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Synthesis of mullite nanofibres by electrospinning of solutions containing different proportions of polyvinyl butyral

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Abstract

In this paper, the synthesis of continuous mullite ($3Al_2O_3 \cdot 2SiO_2$) nanofibres by combination of the sol–gel and electrospinning technique is reported. To find out the optimum viscosity of the electrospinning solution for obtaining the high quality mullite nanofibers, solutions containing different amounts of polyvinyl butyral (PVB, 0–8 wt%) and the precursor sol were prepared for the electrospinning process. The precursor sol was made by using proper amounts of aluminium isopropoxide (AIP), hydrated aluminium nitrate (AN) and tetraethylorthosilicate (TEOS). Crystal phase, microstructure and thermal decomposition behaviour of the electrospun mullite nanofibres were investigated by conventional methods of analysis. The optimal amount of PVB in the electrospinning polymeric solutions was found to be between 4 and 6 wt% and the mullite nanofibres obtained as such were pure, smooth and uniform with diameter sizes of 85–130 nm after calcination at 1200 °C.

Keywords: A. Sol–gel process; Electrospinning; Morphology; Mullite nanofibre; Polyvinyl butyral

1. Introduction

Ceramic fibres contain a broad range of amorphous or crystalline synthetic mineral fibres which exist in both oxide and non-oxide forms and are characterised by their refractory properties (i.e., stability at high temperatures). They are typically made of alumina, silica and other metal oxides (oxide fibres), or non-oxide materials such as silicon carbide (non-oxide fibres) [1]. Ceramic fibres are candidates as reinforcement materials due to their thermal shock damage resistance, dielectric properties, chemical stability and flexibility [2,3]. These ceramics have many applications such as gas turbines, heat exchangers, first containment walls for fusion reactors as well as candle filters for high temperature gas filtration in which no matrix is necessary [4]. But, the excellent properties of non-oxide ceramics, due to their oxidation, subside at high temperatures during long-term applications. Therefore, essentially to overcome oxidation problems at high temperatures, the use of oxide fibres instead of non-oxide fibres has been suggested [5,6].

Among the various of ceramic fibres, alumina and silica fibres are shown to have good mechanical properties, especially at room temperature [3,6]. Despite the stability of alumina fibres at room temperature, they undergo phase changes with increasing temperature, which cause deterioration in their strength at temperatures greater than 1000 °C in corrosive atmospheres [7]. Silica fibres have received considerable attention for their excellent properties such as thermal shock damage resistance, chemical stability and flexibility. However, the disadvantage of the silica fibres is that they degrade at high temperature processing and therefore, became unstable at high temperatures [3]. When alumina and silica fibres mixed together they form a composite that is resistant to phase change at high temperatures. Combining alumina and silica for production of fibres began in the early 1970s for making high temperature insulators [1]. It is found that the only stable combination of Al_2O_3–SiO_2 from medium up to high temperatures at ambient pressure is mullite [8].

Recently, continuous mullite fibres have attracted the attention of many researchers because of their unique important properties [6,9,10]. The most prominent characteristics of these

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fibres are their good thermal shock and refractory properties, creep and stress resistance, low thermal conductivity and expansion coefficient, good strength at high temperature applications, good dielectric and chemical stability. Therefore, mullite fibres have found extensive applications in the adiabatic insulating material [11], high temperature structural material [11,12], high temperature plasticizing structural ceramics [11] and reinforcement of metal, ceramic and resins [13,14]. Morphology and size of mullite nanofibres are important factors to direct applications of this refractory in different specific areas [9].

There are many successful methods that have been reported for synthesis of ceramic fibres such as the sol–gel method [5], melt spinning and solution spinning [6,9] and the electrospinning method [10,15]. One of the most useful methods for fabricating mullite fibres is the sol–gel process [16]. The sol–gel method is an attractive process for its good properties, such as low technical temperature, good homogeneity and high purity of products [17,18]. However, the length of the fibres obtained from this method is in micron range and for producing fibres, it requires special and expensive reagents [15,16]. The melt-spinning method was used for the synthesis of low melting point ceramic fibres. It is difficult to prepare fibres of metal oxides or refractory oxides fabricated from starting materials with high melting points. Therefore, this method is not considered to be suitable for synthesis of mullite fibres [19]. Unlike the melt-spinning method, the solution spinning technique has been used for synthesis of high melting point ceramics. But the disadvantage of this technique is that it results nanofibres with uncontrollable size and cracks [13].

Electrospinning preparation of nanofibres has attracted widespread attention in the past decades. This method is simple, versatile and cost-effective for fabricating one-dimensional polymeric fibres with diameter in the nano and micrometre ranges [20]. Since electrospinning has ability to produce ultrafine fibres, it has been used for scientific applications, such as wound dressings, drug delivery, tissue scaffolds, filtration and protective clothing for the military applications [21]. Among the many parameters which control the process of electrospinning [21,22], those related to the electrospinning solution, such as concentration and viscosity have direct impact on the morphology of the electrospun fibres [9].

Among the many sources for supplying alumina and silica in the binary mullite system, aluminium isopropoxide (AIP) and tetraethylorthosilicate (TEOS) were mainly selected as Al and Si sources, respectively [6,10]. AIP polymerisation can provide appropriate viscosity for spinning [10] and hydrolyses much faster than TEOS, and therefore, this non-concurrency in hydrolysis rate causes chemical heterogeneity in the gel fibres, which could slightly impact on the high temperature properties of the mullite fibres, especially on the creep resistance. To overcome this problem, one can use homogeneous sol which could be prepared from an aqueous solution of aluminium isopropoxide, aluminium nitrate (AN) and TEOS [17]. Furthermore, AIP could not participate in hydrolysis and condensation polymerisation reactions without the presence of AN and therefore the AIP sol has no spinnability property. In fact, to hydrolysis of AIP, the sol should be acidic and it could increase with the increase of AN amount in the sol [11,18,19,23]. Nishio et al. were the first researcher group published the technique for the synthesis of mullite fibres from the AN/AIP/TEOS system [24,25].

Dharmaraj et al. [6] studied the fabrication of mullite nanofibres, using only a known viscous polyvinyl alcohol (PVA) solution in the electrospinning process followed by calcination of the fibres at different temperatures. Lin et al. [9] have reported the fabrication of the nanofibres, which focused on different viscosities of polyvinylpyrrolidone (PVP) solutions and they used only a single temperature for the sintering step. By taking into account the selected starting materials reported in the work conducted by Nishio et al. [24,25] and the electrospinning method of synthesis reported by Dharmaraj et al. [6] and Lin et al. [9], the present work reports the synthesis of mullite nanofibres, using different amounts of polyvinyl butyral (PVB) in the prespinning solutions to find out the most suitable viscosity of the solutions for the electrospinning process to obtain the most uniform, pure, smooth and small size nanofibres at proper sintering temperatures.

2. Experimental

2.1. Preparation of mullite nanofibres

AIP ($C_9H_{21}O_3Al$, MERCK) and AN ($Al\ (NO_3)\cdot 9H_2O$, MERCK) as the alumina sources, TEOS ($SiC_8H_{20}O_4$, MERCK) as the silica source and PVB ($(C_8H_{14}O_2)_n$, Sigma-Aldrich) were used as the precursors.

The proportion of the two different alumina sources impresses the dissolvability, homogeneity and spinnability of the related precursor sol. With decreasing the AIP/AN ratio, the fibres become shorter and finally cannot be spinned when the $AIP/AN < 0.5$ [5]. This ratio was selected in the experiment to be 2:1. The molar ratios of AIP/AN/TEOS/deionized water/ethanol were chosen to be 2:1:1:25:25 in the sol [9]. A diluted sol was prepared from AN and then, AIP and TEOS were added and stirred vigorously at room temperature for 20 h, till AIP completely dissolved to afford a clear sol. The resulting sol was heated at 90 °C, using an oil bath under reflux condition to complete the hydrolysis process. Polymeric solutions with different amounts of PVB (0, 2, 4, 5, 6, 7 and 8 wt%) were prepared for the electrospinning step. The electrospinnable solutions were prepared by mixing polymeric solutions/sol, 3/1, stirred and aged at 60 °C for 1 h [13], resulting viscous semilucent solutions. A voltage of 10 kV was applied to each solution and the distance of the tip to collector was selected to be 13 cm with the rate of ejection of 0.2 ml/h. Dense webs of the fibres were collected on the aluminium target and calcined at 800, 1000, 1200 and 1400 °C for 2 h to obtain the mullite nanofibres.

2.2. Characterizations

The surface morphology of the nanofibres was investigated by scanning electron microscopy (SEM) at an accelerating voltage of 20 kV. A small section of the electrospun mullite mat was placed on the SEM sample holder and coated with gold. X-ray diffraction (XRD) patterns were obtained by Siemens D-500 X-ray diffractometer using Cu radiation with 2θ (°) values between 15 and 80. The viscosity of the precursor solutions was measured at room temperature, pressure of 1 atm and humidity of 26% by using a Modular Compact Rheometer (MCR301, Phusica, made by Anton Paar Company). The rheological behaviour of prepared sols was measured in the shear rate between 1 and 1000 (1/S). Simultaneous thermal analysis (STA) was obtained by a PL-STA-1640 by heating from 50 to 1200 °C under airflow with a heating rate of 5 °C/min.

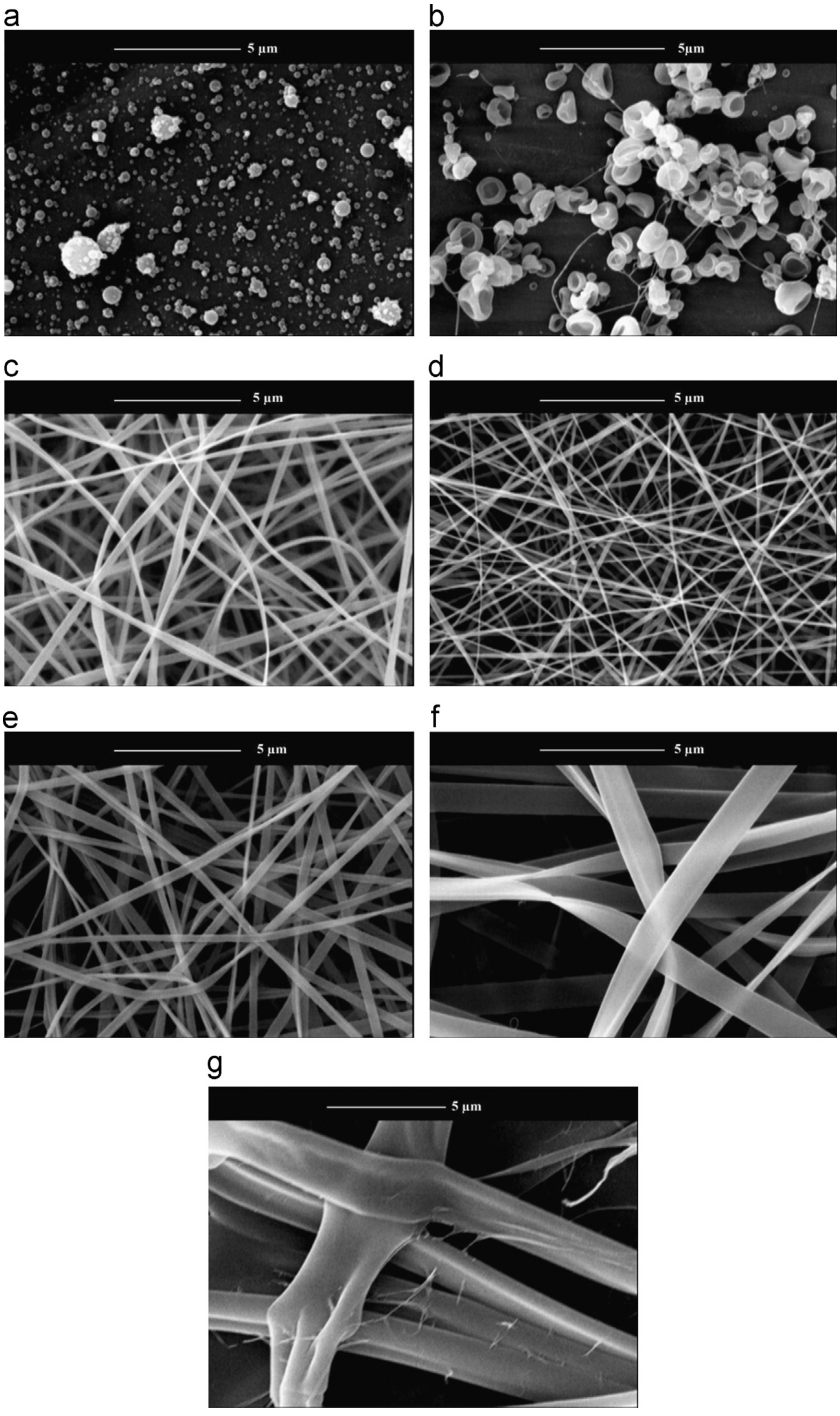

Fig. 1. Morphologies of electrospun fibres with (a) 0 wt%, (b) 2 wt%, (c) 4 wt%, (d) 5 wt%, (e) 6 wt%, (f) 7 wt% and (g) 8 wt% of PVB.

Fourier transform infrared spectroscopy (FT-IR) spectra of the fibres were taken in the range of 4000–400 cm^{-1} by using BRUKER VECTOR 33. The nanofibrous mats were calcined in air at different temperatures from 800 to 1400 °C for 2 h with heating rate of 10 °C/min.

3. Results and discussions

Fig. 1 illustrates SEM photographs of electrospun nanofibre with different PVB contents. Fig. 1(a) and (b) indicates that a large amount of completely beads and partially beaded were obtained when PVB contents were less than 4 wt%. Continuous nanofibres with common cylindrical morphology were obtained with PVB content ranging from 4 to 6 wt%, as shown in Fig. 1(c)–(e). Further increase of PVB content to 8 wt% led to the appearance of wide and flat ribbon morphologies of the nanofibres, Fig. 1(f) and (g).

The change in viscosity of the precursor sols with increase of shear rate is shown in Fig. 2. When PVB was less than 4 wt %, the change in viscosity of the sols was very low, exhibiting the Newtonian flow behaviour. At higher PVB content (from 4 to 8 wt%), the viscosity increased and followed the shear thinning behaviour, meaning that viscosity decreases with increasing shear rate. The consistent results from SEM and viscosity tests suggest that continuous nanofibres could be obtained only when the rheological behaviour of the sols followed the shear thinning behaviour.

According to Figs. 1 and 2, the morphology of nanofibres can be directly adjusted by changing the viscosity of the electrospinning solutions. The polymeric solution is stretched during electrospinning when the jet leaves the needle tip towards the collection plate. The entanglement of molecule chains provides a continuous electrically driven jet and prevents the jet from breaking up and dripping. Moreover, when the viscosity of the sols becomes too high as the result of increasing polymeric chain entanglements, the solution may dry up at the tip of the needle before initiation of the electrospinning and therefore, a proper viscosity of the polymeric solution is necessary for the suitable electrospinning process.

The thermal behaviour of electrospun mullite from room temperature to 1200 °C is shown in Fig. 3. The DTA curve shows three exothermic reactions occurred at 210, 228 and 1000 °C. The first reaction which occurred between 150 and 210 °C is related to loss of water and organic groups. The second reaction occurred between 210 and 580 °C which is related to the degradation of PVB side chain by elimination of

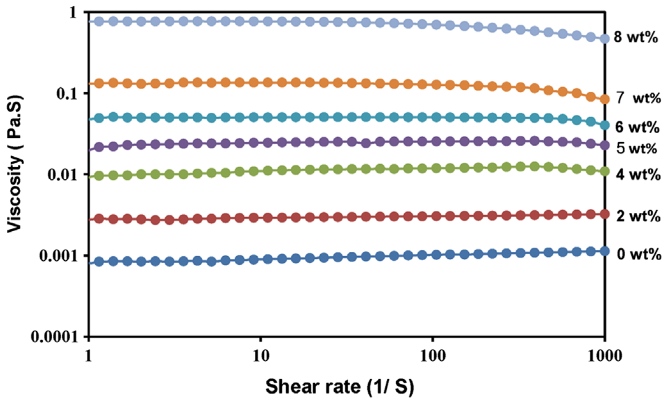

Fig. 2. Plots of viscosity rate versus shear rate.

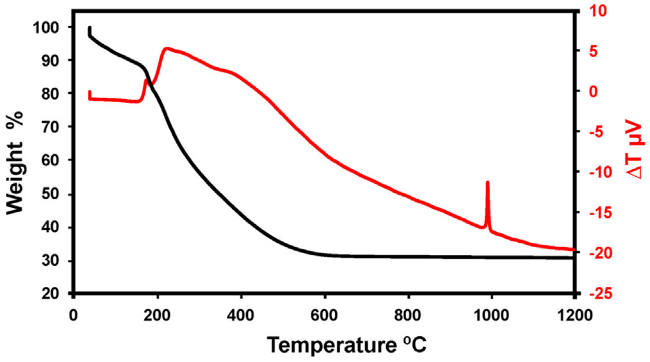

Fig. 3. Thermal behaviour of electrospun mullite.

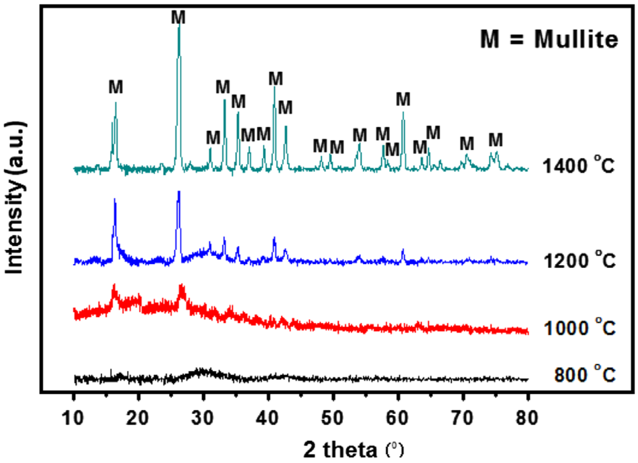

Fig. 4. XRD patterns of various mullite nanofibres samples in different temperatures.

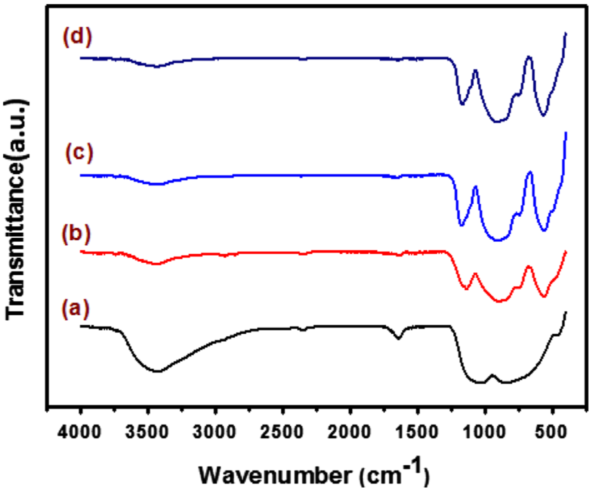

Fig. 5. FT-IR spectrum of the electrospun mullite nanofibres after calcination at (a) 800 °C, (b) 1000 °C, (c) 1200 °C and (d) 1400 °C.

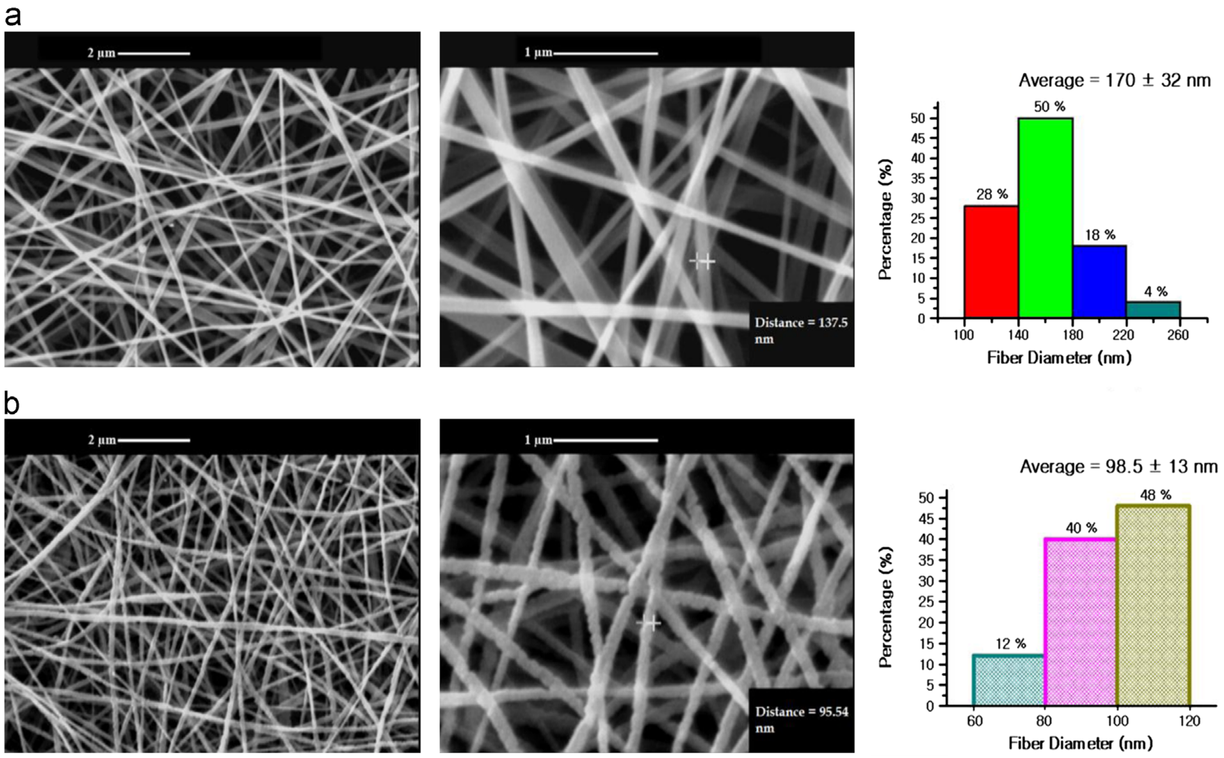

Fig. 6. SEM images of the electrospun mullite nanofibres before (a) and after (b) calcination at 1200 °C in various magnifications.

water. The last reaction can be associated to crystallisation of mullite which occurred at 1000 °C. The TG curve shows three steps weight loss as well. The first step is due to loss of water and organic groups (as explained in DTA curve, occurs in the range of 150–210 °C), the next step occurred in the temperature range of 210–400 °C is for the degradation of PVB side chain and at last, decomposition of PVB main chain occurred above 400 °C. At temperatures above 580 °C, there is no change in weight loss up to 1200 °C, indicating that the PVB has been completely removed from the sample.

XRD pattern of the sample which was calcined in the range of 800–1400°C for 2 h, is shown in Fig. 4. No diffraction peaks of mullite are observed in sample calcined at 800 °C. As the calcination temperature increased gradually to 1000°C, the characteristic peaks of mullite appeared and became more pronounced and sharper with increasing the temperature from 1000 to 1400 °C.

Fig. 5 shows FT-IR spectra of the electrospun mullite nanofibres at different calcination temperatures. A broad peak at 3464 cm^{-1} (Fig. 5a) belongs to absorbed water, which gradually disappears as the temperature increases to 1200 °C. The spectrum of the mullite obtained at 1400 °C has almost no peak at this wavelength which is exactly identical to that reported previously in the literatures [26,27].

Fig. 6 shows the SEM images of electrospun mullite nanofibres in various magnifications before and after calcination at 1200 °C. As shown in Fig. 6(a) and (b), the size of the nanofibres before and after calcination at 1200 °C is in the range of 140–200 nm and 82–113 nm, respectively. The dramatic reduction in the size of the nanofibres can be attributed to burning-out of PVB after calcination at 1200 °C.

4. Conclusions

Mullite nanofibres can be easily synthesised by the electrospinning method followed by calcination at 800, 1000, 1200 and 1400 °C for 2 h. The viscosity of the PVB prespinning solutions played an important role on the morphology of the mullite nanofibres. The continuous electrospun nanofibres were obtained when PVB contents were chosen to be between 4 and 6 wt%. Further increasing the amount of PVB led to excessively high viscosity level of the prespinning solutions, resulting wide and flat ribbon shaped mullite fibres. The size of the nanofibres was in the range of 82–113 nm after calcination at 1200 °C.

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