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Hybrid ZnO/ZnO-NPs nanofibres fabricated via electrospinning

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ABSTRACT

Purpose: Due to the growing interest and multitude of possible applications, zinc oxide nanowires, including those doped with ZnO nanoparticles, can became, alongside carbon nanotubes, a very desirable material which use is predicted in the construction of nanogenerators, dye sensitized solar cells, optoelectronics or ultrasensitive gas detectors.

Design/methodology/approach: The electrospinning process allows for low-cost and scalable production of fibrous mats with diameters from a few to several hundred nanometers. What is more, electrospinning method has gained popularity also due to its versatility, now it is possible to produce fibres from almost every known polymer and the simplicity and lack of any additional functionalization of the obtained nanomaterials. The application of the calcination process to remove the polymer matrix from the obtained nanofibres results in the creation of ceramic nanofibres.

Findings: Among the existing methods for the production of ceramic nanostructures, including the hydrothermal, physical and chemical vapour deposition methods, nanolithography or molecular self-assembly, the electrospinning process creates the possibility of fabricating one-dimensional nanostructures with unprecedented properties, good quality, no additional functionalization and purification.

Research limitations/implications: Due to ongoing research on the potential applications of zinc oxide nanostructures, including photovoltaics, sensorics and electronics, the most predictable behaviour and properties of ZnO nanowires characterize those nanomaterials that exhibit a periodic structure of the crystal lattice. Considering the optimization of the parameters of the method of producing ceramic zinc oxide nanowires doped with crystalline ZnO nanoparticles, it is worth analysing the thermal treatment parameters of nanofibres.

Practical implications: Although amorphous structure, hybrid ZnO nanofibres could be used as humidity sensors with much higher sensing properties than crystalline ZnO nanostructures.

Originality/value: Low-cost, scalable production of ceramic nanofibres for most technical applications.

Keywords: Nanomaterials, Electron microscopy, Amorphous materials, Zinc oxide

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MATERIALS

1. Introduction

Known since the beginning of the 20th century, the electrospinning process is a method of obtaining nanomaterials in the form of fibrous mats. The essence of the process is the electrostatic field, under the influence of which a drop of spinning solution is elongated and accelerated, forming the final material – nanofibres. One of the main advantages of this method of producing nanostructures is the possibility of using the obtained fibrous mats without additional functionalization or purification. The second significant feature of the described process is its high efficiency and low costs, which means that the method itself can be used in large-scale production, while maintaining high quality of produced material. Another advantage of electrospinning is the fact that this process is carried out at room temperature, in the atmosphere most often air, and the procedure for preparing the spinning solution does not require complicated preparations, only magnetic stirrers. An additional advantage of the electrostatic spinning technique is the ability to control and optimize the parameters of the process itself, which significantly affect the morphology and structure, as well as the properties of the produced nanofibres [1,2].

The group of one-dimensional (1D) nanomaterials include nanofibres, nanowires and nanowires. A characteristic feature connecting these nanostructures are diameters ranging from a few to a thousand nanometers and a length significantly exceeding the limits of the nanometric scale.

The ever-growing interest in one-dimensional nanostructures is caused by unique applications in mesoscopic physics and in the production of devices on a nanometric scale. It is assumed that 1D nanomaterials are good systems for studying the relationship of electrical and thermal transport, due to their dimensions and shape. The most important features of one-dimensional nanostructures include the ratio of their surface area to the volume they occupy, which plays a key role in the design of nanosystems. In addition, their high porosity is also a desirable property when designing and manufacturing nanostructures, which further increases the specific surface area of nanostructures [3]. 1D nanomaterials can be produced using both bottom-up and top-down methods, and the most commonly used techniques include chemical and physical vapour deposition, magnetron sputtering, nanolithography, hydrothermal method, template synthesis, molecular self-assembly, sol-gel technique or electrospinning [4-6].

Ceramic metal oxide nanofibres have recently gained popularity from researchers around the world due to their outstanding electrical, optical, thermal, photoluminescent and mechanical properties. It is assumed that one-dimensional nanostructures, including nanowires, are ideal systems for studying phenomena occurring at the nanometer scale, among others quantum effects, as well as size and dimensional relationships for potential applications [7]. The process of obtaining ceramic one-dimensional nanostructures by electrospinning involves the preparation of a spinning solution, which includes a polymeric reagent that allows the solution to obtain the right viscosity, which cannot be ensured by a clean solution of the ceramic nanomaterials precursor compound. Ceramic elements added to the solution are in the form of nanoparticles or precursors, importantly, there are no restrictions on the amount and type of metal oxides added, which results in the formation of hybrid nanowires combining the properties of each added ceramic element. The production of ceramic nanofibres or nanowires in the process of electrospinning allows for the preparation of structures with a specific classification due to their morphology, microstructure, chemical composition and properties that allow their use in many areas [8,9].

Zinc oxide (ZnO) is a material from groups II-IV of n-type semiconductors with an energy gap width of 3.37 eV at room temperature. ZnO has particularly high thermal and chemical stability, which makes zinc oxide nanostructures, including nanowires and nanofibres, next to carbon and silicone nanotubes are number one in terms of application possibilities and tested properties. In addition, it is one of the most important functional oxides, showing the emission of near ultraviolet. An important feature of zinc oxide is its biocompatibility and biocompatibility, which allows its use in the biomedical area.

Among ceramic nanofibres, one-dimensional zinc oxide nanostructures play an important role, which are distinguished by physical, including optical, photoluminescent, semiconductor, and chemical properties. For this reason, scientists involved in the production of ZnO nanofibres are investigating their possible applications, among others, in photoelectronic devices, gas sensors, photocatalysis, optics and piezoelectric nanogenerators [10-16].

2. Materials and methodology

The first stage in the production of ZnO/ZnO-nanoparticles hybrid nanofibres (ZnO/ZnO-NPs) was the production of composite nanofibres doped with ZnO nanoparticles. The spinning solution was prepared as follows: 1.125 g of zinc oxide nanoparticles (30% wt. in respect of the polymer mass) (ZnO, Sigma Aldrich) was added to 30 ml of dimethylformamide (DMF, purity of 99.8%, Sigma Aldrich). The suspension thus prepared was subjected to sonication, to remove the agglomerates of particles for 20 minutes. After the sonication process, measured powders were added: polyvinylpyrrolidone polymer (PVP, Mw=1.300.000 g/mol, purity of 99%, Sigma Aldrich) and zinc acetate dihydrate ($Zn(CH_3COO)_2$ x 2 H_2O, purity of 98%, Sigma Aldrich), in mass amounts, respectively: 3.75 g and 11 g. The final solution was stirred on a magnetic stirrer for 24 hours. Immediately after the end of the mixing process, the spinning solution PVP/ZnO/ZnO-NPs/DMF was subjected to the process of spinning in an electrostatic field on a FLOW – Nanotechnology Solutions Electrospinner 2.2.0 – 500 device, with strictly defined parameters: distance between the nozzle with solution and collector – 20 cm, solution feeding rate 1.5 ml/h, potential difference between electrodes – 23 kV.

The second stage in the production of hybrid ZnO/ZnO-NPs nanostructures was the calcination process of the obtained in the electrospinning process PVP/ZnO/ZnO-NPs fibrous mats in a HT-2100-G-Vac-Graphit-Special high-temperature furnace in a high vacuum atmosphere at 550°C for 10 hours.

The analysis of the morphology and chemical composition of the obtained PVP/ZnO/ZnO-NPs and ZnO/ZnO-NPs nanofibres was carried out using a scanning electron microscope (SEM, Zeiss Supra 35) using an SE detector and a characteristic X-ray detector EDS (Trident XM4 from EDAX). In addition, a transmission electron microscope (TEM, TITAN 80-300, FEI) was used to evaluate the structure and crystallinity of nanofibres. Observations were carried out in the scanning-transmission mode (STEM), in the light and dark fields and in the high-resolution transmission electron microscope mode (HRTEM), while nanofibres diffraction was performed to determine the crystallinity of ZnO/ZnO-NPs nanostructures. Then, in order to determine the impact of ZnO semiconductor nanoparticles on the morphology of ZnO/ZnO-NPs ceramic nanostructures, a 100-fold measurement of the diameters of produced polymer-ceramic and ceramic nanofibres was made, based on which histograms with the diameter distribution of one-dimensional nanomaterials were made.

3. Results and discussion

3.1. Analysis of morphology and structure of doping phase

The doping phase, both in PVP/ZnO/ZnO-NPs polymer-ceramic nanofibres and in ZnO/ZnO-NPs hybrid nanofibres, were zinc oxide nanoparticles with the morphology of cylindrical structures, which was confirmed by observations from a scanning electron microscope. In addition, the chemical composition of ZnO nanoparticles was examined using an EDX detector for X-Ray microanalysis, which confirmed the purity of ZnO material, showing presence of two elements present in the molecule nanostructures, zinc (Zn) and oxygen (O) (Fig. 1).

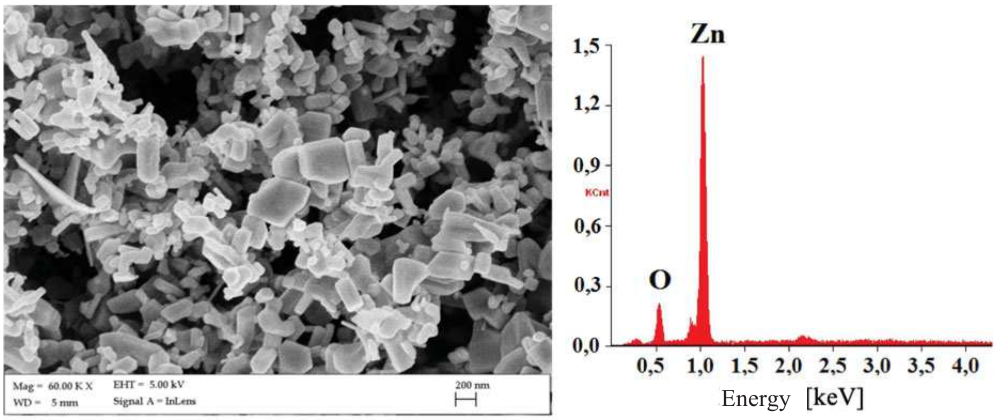

Fig. 1. SEM image of ZnO nanoparticles and EDX graph showing chemical composition of ZnO-NPs

ZnO particle diffraction study was also performed, which allowed determination of the phase composition of the tested material. Based on the diffractogram plotted for an angle of 2θ, in the range from 20 to 90º, it was found that the analysed zinc oxide nanoparticles were characterized by hexagonal crystal structure (Fig. 2).

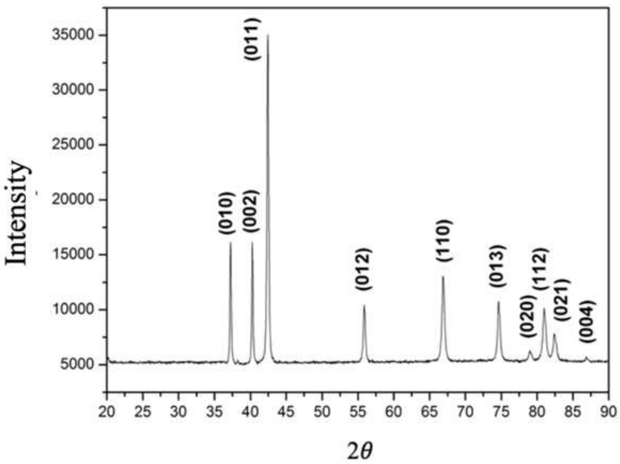

Fig. 2. Diffraction pattern of ZnO nanoparticles

During the X-ray diffraction test, the following diffraction lines for the 2θ angle were recorded: 37.073º, 40.206º, 42.371º, 55.834º, 66.821º, 74.55º, 80.948º and 82.391º, which correspond to Miller's planes in sequence (010), (002) , (011), (012), (110), (013), (112) and (021) belonging to the space group P 63m c, according to JCPDS 98-018-5827.

3.2. Analysis of morphology and chemical composition of polymer-ceramic nanofibres

The use of specific parameters of the electrospinning process allowed the production of polymer-ceramic nanofibres, from which hybrid ZnO/ZnO-NPs nanostructures were obtained in the next stage. Polymer-based nanofibres obtained from a PVP/$Zn(CH_3COO)_2$ ZnO/DMF solution were characterized by the lack of structural defects and uniform diameter values over the entire length of the fibres. In addition, the analysed area of the fibrous hybrid mat allowed the analysis of the distribution of ZnO nanoparticles in fibres. The studied area of SEM images of polymer-ceramic nanostructures showed even distribution of nanoparticles of the doping phase in the entire volume of nanofibres (Fig. 3).

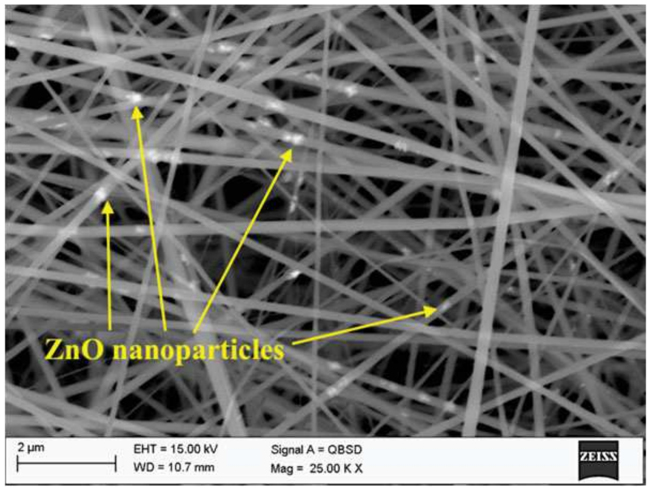

Fig. 3. SEM image of electrospun polymer-ceramic nanofibres

Measurement of the diameter of polymer-ceramic nanofibres enabled an analysis that showed that the average diameter of nanostructures was 135.5 nm. In addition, the largest diameter values were in the range of 120-160 nm, which is 33% of all diameter values (Fig. 4). Examination of composite nanofibres with the EDX detector showed the presence of several chemical elements characteristic for the analysed PVP/ZnO/ZnO-NPs nanostructures: zinc (Zn) and oxygen (O) derived both from the doping phase in the form of zinc oxide nanoparticles and the ceramic precursor in the form of zinc acetate dihydrate, aluminium (Al) – a film onto which nanofibres were deposited, as well as gold (Au) and palladium (Pd), which were a mixture of a film sputtered on a sample to examine a non-conductive object, as well as carbon (C) which is one of atoms of polyvinylpyrrolidone molecular structure (Fig. 4).

3.3. Analysis of morphology, chemical composition and structure of hybrid ceramic nanofibres

Subjecting PVP/ZnO/ZnO-NPs nanofibres to calcination process at 550°C, in a high vacuum atmosphere, allowed obtaining ceramic zinc oxide nanofibres doped with ZnO nanoparticles. Analysis of the morphology of hybrid nanostructures showed that they were characterized by a structure similar to ribbons, which was found on the basis of SEM images (Fig. 5). In addition, based on the analysed area of the ZnO/ZnO-NPs nanofibre mat, an even distribution of nanoparticles of the doping phase was found throughout the entire volume of nanostructures, which confirms the correctly performed calcination process and the process of degradation and evaporation of the polymeric reagent and solvent from the volume of nanofibres, and the sintering process of the doping phase. Zinc oxide nanostructures were free of structural defects.

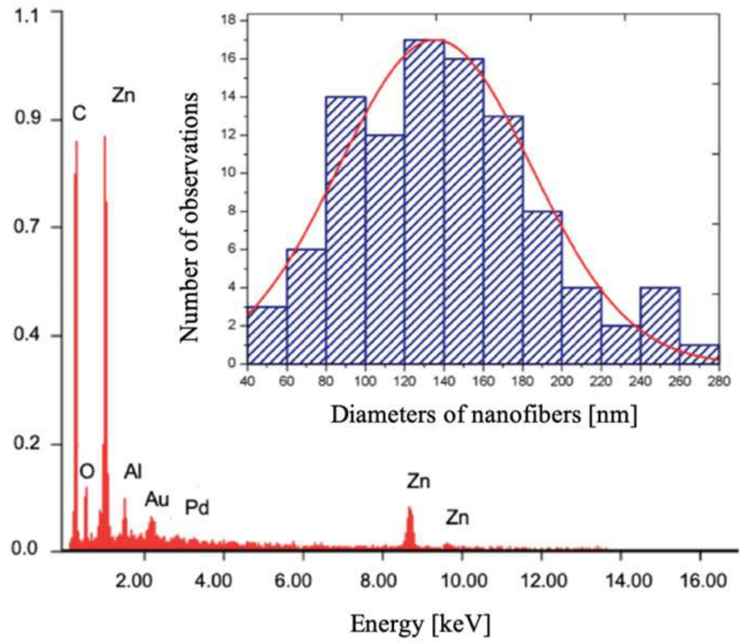

Fig. 4. EDX graph showing chemical composition of PVP/ZnO/ZnO-NPs nanofibres and histogram with distribution of diameter values of polymer-ceramic nanostructures

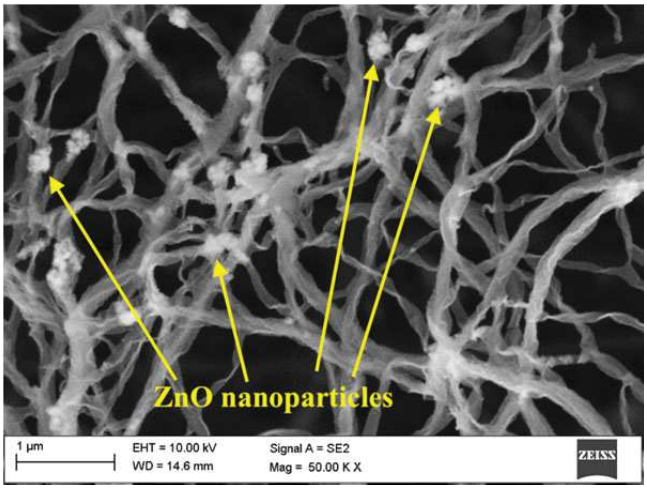

Fig. 5. SEM image of hybrid ceramic nanostructures

The average value of diameters of ceramic nanofibres was 108.8 nm, which is a decrease in the average value relative to the diameters of polymer-ceramic nanofibres by almost 20%, which is also confirmed by the results in [17,18]. This decrease is caused by the degradation and evaporation of the polymer reagent and the solvent spinning solutions used in the preparation. In addition, the range of nanofibre diameters was in the range of 40 to 220 nm, while 50% of all values were nanostructures with diameters from 80 to 120 nm (Fig. 6).

The analysis of the energy dispersion of the characteristic X-ray radiation confirmed the presence of elements present in the produced nanomaterial: zinc (Zn) and oxygen (O), originating from ceramic nanowires, aluminium (Al) being the residue of the collector material obtained in the first stage of hybrid nanofibres, as well as gold (Au) and palladium (Pd) – elements present in the conductive layer enabling the study of non-conductive objects on a scanning microscope, as well as carbon (C), whose presence may be due to sample contamination (Fig. 6).

Figures 7 and 8 show TEM images of individual tested ZnO/ZnO-NPs nanostructures, made using a transmission electron microscope, in STEM mode, with light and dark field observations. The results and analysis of electron diffraction spectra obtained using analytical microscopy in nano-areas, in the form of fuzzy circles, obtained for zinc oxide nanofibres doped with ZnO nanoparticles, indicates their amorphous structure. The morphology analysis of the studied ZnO/ZnO-NPs nanostructures showed a ribbon structure, which was also confirmed by observations from a scanning electron microscope, and the average diameter was about 118 nm.

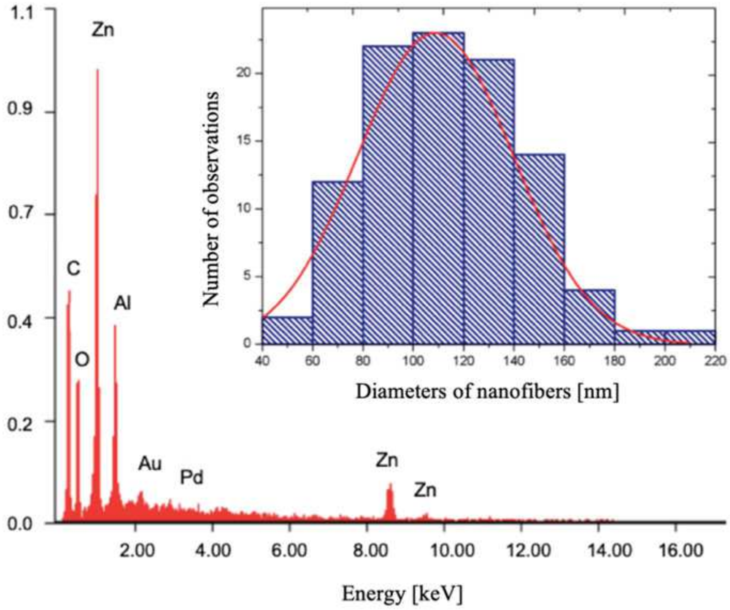

Fig. 6. EDX graph showing chemical composition of ZnO/ZnO-NPs nanofibres and histogram with distribution of diameter values of hybrid nanostructures

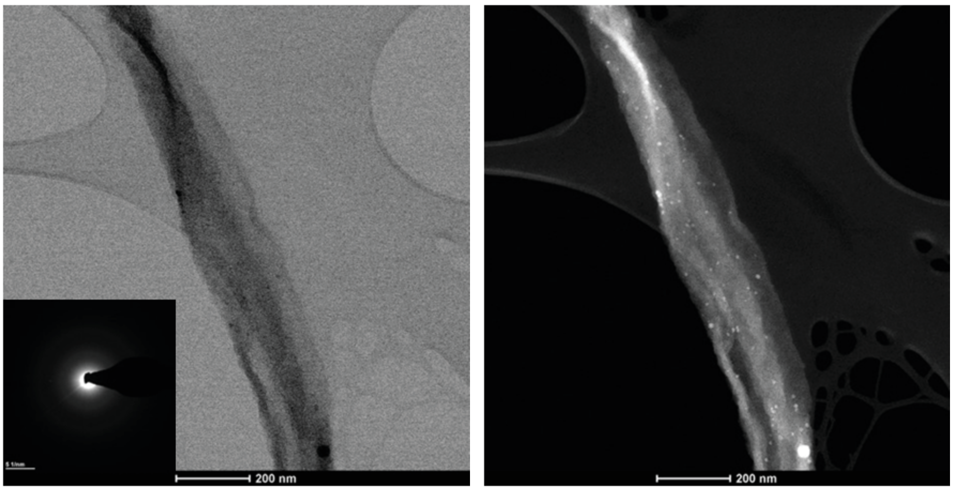

Fig. 7. TEM images of ZnO/ZnO-NPs single nanofibre made in STEM mode (BF, DF and diffraction)

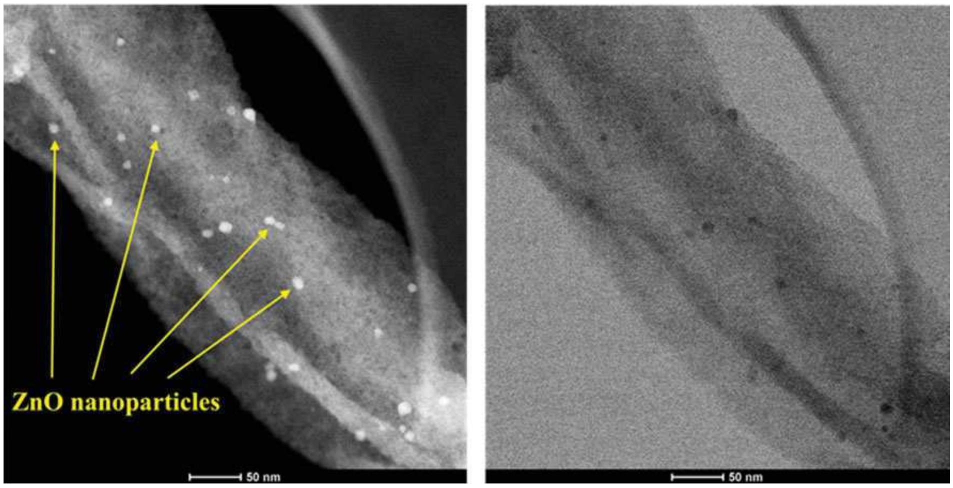

Fig. 8. TEM images of hybrid single nanostructure made in STEM mode (BF and DF)

In addition, the analysed areas of images obtained on a transmission electron microscope allowed to confirm the uniform distribution of particles of the doping phase, both in the entire volume of nanostructures and on their surface. TEM images of single ceramic ZnO nanostructures containing doping phase in the form of zinc oxide nanoparticles, which were obtained in the calcination process of PVP/Zn/ZnO-NPs composite nanofibres showed that the obtained structures can be classified as ceramic nanofibres.

4. Conclusions

The paper presents a method of producing hybrid ceramic zinc oxide nanofibres doped with ZnO nanoparticles, using a combination of sol-gel technique and electrospinning methods from a solution and the calcining process. The obtained ZnO/ZnO-NPs ceramic nanofibres were characterized by uniform dispersion of ZnO nanoparticles in the entire volume of the structures studied, which testifies to correctly selected parameters of both the electrostatic spinning process and the calcining process. The morphology of polymer-ceramic nanostructures in a high-temperature process changed from smooth nanofibres with uniform diameters along the entire length to ribbon-shaped structures, which were ceramic nanofibres. As a result of evaporation of solvents and sintering of nanoparticles of the doping phase, the diameter of the fibrous structures was reduced by 20%, which was confirmed by measuring the diameter values based on the images obtained from the scanning electron microscope. Analysis of the results from the transmission electron microscope confirmed the uniform distribution of ZnO particles in the entire volume of ceramic nanofibres and showed the amorphous nature of the produced material. Although, nowadays most applications of nanomaterials provide possibility of using crystalline structures, due to predictable behaviour of such materials, there are some evidences that indicate to use amorphous structures. In this paper [19], Authors prove better sensing properties in humidity sensor for amorphous ZnO nanostructures than that of crystalline structure.

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