Morphology and structure characterization of crystalline SnO_2 1D nanostructures

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Abstract—In recent years, many attempts have been made to improve the sensory properties of SnO_2, including design of sensors based on one-dimensional nanostructures of this material, such as nanofibers, nanotubes or nanowires. One of the simpler methods of producing one-dimensional tin oxide nanomaterials is to combine the electrospinning method with a sol-gel process. The purpose of this work was to produce SnO_2 nanowires using a hybrid electrospinning method combined with a heat treatment process at a temperature of 600°C and to analyze the morphology and structure of the one-dimensional nanomaterial produced in this way. Analysis of the morphology of composite one-dimensional tin oxide nanostructures showed that smooth, homogeneous and crystalline nanowires were obtained.

Gas sensors based on semiconductor metal oxides (MOS) are widely used in many areas, which includes the control of chemical pollution in the air and rooms, alarms of hazardous substances, and medical diagnostics based on the patient's breath. This type of sensor is very popular due to its high sensitivity, low manufacturing cost, simplicity, as well as compatibility with modern electronic devices. One of the most considered metal oxides in addition to ZnO or In_2O_3 is SnO_2. Tin oxide is characterized by simultaneous optical transparency and electrical conductivity, an energy band gap of 3.6–4.0 kV and high sensitivity. Recently, scientists have been trying to improve the detection properties of SnO_2-based sensors by using one-dimensional nanostructures, such as nanofibers, nanotubes or nanowires. One of the simplest methods of producing one-dimensional tin oxide nanomaterials is to combine the solution electrospinning method with a sol-gel process [1-4]. In the first stage, using the electrospinning process, composite nanofibers made of a polymer matrix and reinforcement in the form of the metal oxide precursor nanoparticles are prepared. The electrospining technique involves the use of an electrostatic field induced between the electrodes (nozzle and grounded collector) under the influence of high voltage to form and stretch a drop of the spinning solution to form a fiber settling in a spiral motion on the collector, resulting in a fibrous (nano)mat receiving. Then, fibers are subjected to a heat treatment process, which leads to degradation of the organic phase and obtaining ceramic one-dimensional nanomaterials [5]. The first attempts to use electro-spun SnO_2 nanofibers for the construction of gas sensors were described in 2008 by Y. Zhang *et al*. [5]. Nanofibers were spun from a solution of poly(vinyl acetate) (PVA) and $SnCl_4 \cdot 5H_2O$ in ethanol and *N*, *N*-Dimethylformamide, after that as-obtained mats were calcined at various temperatures for 4 hours. The properties of the SnO_2-coated ethanol detection sensor were tested and it was shown that the newly developed sensor was characterized by very high sensitivity (detection limit <10 ppb at 330°C), fast response (<14 s) and high repeatability. These results confirmed that one-dimensional nanomaterials based on SnO_2 produced by electrospinning could be successfully used in sensors construction. Sensors based on coreless SnO_2 nanofibers manufactured by W.Q. Li *et al*. also showed high sensitivity to detect acetone detection [6]. Further researches focused on improving gas detection of SnO_2-based detectors, by modifying the solution or process by changing the size of crystallites or increasing the specific surface area of anode material. However, the most effective method of improving the sensors response is doping with various metals (Fe, Ce, Pr), forming composites by using two or more metal oxides (ZnO, TiO_2, CuO, In_2O_3), as well as doping with carbon materials [7-13].

The aim of this work was to manufacture small diameter SnO_2 nanowires using a hybrid electrospinning method combined with the sol-gel process and to analyse the morphology and structure of one-dimensional nanomaterials produced in this way. In order to prepare a spinning solution the following reagents were used: polyvinylpyrrolidone (PVP, 99% purity, Mw = 1 300,000 g/mole), *N*, *N*-Dimethylformamide (DMF, 99.8% purity), ethanol (EtOH, 99.8% purity) and tin chloride ($SnCl_4 \cdot 5H_2O$, 98% purity). All reagents and the polymer were purchased from Sigma-Aldrich. First, the homogenous mixture of 2 g of tin chloride and 10 ml of *N*, *N*- Dimethylformamide was prepared by magnetic stirring for 48 h, at the same time 2 g of PVP was dissolved in 10 ml of ethanol. After 48 h of stirring, PVP/EtOH mixture was added to DMF/$SnCl_4$ and this mixture was subjected to magnetic stirring for next 48 h. Directly after that, the composite PVP:$SnCl_4$ nanofibers were obtained using the FLOW – Nanotechnology Solutions Electrospinner 2.2.0-500 device, with the following parameters: the distance and voltage between the nozzle and collector of 15 cm and 26 kV and the solution flow rate 0.45 ml/h. Then, the

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obtained nanofibrous mat was dried at room temperature. After this, calcination in a high-temperature furnace First Nano Furnace (EasyTube 2000 System) at a temperature of 600 °C with a heating rate of 2 °C/minute for 10 h was performed. This caused the polymer to degrade and to form pristine SnO_2 nanowires (Fig. 1). Manufactured one-dimensional tin oxide nanomaterial was subjected to topography analysis using a scanning electron microscope (SEM) of Zeiss Supra 35. Based on images taken with the help of SEM at 50 000x magnification, the diameters of 100 randomly selected nanofibers were measured using the Digital Micrograph program. Measurements were compiled in the form of a diameter distribution histogram and the average diameter of 1D structure of each material type was determined. In order to analyse the morphology and structure of the obtained materials, the TITAN 80–300 FEI high-resolution transmission electron microscope (TEM) was used for imaging in the transmission mode as well as the scanning-transmission mode, with the use of a bright field (BF), HAADF detector and analytical electron microscopy in nanoareas in STEM mode. Identification of chemical bonds and functional groups in the structure of obtained one-dimensional composite and ceramic nanostructures was carried out using Fourier transform infrared spectroscopy (FTIR). Using the Nicolet™ iS50 FTIR Spectrometer from Thermo Scientific™, absorbance spectra were recorded, as a function of wavenumber in the range from 400 to 3500 cm^{-1}. A summary of the manufacturing process and research methodology is presented in Fig. 2.

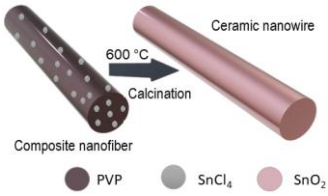

Fig. 1. Schematic representation of SnO_2 nanowires formation.

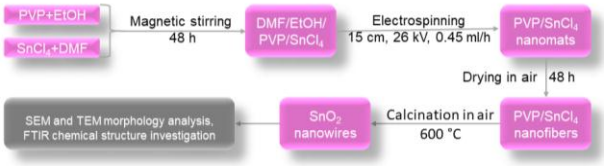

Fig. 2. Scheme of the methodology for the production and study of one-dimensional SnO_2 nanomaterials.

Analysis of the morphology of composite PVP/$SnCl_4$ performed with the use of SEM microscope has shown that the obtained nanostructures were smooth, homogenous and free from structural defects in the form of beads (Fig. 3). Measurements of nanofibers diameters in this sample, repeated 100 times, have shown that these fibers were characterized by diameters in the range of 31–114 nm with an average value of measured diameters of 60 nm (Fig. 4). This demonstrates the preparation of solutions with sufficiently high viscosity and the selection of appropriate parameters for the electrospinning process.

Based on SEM observations of one-dimensional morphology of SnO_2 nanostructures, it was noticed that nanowires have a rough developed surface, but they are homogeneous and have the same diameter over the entire length of the fiber (Fig. 5). A hundredfold diameter measurement of randomly selected SnO_2 nanowires showed that the measured diameters ranged from 19 to 80 nm with the average diameter of 40 nm (Fig. 6). The reduction in diameters size after the calcining results from the removal of the polymer matrix and obtaining pure SnO_2 nanowires, which indicates that the calcination temperature was selected properly.

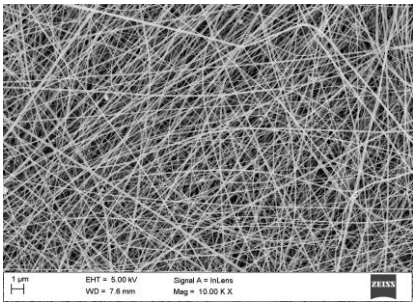

Fig. 3. SEM image of electrospun composite PVP/$SnCl_4$ nanofibers.

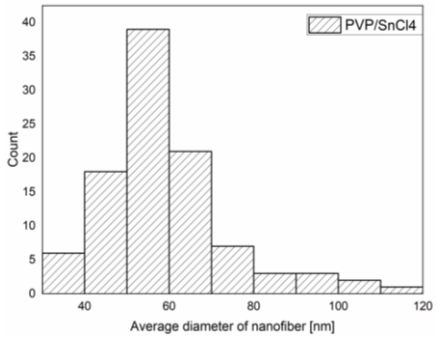

Fig. 4. Histogram showing the distribution of the measured PVP/$SnCl_4$ nanofibers.

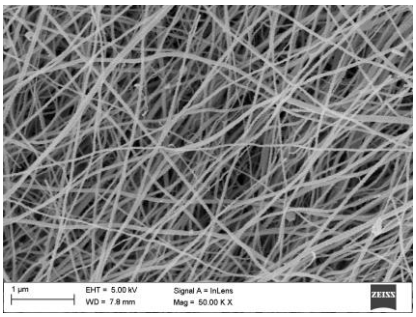

Fig. 5. SEM image of ceramic SnO_2 nanowires after calcination in 600°C.

Figure 7 presents TEM images, based on which it was found that the obtained nanowires are polycrystalline, made of crystallites with a size of about 10 nm. In addition, the diffraction analysis performed in the selected nanoarea showed that SnO_2 nanowires present a tetragonal structure.

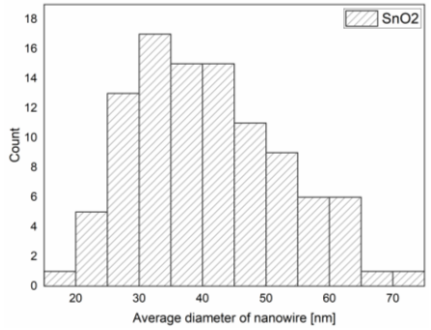

Fig. 6. Histogram showing the distribution of the measured SnO_2 nanowires.

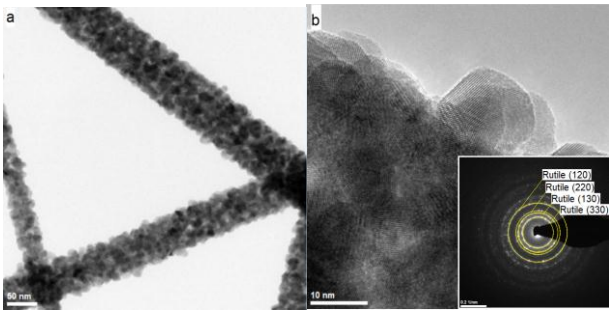

Fig. 7. TEM pictures of polycrystalline SnO_2 nanowires: a) in the bright field, b) HRTEM image with solved diffraction of polycrystalline SnO_2 nanowires with tetragonal structure.

The above analysis of morphology and structure indicates that the nanowires obtained by us, compared to those presented in other works [14-16], are characterized by a much smaller wire diameter and crystallite size.

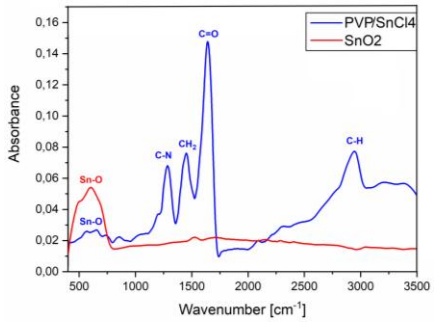

Fig. 8. FTIR spectra of composite PVP/$SnCl_4$ nanofibers and ceramic SnO_2 nanowires.

The absorbance spectra as a function of wavenumber in the range of 400–3500 cm^{-1} graphs were recorded for the obtained composite and ceramic nanomaterials with some characteristic peaks for individual vibration molecules or functional groups (Fig. 8). In the spectrum recorded for PVP/$SnCl_4$ nanofibers, the occurrence of the peaks: at 1286 cm^{-1} may be assigned to C-N bond, at 1438 cm^{-1} due to CH_2 bending vibration, at 1636 cm^{-1} is a result of C=O stretching vibration occurrence and at 2945 cm^{-1} can be assigned to C-H asymmetric stretching vibration [17]. The presence of these peaks is characteristic of a PVP polymer material. In addition, at position 550-660cm^{-1}, a characteristic band for Sn-O bond is visible, indicating the presence of a precursor in PVP nanofibers. In the case of spectrum obtained for pure SnO_2, only a wide band at a position of about 600 cm^{-1} can be observed, which indicates the presence of a Sn-O bond [18]. The absence of bonds and functional groups characteristic of PVP confirms the removal of the polymer in the calcining process.

The paper presents a simple, versatile method to produce one-dimensional tin oxide ceramic nanostructures using a combination of sol-gel and electrospinning from PVP/$SnCl_4 \cdot 5H_2O$/DMF/EtOH solution. The diameter of the obtained SnO_2 nanowires does not exceed 80 nm, moreover they are homogeneous and free of structural defects, which proves correctly selected process parameters. According to the review and knowledge of the authors, no SnO_2 nanowires made by electrospinning with such a small diameter and small crystallite size have been presented so far. The obtained results may be the basis for further considerations on the use of this type of one-dimensional nanomaterials in sensors or other optoelectronic devices.

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