

Synthesis and characterisation of ceramic core/shell nanofibres via single stage co-axial electrospinning

Hojjat Rafieipour¹, Mohammad Reza Vaezi¹, Asghar Kazemzadeh² ✉

¹Department of Nanotechnology and Advanced Materials, Materials and Energy Research Center, Karaj 3177983634, Iran

²Department of Semiconductors, Materials and Energy Research Center, Karaj 3177983634, Iran

✉ E-mail: asg642001@yahoo.com

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SnO₂/ZnO core-shell nanofibres were synthesised by single-stage electrospinning technique. For synthesis of these nanofibres, the hydrophilic solutions of precursors were injected by two injectors through coaxial needles which were connected to separate syringes. The precursor's solutions were prepared by solving zinc acetate and tin chloride in polyvinyl alcohol solution, separately. The morphology and structure of nanofibres were observed by field emission scanning electron microscope, transmission electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction techniques, before and after calcination. The final core/shell structure of the nanofibres was established as SnO₂/ZnO, after calcination. Average diameters of the as-electrospun and calcined core/shell nanofibres were about 190 and 97 nm, respectively.

1. Introduction: Nanofibres are a branch of materials that have diameters of 100 nm or less, but their length may be several times of their diameter. Therefore, they can be considered as non-homogeneous one-dimensional structures [1–8]. Electrospinning represents a relatively simple and versatile method for generating fibular nanostructures, and the unique features of the obtained electrospun nanofibres provide especial interest for both of the technique and the resultant products. It has been mainly applied to pure organic polymers, but functional inorganic nanofibres can be produced by using sol-gel composed of metal(s), precursor(s) and proper polymer(s) [9].

Fibres can be synthesised as complex architectures by electrospinning, e.g. nanofibres, continuous hollow fibres, hierarchical and core-shell nanofibres [5, 9, 10–12]. Core/shell structure is fabricated with a variety of methods, i.e. the synthesis of particles as core and deposition of shell on them, synthesis of core by electrospinning technique and deposition of shell on it (two-stage method); and core-shell synthesis at the moment (one-step method) [5, 8].

Many researchers have been working on core-shell structure such as Li *et al.* [13], Choi *et al.* [14] and Pan *et al.* [15] and they synthesised nanofibres in the two steps. For example, Li *et al.* synthesised core by electrospinning and shell by hydrothermal methods (ES + HT). Choi *et al.* and Pan *et al.* synthesised core by electrospinning and shell by ALD (atomic layer deposition) methods too. Song *et al.* [16] fabricated coaxial electrospun polycaprolactone/polyvinyl alcohol (PVA) core-sheath nanofibres. The core/shell nanofibres were synthesised in the one step without any precursor. Tharsika *et al.* [17] fabricated SnO₂/ZnO core/shell nanowires. They synthesised nanowires by a single-step carbothermal reduction method, at high temperature (900°C), but our work's conditions are at room temperature and ambient atmosphere.

Reneker *et al.* [18] has expressed the core-shell nano/mesofibres were first produced by co-electrospinning of two materials by Sun. Many parameters to play roles in governing successful electrospinning of fibres. Solution parameters, processing parameters and environment parameters have impacts on the electrospinning process [19]. Solution concentration is the main factor in determining the outcome of this procedure. It determined for PVA in this work 6–15 wt% by Mark-Houwink formula [20]. Core-shell nanofibres have many applications in oil and gas industry, petrochemical, diagnosis illness, tissue engineering, drug delivery, catalysts,

sensors and so on [12, 15, 21, 22]. To generate well-controlled and high-quality ceramic nanofibres by electrospinning, one typically process has to use the following procedure: (i) preparation of an electrospinning solution containing a polymer and sol-gel precursor of the ceramic material, (ii) electrospinning of the solution under appropriate conditions, generate precursor nanofibres containing inorganic precursor and polymer assistant materials and (iii) calcination of the precursor nanofibres at high temperature to remove polymers and obtain the ceramic phase [4].

Many studies concluded that two immiscible components favoured well defined core/shell structure via co-axial electrospinning [23–30]. For lowering liquid-liquid interfacial tension, miscible fluids have been often co-axially electrospun to core/shell fibres. Yu *et al.* [31] mentioned that interaction between core and shell fluids during co-axial electrospinning was probably negligible, as electrospinning was such a rapid process that it could not provide sufficient time for the two fluids to diffuse into each other. It was emphasised that miscible fluids, even in the same solvent, served to reduce the interfacial tension, producing thinner fibres. The interaction between core and shell solutions (polymers or solvents) is very important parameter. It should be considered before selecting the desired set of solutions for co-axial electrospinning. The solvent of either of the solutions should not precipitate the polymer from the other solution when the solutions meet at the tip of the capillary.

The interfacial tension between the shell and the core should be as low as possible for the generation of the stabilised compound Taylor cone. [32] Sun *et al.* [33] showed that 'the characteristic time of diffusion spreading of a boundary' between two miscible solutions was greater than that of the electrospinning process and therefore, no mixing took place. A subsequent study by Yu *et al.* [31] was in agreement with this finding and they added that using the same solvent might also help to reduce the interfacial tension between the two solutions, which should further favour the development of a uniform core/sheath fibre. Li and Xia [23] in their study reported that mixing between the solutions could occur during the process if they were miscible. In our research, SnO₂/ZnO core/shell nanofibres were synthesised in a 'one step' method without any mixing by the same polymeric solutions.

In this work, we synthesised oxide nanofibres via single stage, not only eliminate some of shell steps fabrication, but also nanofibres were fabricated faster and easier in our procedure which is very cost effective. This method for synthesising the core/shell oxide

Table 1 Solution and processing parameters

<i>d</i> , cm	<i>V</i> , kV	Tin chloride, wt%	Zinc acetate, wt%	<i>R</i> , ml/h		<i>N</i> , Pa s		PVA, wt%	
				Core	Shell	Core	Shell	Core	Shell
12	12	10	10	0.02	0.20	0.20	0.25	9	15

nanofibres is a new method. The other processes for producing the core/shell nanofibres are two-step methods (e.g. electrospinning + ALD). Several times deposition (up to 800 times) is needed for shell fabrication, and subsequent clean-up is required by various gases after forming each layer [6, 14, 34], so it has been a long and costly process. However, in this Letter, these costs are eliminated and core/shell nanofibres are synthesised fast. We prepared two aqueous solutions of PVA at first, and then tin chloride and zinc acetate were added to either of them. Then, these precursor solutions were electrospun by a home-made co-axial needle and after calcination core-shell nanofibres were synthesised. We intend to use nanofibres made in gas sensors.

2. Experimental

2.1. Materials: PVA with an average molecular weight of 72,000 g/mole (Art. No.821038 Merck, Germany), zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) (Art. No.A769302639), tin chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) (Sigma-Aldrich, 14550) and distilled water was used to prepare the PVA/precursor aqueous solutions.

2.2. Equipment: A high-voltage power supply (Hi-V) FC60P2-Glassman Co., USA that provides 60 kV power supply. Two syringe pumps, Top5300-Japan, and other, SP 1000 HSM-Iran, were used for different flow rates.

2.3. Solution preparation

(a) *Core solution preparation:* An aqueous solution was prepared by dissolving 0.60 g PVA granules in 9.40 ml distilled water, and stirred by magnet bar with 400 rpm at 60°C for 4 h. Then, 1 g of tin chloride was added to this solution and stirred for 1 h at ambient temperature and then was loaded into a 10 ml polyethylene syringe.

(b) *Shell solution preparation:* An aqueous solution was prepared by dissolving 1.50 g PVA granules in 8.50 ml distilled water as the same condition as the core solution, and then 1 g zinc acetate was added and solution was stirred for 1 h at ambient temperature and then was loaded into another 10 ml polyethylene syringe.

The distance between the tip of the syringe needle and an aluminium foil collector was fixed at 12 cm and feeding rates were adjusted at two constant rates 0.02 and 0.20 ml/h for core and

shell solutions, respectively. Applied voltage was adjusted at 12 kV. Test conditions are summarised in Table 1.

A homemade stainless steel coaxial needle was used with a vertically upward configuration as is shown in Fig. 1.

The positive pole was at the needle tip and the negative pole was located at the top on the aluminium foil and nanofibres will gather on aluminium foil on the top plate (Fig. 1) [35].

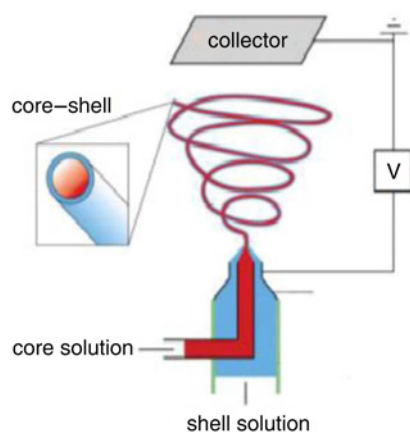
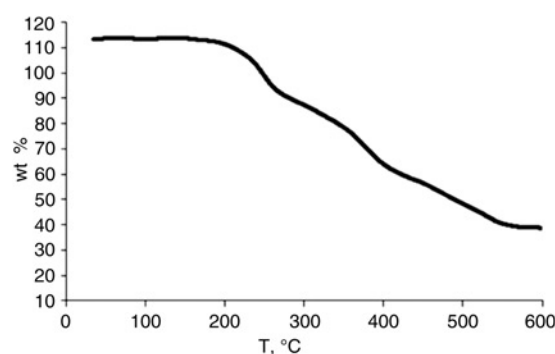
2.4. Characterisation: The morphologies and chemical composition of the SnO_2/ZnO nanofibres were investigated by using a field emission scanning electron microscope (FE-SEM) (Mira 3-XMU, Czech). The core-shell structure was studied by 80 kV transmission electron microscope (TEM), (EM10C-Zeiss-Germany) and SnO_2 , ZnO phases were determined by X-ray diffraction (XRD), (Philips-PW 3710-Netherlands), $\text{CoK}\alpha$, $\lambda = 0.1789$ nm. Chemical composition was analysed by energy dispersive spectroscopy (EDS). Thermo gravimetric analysis (TGA) was accomplished by using BÄHR-STA503-Germany Instrument. Synchronous DSC/TG, which measures the weight loss in a material dependent on temperature or time under a controlled environment condition. TGA samples were annealed from room temperature to 600°C at a rate of 5°C/min in air. The statistical analysis was done by using Image J and Origin pro 8.1 software's.

3. Results and discussion

3.1. Thermal characterisation: TGA was accomplished to distinguish appropriate calcination temperature for as-spun nanofibres. The TG curve in Fig. 2 shows a weight decrease in the limited area of <250°C, for H_2O vaporisation in the as-spun nanofibres.

Between 250°C and 575°C, PVA and CH_3COO groups of zinc acetate decomposed and some vaporisable tin persulfate such as chloride blend evaporated. The phase conversion from amorphous (i.e. as-spun nanofibres) to calcined nanofibres also happen at this temperature. It should be leaded that there is no weight decreases above 575°C, disclosing that a calcination temperature of ~575°C is required to eliminate the solvent and polymer also to entirely disintegrate zinc acetate and tin chloride to pure ZnO-SnO_2 phases.

3.2. Calcination: Thermal treatment is essential to remove water and organic species of the as-spun nanofibres also conversion the precursors to their form oxide phases. Calcination temperature

**Fig. 1** Schematic of vertical upward electrospinning process [35]**Fig. 2** TG curve of core/shell nanofibres

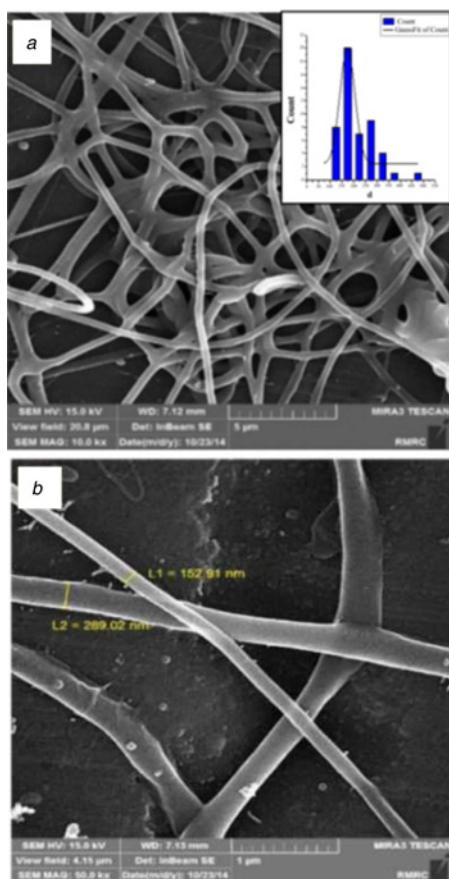
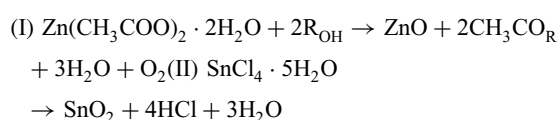


Fig. 3 FE-SEM images of electrospun SnO_2/ZnO core-shell nanofibres at *a* 10.0 kx. Inset: distribution of nanofibres *b* 50.0 kx

was meliorated to 600°C founded on the TGA results. After calcination in air for 2 h, the chiselled nanofibres get stiff and thinner owing to the disintegration of PVA and the alteration of the metal precursors to their metal oxides.

Thermal decomposition reactions of tin chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) and zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) are as follows:



To synthesise the ceramic nanofibres, a conductive polymer is required. In this Letter, the polyvinyl alcohol that is used as R-OH, and R-OH reacts with zinc acetate dehydrate. The role of R-OH in the synthesis of nanofibres is defined as a solvent.

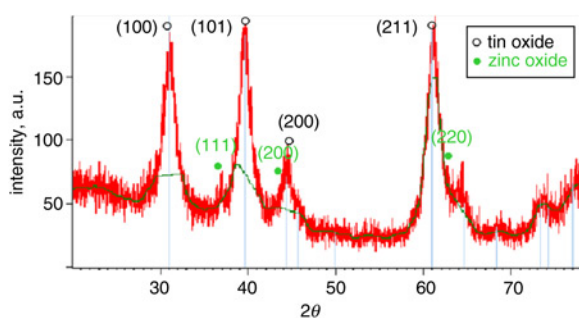


Fig. 4 XRD patterns of the core/shell $\text{SnO}_2/\text{ZnO}_2$ nanofibres, calcined at 600°C for 3 h

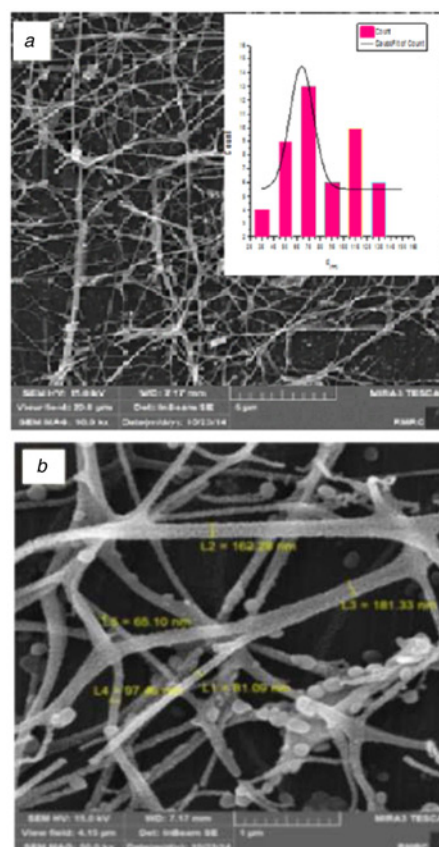


Fig. 5 FE-SEM images of calcined SnO_2/ZnO core/shell nanofibres at *a* 10.0 kx. Inset: distribution of nanofibres *b* 50.0 kx

Acetate group will be decomposed and PVA side chain will be degraded by elimination of water in calcination step [36, 37].

3.3. Structural and morphological characterisation: Prior to the electrospinning of the PVA/ SnO_2 and PVA/ ZnO solutions together, the system parameters have been optimised with either of PVA/ SnO_2 and PVA/ ZnO solutions to produce smooth and thin fibres without beads and drops. The best optimised conditions were used for the fabrication of the fibres using. The optimised parameters are showed formerly (Section 2.3). These parameters yielded fibres with diameters of 160–490 nm, measured from the FE-SEM micrographs. The FE-SEM micrographs of the as-electrospun PVA/ SnO_2/ZnO core-shell nanofibres are shown in Figs. 3*a* and *b*.

The crystalline structure including the phase purity and morphological features of the synthesised nanofibres were examined using XRD is shown in Fig. 4.

Index planes (111), (200) and (220) are the main planes in zinc oxide with cubic structure, and this XRD pattern is correlated with JCPDS Card No. 01-077-2414. The lattice constants of cubic structure are as follows: $a = b = c = 4.871 \text{ \AA}$. Index planes (110), (101), (200) and (211) are the main planes in SnO_2 crystals with tetragonal rutile structure with lattice constants: $a = b = 4.737$

Table 2 Statistical analysis of the as-electrospun and calcined nanofibres

State	No	SD	Sum, nm	Min, nm	Ave, nm	Max, nm
as-electrospun	50	73.95	10,302	103	190	460
calcined	50	29.64	4249	25	97	151

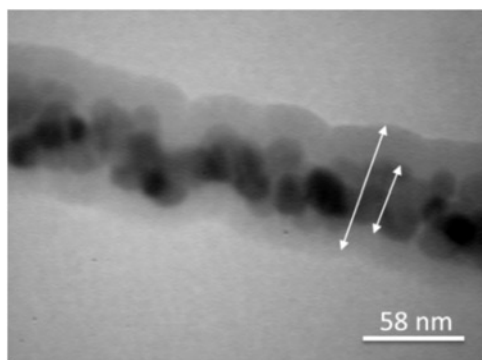


Fig. 6 TEM image of SnO_2/ZnO core/shell nanofibre

\AA , $c = 3.187 \text{ \AA}$ and this XRD pattern is correlated with JCPDS Card No. 01-072-1147.

The FE-SEM images of calcined SnO_2/ZnO core-shell are shown in Figs. 5a and b. It can be seen that after calcination, the surface of nanofibres is rough, as the organic constituents were removed from the as-spun nanofibres web through calcination [38]. Distribution of fibres was evaluated by histogram chart and Gaussian model for both the as-electrospun and calcined fibres and the results are shown in the inset of Figs. 3 and 5, respectively.

After calcination, the diameter of fibres is decreased, because the removal of superficial and structural water in the precursors [38], decomposition of PVA and zinc acetate will occur according to the reactions (I and II), and reduces the diameter of the fibres [36, 37].

The reduced diameter increases the surface-to-volume ratio [39], and leads to improve the performance in different filtration industries, such as gas sensors, drug delivery, tissue engineering [12, 22], water treatment and so on [39, 40]. It is necessary to note that the nanofibres synthesised in this research will be used in gas sensors.

Distribution, maximum, minimum, average diameter and standard deviation of the non-woven nanofibres web are given in Table 2 and d is the distance between needle and collector, R is the feed rate, V is the applied voltage and ν is the viscosity are given in Table 1.

According to statistical results, average diameters of the as-electrospun and calcined nanofibres were 190 and 97 nm, respectively.

TEM image was used to show the nanostructure details of the core and the shell parts of the fibres (Fig. 6).

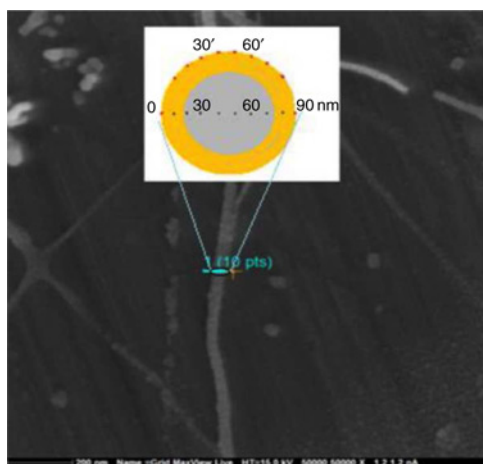


Fig. 7 Ten positions on the energy dispersive X-ray spectroscopy (EDXS) fibre profile, inset: line scan position of the fibre

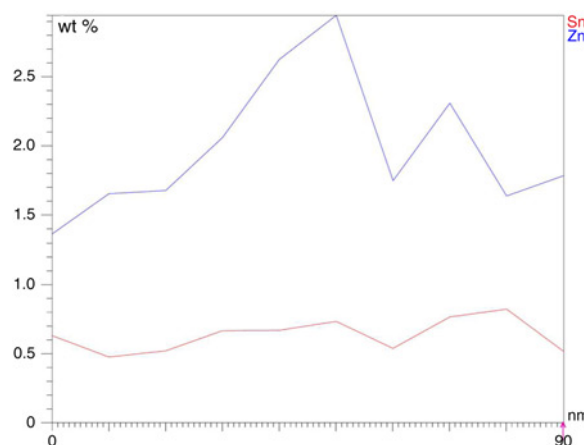


Fig. 8 EDXS analysis line scan profile of a fibre

The ten points on backbone of one fibre were line scanned. These points are shown in Fig. 7 and the profile EDS analysis is shown in Fig. 8.

According to Figs. 7 and 8, the maximum amount of ZnO and SnO_2 are in the middle of the fibre and toward the edges, the amount of ZnO decreases as its thickness gradually decreases, but, the amount of SnO_2 is uniform, approximately, and decreases toward the edge, except the first 10 nm of the left edge.

4. Conclusion: The following results can be deduced accordingly:

(a) The $(\text{SnO}_2/\text{ZnO})$ nanofibres with core/shell structure have been fabricated by single-stage electrospinning technique, for the first time, and the diameter of the synthesised nanofibres are in nanoscale.

(b) It was found that, the maximum amount of Zn is in the middle of the fibre and reduces toward the edges, but the amount of Sn at the middle of the fibre is uniform approximately, and at the sides (except the first point) are minimum too.

(c) The TEM image showed that the SnO_2 and SnO_2/ZnO diameters are about 45 and 85 nm, respectively.

(d) The reducing diameter of calcined nanofibre was synthesised by two-stage methods were reported in other papers. However, diameter reduction of core/shell nanofibre oxides, not only was not mentioned, but also not synthesised by one-step in all references. However, in this work, diameter reduction of 49% was achieved, approximately.

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6 References

- [1] Khorami H.A., Keyanpour-Rad M., Vaezi M.R.: 'Synthesis of sensing properties', *Appl. Surf. Sci.*, 2011, **257**, pp. 7988–7992
- [2] Hwang I.S., Kim S.J., Choi J.K., *ET AL.*: 'Synthesis and gas sensing characteristics of highly crystalline ZnO-SnO_2 core-shell nanowires', *Sens. Actuators*, 2010, **B148**, pp. 595–600
- [3] Huang J., Wan Q.: 'Gas sensors based on semiconducting metal oxide one-dimensional nanostructures', *Sensors*, 2009, **9**, pp. 9903–9924
- [4] Wu H., Pan W., Lin D., *ET AL.*: 'electrospinning of ceramic nanofibers: fabrication, assembly and applications', *Adv. Ceram.*, 2012, **1**, (1), pp. 2–23

- [5] Guorui Y., Wei Y.: 'The preparation of core/shell nanofibers by electrospinning: applications in tissue engineering and drug delivery', 2010, pp. 1–14, <http://www.paper.edu.cn>
- [6] Park J.Y., Choi S.W., Lee J.W., *ET AL.*: 'Synthesis and gas sensing properties of TiO₂-ZnO core-shell nanofibers', *J. Am. Ceram. Soc.*, 2009, **92**, (11), pp. 2551–2554
- [7] Wang Y., Aponte M., Leon N., *ET AL.*: 'Synthesis and characterization of tin oxide microfibres electrospun from a simple precursor solution', *Semicond. Sci. Technol.*, 2004, **19**, pp. 1057–1060
- [8] Kumar A.: 'Nanofibers', Chapter 22, Intech, Olajnica 19/2, 32000 Vukovar, Croatia, (published in India, 2010)
- [9] Tolba G.M.K., Barakat N.A.M., Bastaweesy A.M., *ET AL.*: 'Hierarchical TiO₂/ZnO nanostructure as novel non-precious electrocatalyst for ethanol electrooxidation', *J. Mater. Sci. Technol.*, 2015, **31**, (1), pp. 97–105
- [10] Zhuo H.T., Hu J.L., Chen S.J.: 'Coaxial electrospun polyurethane core-shell nanofibers for shape memory and antibacterial nanomaterials', *EXPRESS Polymer Lett.*, 2011, **5**, pp. 182–187
- [11] Lee B.S., Son S.B., Park K.M., *ET AL.*: 'Fabrication of Si core/C shell nanofibers and their electrochemical performances as lithium-ion battery anode', *J. Power Sources*, 2012, **206**, pp. 267–273
- [12] Hong Z., Guang Z.C., Hui Z.Y., *ET AL.*: 'Electrospinning of ultrafine core/shell fibers for biomedical applications', *Sci. Chin. Chem.*, 2010, **53**, pp. 1246–1254
- [13] Li W., Ma S., Li Y., *ET AL.*: 'Enhanced ethanol sensing performance of hollow ZnO-SnO₂ core-shell nanofibers', *Sens. Actuators*, 2015, **B 211**, pp. 392–402
- [14] Choi S.W., Park J.Y., Kim S.S.: 'Synthesis of SnO₂-ZnO core-shell nanofibers via a novel two-step process and their gas sensing properties', *Nanotechnology*, 2009, **20**, pp. 1–6
- [15] Pan K.Y., Lin Y.H., Lee P.S., *ET AL.*: 'Synthesis of SnO₂-ZnO core-shell nanowires and their optoelectronic properties', *Nanomaterials*, 2012, **2012**, pp. 1–6
- [16] Song W., Yu X., Markel D.C., *ET AL.*: 'Coaxial PCL/PVA electrospun nanofibers: osseointegration enhancer and controlled drug release device', *Biofabrication*, 2013, **5**, pp. 1–11
- [17] Tharsika T., Haseeb A.S.M.A., Akbar S.A., *ET AL.*: 'Catalyst free single-step fabrication of SnO₂/ZnO core-shell nanostructures', *Ceram. Int.*, 2014, **40**, pp. 7601–7605
- [18] Reneker D.H., Yarin A.L., Zussman E., *ET AL.*: 'Electrospinning of nanofibers from polymer solutions and melts', 2007, p. 152
- [19] Bhardwaj N., Kundu S.C.: 'Electrospinning: a fascinating fiber fabrication technique', *Biotechnol. Adv.*, 2010, **28**, pp. 325–347
- [20] Koski A., Yim K., Shivkumar S.: 'Effect of molecular weight on fibrous PVA produced by electrospinning', *Mater. Lett.*, 2004, **58**, pp. 493–497
- [21] Reneker D.H., Yarin A.L.: 'Electrospinning jets and polymer nanofibers', *Polymer*, 2008, **49**, pp. 2387–2425
- [22] Nikan E., Khodadadi A.A., Mortazavi Y.: 'Highly enhanced response and selectivity of electrospun ZnO-doped SnO₂ sensors to ethanol and CO in presence of CH₄', *Sens. Actuators*, 2013, **B 184**, pp. 196–204
- [23] Li D., Xia Y.N.: 'Direct fabrication of composite and ceramic hollow nanofibers by electrospinning', *Nano Letters*, 2004, **4**, (5), pp. 933–938
- [24] Li D., McCann J.T., Xia Y.N.: 'Use of electrospinning to directly fabricate hollow nanofibers with functionalized inner and outer surfaces', *Small*, 2005, **1**, (1), pp. 83–86
- [25] Li D., Babel A., Jenekhe S.A., *ET AL.*: 'Nanofibers of conjugated polymers prepared by electrospinning with a two-capillary spinneret', *Adv. Mater.*, 2004, **16**, (22), pp. 2062–2066
- [26] McCann J.T., Marquez M., Xia Y.N.: 'Melt coaxial electrospinning: a versatile method for the encapsulation of solid materials and fabrication of phase change nanofibers', *Nano Letters*, 2006, **6**, (12), pp. 2868–2872
- [27] Babel A., Li D., Xia Y.N., *ET AL.*: 'Electrospun nanofibers of blends of conjugated polymers: morphology, optical properties, and field-effect transistors', *Macromolecules*, 2005, **38**, (11), pp. 4705–4711
- [28] Kim G.H., Min T.J., Park S.A., *ET AL.*: 'Coaxially electrospun micro/nanofibrous poly (ϵ -caprolactone)/eggs hell-protein scaffold', *Bioinsp. Biomim.*, 2008, **3**, (1), pp. 1–8
- [29] Li X.Q., Su Y., Chen R., *ET AL.*: 'Fabrication and properties of core-shell structure P (LLA-CL) nanofibers by coaxial electrospinning', *J. Appl. Polym. Sci.*, 2009, **111**, (3), pp. 1564–1570
- [30] Di J.C., Chen H.Y., Wang X.F., *ET AL.*: 'Fabrication of zeolite hollow fibers by coaxial electrospinning', *Chem. Mater.*, 2008, **20**, (11), pp. 3543–3545
- [31] Yu J.H., Fridrikh S.V., Rutledge G.C.: 'Production of submicrometer diameter fibers by two-fluid electrospinning', *Adv. Mater.*, 2004, **16**, (17), pp. 1562–1566
- [32] Díaz J.E., Barrero A., Márquez M., *ET AL.*: 'Controlled encapsulation of hydrophobic liquids in hydrophilic polymer nanofibers by co-electrospinning', *Adv. Funct. Mater.*, 2006, **16**, pp. 2110–2116
- [33] Sun Z., Zussman E., Yarin A.L., *ET AL.*: 'Compound core-shell polymer nanofibers by co-electrospinning', *Adv. Mater.*, 2003, **15**, pp. 1929–1932
- [34] Kayaci F., Ozgit-Akgun C., Donmez I., *ET AL.*: 'Polymer-inorganic core-shell nanofibers by electrospinning and atomic layer deposition: flexible Nylon-ZnO core-shell nanofiber mats and their photocatalytic activity', *Appl. Mater. Interfaces*, 2012, **4**, pp. 6185–6194
- [35] Ova L.V., Buzgo M., Mohroval J., *ET AL.*: 'Productivity enhancement of core/shell nanofibers', 2012, **10**, pp. 23–25
- [36] Alizadeh M.M., Keyanpour-Rad M., Ebadzadeh T.: 'Effect of viscosity of polyvinylalcohol solution on morphology of the electrospun mullite nanofibers', *Ceram. Int.*, 2014, **40**, pp. 5461–5466
- [37] Esmailpour ganji M., Bazargan A.M., Keyanpour-rad M., *ET AL.*: 'Morphological and optical characterization of electrospun zinc oxide nanofibers', *Functional Mater. Lett.*, 2010, **3**, (2), pp. 141–145
- [38] Yan S.H., Ma S.Y., Li W.Q., *ET AL.*: 'Synthesis of SnO₂-ZnO heterostructured nanofibers for enhanced ethanol gas-sensing performance', *Sens. Actuators B*, 2015, **221**, pp. 88–95
- [39] Ma G., Wang X.: 'Synthesis and applications of one-dimensional porous nanowire arrays: a review', *Nano*, 2015, **10**, (1), pp. 1–26
- [40] Ghelich R., Keyanpour Rad M., Yuzbashi A.A., *ET AL.*: 'Preparation and characterisation of NiO-Ce_{0.8}Gd_{0.2}O_{1.9} composite nanofibres via electrospinning', *Micro Nano Lett.*, 2012, **7**, (12), pp. 1316–1319