

ELECTROSPUN ZNO NANOFIBERS FROM PVA/ZINC NITRATE PRECURSORS: EFFECTS OF PRECURSOR CONCENTRATION

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ABSTRACT

Electrospinning was used to prepare poly(vinyl alcohol) (PVA)/zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] fibers to evaluate the influence of zinc nitrate concentration on their morphology. The ZN2, ZN4, and ZN6 formulations had initial $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ concentrations of 2%, 4%, and 6% w/v relative to the water volume and approximate final concentrations of 1.01%, 2.04%, and 3.09% w/v relative to the total precursor-mixture volume, respectively. The mixtures were electrospun for 2 h onto silicon substrates, and the resulting specimens were thermally treated at 500 °C for 6 h using a heating rate of 10 °C min⁻¹. Optical and scanning electron microscopy showed that ZN4 produced greater observed substrate coverage and a more interconnected fibrous network under the investigated conditions. In contrast, ZN2 generated heterogeneous deposits containing clusters, short needle-like structures, bundles, and agglomerates, whereas ZN6 produced sparse deposits containing bundles and curved or segmented features. Non-contact atomic force microscopy of ZN4 showed apparent fiber widths of approximately 1.5–2.0 μm before thermal treatment and 120–380 nm after treatment. Separately, non-electrospun powder products obtained by thermally treating ZN6 precursor-solution aliquots exhibited Raman bands near 100, 332, and 438 cm⁻¹ from 500 °C onward, consistent with the characteristic vibrational modes of wurtzite ZnO. Qualitative EDS measurements provided complementary evidence of zinc-containing material. The results demonstrate that precursor concentration substantially influences the coverage, interconnectivity, and heterogeneity of the deposited fibrous structures.

Keywords: Zinc Oxide, Nanofibers, Metal Oxide

Nanofibras de ZnO electrohiladas a partir de precursores de PVA/nitrato de zinc: efectos de la concentración del precursor

RESUMEN

Se utilizó electrohilado para preparar fibras de poli(alcohol vinílico) (PVA) y nitrato de zinc hexahidratado [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], y para evaluar la influencia de la concentración de nitrato de zinc sobre su morfología. Las formulaciones ZN2, ZN4 y ZN6 tuvieron concentraciones iniciales de $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ de 2 %, 4 % y 6 % p/v con respecto al volumen de agua, y concentraciones finales aproximadas de 1,01 %, 2,04 % y 3,09 % p/v con respecto al volumen total de la mezcla precursora, respectivamente. Las mezclas se electrohilieron durante 2 h sobre sustratos de silicio y las muestras resultantes se trataron térmicamente a 500 °C durante 6 h, empleando una velocidad de calentamiento de 10 °C min⁻¹. Las microscopías óptica y electrónica de barrido mostraron que ZN4 produjo una mayor cobertura observable del sustrato y una red fibrosa más interconectada bajo las condiciones estudiadas. En contraste, ZN2 generó depósitos heterogéneos con agrupaciones, estructuras cortas similares a agujas, haces y aglomerados, mientras que ZN6 produjo depósitos dispersos con haces y características curvas o segmentadas. La microscopía de fuerza atómica en modo no contacto de ZN4 mostró fibras de aproximadamente 1,5–2,0 μm antes del tratamiento térmico y de 120–380 nm después del tratamiento. De manera independiente, los productos en polvo no electrohilados, obtenidos mediante el tratamiento térmico de la solución precursora ZN6, presentaron bandas Raman cercanas a 100, 332 y 438 cm⁻¹ a partir de 500 °C, consistentes con los modos vibracionales característicos del ZnO tipo wurtzita. Las mediciones cualitativas mediante EDS proporcionaron evidencia complementaria de la presencia de material con contenido de zinc. Los resultados demuestran que la concentración del precursor influye considerablemente en la cobertura, interconectividad y heterogeneidad de las estructuras fibrosas depositadas.

Palabras claves: Óxido de Zinc, Nanofibras, Óxidos metálicos

INTRODUCTION

Zinc oxide (ZnO) is a II–VI semiconductor with a direct wide band gap of approximately 3.3 eV and an exciton binding energy of about 60 meV at room temperature [1]. Its distinctive electrical, optical, piezoelectric, and chemical properties have enabled its use in optoelectronic devices, ultraviolet photodetectors, solar cells, photocatalytic systems, sensors, and energy-harvesting technologies [2].

The performance of ZnO-based materials is strongly influenced by their morphology and characteristic dimensions [3]. Nanostructuring substantially increases the specific surface area and the number of active surface sites available for adsorption, charge transfer, and catalytic reactions [4], [5]. These characteristics are particularly advantageous in sensing and photocatalytic applications [6], in which the interaction between the material surface and the surrounding environment determines device performance. At the nanoscale, grain boundaries, surface defects, oxygen vacancies, and interface states can also modify charge-carrier transport and optical emission. Quantum-confinement effects may additionally occur when the relevant crystalline dimensions approach the exciton Bohr radius of ZnO; however, these effects should not be assumed for conventional electrospun fibers with diameters of several tens or hundreds of nanometers [7]. In such fibers, surface-related phenomena, crystallite size, porosity, and defect chemistry generally exert a greater influence on their electrical and optical behavior [8], [9]. Among the different ZnO nanostructures, nanofibers are particularly attractive because they combine a high aspect ratio with large surface-to-volume ratios, interconnected porous networks, and potentially continuous pathways for charge transport. Electrospun ZnO nanofibers have consequently been investigated for humidity, ethanol, hydrogen, acetone, and volatile-organic-compound sensing, as well as for photocatalysis, ultraviolet protection, energy storage, solar cells, and functional textile coatings [10]. Their porous morphology facilitates

gas diffusion and increases the number of accessible adsorption sites [11], thereby improving sensor response [12], [13]. However, although the nanofibrous architecture generally enhances sensitivity, selectivity must usually be tailored through surface functionalization, elemental doping, catalyst loading, or heterojunction formation.

Electrospinning is one of the most versatile approaches for producing continuous fibers with diameters ranging from the micrometer to the nanometer scale. In the fabrication of ceramic nanofibers, a metal precursor is commonly combined with a polymer that provides the viscosity and chain entanglement required for stable fiber formation. The electrospun composite fibers are subsequently calcined to remove the organic phase and convert the inorganic precursor into crystalline ZnO. Solution properties—including viscosity, conductivity, surface tension, polymer concentration, and precursor content—as well as processing parameters such as applied voltage, solution flow rate, needle-to-collector distance, collector configuration, temperature, and relative humidity, strongly influence fiber diameter, morphology, uniformity, and alignment [14], [15]. In addition, the calcination temperature and heating conditions determine polymer decomposition, ZnO crystallization, grain growth, porosity, and the preservation or collapse of the fibrous structure [8], [12].

Several studies have demonstrated the feasibility of producing ZnO nanofibers through electrospinning followed by thermal treatment [7], [16], [17]. Park et al. fabricated polycrystalline ZnO nanofibers from an electrospun sol–gel/polymer precursor system and reported fiber diameters ranging from approximately 35 to 100 nm after annealing above 600 °C. They also found that crystallinity increased with annealing temperature and demonstrated the detection of CO at concentrations as low as 1.9 ppm [18]. Di Mauro et al. subsequently synthesized ZnO nanofibers using zinc acetate and polyvinylpyrrolidone (PVP) through a combined sol–gel and electrospinning route. Calcination between 350 and

650 °C promoted polymer removal and the formation of polycrystalline ZnO, while fibers annealed at 550 °C exhibited an average diameter of approximately 50 nm [2]. Blachowicz and Ehrmann later reviewed several ZnO nanofiber fabrication strategies, including the electrospinning of PVP/zinc nitrate precursor solutions followed by calcination to eliminate the organic phase. Their review highlighted the influence of precursor composition and thermal treatment on the morphology and functional properties of the resulting ZnO fibers [19], [20]. Despite these advances, further research is required to understand how alternative polymer–precursor combinations affect fiber formation, thermal decomposition and ZnO crystallization. In this context, the present work reports the synthesis and characterization of ZnO nanofibers using poly(vinyl alcohol) (PVA) and zinc nitrate as the polymeric carrier and ZnO precursor, respectively.

EXPERIMENTAL

Poly(vinyl alcohol) (PVA; $M_w=130,000 \text{ g mol}^{-1}$) and zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; $M_w=297.49 \text{ mol}^{-1}$], Sigma Aldrich (99% purity), were used as the polymeric carrier and zinc precursor, respectively.

Three aqueous zinc nitrate precursor solutions were prepared by dissolving 0.2, 0.4, and 0.6 g of zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] in 10 mL of distilled water. The zinc nitrate solutions were subsequently mixed with 9.8, 9.6, and 9.4 mL of the 11% PVA stock solution, respectively. Assuming additive volumes, the resulting electrospinning mixtures contained nominal final zinc nitrate concentrations of approximately 1.01%, 2.04%, and 3.09% w/v, respectively, as is shown in Table I. Each mixture was stirred at 70 °C and 685 rpm for 2 h until a homogeneous and viscous PVA/zinc nitrate precursor solution was obtained.

The precursor solution labeled as ZN6 in Table I was calcined in a muffle furnace at temperatures ranging from

200 to 1000 °C for 6 h, and the resulting products were characterized by Raman spectroscopy

TABLE I. Composition of the PVA/zinc nitrate hexahydrate precursor mixtures and their nominal final zinc nitrate concentrations used for electrospinning.

Solution name	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / \text{H}_2\text{O}$	PVA solution	Final zinc nitrate concentration
ZN2	0.2 g/10ml	9.8 mL	1.01% w/v
ZN4	0.4 g/10ml	9.6 mL	2.04% w/v
ZN6	0.6 g/10ml	9.4 mL	3.09% w/v

The electrospinning was carried out using SprayBase equipment with controlled parameters: voltage (9.5 kV), flow rate (0.02 mL/h), needle-collector distance (12 cm), needle diameter of 0.9 mm, and ambient temperature (19 °C). The collector consisted of steel with flat plate geometry and dimensions of 10 x 10 cm. Fibers were deposited onto silicon wafer pieces (1 x 1 cm). The experiments were conducted at 19°C and a relative humidity of 60%. Electrospinning was performed for 2 h. The collected nanofibers were subjected to thermal treatment in a muffle furnace. The calcination was performed at 500 °C for 6 hours with a ramp rate of 10 °C/min to remove organic components and obtain ZnO nanofibers

To characterize the synthesized nanofibers, several complementary techniques were employed to analyze their structural and morphology. Raman spectroscopy was used to confirm the formation and crystalline phase of zinc oxide (ZnO) after the calcination process, with characteristic peaks identified from 500 °C onwards. Scanning electron microscopy (SEM) was used to observe the surface morphology of the nanofibers and assess their density and uniformity based on precursor concentration. Atomic force microscopy (AFM) provided high-resolution topographical images, allowing the evaluation of fiber diameter and surface texture before and after calcination.

RESULTS

Raman Spectroscopy

Raman measurements were performed at room temperature using a LabRAM HR Evolution confocal Raman microscope (HORIBA Scientific). The powder products obtained by calcining aliquots of the precursor solution prepared from the ZN6 sample at 200, 300, 400, 500, 600, 700, 800, 900, and 1000 °C for 6 h were analyzed. A ZnO powder reference was also measured under the same experimental conditions. A 633 nm laser, set to 25% of the instrument output power, was focused on the samples using a 50X microscope objective. The Raman spectra were collected over the range of 20–2000 cm^{-1} . An integration time of 15 s and 15 accumulations were used for each spectrum to improve the signal-to-noise ratio.

Figures 1(a)–1(c) show the Raman spectra of ZN6 solution calcined at different temperatures, comparing them with the Raman spectrum of ZnO powder. In Figure 1(a), it is observed that the Raman spectrum of ZnO powder has specific peaks, such as 100, 332, and 438 cm^{-1} , indicating the characteristic vibrations of ZnO. At 200 °C, the ZnO peaks are not observed as in the Raman spectrum of ZnO powder, suggesting that there is still no complete decomposition of PVA and zinc nitrate, and therefore no formation of ZnO at this calcination temperature.

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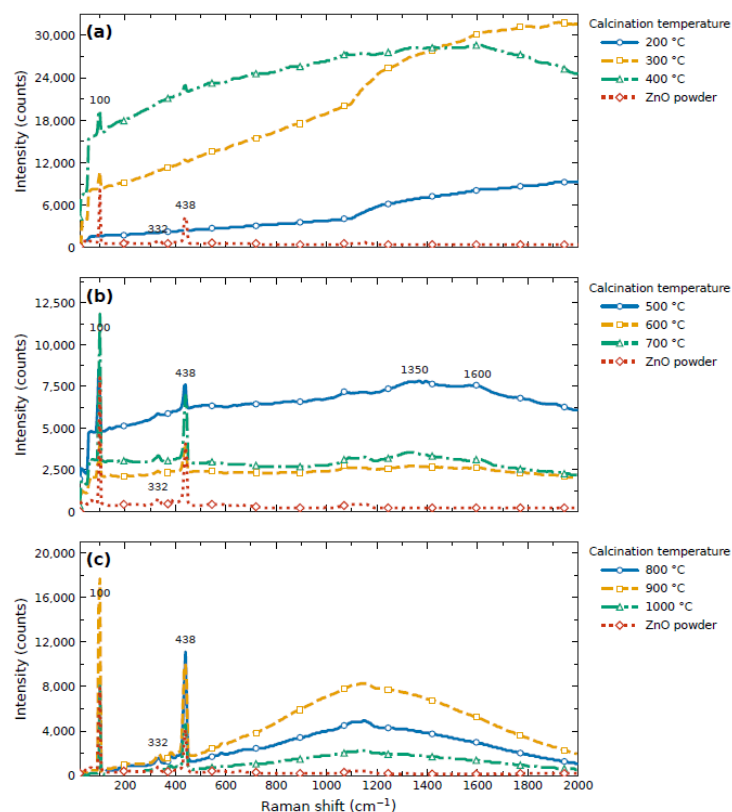


Figure 1. Raman spectra of ZN6 sample calcined at (a) 200–400 °C, (b) 500–700 °C, and (c) 800–1000 °C, together with the spectrum of ZnO powder used as a reference.

As the temperature increases to 300 °C, peaks such as 100 and 439 cm^{-1} become more prominent in the spectrum, and the overall intensity increases. This may indicate a greater interaction between PVA and zinc nitrate or the initial formation of ZnO. At 400 °C, the intensity of the peaks such as 100 and 439 cm^{-1} is even higher in the spectrum, suggesting that a significant amount of ZnO is forming from the thermal decomposition of zinc nitrate at this temperature. The shape and location of the peaks may resemble those of the ZnO powder Raman spectrum, confirming the formation of ZnO. Finally, in the spectra taken at different calcination temperatures, a gradual increase in intensity from approximately 1000 cm^{-1} to 2000 cm^{-1} is observed, indicating fluorescence due to the intact presence of the PVA matrix or impurities [21].

In Figure 1(b), at 500 °C, a significant increase in the intensity of the 100, 332, and 438 cm^{-1} peaks is observed

compared to the spectra at lower temperatures. This suggests considerable formation of ZnO from the decomposition of zinc nitrate [22]. The similarity of the peaks to ZnO powder indicates effective formation of ZnO. At 600 °C, the peak intensity in this spectrum is slightly lower than in the 500 °C spectrum. The presence of peaks similar to those in the ZnO powder Raman spectrum confirms that the material remains ZnO, but with possible variations in morphology or particle size. At 700 °C, the intensity of the peaks decreases further, which could be due to an increase in the grain size of ZnO, reducing the specific surface area and, therefore, the Raman spectrum intensity. Despite this, the characteristic peaks of ZnO powder are present, confirming the stability of ZnO at this temperature. Finally, the fluorescence effect is no longer observed in all spectra, suggesting the complete decomposition of PVA, but the presence of residual carbon, characterized by peaks at 1350 and 1600 cm^{-1} , is observed.

At 600 °C, the Raman spectrum exhibits the characteristic ZnO bands near 100, 332, and 438 cm^{-1} , confirming that the zinc-containing precursor has been converted into crystalline wurtzite ZnO [23]. The band near 100 cm^{-1} is assigned to the $E_2(\text{low})$ mode, which is predominantly associated with vibrations of the Zn sublattice, whereas the intense band near 438 cm^{-1} corresponds to the $E_2(\text{high})$ mode associated mainly with oxygen-sublattice vibrations [24]. The weaker feature near 332 cm^{-1} is attributed to a second-order $E_2(\text{high})$ - $E_2(\text{low})$ Raman process [21], [25]. At 700 °C, the $E_2(\text{low})$ and $E_2(\text{high})$ bands became considerably more prominent and better defined relative to the local spectral background [26], [27].

In Figure 1(c), at 800 °C a significant increase in the intensity of the 100, 332, and 438 cm^{-1} peaks is observed compared to samples treated at lower temperatures. This suggests considerable formation of ZnO from the decomposition of zinc nitrate. The similarity of the peaks to the ZnO powder Raman spectrum indicates effective formation of ZnO. At 900 °C, the intensity of the peaks in

this spectrum is higher than in the 800 °C spectrum, indicating a greater amount of ZnO formed at this temperature. The presence of characteristic peaks similar to those in the ZnO powder Raman spectrum confirms that the material remains ZnO. Finally, at 1000 °C, the intensity of the peaks slightly decreases compared to the 900 °C spectrum, which may be due to increased sintering and growth of ZnO particles. Despite this, there are peaks similar to those in the ZnO powder Raman spectrum are present, confirming the stability of ZnO at this temperature. Finally, between 1100 and 1200 cm^{-1} , there is an elevation in each Raman spectrum of the calcined solution caused by the carbon formed during the calcination process.

Optical microscopy and electrospinning morphology.

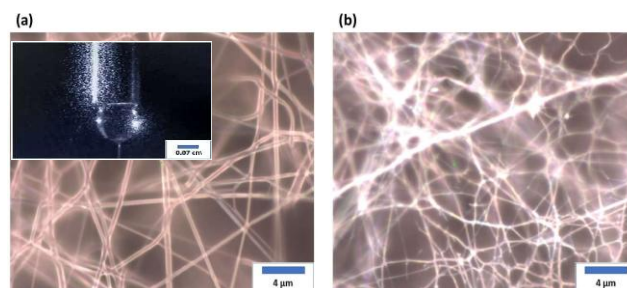


Figure 2: Optical micrographs of electro spun fibrous networks prepared from ZN4 solution, (a) as-spun PVA/zinc nitrate precursor fibers and (b) the resulting fibrous structures after calcination at 500 °C for 6 h.

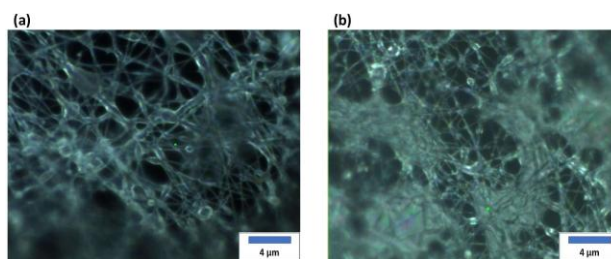


Figure 3: Optical micrographs of as-spun PVA/zinc nitrate fibrous structures prepared from (a) the ZN2 sample, and (b) the ZN6 sample. Intermittent dripping was observed during electrospinning of both formulations.

Optical microscopy revealed a clear influence of the zinc nitrate concentration on the morphology and spatial distribution of the electrospun structures. The as-spun

sample prepared from the ZN4 solution (Figure 4(a)) exhibited a highly interconnected network composed predominantly of long and continuous fibers, with comparatively few optically detectable beads or agglomerates. After calcination at 500 °C for 6 h, the fibrous architecture remained recognizable, indicating that the precursor network was preserved during thermal treatment (Figure 4(b)). The morphological changes observed after calcination are consistent with the removal of the PVA matrix, decomposition of the zinc nitrate precursor, and formation of ZnO, processes that are expected to produce substantial fiber shrinkage.

In comparison, the samples prepared from the ZN2 solution and ZN6 solution exhibited less homogeneous fiber distributions, localized agglomeration, and regions with poorly defined or discontinuous structures (Figure 5(a)-5(b)). Intermittent dripping observed during electrospinning indicates an unstable Taylor cone and a transition between continuous electrospinning and droplet-assisted deposition. Overall, the intermediate ZN4 solution provided the most favorable conditions for producing a continuous and comparatively uniform fibrous network.

Atomic Force Microscopy Analysis

Atomic force microscopy measurements were performed on the uncalcined and calcined samples prepared from the ZN4 solution using a Park Systems atomic force microscope NX7 operated in non-contact mode. A silicon PPP-NCHR cantilever with a nominal spring constant of approximately 42 N m⁻¹, a nominal resonance frequency of approximately 330 kHz, and a nominal tip radius of approximately 7 nm was used. Scan rates of 0.19 Hz and 0.42 Hz were used for the uncalcined and calcined samples, respectively.

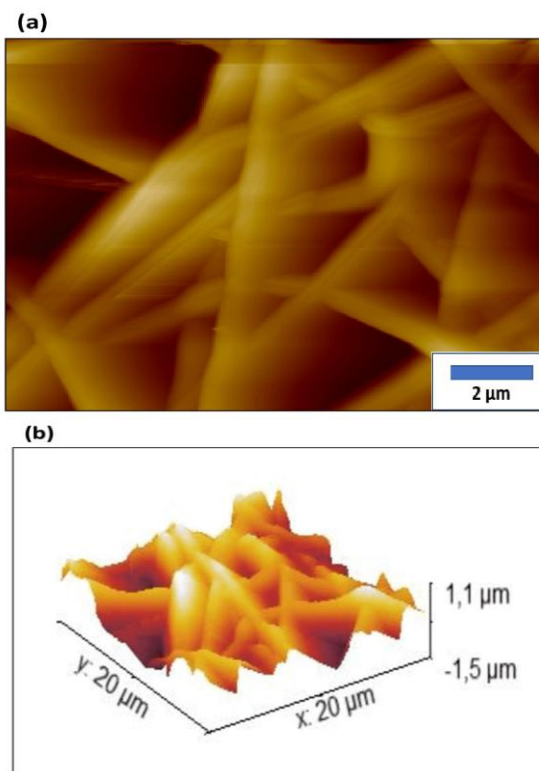


Figure 4: AFM topography of the uncalcined PVA/zinc nitrate precursor fibers prepared from ZN4 solution: (a) two-dimensional height image and (b) three-dimensional reconstruction of the (20x20μm²) scanned area. The images reveal a dense, randomly oriented, and multilayered fibrous network.

The 2D and 3D AFM images, recorded over a scanning area of 20 × 20 μm², are illustrated in Figure 4(a) and 4(b). In the 3D image, a fibrous structure is observed, by manually measuring the diameter of some nanofibers, the diameters of the nanofibers range from 1500 to 2000 nm. The fibers extend over several micrometers and exhibit numerous intersections and overlapping regions. The brighter regions in the height image correspond to topographically elevated features, particularly at fiber crossings. The three-dimensional reconstruction confirms the pronounced surface relief of the deposited network, with an overall peak-to-valley height range of approximately 2.6 μm.

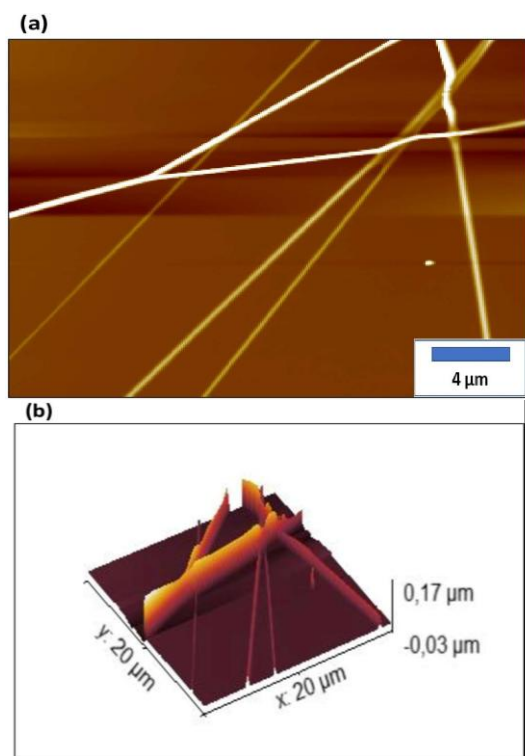


Figure 5. AFM topography of the composite fibers after calcination prepared from ZN4 solution: (a) two-dimensional height image and (b) three-dimensional reconstruction of the ($20 \times 20 \mu\text{m}^2$) scanned area.

The surface topography of composite fibers after calcination was also studied using non-contact atomic force microscopy. The 2D and 3D AFM images, recorded over a scanning area of $20 \times 20 \mu\text{m}^2$, are illustrated in Figure 5(a) and 5(b). By manually measuring the diameter of some nanofibers, the diameters of the nanofibers range from 120 to 380 nm. It can be observed that the diameter of ZnO nanofibers after 6 hours of calcination was reduced by almost 90%.

The AFM phase images, shown in figure 6, reveal differences in the tip–sample interaction response between the uncalcined PVA/zinc nitrate precursor fibers (Figure 6(a)) and the calcined ZnO fibers (Figure 6(b)).

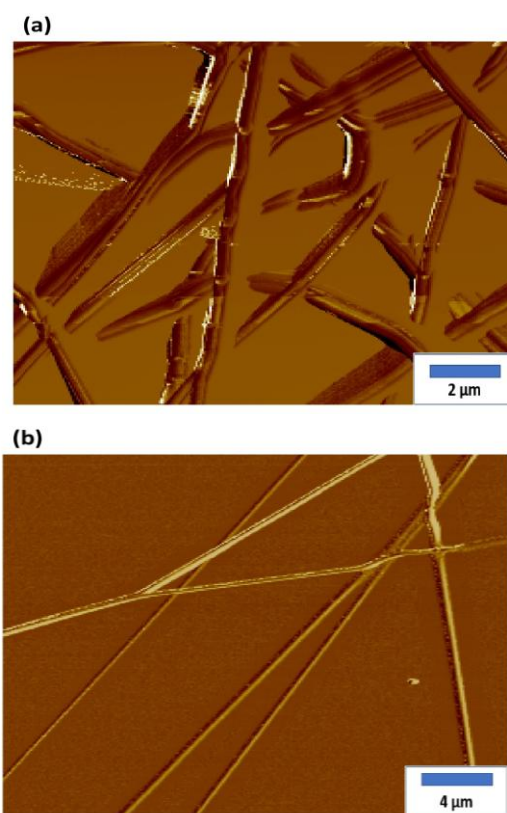


Figure 6: AFM phase images of (a) the uncalcined PVA/zinc nitrate precursor fibers and (b) the composite fibers after calcination

The uncalcined sample exhibits a dense network of relatively broad fibers with heterogeneous phase contrast and longitudinal variations. In contrast, the calcined sample shows a more dispersed network of thinner fibers with a comparatively uniform phase response along their length. In both samples, the strongest contrast occurs predominantly at fiber edges, steep topographic slopes, and intersection points, indicating a significant contribution from topography–phase cross-talk and feedback response.

The dimensions and morphology of electrospun ZnO structures depend strongly on the polymer–precursor system, solution composition, electrospinning conditions, and thermal-treatment schedule. Using a PVA/zinc acetate precursor, Ghafari et al. reported average diameters of approximately 400 nm before annealing and approximately 232, 145, 120, and 60 nm after treatment at 80, 300, 500, and 700 °C, respectively [28]. At 500 °C, an

average diameter of approximately 90 nm was obtained after 4 h, followed by comparatively small changes at longer dwell times. Ramos et al. employed PVA and zinc acetate dihydrate and obtained interconnected structures composed of ZnO particles with mean dimensions of approximately 45–80 nm after calcination at 600 °C for 3 h [29]. Oliveira et al. investigated PVA/zinc acetate systems thermally treated at 500–700 °C for 2 h in air and observed connected or agglomerated grains retaining a fiber-like morphology, with residual organic material under some 500 °C conditions [30]. In a related PVP/zinc acetate system, Mhetre et al. obtained diameters of approximately 49.63–95.63 nm after calcination at 350 °C for 2 h in air [31].

In the present PVA/ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ system, thermal treatment at 500 °C for 6 h produced fibrous structures with apparent AFM widths of approximately 120–380 nm. The observed morphology included interconnected regions, bundles, ribbon-like structures, fused junctions, fragments, and partially segmented features. The measured range is comparable to, but broader than, values reported for several PVA/zinc acetate-derived ZnO systems.

Scanning electron microscopy (SEM)

The morphology of the electrospun samples prepared from ZN2, ZN4, ZN6 solutions was examined using a JEOL JSM-IT100 scanning electron microscope (SEM). Secondary-electron images were acquired at an accelerating voltage of 20 kV and at magnifications ranging from approximately 750× to 3000×. Qualitative elemental analysis was performed using the energy-dispersive X-ray spectroscopy (EDS) system integrated into the microscope at an accelerating voltage of 20 kV. The sample prepared from the ZN2 solution (Figure 7(a)) exhibits a highly heterogeneous and discontinuous morphology. Fiber formation is mainly localized in small clusters, while a large fraction of the substrate remains uncovered. The observed structures include short, needle-

like fibers, partially interconnected bundles, and irregular particulate agglomerates.

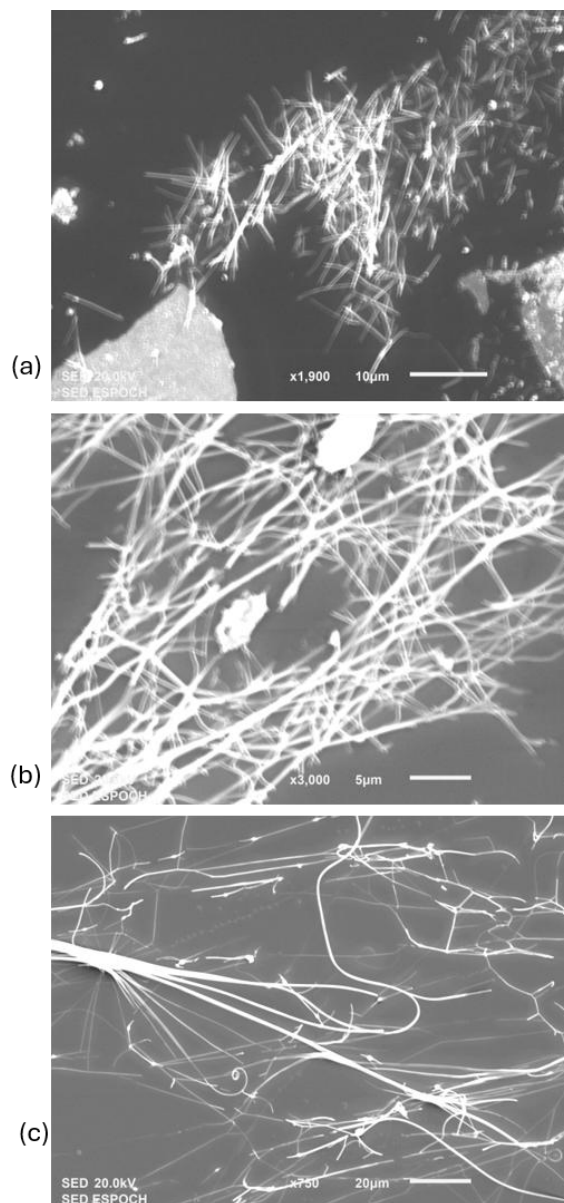


Figure 7: SEM micrographs of the calcined products obtained from PVA/zinc nitrate precursor solutions prepared with (a) ZN2, (b) ZN4, and (c) ZN6. Scale bars: (a) 10 μm, (b) 5 μm, and (c) 20 μm.

The sample prepared from ZN4 solution (Figure 7(b)) displays the highest fiber density and substrate coverage. A randomly oriented, interconnected fibrous network extends throughout the observed region, with substantially fewer uncovered areas than in the ZN2 and ZN6 solution samples. Most fibers appear ribbon-like structures and form numerous intersections, producing a porous,

nonwoven architecture. Nevertheless, some thicker segments, fused junctions, and particulate agglomerates are also visible, indicating that the morphology is not completely uniform. Among the three investigated formulations, the ZN4 solution condition provides the most favorable balance for the formation of a dense and interconnected fiber network.

In contrast, the sample prepared from the ZN6 solution formulation (Figure 7(c)) exhibits a sparse and heterogeneous distribution of relatively long fibers, with extensive regions of exposed substrate. Several fibers appear grouped into thicker bundles, while other regions contain isolated, curved, or partially fractured structures. Overall, the SEM observations indicate that the ZN4 solution produced the most continuous, dense, and interconnected fibrous morphology under the investigated electrospinning conditions. The ZN2 solution resulted mainly in localized fiber clusters and particulate agglomerates, whereas the ZN6 solution produced long but sparsely distributed fibers and bundles.

The EDS spectra of the samples prepared from the ZN2, ZN4, ZN6 solutions are dominated by the Si K α peak at approximately 1.74 keV, which originates from the silicon substrate, the predominance of this signal indicates that the electron interaction volume extended through the relatively thin or discontinuous fibrous deposits into the substrate, weak carbon and oxygen signals were also detected; however, carbon may arise from residual organic material or adventitious surface contamination, while oxygen may originate from both the deposited zinc-containing material and the native silicon oxide layer. The low-energy signal near 1.0 keV cannot be assigned unequivocally because the Na K α line overlaps strongly with the Zn L α and Zn L β lines[32], [33].

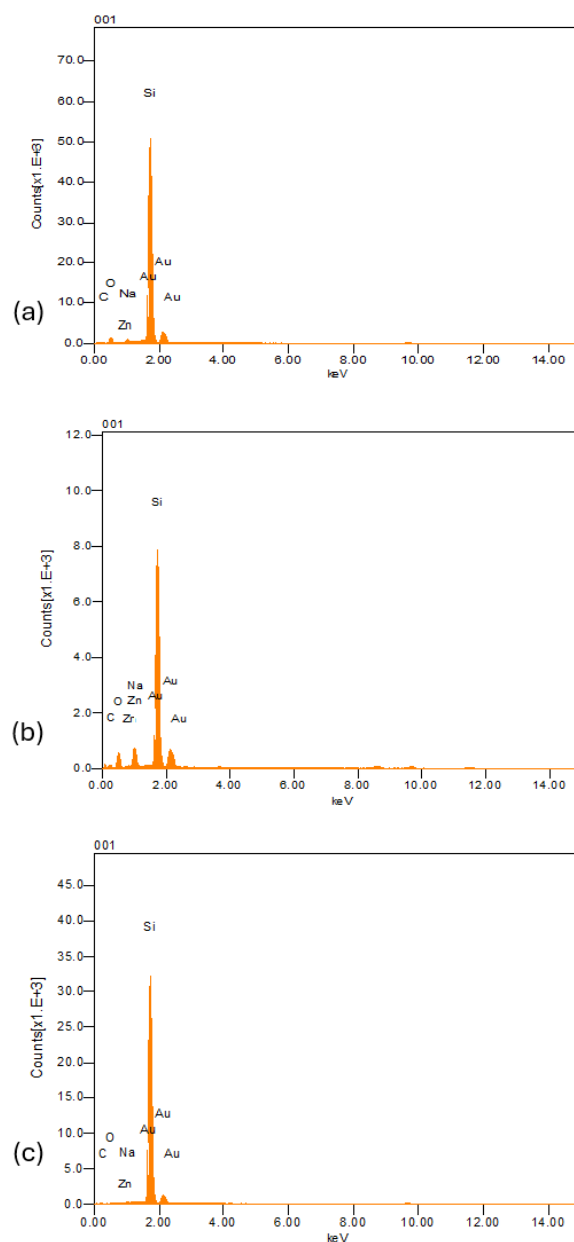


Figure 8. EDS spectra of the calcined products obtained from PVA/zinc nitrate precursor solutions prepared from (a) ZN2, (b) ZN4, and (c) ZN6 solutions

Therefore, the EDS results should be regarded as qualitative evidence of a possible zinc contribution rather than definitive confirmation of ZnO composition or stoichiometry. The automatic Au assignments were excluded because no gold coating or Au-containing material was used during sample preparation.

CONCLUSIONS

PVA/zinc nitrate fibrous structures were produced by electrospinning under fixed processing conditions, and their morphology was strongly influenced by the zinc nitrate content of the precursor mixture. Among the investigated formulations, the nominal ZN4 formulation, corresponding to an approximate final $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ concentration of 2.04% w/v, produced the most continuous, interconnected, and comparatively uniform fibrous network. In contrast, the ZN2 and ZN6 formulations exhibited intermittent dripping during electrospinning and generated more heterogeneous deposits, including sparse fibers, bundles, discontinuous structures, and localized agglomerates.

Raman spectroscopy revealed the characteristic ZnO bands near 100, 332, and 438 cm^{-1} , which became clearly defined from $500\text{ }^\circ\text{C}$ onward, this analysis also suggested the presence of residual carbonaceous and nitrate species. Calcination caused a substantial reduction in fiber diameter, from approximately $1.5\text{--}2.0\text{ }\mu\text{m}$ in the precursor fibers to $120\text{--}380\text{ nm}$ in the ZnO fibers. AFM and SEM observations confirmed that the optimized formulation retained a dense and interwoven nanofibrous structure after calcination.

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