Investigation of the influence of calcination temperature on morphology and structure of electrospun 1D SnO$_2$ nanostructures

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Abstract. The aim of the study was to manufacture the SnO$_2$ one-dimensional nanostructures via the sol-gel technique and electrospinning methods from a solution of polyvinylpyrrolidone (PVP), tin chloride pentahydrate (SnCl$_4$·5H$_2$O), N, N-dimethylformamide (DMF) and ethanol (EtOH). The as obtained fibrous mats consisting of polymer and precursors particles were subjected to the heat treatment in air in the following temperatures 500, 600 °C to obtain pristine tin oxide nanowires. The scanning electron microscope (SEM) was used to determine the effect of calcination temperature on the morphology and structure of produced 1D SnO$_2$. The energy dispersive spectrometry (EDX) and Fourier-Transform Infrared spectroscopy (FTIR) were performed to investigate the chemical composition and structure of manufactured nanomaterials, respectively.

1 Introduction
Recently, increased interest in one-dimensional nanomaterials has been observed, which is primarily due to their extraordinary properties that distinguish them from other types of nanomaterials. The limited electron movement to two quantum directions and the high density of energy states are often responsible for optical, electrical, magnetic, and electrochemical properties of these nanostructures, which are much better than zero, two and three-dimensional nanomaterials. Ceramic semiconductor nanomaterials based on such compounds as titanium oxide (TiO$_2$), zinc oxide (ZnO), silicon oxide (SiO$_2$), bismuth oxide (Bi$_2$O$_3$) as well as tin oxide (SnO$_2$) are particularly popular among one-dimensional nanostructures [1-7].

As of today, based on literature study, it should be noted that SnO$_2$, despite the equally interesting as other oxides, optical and electrical properties (energy band gap, refractive index and dielectric constant) is much less studied, and analysis mechanisms responsible for their structure and properties are still a challenge for scientists. This is why this material should be given special attention, as it can be an ideal alternative to popular TiO$_2$ or ZnO in terms of optical properties. Tin oxide nano-materials are n-type semiconductor characterised by large surface-to-volume ratio, high optical transmission in the visible range, energy band gap in the range of 3.0–3.9 eV and good mechanical, chemical and thermal stability [7, 8].

For this reason, nanostructures have a wide application potential, which includes the construction of modern electronic and optical devices such as sensors or photovoltaic cells, as well as photocatalytically assisted water and air purification processes [7-10]. Therefore, in order to obtain SnO$_2$ nanowires with the desired morphology and physical properties, the influence of the parameters of the manufacturing process should be carefully studied. The
particular attention should be paid to the calcination temperature, which significantly affects the diameter and optical properties of SnO$_2$ nanowires, which was presented in this work.

2 Materials and methods
To prepare spinning solutions, in order to produce one-dimensional tin oxide nanostructures, the following reagents were used: poly(vinylpyrrolidone) (PVP, purity of 99%, Mw = 1,300,000 g/mole), N,N-dimethylformamide (DMF, purity of 99.8%), ethanol (EtOH, purity of 99.8%) and tin chloride pentahydrate (SnCl$_4$·5H$_2$O), purity of 98%). All substrates were purchased from Sigma-Aldrich.

In the first step, the mixture of 6 g of tin chloride pentahydrate and dimethylformamide (10 ml) was made using magnetic stirrer for 48 h; mixture of ethanol (10 ml) and 2 g of PVP was prepared and then added to the above mixture and such homogenous solution was subjected to magnetic stirring for 48 h. The composite nanofibers polymer/precursor were obtained using the FLOW – Nanotechnology Solutions Electrospinner 2.2.0-500 device, with the following parameters: the distance and voltage between the electrodes of 15 cm and 24 kV, respectively and the flow rate of 0.45 ml/h. Directly after the fibrous mat production process, drying at room temperature was performed. After this, calcination in a high-temperature furnace EasyTube 2000 provided by first nano at temperatures of 500 and 600 °C (heating rate of 2 °C/min) for 6 h in air was conducted. The manufactured samples were left in a furnace to cool down completely.

In order to image the topography nanostructures and analyse the chemical composition of the prepared composite and ceramic one-dimensional nanostructures, the (SEM) Zeiss Supra 35 scanning electron microscopes with the Trident XM4 series (EDX) X-ray spectrometer were used. Based on the SEM images, a measurement of one hundred randomly selected diameter values of the obtained nanomaterials using DigitalMicrograph was provided. In addition, to analyse the oscillatory transitions of atoms vibrating between the oscillatory levels in the molecules of the produced nanomaterials, and to determine the functional groups existing therein, Fourier-Transform Infrared spectroscopy (FTIR) (Nicolet™ iST™ 50 FTIR Spectrometer, Thermo Fisher Scientific) was used.

3 Results and discussion
3.1 Morphology, structure and chemical composition
An analysis of the morphology and structure of nanofibers prior to the calcination process demonstrated that PVP/SnO$_2$ nanofibers are devoid of structural defects and have a constant diameter along the entire length, which results from the preparation of a solution of appropriate viscosity and the correct selection of electrospinning parameters (figure 1a). Using both calcination temperatures during the calcination process, of 500 and 600 °C, allowed for obtaining homogenous one-dimensional SnO$_2$ nanowires without visible structural defects in the form of agglomerates or welded nanowires (figure 2, 3).

The analysis of the morphology of the obtained PVP/SnCl$_4$ nanofibers made on the basis of a hundredfold measurement of the diameters of randomly selected one-dimensional composite nanostructures with a polymer matrix, showed that the nanofibers were characterised by diameters in the range of 40–320 nm, an average diameter was 180 nm. In addition, the largest group was nanofibers with diameters ranging from 160 to 240 nm (figure 1, histogram).

Analysis of the morphology of SnO$_2$ nanowires calcined in 500 °C, performed on the basis of 100-times measurements of their diameters, has shown that wires diameters ranged between 50 and 250, with wires ranging between 125 and 175 nm making up the most numerous group of 36% of nanowires. The average wire diameter was 138 nm (figure 2, histogram).
Figure 1. SEM surface morphology images, histograms showing the distribution of hundredfold measurement of the diameter and chemical composition of the produced PVP/SnCl₄ composite nanofibers

A hundredfold diameter measurement of random SnO₂ wires obtained from calcination in 600 °C showed that the measured diameters ranged from 15 to 75 nm, with the most common values for the diameter (60% of all measured values of diameters) contained in the range from 25 to 45 nm and an average diameter of 40 nm (figure 3, histogram). Therefore, a strong shrinkage of nanowires is noticeable as a result of the calcination process.

The observed decrease in the diameter of nanowires after calcination compared to the diameter of the fibers just after electrospinning results from the removal of the polymer matrix and obtaining pristine SnO₂ nanowires. In addition, the higher calcination temperature made it possible to obtain nanowires with a much smaller diameter than for wires calcined at 500 °C [11, 12].

The EDX spectra confirmed the formation of non-contaminated, pristine SnO₂ nanowires from z PVP/SnCl₄ nanofibers, because chlorine from the precursor nanoparticles does not appear in the spectra recorded for nanowires (figure 1-3).
Figure 2. SEM surface morphology images, histograms showing the distribution of hundredfold measurement of the diameter and chemical composition of the produced SnO$_2$ nanowires calcined in 500 °C.

The absorbance spectra in the function of wavenumber in the range of 400–3500 cm$^{-1}$ graphs were plotted for composite PVP/SnCl$_4$ nanofibers and SnO$_2$ nanowires with some characteristic peaks for individual vibration molecules or functional groups (figure 4). In the spectrum obtained for composite nanofibers we observe characteristic peaks at 558 cm$^{-1}$ that may be assigned respectively to N-C=O bending. The peaks at 1298 and 1632 cm$^{-1}$ proved the existence of C-N and stretching of C=O, respectively. All characteristic peaks for $-\text{CH}_2-\text{CH}$ groups of PVP at 1456, and 2957 cm$^{-1}$ were observed, respectively. The FTIR spectrum of PVP/SnCl$_4$ had a peak at 3169 cm$^{-1}$ which indicates O-H stretching. At 670 cm$^{-1}$ Sn-O bond from precursor occurrence in nanofibers can be observed [13, 14].

In the case of FTIR spectra recorded for both SnO$_2$ samples, the occurrence of broad peaks at 639 and 667 cm$^{-1}$ confirms generation of Sn-O bond. In addition, no characteristic peaks from PVP are observed, which confirms the degradation of the polymer during the calcination in both temperatures.
Figure 3. SEM surface morphology images, histograms showing the distribution of hundredfold measurement of the diameter and chemical composition of the produced SnO$_2$ nanowires calcined in 600 °C.

Figure 4. FTIR spectrum for PVP/SnCl$_4$ composite nanofibers and SnO$_2$ nanowires calcined in 500 and 600 °C.
4 Conclusion
The aim of this work was to prepare, using combination method of sol-gel technique and electrospinning from solutions PVP/SnCl$_4$/DMF/EtOH, and examine the morphology and structure of SnO$_2$ nanowires. The performed morphology and structure analysis of the obtained after calcination in 500 and 600°C one-dimensional tin oxide nanostructures using scanning (SEM) revealed that SnO$_2$ nanowires were characterised by a lack of structural defects and constant diameter values along the entire lengths. Moreover, the increase in the annealing temperature is associated with a decrease in the nanowire diameter values, respectively 138 nm for 500°C and 40 nm in the case of 600°C.

Both, EDS and FTIR analysis confirmed that pristine, undoped SnO$_2$ nanowires were obtained, which confirms that the presented method allows control the morphology and chemical composition of the produced one-dimensional nanostructures. This work is a good basis for further research on the electrical and optical properties of SnO$_2$ nanowires depending on the parameters of the electrospinning and calcination process.

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