVP [(C₆H₉NO)_n, 20 wt%] and AMT ((NH₄)₆[H₂W₁₂O₄₀]·nH₂O, 50 wt%). AMT (Fluka, 99% purity) and PVP (Alfa Aesar, *M_w*: 1300,000) were used as received. The needle voltage was 14.4 kV. The polymer fibers were collected on a rotating drum 15 cm from the needle.

The thermal decomposition of the nanofibers was studied by a TG/DTA-MS apparatus consisting of an STD 2960 simultaneous TG/DTA (TA Instruments Inc.) thermal analyzer and a Thermostat GSD 200 (Balzers Instruments) quadrupole mass spectrometer. During the measurement, an open platinum crucible, sample size of 4.5 mg and heating rate of 10 °C min⁻¹ were used, and the thermoanalytical furnace was purged with flowing air (130 mL min⁻¹). On-line coupling of the two parts (TG/DTA and MS) was provided through a heated (*T* = 200 °C) 100% trimethylsilyl deactivated fused silica capillary tube with an inner diameter of 0.15 mm. A mass range between *m/z* = 1–64 was monitored through 64 channels in multiple ion detection mode (MID) with a measuring time of 0.5 s/channel. The components of the released gas mixtures were monitored and identified on the basis of their MS reference gas spectra [22].

Annealing of the as-prepared PVP/AMT nanofibers was done in a Nabertherm N7 furnace equipped with a Logotherm S19 heating program controller. The fibers were heated with 10 or 1 °C min⁻¹ heating rate to 500, 550, or 600 °C (i.e., the heating period ranged between 48 min and 9.5 h), and the samples were kept at the set temperature for 1 h.

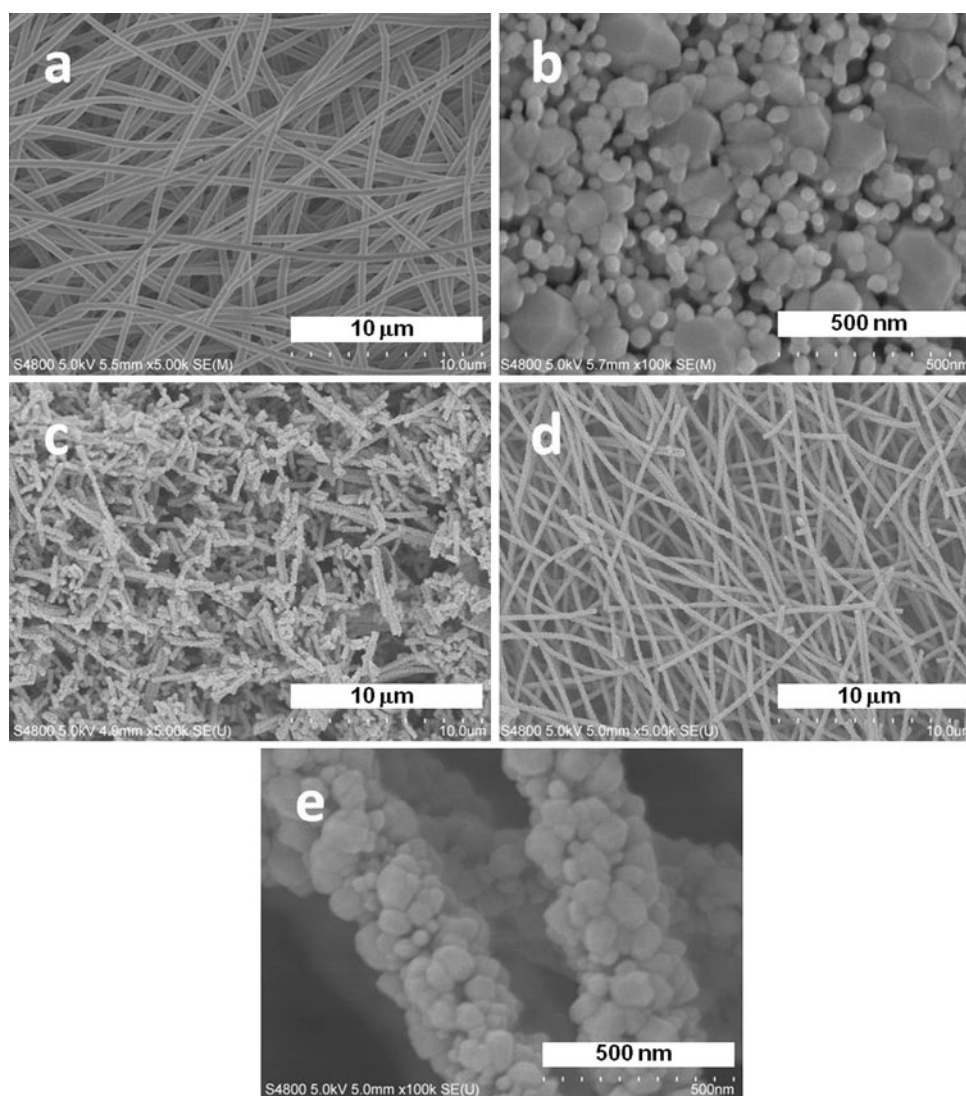
The XRD patterns were recorded by a PANalytical X'pert Pro MPD X-ray diffractometer using Cu K_α radiation and grazing incidence angle mode.

The morphology of the nanofibers was investigated by a Hitachi S-4800 field emission scanning electron microscope (FESEM).

The FTIR measurements were conducted with a Bruker Vertex 80 FTIR spectrometer (liquid nitrogen cooled MCT detector, KBr beamsplitter and Globar light source). The spectral resolution was 2 cm⁻¹ and 100 scans were accumulated for one spectrum.

The Raman spectra were recorded with a LabRam HR confocal microscope (Horiba Jobin Yvon) using excitation at 488 nm of an Ar-ion laser (0.1–1 mW on sample), 100× objective and spectral resolution 2 cm⁻¹.

Fig. 1 **a** SEM images of electrospun PVP/AMT nanofibers, **b–e** SEM images of WO_3 nanofibers obtained by annealing PVP/AMT nanofibers in air **b** at $600\text{ }^\circ\text{C}$ using $10\text{ }^\circ\text{C min}^{-1}$ heating rate and 4 h isothermal stage, **c** at $600\text{ }^\circ\text{C}$ using $1\text{ }^\circ\text{C min}^{-1}$ heating rate and 1 h isothermal stage, and **d, e** at $550\text{ }^\circ\text{C}$ using $1\text{ }^\circ\text{C min}^{-1}$ heating rate and 1 h isothermal stage



Results and discussion

Thermal decomposition and oxidation of PVP/AMT nanofibers

Electrospinning of the PVP/AMT polymer/inorganic solution was successful, and homogenous nanofibers were produced. The diameter of the PVP/AMT fibers was 400–600 nm, and the fibers were several tens of micrometers long (Fig. 1a).

We studied in detail the thermal behavior of the as-spun PVP/AMT nanofibers in air, so that we could determine the annealing temperature, where the organic part of the fibers decomposes and burns out completely. The TG/DTA curves of the thermal decomposition and combustion of PVP/AMT nanofibers in air are shown in Fig. 2, while the evolved gas analytical (EGA) curves of selected ions, recorded with the on-line coupled mass spectrometer, are

presented in Fig. 3. Note that the EGA curves show only qualitative information, and they are scaled so that all features can be seen.

The PVP/AMT decomposed and oxidized in four main steps. To explain the steps, the measured thermoanalytical curves were compared with previous data published about the thermal decomposition of PVP and AMT.

There is abundant information available about the thermal decomposition of PVP and PVP/inorganic composites, as they have applications in many areas (e.g., nanotechnology [23], materials science [24], fuel cells [25], pharmaceutical and biomedical applications [26–28], and cosmetics [29]). The decomposition of PVP and PVP/inorganic composites (including electrospun fibers) was studied previously both in air and N_2 , and mostly TG [30–37] and TG/DTA studies were published [2, 10–12, 18–20, 38–44] and only one evolved gas analytical report exists [45].

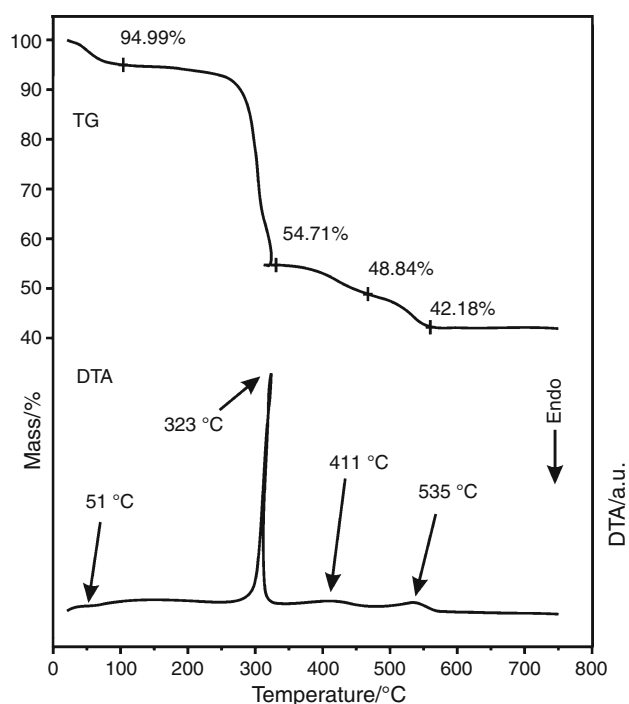


Fig. 2 Simultaneous TG/DTA curves of PVP/AMT nanofibers measured in air (130 mL min^{-1} , $10 \text{ }^\circ\text{C min}^{-1}$, open Pt crucible, 4.5 mg)

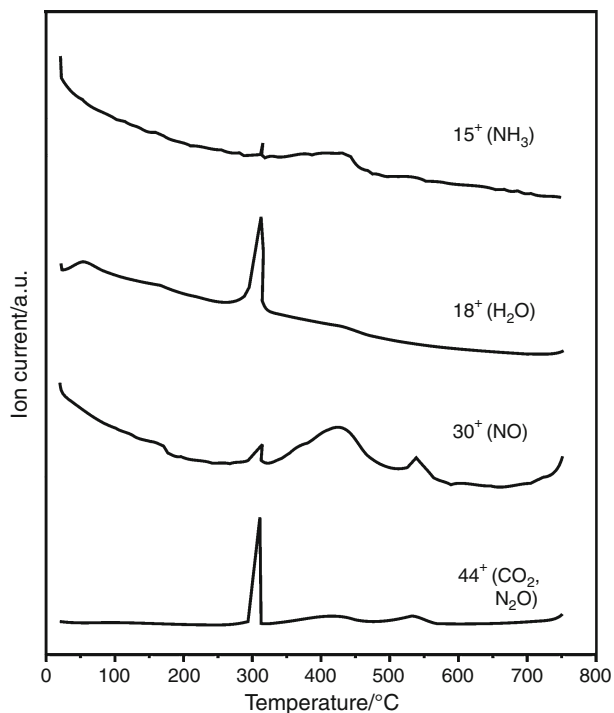


Fig. 3 Evolved gas analytical (MS ion) curves of PVP/AMT nanofibers measured in air (130 mL min^{-1} , $10 \text{ }^\circ\text{C min}^{-1}$, open Pt crucible, 4.5 mg)

There are much less published data about the thermal behavior of AMT. To the best of our knowledge, no thermal study has been performed on pure AMT. However,

AMT was reported to be a decomposition intermediate of ammonium paratungstate (APT), $(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 4\text{H}_2\text{O}$ at $200\text{--}250 \text{ }^\circ\text{C}$ [46, 47], though other studies could not confirm this [48]. The thermal behavior of APT is very well known as it is an important starting material for making tungsten oxides, tungsten carbides and tungsten metal for catalysis, hardmetals, and light source industry [49]. The thermal decomposition of APT has been characterized by various thermoanalytical (TG, DTA, and evolved gas analysis) and further techniques (e.g., XRD, SEM, FTIR, Raman, etc.) in oxidative, inert, and reductive atmospheres (see [48, 50–54 and the references therein]). Thus, it was expected that the thermal decomposition of AMT should be similar to that of APT above $200\text{--}250 \text{ }^\circ\text{C}$.

Here in our study, at the first decomposition step ($25\text{--}100 \text{ }^\circ\text{C}$) adsorbed water was released from both PVP and AMT (5% mass loss) in an endothermic reaction, shown by a small peak in the H_2O EGA curve (18^+ , H_2O^+).

The second decomposition step took place between 250 and $330 \text{ }^\circ\text{C}$, where the largest mass loss occurred (40%). According to the previous thermal studies on PVP [2, 12, 18–20, 31, 37, 39, 44] in air, the main decomposition of PVP takes place in this temperature range. The dramatic weight loss in the TG curve was the result of the breakdown of the sidegroups (pyrrolidone) of PVP, which were released and oxidized immediately. The combustion of the evolved gaseous species was responsible for the sharp peaks in the CO_2 (44^+ , CO_2^+) and H_2O EGA curves, and it also explained the very sharp exothermic heat effect in the DTA curve, which occurred at $323 \text{ }^\circ\text{C}$. However, at this step not just PVP started to decompose, but also AMT. In the NH_3 (15^+ , NH^+) curve a small peak was observable, which suggested that part of the NH_4^+ ions of AMT was released here.

At the third decomposition step ($350\text{--}450 \text{ }^\circ\text{C}$), the main decomposition of AMT took place. This explanation was supported by that the largest peaks in the NH_3 and NO (30^+ , NO^+) EGA curves were observable in this region. Most probably NH_4^+ ions and also H_2O molecules, which linked the large metatungstate ions, were released at this step (similar to the decomposition of APT), and in air they were burnt right away. In the case of the oxidation of APT [52], NO and N_2O (44^+ , N_2O^+) were the main combustion products of as-released NH_3 [55], and this was the case in the thermal oxidation of AMT as well. In parallel to the gas release, hexagonal (h-) WO_3 or oxidized $(\text{NH}_4)_x\text{WO}_3$ could form at $460 \text{ }^\circ\text{C}$, similarly to the case of annealing APT. It has recently been proven that h- WO_3 still contains small amount of impurities (NH_4^+ or alkaline ions depending on the type of precursor), which stabilize its metastable structure [56]. Therefore, $(\text{NH}_4)_x\text{WO}_3$ and h- WO_3 are

basically the same compounds [56, 57], the only difference between them is that the longitudinal hexagonal channels of $(\text{NH}_4)_x\text{WO}_3$ are more packed with NH_4^+ ions than that of h- WO_3 .

It is worth mentioning that the main decomposition of AMT happened at 50–80 °C higher temperature than expected, based on previous results on APT. In general, the main decomposition of the APT bulk takes place between 250 and 350 °C [48, 50–54], and an amorphous phase forms. From this, h- WO_3 or oxidized $(\text{NH}_4)_x\text{WO}_3$ form in another decomposition step between 350 and 450 °C. In the case of AMT, these two stages could happen continuously in one step and at higher temperature than with APT, for which the presence of PVP might be responsible.

Based on previous results, the degradation of the residual hydrocarbon polymer chain of PVP also took place at the third step, but it could not be seen directly from the TG/DTA and EGA curves, as the decomposition of AMT was more intense, and the mass spectrometric signals of N_2O overlapped with CO_2 . At the third decomposition stage, the combustion of NH_3 and the organic material as well as the crystallization of $(\text{NH}_4)_x\text{WO}_3$ and h- WO_3 [51, 52] resulted again in an exothermic DTA peak (411 °C), which was smaller than that at the second step.

At the last decomposition step (460–570 °C) the carbonized residue of PVP was burnt. In this final decomposition process, the as-formed h- WO_3 and $(\text{NH}_4)_x\text{WO}_3$ could release their residual NH_4^+ content, and transform into monoclinic (m-) WO_3 . Again, a small exothermic peak was detected in the DTA curve in this region, the origin of which was the combustion of residual carbon and as-released NH_3 , and also the exothermic hexagonal–monoclinic WO_3 phase change [56].

The decomposition of the electrospun PVP/AMT nanofibers ended between 550 and 570 °C, and no further thermal processes were observed at higher temperatures up to 800 °C.

Optimizing the annealing conditions of PVP/AMT electrospun nanofibers

According to the TG/DTA-MS study, the organic content of the PVP/AMT nanofibers was burnt away completely by 550–570 °C. Therefore, it was straightforward to anneal the PVP/AMT fibers in a furnace at 600 °C, for which a 10 °C min^{-1} heating rate (the same as at the TG/DTA-MS study) was used, and then the fibers were kept at 600 °C for 4 h. According to SEM images (Fig. 1b), the organic content was burnt completely and WO_3 formed, but the WO_3 nanofibers disintegrated, and only 50–250 nm WO_3 particles were visible. This clearly demonstrated that a too high heating rate and too high annealing temperature might destroy the ceramic nanofibers, as was also mentioned and

shown in some previous electrospinning studies [11, 13, 17].

Therefore a much lower (1 °C min^{-1}) heating rate was applied, and the PVP/AMT fibers were annealed at lower temperatures as well, i.e., at 550 and 500 °C and a shorter, 1 h long isothermal stage was used. At 600 °C and with a 1 °C min^{-1} heating rate, the WO_3 nanofibers did not disintegrate, but they still broke into 1–5 μm long and 250 nm wide nanorods, which were made up of 20–80 nm large particles (Fig. 1c). At 550 °C (Fig. 1d, e) and at 500 °C (not shown here), several ten micrometer long WO_3 nanofibers were formed. These fibers were also 250 nm in diameter and were built up of 20–80 nm particles, just as those annealed at 600 °C. Larger 50–80 nm large particles were located at the surface of the fibers, while the inner part of the fibers was packed with smaller, 20–50 nm particles. The reason for such a size distribution of nanoparticles can be that higher mobility of particles at the surface of the fibers favors more intense grain growth.

The XRD patterns of the PVP/AMT fibers annealed at 500, 550, and 600 °C (1 °C min^{-1} heating rate, 1 h isothermal stage) are shown in Fig. 4. All diffractograms correspond to pure, crystalline m- WO_3 (ICDD 43-1035 [58]). It is visible that as the annealing temperature rose, the XRD peaks got sharpened, i.e., the structure of m- WO_3 became more ordered. At 500 °C, the structure was considerably less crystalline than at 550 and 600 °C, and here the sample had a greenish-yellow color, suggesting an incompletely oxidized structure [56, 57]. The samples annealed at both 550 and 600 °C were yellow, thus fully

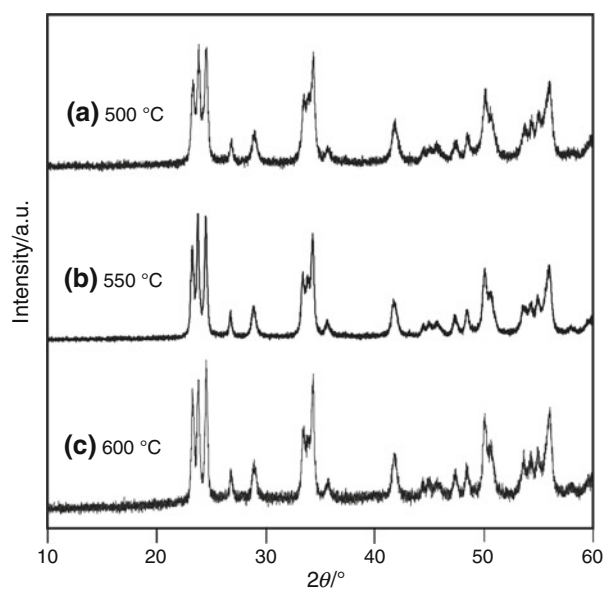


Fig. 4 XRD patterns of WO_3 nanofibers obtained by annealing PVP/AMT nanofibers using 1 °C min^{-1} heating rate and 1 h isothermal stage in air at (a) 600 °C, (b) 550 °C, and (c) 500 °C

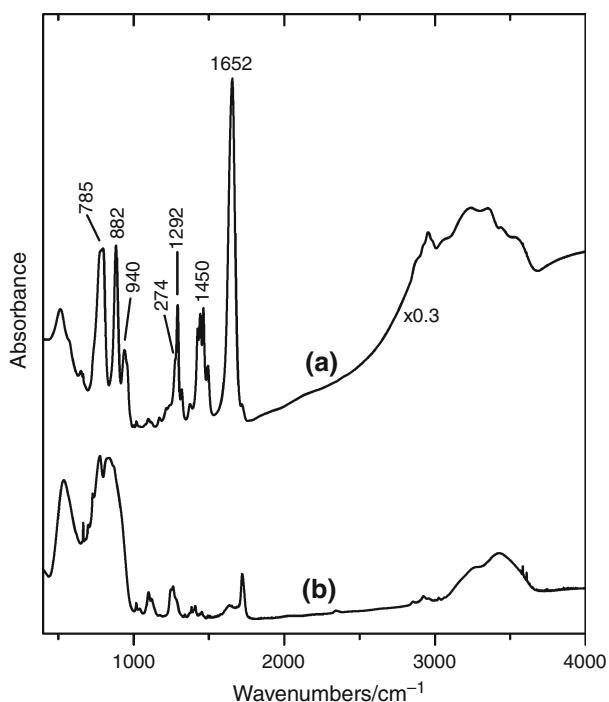


Fig. 5 (a) IR spectrum of electrospun PVP/AMT nanofibers, (b) IR spectrum of WO₃ nanofibers obtained by annealing PVP/AMT nanofibers in air at 550 °C using 1 °C min⁻¹ heating rate and 1 h isothermal stage

oxidized, and the difference between their crystallinity was not quite significant.

As a fair compromise, 550 °C was selected for the annealing temperature of PVP/AMT nanofibers, and the heating rate was chosen to be 1 °C min⁻¹. Under these conditions the structure was as crystalline as possible, while the nanofiber arrangement of WO₃ was still preserved.

Finally, to double-check the completeness of annealing (removal of organic species and formation of well-ordered structure of m-WO₃), the as-spun PVP/AMT fibers and the WO₃ nanofibers prepared at 550 °C (1 °C min⁻¹ heating rate, 1 h isothermal stage) were also studied with FTIR and Raman spectroscopy.

The FTIR spectrum of PVP/AMT (Fig. 5a) was dominated by the bands of PVP [19, 26, 33, 35, 39]. The broad multiband region at 3100–3450 cm⁻¹ (3200, 3330, and 3413 cm⁻¹) was ascribed to the OH stretching vibrations of both PVP and AMT, while the band at 3540 cm⁻¹ could be explained by the NH stretching modes of AMT. The bands at 2850–3000 cm⁻¹ (2860, 2913, 2944, and 2962 cm⁻¹) were explained by the CH stretching vibrations of CH and CH₂ in PVP. The most intense peak of PVP was the C=O stretching band at 1652 cm⁻¹. Four IR modes at about 1450 cm⁻¹ (1422, 1440, 1462, and 1473 cm⁻¹) were due to the bending CH modes of CH₂ of PVP and the

deformation mode of the NH₄⁺ ion [53] of AMT. The peak at 1292 cm⁻¹ and the shoulder at 1274 cm⁻¹ could be explained by the C–N and C–O stretching bands of PVP, respectively. The bands of AMT were observable mostly below 1000 cm⁻¹. The W=O vibrations were detected at about 940 cm⁻¹ (930, 955 cm⁻¹), and the W–O bands were visible at 700–900 cm⁻¹ (785, 882 cm⁻¹). These bands were identified based on the FTIR data of polytungstates and WO₃ [59–63], as the FTIR spectrum of AMT has not been published yet.

When the composite fibers were annealed at 550 °C (Fig. 5b), the PVP bands (e.g., at 1652 cm⁻¹) disappeared almost completely showing the effective removal of the organic material. Traces of organic fragments were suggested only by very weak bands at 1652 and 2850–3000 cm⁻¹. However, the amount of these trace organics (in this study the absorbance of the peak at 1652 cm⁻¹ reduced 50 times from 3.13 to 0.06, when PVP/AMT was annealed at 550 °C) was as low or even less than in other electrospinning studies [11, 18, 20, 21]. The broad peak between 700 and 1000 cm⁻¹ (723, 752, 805, and 852 cm⁻¹) in the FTIR spectrum of the sample annealed at 550 °C belonged to the W=O and W–O vibrations.

In the Raman spectrum of PVP/AMT (Fig. 6a), the bands of AMT were much more intense than the bands of PVP, which was in contrast to the FTIR results. Similar to

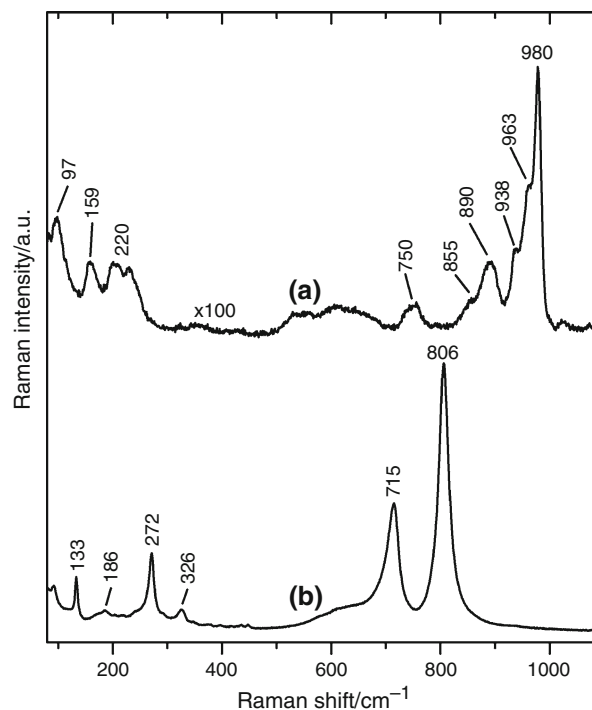


Fig. 6 (a) Raman spectrum of electrospun PVP/AMT nanofibers, (b) Raman spectrum of WO₃ nanofibers obtained by annealing PVP/AMT nanofibers in air at 550 °C using 1 °C min⁻¹ heating rate and 1 h isothermal stage

the FTIR, the Raman spectrum of pure AMT has not been published yet, however, the supposed Raman bands of AMT could be identified based on the known Raman spectra of polytungstates [48, 61, 64–67]. The peak at 980 cm^{-1} with shoulders at 963 and 938 cm^{-1} (W=O bands) and the peak at 890 cm^{-1} with a shoulder at 855 cm^{-1} (W–O bands) are characteristic to polytungstates [48, 61, 64–67]. Similar to paratungstates [60, 64, 65], the weaker Raman peaks at 500 – 700 cm^{-1} (657 , 618 , 571 , 540 , 360 , and 337 cm^{-1}) and about 220 cm^{-1} (235 , 210 cm^{-1}) could also be assigned to AMT. One of the characteristic Raman peaks of PVP, the pyrrolidone ring breathing mode at 934 cm^{-1} [13, 26–28, 40, 68], could not be observed, because the more intense Raman peaks of AMT between 850 and 1000 cm^{-1} covered it completely. Similarly, the Raman peaks of PVP at 858 and 556 cm^{-1} [26, 40, 68] were overlapped by the AMT bands. Nevertheless, the C–N vibration band at 750 cm^{-1} [26, 27, 40, 68] clearly showed the presence of PVP, and some other Raman peaks of PVP could also be detected at 371 , 159 , and 97 cm^{-1} [40, 68].

When the PVP/AMT polymer was annealed at $550\text{ }^{\circ}\text{C}$ (Fig. 6b), all the Raman bands of PVP disappeared, and only the Raman bands of pure m- WO_3 were present [58, 69–72]. The main bands at 806 and 715 cm^{-1} were the O–W–O stretching vibrations, and additional peaks of m- WO_3 were also detected, i.e., the O–W–O deformation vibrations at 326 and 272 cm^{-1} , lattice modes at 186 and 133 cm^{-1} . The sharp Raman peaks confirmed the XRD results that m- WO_3 was highly crystalline and ordered.

Conclusions

The PVP ($\text{C}_6\text{H}_9\text{NO}$) $_n$ and AMT (NH_4) $_6$ [$\text{H}_2\text{W}_{12}\text{O}_{40}$] $\cdot n\text{H}_2\text{O}$ composite nanofibers were prepared by a newly developed electrospinning process from aqueous solutions of PVP and AMT. Our aim was to find the optimal annealing conditions of the PVP/AMT fibers to get high-quality WO_3 nanofibers. We also intended to demonstrate in general the importance of appropriate heating conditions for organic/inorganic electrospun fibers to avoid disintegration of the obtained ceramic nanofibers.

The as-spun PVP/AMT fibers and their annealing were characterized by TG/DTA-MS, XRD, SEM, Raman, and FTIR. The PVP/AMT fibers were 400 – 600 nm thick and dozens of micrometer long. According to TG/DTA-MS results, the composite fibers thermally decomposed and oxidized in air in four steps between 25 and $570\text{ }^{\circ}\text{C}$. Based on these results, the PVP/AMT fibers were annealed in a furnace between 500 and $600\text{ }^{\circ}\text{C}$ and pure m- WO_3 nanofibers were obtained. When $10\text{ }^{\circ}\text{C min}^{-1}$ heating rate was used at $600\text{ }^{\circ}\text{C}$, the WO_3 nanofibers completely

disintegrated. At $600\text{ }^{\circ}\text{C}$ and with a $1\text{ }^{\circ}\text{C min}^{-1}$ heating rate, the fibers broke into rods, while at 500 and $550\text{ }^{\circ}\text{C}$ high quality, 250 nm thick and tens of micrometer long WO_3 nanofibers were obtained. The fibers consisted of 20 – 80 nm particles. At $500\text{ }^{\circ}\text{C}$ the crystalline structure was not ordered enough, therefore $550\text{ }^{\circ}\text{C}$ and $1\text{ }^{\circ}\text{C min}^{-1}$ heating rate were found to be the optimal annealing conditions for this set of electrospun nanofibers.

According to the FTIR and Raman spectra, PVP disappeared after annealing at $550\text{ }^{\circ}\text{C}$, and based on FTIR only traces of organics were still present. These results confirmed that with optimized heating parameters the organic matter can be effectively removed from the inorganic nanofibers. In harmony with the XRD results, the Raman data also showed that at $550\text{ }^{\circ}\text{C}$ m- WO_3 was present in highly crystalline and ordered form.

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