FABRICATION OF ZnO NANOFIBERS USING ELECTROSPINNING METHOD

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Abstract. *Zinc oxide (ZnO) nanofibers have attracted significant attention due to their unique properties and diverse applications in fields such as electronics, photonics, and sensing. Fabrication parameters play a crucial role in determining the morphology, structure, and properties of ZnO nanofibers synthesized via the electrospinning method. This mini-review systematically discusses the impact of critical parameters on the electrospinning process and the resulting characteristics of ZnO nanofibers. Parameters such as polymer concentration, solvent selection, applied voltage, spinning distance, and post-processing conditions are examined in detail. Furthermore, the influence of these parameters on the morphology, diameter distribution, crystallinity, and functional properties of ZnO nanofibers is elucidated. Strategies for optimizing these parameters to achieve desired morphologies and properties are also discussed. Understanding the interplay between fabrication parameters and ZnO nanofiber characteristics is essential for tailoring these materials to specific applications and advancing their technological relevance. This review provides valuable insights into the fabrication of ZnO nanofibers via electrospinning, guiding researchers and engineers toward effective synthesis strategies and future developments in this exciting field.*

Keywords: *Nanofiber synthesis, ZnO precursor, polymer concentration, applied voltage, spinning distance*

Introduction

Zinc oxide (ZnO) nanofibers have garnered significant attention in recent years owing to their unique properties and versatile applications in fields ranging from electronics and photonics to biomedicine and environmental remediation. Among the various methods available for synthesizing ZnO nanofibers, electrospinning has emerged as a prominent technique due to its simplicity, scalability, and ability to produce continuous and uniform nanofibers. The electrospinning process involves applying a high voltage to a polymer solution, resulting in the formation of ultrafine fibers through the stretching and solidification of the polymer jet.

However, the properties and performance of ZnO nanofibers synthesized via electrospinning are heavily influenced by the choice of fabrication parameters. These parameters encompass a wide range of variables, including polymer concentration, solvent selection, applied voltage, spinning distance, and post-processing conditions. Each of these parameters plays a crucial role in determining the resulting ZnO nanofibers' morphology, structure, crystallinity, and functional properties.

In this review, we aim to provide a comprehensive overview of the fabrication parameters involved in the electrospinning method for the synthesis of ZnO nanofibers. We systematically explore the influence of each parameter on the electrospinning process and elucidate its impact on the characteristics of the synthesized nanofibers. By understanding the interplay between these fabrication parameters and the resulting properties of ZnO nanofibers, researchers and engineers can effectively tailor the synthesis process to achieve desired morphologies, structures, and

functionalities. The parameters collected and the results obtained over the years are presented in Table 1.

Through a critical analysis of existing literature and experimental findings, this review aims to shed light on the optimization strategies and challenges associated with fabricating ZnO nanofibers via electrospinning. By providing valuable insights into the synthesis process, this review seeks to facilitate further advancements in developing and utilizing ZnO nanofibers for a wide range of applications, including sensors, catalysis, energy harvesting, and tissue engineering.

Table 1.

Electrospinning parameters for ZnO nanofibers synthesis

Ref	Material	$T_{annealing}$, °C	Applied voltage, kV	Distance, cm	Flow solution, µl*min^{-1}	Diameter before annealing, nm	Diameter after annealing, nm
[1]	$(Zn(CH_3COO)_2 \cdot H_2O)$+ PVP	550	18	16	5	156	50
[2]	$(Zn(CH_3COO)_2 \cdot H_2O)$+ PVA	480	25	15	5	278	124
[3]	ZnO(nanoparticle)+PA N+DMA (solvent)	-	1	8	10	500-1000	-
[4]	Zn(CH3COOH)2*2H2 O+PEO	600	1	23	20	-	55-70
[5]	$(Zn(CH_3COO)_2 \cdot H_2O)$+ PVA	550	1	15	6	-	120
[6]	$Zn(CH_3COO)_2 \cdot 2H_2O$+ ZnO (NPs)+PVP	550	23	20	25	220	120
[7]	Zn(CH3COO)2 * 2H2O+ PVP+ ethanol	550	25	25	-	300	90
[9]	$Zn(NO_3)_2 \cdot 6H_2O$+PVP+ ethanol	520	15	15	17	400	160

The materials and the concentration of the solution.

One of the essential parameters for electrospinning is the solution concentration and type of materials. In many cases, solutions from tree-based materials, such as ZnO precursor, polymer, and solvent, were used in different concertations depending on the application scope to obtain ZnO nanofibers. Was properly demonstrated the importance of the concentration of zinc acetate/polymer by Di Mauro A. et al. [1], who reported morphology changed in high concentrations of zinc acetate (14 wt%), becoming a rope-like structure. However, at the same time, Imran M. et al. [2] reported that the concentration of zinc acetate from 5 to 15 wt% does not show any effect on the morphology, but the diameter of nanofibers is affected from 278nm to 423nm, characterized by a broader distribution of nanofibers, due to the high viscosity which causes non-uniform ejection of the jet.

As ZnO precursors are zinc acetate [1,2,4,5,7], zinc nitrate [9,10], ZnO NPs [3], and in some cases can be used hybrid precursor [6], which combines zinc acetate and ZnO nanoparticles, which can offer certain advantages in obtaining ZnO nanofibres. The combination of zinc acetate and ZnO nanoparticles allows more precise control of the composition and morphology of the resulting nanofibrils, which was reported by W. Matysiak and M. Zaborowska, obtaining a more uniform and better-defined ceramic structure with free structural defects [6]. In the case of zinc nitrate, structural defects were observed due to oxygen deficiency [9], which is not good when using ZnO nanofibers as a sacrificial material to grow another material such as GaN.

The type of polymer used for electrospinning has one of the most critical roles in nanofiber fabrication: it serves as a matrix or support for the ZnO precursors, which facilitates the electrospinning process and allows the obtaining of ZnO nanofibres with controlled dimensions,

as well as the control of the morphology, size, and alignment of the ZnO nanofibres. There are reports on a variety of polymers that can be used in the electrospinning process, such as polyacrylonitrile (PAN) [3], polyethylene oxide (PEO) [4], polyvinylpyrrolidone (PVP) [1,6], and polyvinyl alcohol (PVA) [2,5]. This versatility allows the electrospinning process to be adapted to the specific requirements of each application.

As solvents, more often used ethanol [7,9], distilled water (DW) [2,5], and dimethylformamide (DMF) [1,3,4,6], these types of solvents depend on the field of application and the dimensions of the desired nanofibers. Compared ethanol with DMF, the first one has low density and viscosity due to the simple molecule and can be used to obtain thinner fibers. In contrast, DMF has higher viscosity due to its complex molecular structure than ethanol. As a result, using DMF can get thick, non-uniform structures with beads.

The applied voltage.

Adequate voltage is required to ensure the jet formation and stability and to allow polymer extraction from the solution. A higher tension can lead to a smaller diameter of the nanofibers, while a tension that is too high can generate cracks or discontinuities in the resulting fiber. Nevertheless, at the same time, applied voltage depends more partly on the solution's viscosity; if high viscosity is required, adequate high voltage is necessary to form a uniform structure.

It must be controlled to avoid unwanted phenomena such as electrospray or droplet formation, leading to non-uniform or low-quality nanofibril structures.

The flow of the solution and the distance between the tip of the spinneret and the collector

The precursor solution flow rate is the amount of solution flowing from the spinneret tip in a given interval. This parameter determines the amount of material deposited on the collector and influences the thickness and density of the nanofiber layer. A higher flow rate can lead to the formation of thicker layers of nanofibers, while a lower flow rate can lead to the deposition of thinner layers. Suyitno S. et al. [7] report the importance of flow rate and its influence on nanofibers dimensions in their work. Investigated flow rate from 2 ul/min to 6 ul/min demonstrates that the high flow rate increases fiber diameter, in the same time in case of 6 ul/min, the tip of the needle formed a giant bubble size, which caused larger fibers to be drowned without any sufficient stretching for the same magnitude of the electrostatic field.

The distance between the spinneret tip and the collector influences the length the precursor solution jet traveled to the collector and the nanofibrils' degree of stretching and alignment. A smaller distance may favor the uniform spreading of the precursor solution on the collector and the formation of thinner and more uniform nanofibers. On the other hand, a too-small distance can lead to the aggregation of nanofibrils and the formation of improper layers.

Calcification

The calcination temperature used to obtain ZnO nanofibrils by the electrospinning method is a critical parameter influencing the nanofibrils' properties and characteristics. Calcification is the process of transforming the ZnO precursor into crystalline zinc oxide. The calcination temperature affects the degree of crystallinity and purity of the resulting ZnO. Higher temperatures can promote complete calcination and higher crystallinity of ZnO, which can lead to improved performance in further applications.

The calcination temperature can affect the size and morphology of ZnO nanofibrils. Sometimes, a temperature that is too high may lead to retraction or fusion of nanofibers. At the same time, a too low temperature may not ensure complete calcination or allow the formation of high-quality crystalline ZnO. A. Di Mauro et al. [1] anneal material at different temperatures, from 350 to 650 ˚C. In the case of 450 ˚C was determined, very low crystal quality with the presence of a partially amorphous state. At the same time, in the case of 650 ˚C, materials have high

crystallinity but are impossible to use in any application due to the high fragility of the material. As a result, an optimal temperature was reported at 550 ˚C, an equilibrium between crystal quality and the fragility of the material.

Another important aspect is the thermal and chemical stability of the obtained ZnO nanofibers. By calcining at suitable temperatures, ZnO's increased thermal and chemical stability can be ensured, which can be crucial in various applications.

Conclusion

The fabrication of ZnO nanofibers using the electrospinning method involves a multitude of parameters that significantly influence the morphology, structure, and properties of the resulting nanofibers. This review reveals that careful control and optimization of these parameters are essential for achieving desired characteristics and functionality in ZnO nanofibers.

Parameters such as solution properties, including polymer concentration, solvent type, and ZnO precursor concentration, play a critical role in determining the solution's spinnability and the nanofibers' final morphology. Additionally, the electrospinning process parameters such as applied voltage, flow rate, distance between the spinneret and collector, and environmental conditions (temperature and humidity) exert profound effects on fiber diameter, orientation, and uniformity.

Furthermore, post-treatment techniques such as calcination, annealing, and surface modification can further tailor the properties of ZnO nanofibers, enhancing their crystallinity, surface area, and chemical reactivity for specific applications.

However, the review reveals that optimizing these parameters is often challenging due to their complex interplay and the electrospinning process's sensitivity to small variations. Therefore, future research efforts should focus on systematic studies aimed at understanding the underlying mechanisms governing the electrospinning process and the relationship between process parameters and nanofiber properties.

Moreover, the development of advanced characterization techniques and computational modeling approaches can aid in elucidating the intricate dynamics involved in electrospinning ZnO nanofibers, thereby facilitating more precise control and optimization of the fabrication process.

In conclusion, while significant progress has been made in the fabrication of ZnO nanofibers via electrospinning, continued research is necessary to harness the potential of this method fully for various applications. By advancing our understanding of the key parameters and their influence on nanofiber properties, we can unlock new opportunities for the design and synthesis of ZnO nanofibers with tailored characteristics suited for diverse technological applications.

References

[1] A. DI Mauro et al. *Synthesis of ZnO nanofibers by the electrospinning process* //Materials Science in Semiconductor Processing, 2016, vol. 42, pp. 98-101.

[2] M. Imran et al. *Fabrication and characterization of zinc oxide nanofibers for renewable energy applications* //Arabian Journal of Chemistry, 2017, vol. 10, pp. S1067-S1072.

[3] A. Jamil et al. *Fabrication of PAN/ZnO Nanofibers by Electrospinning as Piezoelectric Nanogenerator* //Journal of Physics: Conference Series, IOP Publishing, 2018, vol. 1093, pp. 012024.

[4] P. Samanta, S. Bagchi, S. Mishra *Synthesis and Sensing characterization of ZnO nanofibers prepared by Electrospinning* //Materials Today: Proceedings, 2015, vol. 2(9), pp. 4499-4502.

[5] S. Suyitno et al. *Fabrication and characterization of zinc oxide-based electrospun nanofibers for mechanical energy harvesting* //Journal of Nanotechnology in Engineering and Medicine, 2014, vol. 5(1), pp. 011002.

[6] W. Matysiak, M. Zaborowska *Hybrid ZnO/ZnO-NPs nanofibres fabricated via electrospinning* //Journal of Achievements in Materials and Manufacturing Engineering, 2019, vol. 94(1-2), pp. 5-12.

[7] J. Guo et al. *Fabrication of ZnO nanofibers by electrospinning and electrical properties of a single nanofiber* //Journal of dispersion science and technology, 2010, vol. 31(5), pp.684-689.

[8] J. Park A. et al. *Fabrication and characterization of ZnO nanofibers by electrospinning* //Current Applied Physics, 2009, vol. 9(3), pp. S210-S212.

[9] S. S. Mali et al. *Novel synthesis and characterization of mesoporous ZnO nanofibers by electrospinning technique* //ACS Sustainable Chemistry & Engineering, 2013, vol. 1(9), pp. 1207-1213.

[10] Y. İ. Akgül, Y. Aykut *Partially Transformation of Zinc Nitrate to Zinc Compounds on PVC Nanofibers at Low Temperature Heat Treatment and Investigation of the Products' Optical Properties* //Tekstil ve Mühendis. – 2019. – T. 26. – №. 114. – C. 118-124.