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**ELECTROSPINNING TECHNIQUE
FOR PREPARATION OF TIN DIOXIDE-BASED
NANOFIBERS**

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In this paper, electrospinning is presented as the technique of choice to prepare nanofibers of the (poly(vinylpyrrolidone)) (PVP) / SnO₂ type. This newly proposed nano-material can be prepared using a Sn^{IV}-acetate / PVP-assisted template solution under the controlled conditions of high voltage (HV) applied, the needle-vs.-collection screen distance (L_{n-cs}), suitable binder concentration, $c(\text{PVP})$, and sufficient annealing temperature (T_a); the respective optimal parameters being as follows: HV = 15 kV; distance = 20 cm; $c(\text{PVP})$ = 15% (w/w), and T_a = 400 °C. As shown in comparative experiments, the diameter of nanofibers, their overall web-structure and chemical composition, as well as the resultant quality depends primarily on the annealing temperature chosen. The study has also included

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special characterizations by scanning electron microscopy, X-ray diffraction analysis, and X-ray photoelectron spectroscopy, and all these techniques have considerably contributed to the basic characterization of the nanofibers prepared and their potential applicability in the configurations of industrial gas sensors.

Introduction

Nanotechnology and the other related fields of advanced knowledge could seem to be young and recently discovered. Terms nanostructure, nanotechnology, and others, however, had already appeared in 1959 in the revolutionary investigations by Robert P. Feynman — a physicist awarded by Nobel Prize. Since then, there have been shown many potentialities, applications, and utilizations associated with the nanostructure, nanomaterials, and nano-technologies as such. For some, the production of nano (i.e., 10^{-9} m) “dwarfish-things” may appear very expensive and with high demands for energies and instrumentation. In case of nanofibers, modern approaches based on the so-called electrospinning techniques are the proper choice and a guarantee that mass production of nanofibers is feasible *via* simple, inexpensive methods with elementary devices.

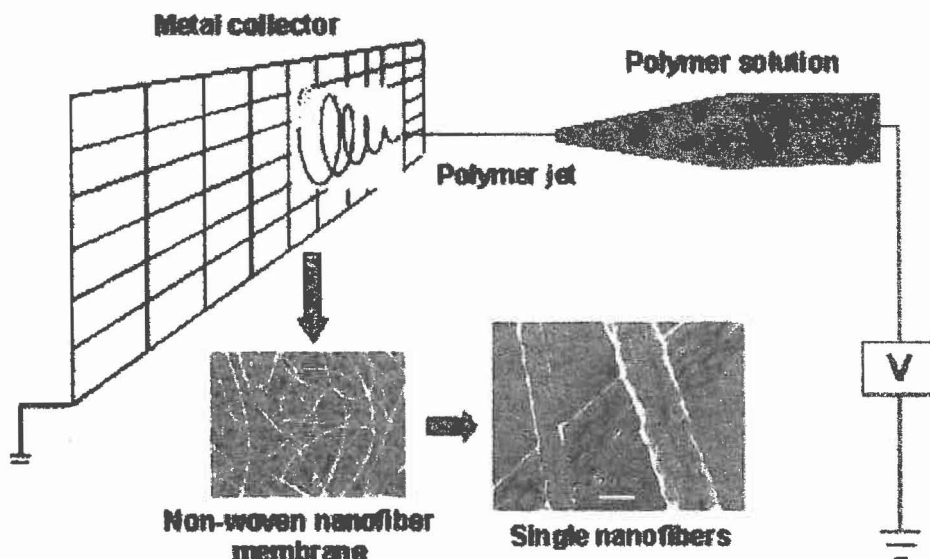


Fig. 1 Scheme of electrospinning process

Electrospinning is a technique involving the use of high-voltage electrostatic field to generate ultra-thin fibers from a variety of materials in the presence of dissolved polymers or melts assisting the formation process. Diameters of fibers electrospun in this way are measured in nanometres and hence, the

resultant fibers are called “submicron fibers”, or — more often — “nanofibers”. The term “electrospinning” (derived from “electrostatic spinning”) was put into practice relatively recently, around 1994, but its basic concept has been known for more than half of a century. Namely, within the period of 1934-1944, Formhals published a series of patents [1-5] concerning experimental set-up for fabrication of polymer fibers using electrostatic forces. Some years later, in 1952, Vonnegut and Neubauer [6], as well as Drozin in 1955 [7], were dealing with behavior of solutions in the electric field with a high electric potential. In 1966, Simons for the first time used the term electrospinning [8] and, together with Baumgarten in 1972, produced fibers with diameters of 0.05-1 micron. His setup became the fundamental concept of all on-going electrospinning equipments, representing merely various modifications of the original device or its technical advanced versions.

However, a real renaissance of electrospinning began in the nineties, most likely due to the interest and rapid progress in nanotechnologies. In general, typical electrospinning equipment consists of a high voltage supply, syringe (or capillary tube with needle) and a collecting screen and its scheme is depicted in Fig. 1.

High voltage (within the kV range) is imposed between a droplet of polymer solution at the tip of needle and the collecting screen. When the forces due to electric field overcome the surface tension of the drop at the needle tip, a narrow stream of polymer solution is ejected. As the stream is being divided into multiple filaments, the solvent evaporates to dryness and a web-like structure of ultrathin fibers is formed (and then collected at the screen).

There are numerous modifications of the electrospinning process as well as various types of electrospun nanofibers and the respective classification, instrumentation, key parameters, and typical applications can be found in special reviews (see, e.g., [10]). As time went by, the idea of electrospun nanofibers has been extended to other configurations based on the effective electrospinning from (i) composite solutions of various hybrid inorganic / organic materials ([11-15]), when the attention is also paid to the preparation of (ii) ceramic “ultrafine” fibers of purely inorganic character. To date, a number of such nanofibers have been reported, involving the use of various metal-oxides: Mn_2O_3 and Mn_3O_4 [16], CeO_2 [17], In_2O_3 [18], Al_2O_3 [19], SiO_2-TiO_2 [20], CeO_2-ZrO_2 [21], Co-doped TiO_2 [22], $BaTiO_3$ [23], or TiO_2 [24]. Besides, nanofibers with interesting properties can also be prepared from some “mixed” oxides like: $Pb(Zr_{0.5},Ti_{0.5})O_3$ [25], $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ [26], $LaMnO_3$ [27], Eu-doped Y_2O_3 [28], V^{IV} -doped TiO_2 , Nb_2O_5 , Ta_2O_5 , $Ta^V Nb^V O_5$, [29,30], or PdO [31].

Prominent positions in both groups (i) and (ii) are then held by tin-dioxide (SnO_2) based nanofibers, where the respective oxide acts as a key-functional compound with attractive properties for optoelectronic devices [32,33], gas sensors [34,35], solar cells and flat panel displays [36-38], or special supported

catalysts [39]. A few procedures have already been described to prepare the SnO₂-fibers by electro-spinning and such nanofibres could be produced from poly(ethyleneoxide) [40] or poly(vinylacetate) assisted polymers [41]. Applicability of PVP as the polymer of choice for electrospinning has also been examined – either for the preparation of “pure” nano-scaled fiber ensembles (i.e., made of PVP only; see, e.g., [42-44]) or for nanofibers based on SnO₂ doped with Sb^{III} [45].

In this article, the results of our recent investigations [46] are summarized, concerning the development of a new method for the preparation of tin-dioxide nanofibers, as well as their basic characterization with the aid of scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The SnO₂-nanofibers described herein were prepared from an Sn^{IV}-acetate solution in the presence of poly(vinylpyrrolidone) (PVP) binder ensuring the appropriate viscosity during the electrospinning process and encapsulating the SnO₂ particles into the polymer structure.

Experimental

Chemicals and Solutions

All the chemicals used to prepare stock and solutions were purchased from Aldrich. The solution of Sn^{IV}-acetate, Sn(CH₃COO)₄, was prepared by dissolving 0.2 g Sn^{IV}-salt in 10 ml of ethanol. Stock solutions of poly(vinylpyrrolidone) were prepared as three ethanolic media, containing 5, 10, and 15 % (w/w) PVP.

Subsequently, 7 ml of the PVP solution were added drop by drop into the Sn^{IV}-acetate solution and stirred with an electromagnetic bar until the medium became a homogenous precursor solution with the appropriate viscosity (see scheme in Fig. 2).

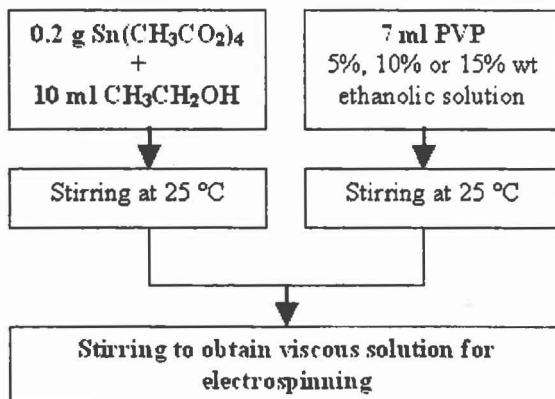


Fig. 2 Schematic diagram for preparation of solutions in electrospinning

Electrospinning Procedure and the Preparation of Nanofibers

The electrospinning proper was performed in a self-made experimental set-up illustrated in Fig. 3. A 1-ml plastic syringe with hypodermic needle (enabling to eject small drops at the tip) was filled with optimally viscous solution and connected with a crocodile clip to a high voltage (HV) power supply (model “ES30P-20W”; *Gamma High Voltage Res.*, USA).

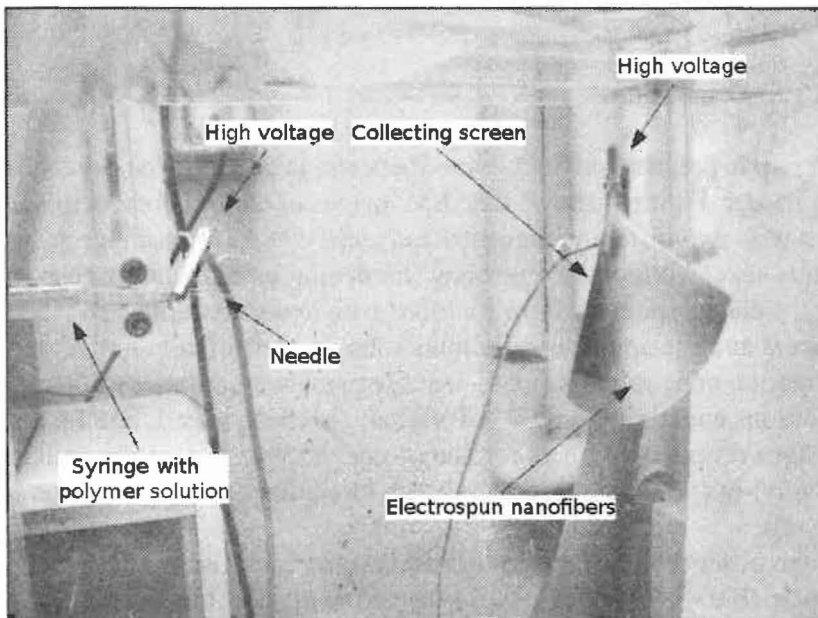


Fig. 3 Laboratory-made equipment for electrospinning. A real photoimage

The electrospun nanofibers were accumulated at a collecting screen, also connected with the HV-power supply and attached to a silicon substrate for clustering the nanofibers formed. Among experimental conditions, the different distance between the needle tip and collecting screen (5-20 cm), different HV applied (5–25 kV), and different concentrations of polymer binder (5, 10, 15% PVP) were of interest. Finally, to decompose PVP-binder and release the SnO₂-nanofibers, the products were annealed in a furnace for 3 hours when using heating at a different temperature regulated at a gradient of 3 °C min⁻¹.

Methods and Procedures for Characterization of Nanofibers

Morphological studies were carried out by employing a high-resolution scanning electron microscope (SEM; *Carl Zeiss SMT AG*, Germany). The X-ray

photoelectron spectroscopy (XPS) measurements serving for chemical and structural analysis were performed using the PHI ESCA system equipped with an Al X-ray source ($h\nu = 1253.6$ eV) with a hemispherical XPS analyzer (both *Perkin Elmer*, USA). The XPS analyses were surveyed in the binding energy range of 0–1300 eV when choosing a $0.8 \text{ mm} \times 0.8 \text{ mm}$ area. Finally, evaluation of the phase formation of the electrospun nanofibers was performed by means of a XRD device (model “D5000”, *Bruker*, USA) operated in the XRD-grazing angle mode. The X-ray source was a sealed X-ray with 1.5 kW Cu-radiation ($\lambda = 1.5406 \text{ \AA}$).

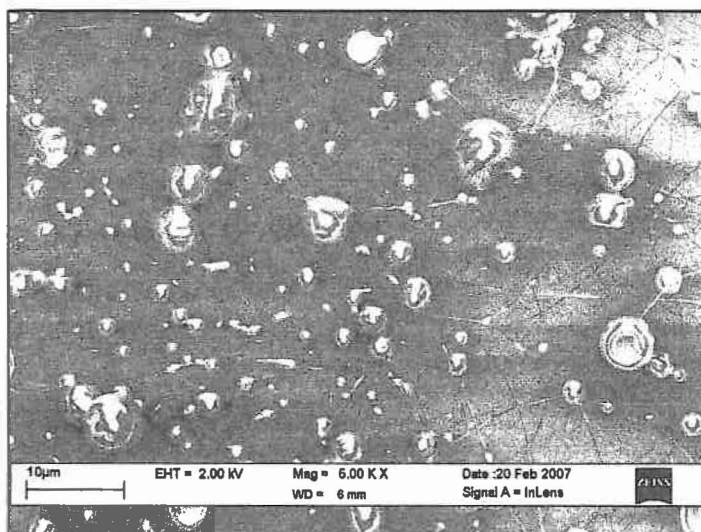
Results and Discussion

The first step in preparation SnO_2 -nanofibers was to optimize the concentration of polymer binder. Figure 4 shows the SEM images of nanofibers electrospun from solutions with two different concentrations: $c(\text{PVP}) = 10 \%$ (image A) and 15% (B); in this case, without the annealing (hardening or calcination, resp.). As can be seen, the electrospinning from solutions with lower content of PVP resulted in “wet” fibers and the appearance of numerous droplets of solvent (A) remaining after formation of nanofibers and their subsequent assembling. (Similar synthesis from solutions containing only 5% PVP had also been tested, but the respective SEM images revealed no fibers formed — not shown.) The lowest concentration of poly(vinyl-pyrrolidone) for the optimum formation of fibers was then found to be 15% (B).

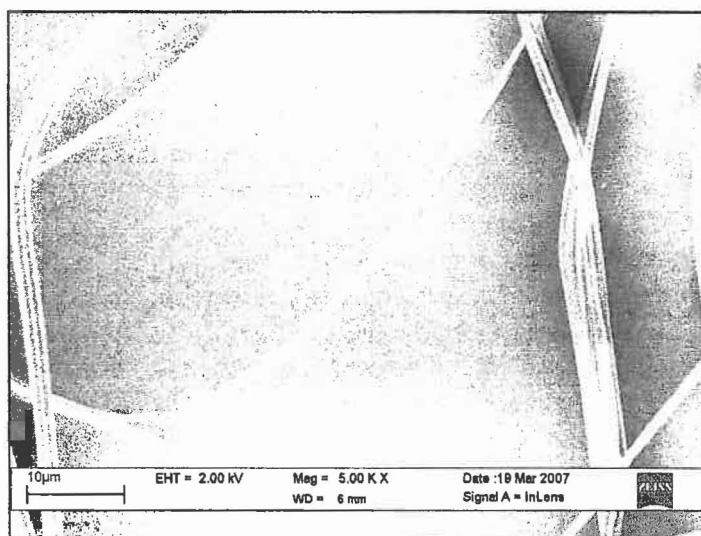
Such observations have confirmed that the electrospinning formation can be quite variable with respect to the composition of solutions tested. And because the deposition from solutions with lower PVP concentrations could not be further improved by changing the HVs applied or distances between needle and the collection screen, all other studies on the electrospinning of SnO_2 -based nanofibers were carried out with solutions containing 15% PVP.

Next investigations were focused on the respective conditions during the preparation of nanofibers, involving the choice of HV, the needle-vs.-collecting screen distance (L_{n-cs}), and the appropriate annealing temperature, tested at three different levels ($T_a = 200 \text{ }^\circ\text{C}$, $300 \text{ }^\circ\text{C}$, and $400 \text{ }^\circ\text{C}$). At first, it was found out that the morphology of nanofibers and, in particular, their diameter depended upon the HV applied; nevertheless, both being rather similar for HVs of 10 and 15 kV, as well as for 20 and 25 kV (see Fig. 5).

In the case of 10 and 15 kV, the diameters of nanofibers increased after annealing at $200 \text{ }^\circ\text{C}$ (compare with the fibers produced in the modus “as deposited”; i.e., without annealing), which was probably owing to “baking” of nanofibers together. Higher annealing temperatures (300 and $400 \text{ }^\circ\text{C}$) then led to a more intimate decomposition and evaporation of PVP residua undesirable in the final product, resulting in a marked decrease of the fibers thickness. With appli-



A



B

Fig. 4 Effect of PVP (polymer binder) concentration; SEM images of PVP / SnO₂ nanofibres. Legend: A) $c(\text{PVP}) = 10\%$, B) 15% (w/w). Electrospinning (ES) conditions: high voltage applied, $HV = 15\text{ kV}$; distance, $L_{n-cs} = 20\text{ cm}$; without annealing

cation of $HV = 20$ and 25 kV , the trends in changing nanofibers diameters after annealing could also be seen, but they were not very pronounced.

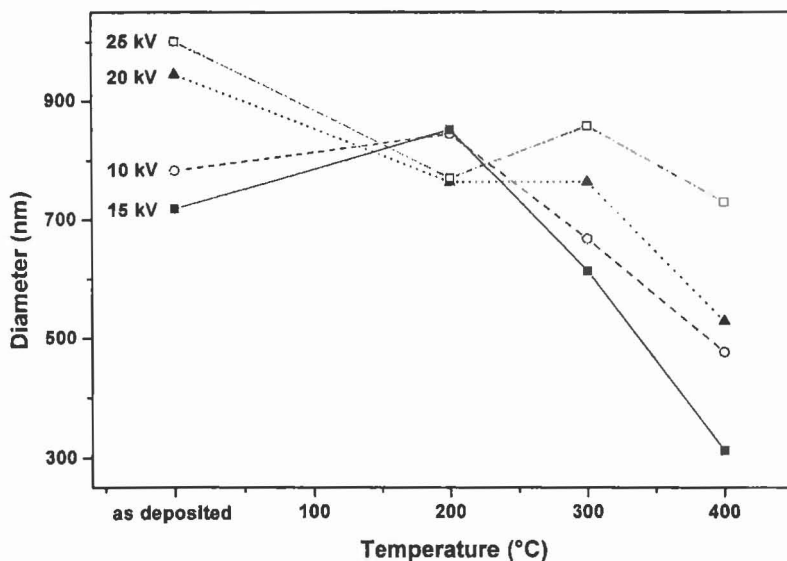


Fig. 5 Effect of annealing temperature and the voltage applied upon the resultant diameter of nanofibres. ES conditions: $L_{nc} = 20$ cm

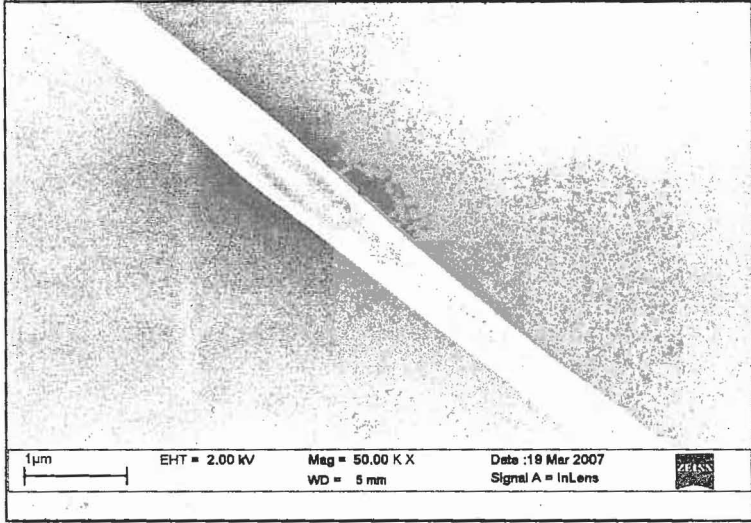
Regarding the temperature, this parameter exhibited a typical “yo-yo” effect — after annealing at 200 °C, one could observe a decrease of the nanofibers diameters, a higher temperature of 300 °C caused the increase, whereas the heating at 400 °C resulted again in a abrupt decrease in the diameters (similarly as with 10 kV and 15 kV HVs).

This characteristic behavior is depicted in Figs. 6 A-D, *via* the respective SEM images.

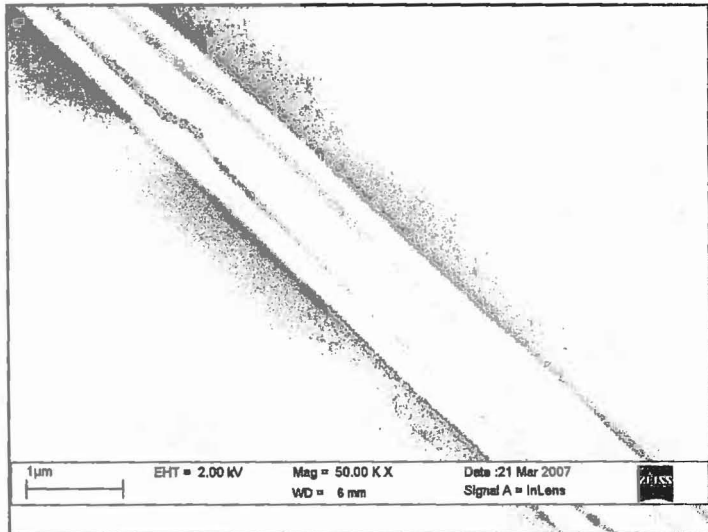
Furthermore, the effect of temperature was evident not only in the changes of fiber diameters, but also in the overall mat structure of the fibers. Their structural alteration began apparent above 200 °C and, when reaching the temperature of 300 °C, the fibers already exhibited the optimal web-structure. A further increasing of the annealing temperature had yet some positive influence upon the fibers diameter; however, the resultant web-structure appeared to be more damaged (see Fig. 7).

Despite this, annealing temperature of 400 °C was chosen as the optimum because it could ensure a complete decomposition of PVP and, therefore, the required purity of the SnO₂-fibers – without molecules of binder. Both lower temperatures tested, 200 and 300 °C, gave rise to the fibers containing some PVP residua and non-encapsulated SnO₂, which was confirmed also by XRD analysis – see below.

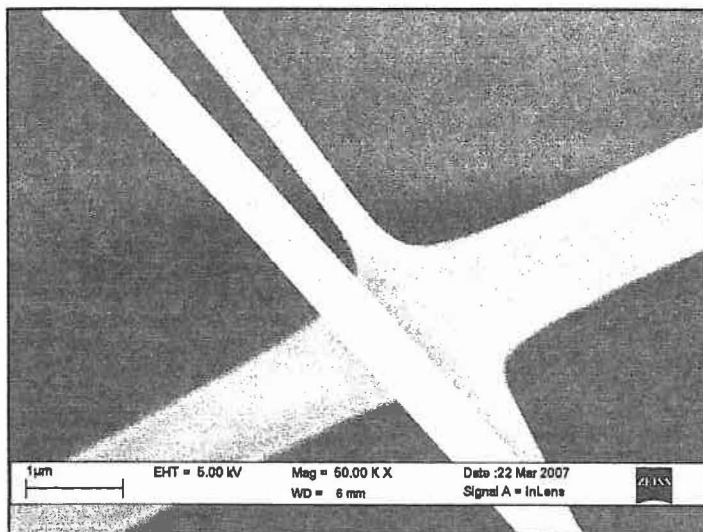
Because of an excess of PVP during the process, there apparently were also some molecules of PVP without encapsulated SnO₂ or, eventually, the fibers with



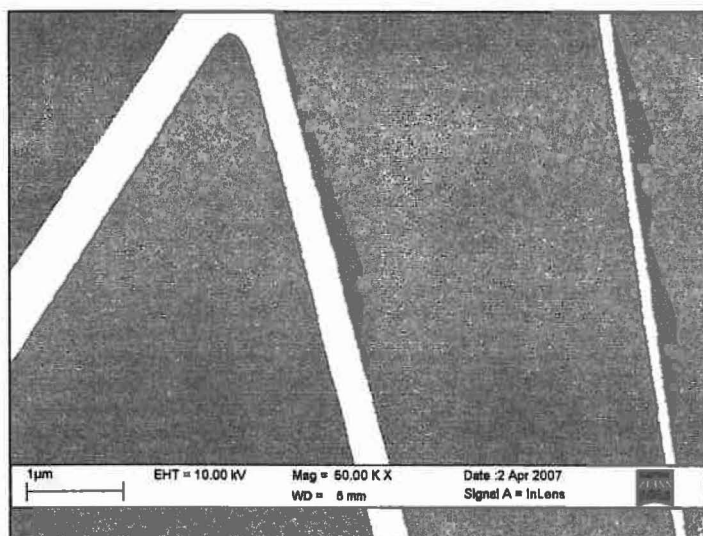
A



B



C



D

Fig. 6 Effect of annealing temperatures onto the fibre morphology; SEM images of PVP / SnO₂ nanofibres. A) "as deposited" (at ambient temperature, without annealing), B) $T_a = 200$ °C, C) 300 °C, D) 400 °C. Other ES conditions: as those in Fig. 4

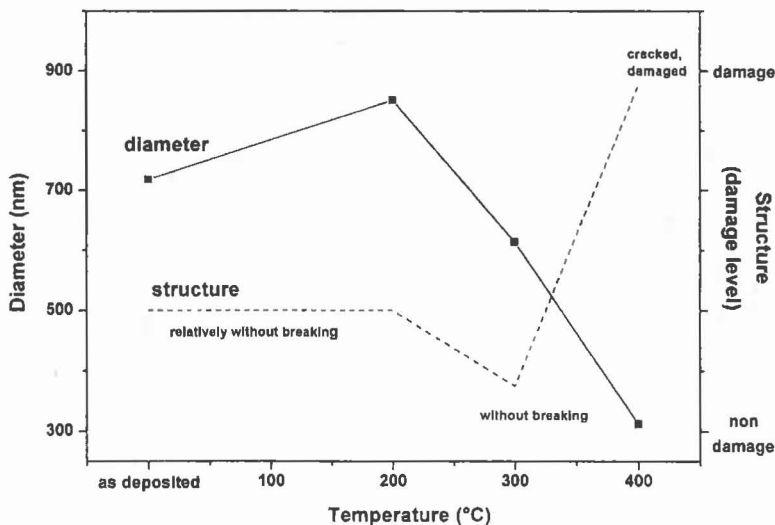


Fig. 7 Effect of annealing temperature upon the diameter and the structure of PVP / SnO₂-nanofibers. ES conditions: see Fig. 4

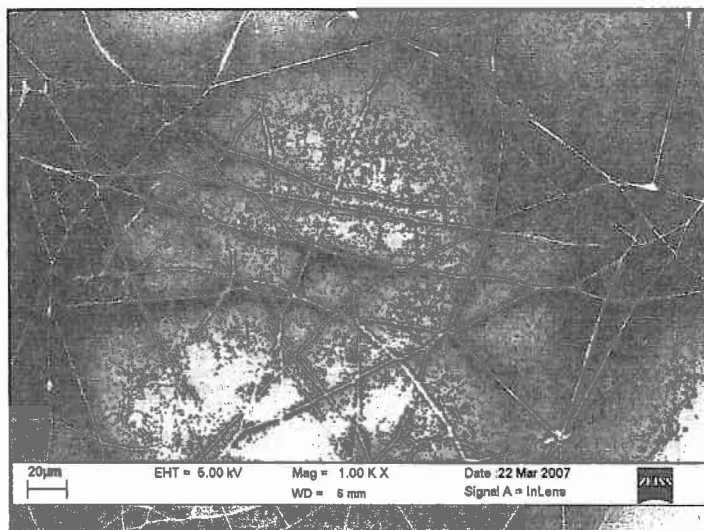
insufficient amount of SnO₂. And, because of instability of “pure” PVP-nanofibers, these structures were decomposed at high temperatures – visibly at 300 °C, completely at 400 °C.

Also, pure products (with a lack of SnO₂) could be identified as such – having formed typically short or cracked fibers. The respective differences between the overall nanostructure of the fibers annealed at both temperatures of 300 °C and 400 °C are then shown in Fig. 8 (A) and (B).

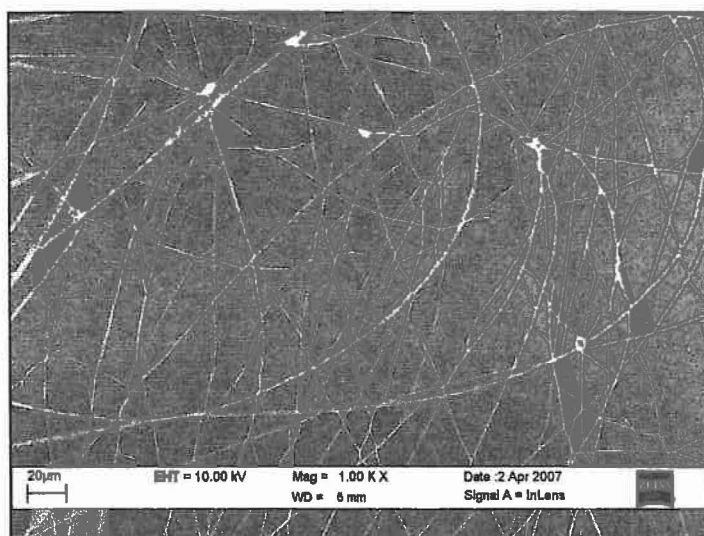
Special morphological studies carried out with the aid of the XRD-spectra are illustrated in Fig. 9 as a function of the corresponding annealing temperatures. The spectra obtained have revealed a characteristic phase constitution of the nanofibers prepared.

As seen, “as deposited” fibers (not hardened by annealing), as well as those annealed at 200 °C are nearly amorphous and do not exhibit any diffraction peaks, which might be due to the presence of PVP and the fibers obscured by the polymer. After annealing at 300 °C, broad diffraction peaks already appeared, indicating undoubtedly the decomposition of PVP binder. Finally, the XRD spectrum of nanofibers annealed at 400 °C comprised also new peaks that were attributed to rutile (allotropic modification of SnO₂) and its tetragonal structure, characterized by the following crystallographic data – (a) Miller indices: (110), (101), (200), (211), and (220); and (b) two lattice constants: $a = 4.736 \text{ \AA}$ and $c = 3.185 \text{ \AA}$.

The X-ray photoelectron spectroscopy was also used to verify chemical composition of the respective nanofibers; the corresponding XPS-analysis is illu-



A



B

Fig. 8 Effect of annealing temperature on the overall web structure of PVP/SnO₂-nanofibers. Legend: A) $T_a = 300\text{ }^\circ\text{C}$, B) $400\text{ }^\circ\text{C}$. Other ES conditions: see Fig. 4

strated in Fig. 10, gathering the spectra for both “as deposited” (A) and annealed (B) modes.

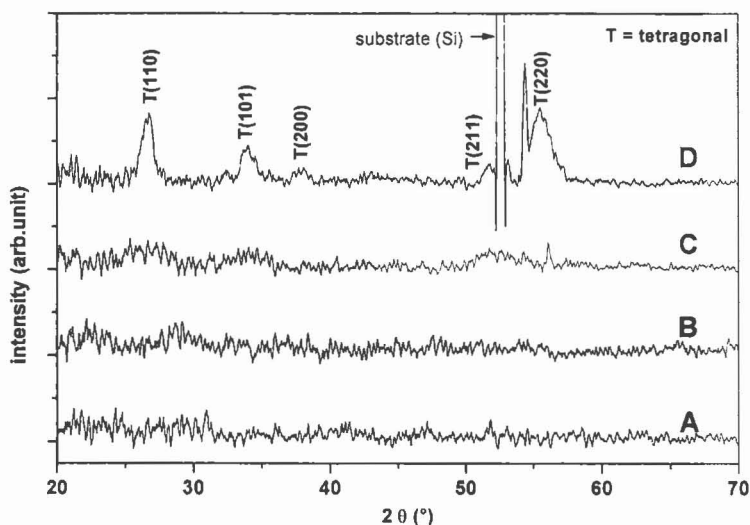


Fig. 9 XRD-spectra obtained by analyzing the PVP/SnO₂ electrospun nanofibres. Legend: A) as deposited, B) $T_a = 200$ °C, C) 300 °C, D) 400 °C. Other ES conditions: see Fig. 4

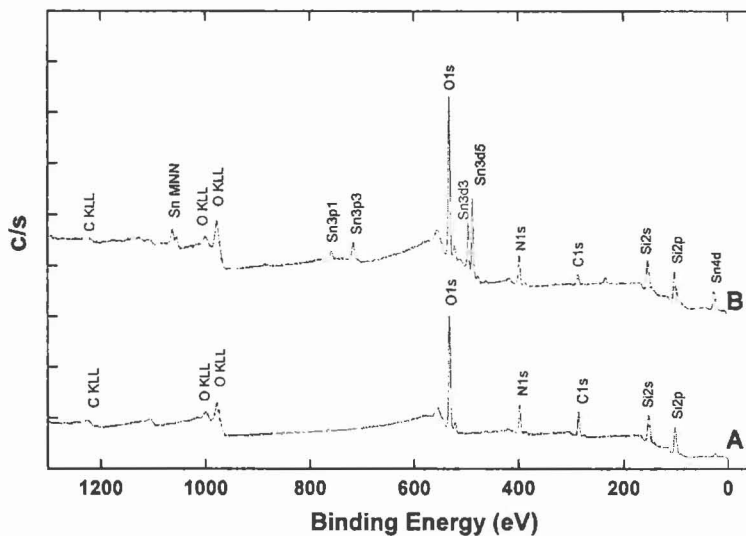


Fig. 10 XPS spectra of PVP / SnO₂ electrospun nanofibres. A) “as deposited”, B) $T_a = 400$ °C. Other ES conditions: see Fig. 4

It can be noticed that, after annealing at 400 °C (B), a set of typical signals for tin compounds were found here; namely, the Auger peaks: Sn3p_{1/2}, Sn3p_{3/2}, Sn3d_{3/2}, Sn3d_{5/2}, 4d, SnM₅N₄₅N₄ and SnM₅N₄₅N₄₅. In both regimes (A) and (B), we could also identify a pair of peaks belonging to elemental silicon (Si2s and Si2p)

and coming from the silicon substrate that had served as the collecting screen for electrospinning. Otherwise, with respect to structural analysis by XPS, no significant trends or changes in the fiber diameters or in overall web-structure were ascertained when changing the needle-screen distance.

Conclusion

In this study, the electrospinning technique was employed to prepare the SnO₂-based nanofibers from newly proposed Sn^{IV}-acetate / PVP (poly(vinylpyrrolidone)) solution, where the latter served as a template (supporting agent or polymer binder) for the electrospinning process.

Due to the annealing step, i.e. application of high temperatures up to 400 °C, the PVP molecules could be decomposed and the desired SnO₂-nanofibers obtained. As found out, the application of higher annealing temperatures, 300 °C and 400 °C, also led to a very significant decrease in the diameter of nanofibers; the highest temperature tested was proved to ensure a complete destruction of non-encapsulating PVP molecules. Investigations on the effect of key-conditions for electrospinning (high voltage applied, the needle-vs.-collection screen distance, and PVP concentration) have resulted in a set of optimal parameters: HV = 15 kV; distance = 20 cm; *c*(PVP) = 15 % (w/w). The whole study has also included special characterizations by scanning electron microscopy (SEM), X-Ray diffraction analysis (XRD), and X-ray photoelectron spectroscopy (XPS), when all these techniques helped to evaluate the resultant electrospinning process, as well as to obtain useful information about the nanostructure and chemical composition of the SnO₂-based fibers.

Regarding the practical usefulness of the results presented, it can be stated that the hitherto-evaluated parameters of SnO₂-based nanofibers prepared from Sn^{IV}-acetate / PVP (poly(vinylpyrrolidone)) media seem to have some promise as a substrate for fabrication of new miniature electrodes — industrial gas sensors. Some preliminary results [46] indicate that the SnO₂-nanofibers would be the substrate of choice for the determination of toxic nitrogen oxides, NO_x, with a detection limit below the ppm concentration level (down to 0.1 ppm). Furthermore, the newest tests with these nanosubstrates have revealed that the respective sensor could also be applicable to the detection of other gaseous analytes like ammonia or ethanol, benzene, and toluene vapours.

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