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ELECTROSPINNING OF ZNO NANOFIBERS FROM ZINC GALVANIZING FLUE DUST

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Abstract

The research investigates the utilization of zinc galvanizing flue dust as a secondary resource for the preparation of ZnO ceramic nanofibers. The applied methodology combined acidic leaching with electrospinning of the obtained zinc solutions, with emphasis on the effect of leaching agents and waste-derived impurities on fiber morphology. Results revealed that 0.5 M HCl produced coarse oval fibers, whereas 0.5 M H_2SO_4 generated hollow ribbon-like nanostructures with increased surface area. Importantly, the presence of impurities in real waste solutions did not adversely affect fiber formation. The study confirms that electrospinning is a viable and low-waste approach for converting industrial zinc residues into advanced ceramic nanomaterials, providing a sustainable pathway for nanotechnology development.

***Keywords**: zinc galvanizing flue dust; electrostatic spinning; ZnO; ceramic nanofibers*

1. INTRODUCTION

Approximately 60 % of global zinc production is used for steel corrosion protection, with hot-dip galvanizing being one of the most important processes [1]. While widely applied, this technology generates significant zinc-rich by-products. Besides bottom and top dross, a fine particulate waste known as zinc galvanizing flue dust is formed [1]. This dust, typically 1–2 μm in size and containing over 20% Zn, originates from the interaction of steel with molten zinc, producing the so-called white smoke [2]. Due to the presence of chlorides and organic residues, it is classified as hazardous waste (KO61) [3]. Industrial-scale treatment of flue dust remains undeveloped. Research has mainly focused on hydrometallurgical methods, investigating leaching in water, HCl, and H_2SO_4 under different conditions [4-8]. Some attempts with pyrometallurgical processing, similar to zinc ash treatment, have also been reported [9].At the same time, electrospinning is emerging as a powerful technique for producing nanofibers with high surface area, porosity, and excellent mechanical–chemical properties. Based on strong electrostatic fields, this process enables fiber formation from liquid precursors and provides a promising route for converting zinc-containing waste into functional ZnO nanomaterials.

1.1 Electrospinning

Electrospinning can be performed by several approaches, including needle-based, needle-free, and rod-assisted techniques, each differing in the way fibers are generated from the polymer solution [10-11]. Needle spinning provides high control and is widely used, while needle-free and rod-based methods enable higher productivity by producing multiple fibers simultaneously. In the

synthesis of ZnO nanofibers, electrospinning is particularly advantageous, as polymer–zinc precursor solutions can be spun into composite fibers and subsequently calcined to remove organic components [12]. This process yields pure ceramic nanofibers with tailored morphology and structural properties [13].

2. MATERIAL AND METHODOLOGY

2.1 Input material

The zinc flue dust sample used in this study was obtained from a Slovak hot-dip galvanizing plant. Prior to analysis, the material was homogenized by particle size adjustment to ensure a representative sample. Elemental composition (Zn, Fe, Al, Cu, Pb) was determined using HRCS AAS, while chloride content was measured by titration. Additional elemental data were obtained by XRF, and the crystalline structure was characterized by XRD. A thermodynamic study was also performed with HSC Chemistry 6.0 to calculate Gibbs free energy changes and construct Eh–pH diagrams [14].

2.2 Leaching and preparation of solutions

For comparison, two feedstocks were used in the leaching experiments – real zinc flue dust and high-purity zinc oxide. Synthetic solutions were prepared by dissolving ZnO (99.6%, Centralchem) in HCl and H_2SO_4 at concentrations of 0.01 M, 0.5 M, and 1 M, targeting a Zn concentration of about 40 g/L. Leaching was carried out at 60 °C for 30 minutes under constant stirring. The same conditions were applied to fine fractions of zinc flue dust, with two liquid-to-solid ratios tested (30:1 and 5:1). After the process, solutions were filtered and subsequently analyzed.

2.3 Electrostatic spinning

Leachates from both synthetic and real sources were used to prepare solutions for electrospinning, containing PVP, ethanol, citric acid, and acetic acid in a weight ratio of 48:6:6:2.6:1. The mixtures were stirred for 48 hours at 25 °C to achieve a homogeneous solution. Electrospinning was performed on a Nanospider™ device using needle-free electrostatic technology at 75–80 kV and an electrode distance of 130–140 mm. The resulting composite fibers were calcined in air at 550–600 °C to remove the polymer matrix. This process yielded ceramic ZnO nanofibers with the desired morphology and chemical properties. Do not put numbers on the pages.

3. RESULTS AND DISCUSSION

AAS analysis revealed that the sample contained 25.33 % Zn and 24.87 % chlorides, while other elements (Al, Fe, Pb, Cu) were present at concentrations below 1 % (see table 1). XRF confirmed the dominant presence of zinc and chlorides, with minor contributions from other elements. X-ray diffraction identified the main zinc-containing phases as complex salts, specifically $(NH_4)_2[ZnCl_4]$ and $[ZnCl_2](NH_3)_2$. Iron was also detected in the form of an ammonium chloride complex, $(NH_4)_3[FeCl_5]$.

Thermodynamic analysis of the Zn–Al–Cl–Fe–H_2O and Zn–Al–Fe–S–H_2O systems at 60 °C confirmed that zinc occurs predominantly as $ZnCl^+$ within the water stability region, up to pH ~ 5 in HCl and up to pH ~ 4.3 in H_2SO_4. Experimental results further indicated that 0.5 M HCl and 0.5 M H_2SO_4 solutions are the most suitable for ZnO nanofiber fabrication.

Table 1. *Chemical composition of zinc galvanizing flue dust*

Sample	**Zn [%]**	**Fe [%]**	**Al [%]**	**Cu [%]**	**Pb [%]**	**Cl^- [%]**	**Residual [%]**
Average	25.33	0.38	0.91	0.006	0.09	24.87	48.41
S	0.46	0.01	0.14	0.0008	0.06	2.07	-
RSD	1.81	2.63	650	750	150	8.32	-

S- Standard deviation
RSD- Relative standard deviation

Figure 1a shows precursor fibers obtained from the real solution (0.5 M HCl), characterized by oval morphology with diameters between 100 and 400 nm. After calcination at 550 °C (Figure 1b), the fibers preserved their fibrous shape but exhibited slight shrinkage. A detailed view in Figure 1c highlights their morphology, displaying a textured and mildly porous surface. At 600 °C (Figure 1d), the fibers retained their structure after complete carbon removal, confirming their thermal stability.

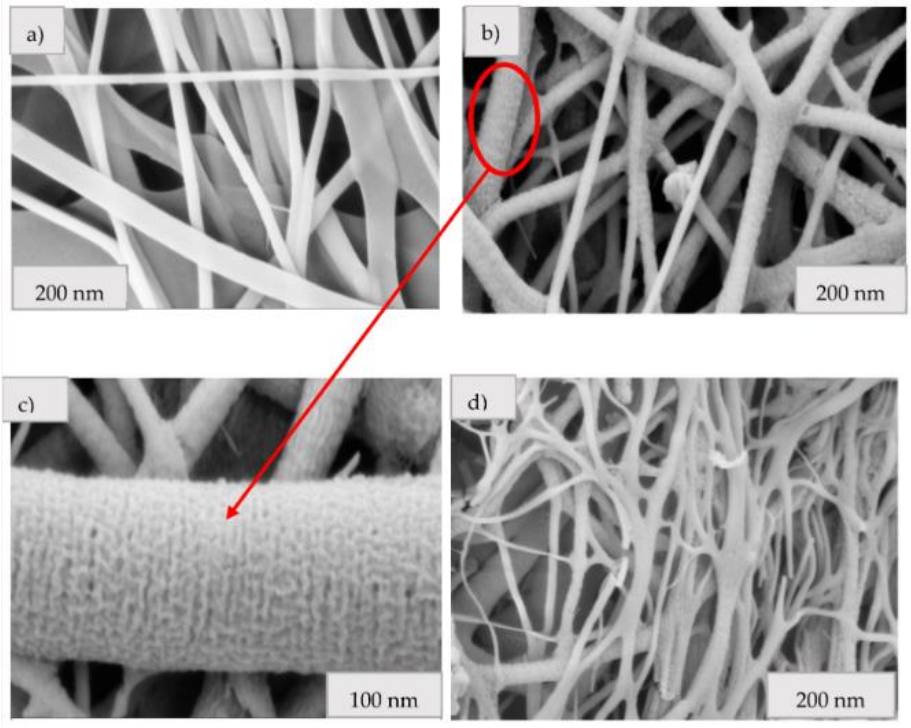

Figure 1. SEM images of (a) precursor fibers 0.5 M HCl, (b) ceramic fiber 0.5 M HCl at the temperature of 550 °C, (c) fiber morphology, (d) ceramic fibers 0.5 M HCl at 600 °C

In Figure 2a, precursor fibers from the real solution of 0.5 M H_2SO_4 are shown. The precursor fibers are very fine, with a thickness of less than 100 nm. Figure 2b shows ceramic nanofibers after calcination at 550 °C, which are highly structured and porous. Figure 2c shows ceramic fibers after calcination at 600 °C, which have a structured surface composed of fine ZnO layers. The detail in Figure 2d highlights the hollow structure of the fibers.

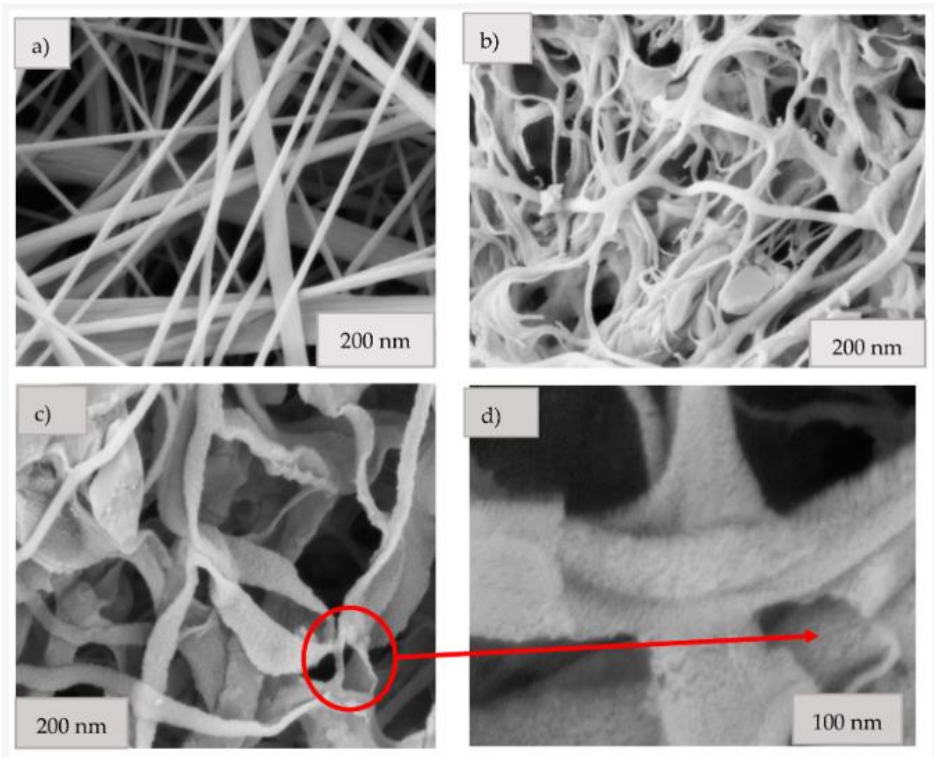

Figure 2. SEM images of (a) precursor fibers 0.5 M H_2SO_4, (b) ceramic fibers 0.5 M H_2SO_4 at the temperature of 550 °C, (c) ceramic fibers 0.5 M H_2SO_4 at the temperature of 600 °C, (d) fiber morphology

3.1 Structural and Morphological Comparison of ZnO Fibers from Synthetic vs. Real Solutions

For the purpose of comparison, ceramic nanofibers obtained from both synthetic and real solutions prepared with 0.5 M HCl and 0.5 M H_2SO_4 were investigated. The results demonstrate that ZnO ceramic nanofibers derived from these conditions exhibit comparable structural characteristics (Figures 3-4), confirming the suitability of the selected acid concentrations for their fabrication. Specifically, nanofibers synthesized using 0.5 M HCl predominantly display oval morphologies with irregular and rough surfaces, whereas the application of 0.5 M H_2SO_4 leads to the formation of hollow ribbon-like fibers, which are expected to provide an increased specific surface area. Complementary XRD analysis verified the presence of the principal crystalline zinc phases (Figure 5), thereby substantiating the successful formation of ZnO nanostructures.

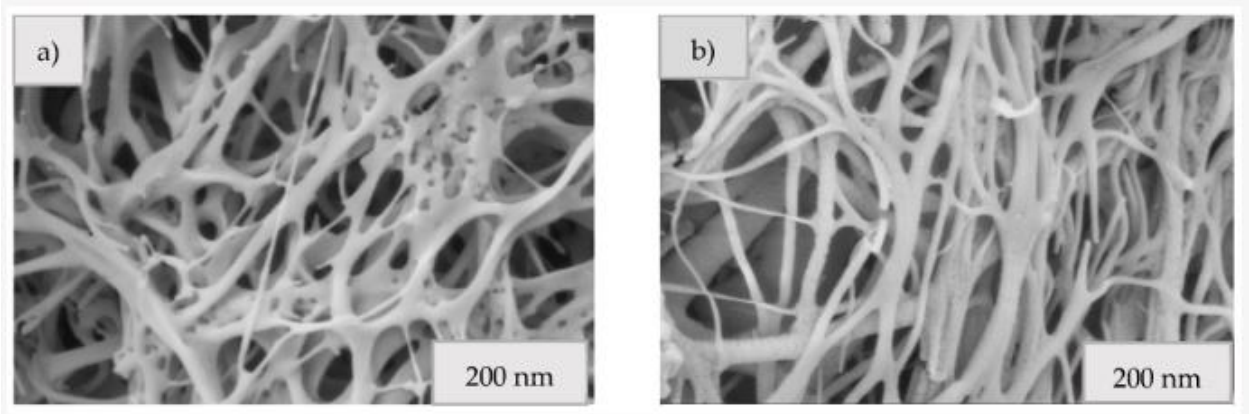

Figure 3. Images of (a) ceramic fibers from synthetic solution of 0.5 M HCl at 600 °C and (b) ceramic fibers from real solution of 0.5 M HCl at 600 °C.

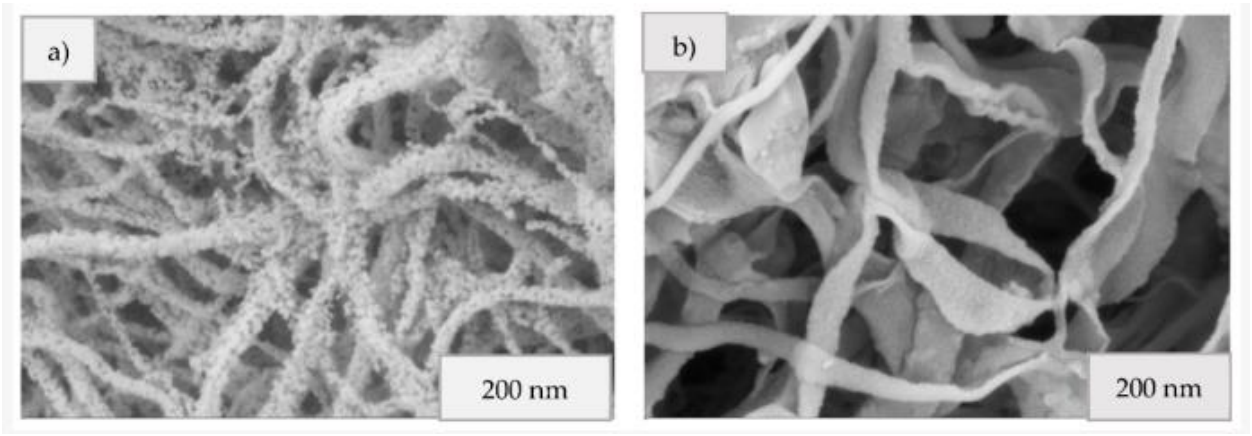

Figure 4. Images of (a) ceramic fibers from synthetic solution of 0.5 M H_2SO_4 at 600 °C and (b) ceramic fibers from real solution of 0.5 M H_2SO_4 at 600 °C.

Complementary XRD analysis verified the presence of the principal crystalline zinc phases (Figure 5), thereby substantiating the successful formation of ZnO nanostructures.

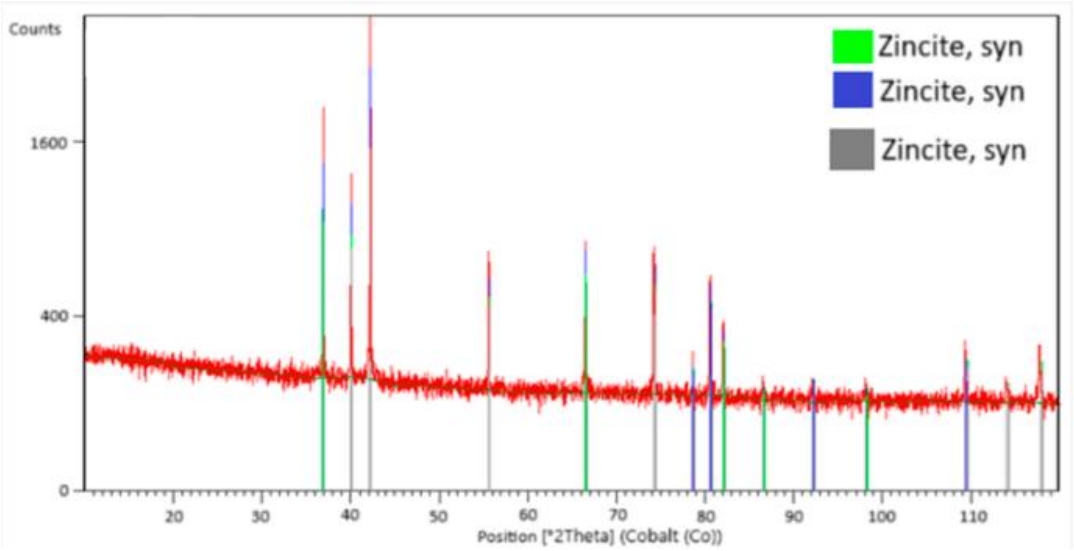

Figure 5. XRD analysis of ceramic nanofibers from the real 0.5 M H_2SO_4 solution.

4. CONCLUSION

This study explores the hydrometallurgical processing of zinc galvanizing flue dust for the fabrication of ceramic ZnO nanofibers. The experiments demonstrated that electrospinning is a reliable method, and the use of flue dust did not compromise nanofiber quality compared to synthetic precursors. The resulting fibers showed comparable morphology and properties, confirming the feasibility of this approach. In addition to reducing waste disposal and associated costs, the method provides an environmentally sustainable route for resource recovery. These findings highlight the potential for industrial application of the process. Overall, the work contributes to innovation in nanotechnology and sustainable waste management.

ACKNOWLEDGEMENTS

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