

ELECTROSPINNING OF 2D AND 3D SILICA NANOFIBRES FROM A COLLOIDAL SOLUTION

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Silica nanofibres were synthesised by electrospinning a commercially available silica solution with an aqueous 5% poly (ethylene oxide) (PEO) solution to produce composite PEO/ silica nanofibres. Using a ratio of 80% PEO solution to 20% silica solution, random nanofibrous silica membrane were produced after being subject to pyrolysis at 800°C for 2 hours. The mean diameter of the silica nanofibres was 256 nm. With a solution of 50% PEO to 50% silica solution, three-dimensional wool-like network of nanofibres was achieved.

INTRODUCTION

Using classical spinning techniques such as wet and melt spinning, tensile, rheological, gravitational, inertial and aerodynamic forces [1] are utilised to obtain filaments in the micrometre diameter range. To obtain fibres in the nanometre range, electrospinning is more effective. Here an electric field is applied to a viscoelastic solution passing through a needle tip, creating an electrified jet. This jet is subjected to bending instability which leads to stretching, elongation and thinning of the solution over a short distance, thereby producing fibres in the nanometre range [2]. The whipping motion of the electrified jet results in the assembly of a nanofibre into a two-dimensional (2D) or three-dimensional (3D) non-woven mat, where the fibres produced are continuous, producing fibres with a diameter lower than 100 nm and lengths up to kilometres [3]

The nanofibres produced by electrospinning exhibit a number of unique features compared to fibres fabricated using other techniques. In addition to being continuous, they may have a high surface area to volume ratio due to their small fibre diameters. They may also have complex architectures, either in 2D or 3D, random or aligned, by manipulating processing conditions such as electrospinning solutions, apparatus configuration and environment (temperature and humidity). These versatile materials may have a number of important applications, including as filter materials for dust, bacteria and viruses [4], as carriers for drug releasing and delivery, as scaffolds in tissue engineering and wound dressing, as components of protective clothing, as supports for

enzymes and catalysts, as sensors in electronic and optical devices [4-6]. Such nanofibres can be made of a variety of materials ranging from polymers, ceramics to composites [5].

Silica nanofibres have many interesting properties. They can be used in biosensors [7], catalysts [8], and dental composites [9]. Previous research focussing on the production of silica nanofibres has utilised the hydrolysis and polycondensation of a silicon alkoxide to produce a sol-gel for electrospinning [10-12] in the presence of an acidic catalyst. Experimental work published by Choi *et al.* used a sol of tetraethylorthosilicate (TEOS)/ ethanol/ water and hydrochloric acid in a 1/2/2/0.01 molar ratio [10]. Scanning electron microscopy demonstrated that the fibres produced had a diameter of between 200 and 600nm. The advantage of this method of producing silica nanofibres is the absence of any polymer binder/ gelation molecules, which must otherwise be removed by calcination in order to obtain pure inorganic nanofibres. Using phosphoric acid as the catalyst fibre mats of poly(vinyl alcohol) (PVA)/silica composite have been produced [11, 12]. Research by Shao *et al.* investigated the effects of calcination at between 400 and 800°C, at a rate of 240°C/ hour, followed by holding at the required temperature for 10 hours, on 59 wt.% PVA/ silica composite nanofibre mats [11]. Scanning electron microscope revealed that the nanofibre mats produced had smaller diameters and rougher surfaces than uncalcinated PVA/silica composite nanofibres and as the calcination temperature increased the nanofibres became smaller and the surface rougher. However, the nanofibres still retained their fibre

morphology, with diameters of between 200 and 300 nm. Composite poly(vinylbutyral)/silica nanofibres have also been produced with diameters ranging from a few nanometres to 100-200 nm [13].

In this communication we report on a simple method for producing silica nanofibres by electrospinning a commercial colloidal silica solution, to produce PEO/silica nanofibres with both 2D random membrane and 3D wool-like structures, followed by high temperature pyrolysis to obtain silica nanofibres.

EXPERIMENTAL

Three potential candidate polymers were investigated to assess their suitability for the electrospinning of a commercial colloidal silica solution (Ludox SM-30, 30% solid loading, Grace Davidson, Columbia, USA). Poly(vinyl pyrrolidone) (PVP) (Mn 40,000, Sigma Aldrich Ltd, Poole, Dorset, UK), poly(vinyl alcohol) (PVA) (Mn 30,000 - 70,000, Sigma Aldrich Ltd, Poole, Dorset, UK) and poly(ethylene oxide) (PEO) (Mn 600,000, Sigma Aldrich Ltd, Poole, Dorset, UK) were prepared in solution by weight with an appropriate solvent. The next stage was to determine whether a 30% colloidal silica solution could be solubilised within each polymer solution and then electrospun. Only an aqueous 5 wt.% PEO solution mixed with a 30% colloidal silica solution resulted in the production of a transparent solution which had a viscosity suitable for electrospinning.

To produce an aqueous 5 wt.% PEO solution, 2 grams of PEO powder were dissolved in 38 grams of distilled water at room temperature and stirred with a magnetic stirrer to aid dissolution. 30 % colloidal silica

solution was then slowly added to produce an 50:50 and 80:20 aqueous 5 wt.% PEO solution with a 30 % colloidal silica solution. Mixing took place at room temperature over a period of 4 hours using a magnetic stirrer at 450 revolutions per minute (rpm). The resulting solution was then centrifuged at 3000 rpm for 2 minutes to remove any air bubbles. The solution was contained in a 5 mL syringe connected to a 24 gauge stainless steel needle using Bohlender[®] PTFE tubing. To produce a 3D network of PEO/silica nanofibres, the needle tip was angled downwards 15cm from a grounded collecting plate and a potential difference of 15 kV was applied across the two. The grounded plate was covered with aluminium foil to collect the resultant nanofibres and a syringe driver was programmed to deliver a solution flow rate of 10 ml/minute during the spinning process.

To produce a 2D membrane of PEO/silica nanofibres, the needle tip was suspended 20cm above a grounded collecting plate and a potential difference of 17.5 kV was applied across the two, with the solution delivered at 10 ml/minute (Figure 1).

Samples of the 80:20 PEO/ silica composite nanofibre mats underwent pyrolysis at a rate of 5°C/ minute, up to 700, 800, 900, 1000 or 1100°C. Once at the desired preset temperature the samples were held at this temperature for 2 hours before cooling to room temperature. The pyrolysed nanofibre membranes were then examined under SEM (Jeol SEM 5600LV, Jeol, Welwyn Garden City, UK) and compared to as-electrospun nanofibres in order to investigate the effect of the differing sintering temperatures on fibre properties, in particular fibre diameter.

Energy dispersive microanalysis was also performed in order to determine the constituent elements of the sintered fibres. For X-ray diffraction measurements, samples of the PEO/silica nanofibres pyrolysed at 700°C and 800°C for 2 hours, and an as-electrospun control sample, were analysed using a Phillips X'pert PRO diffractometer (PANalytical Ltd, Waterbeach, Cambridgeshire, UK).

RESULTS AND DISCUSSION

This investigation firstly studied PVP, PVA and PEO as potential polymers for the electrospinning of a 30% colloidal silica solution. A 10wt% PVP/ethanol solution resulted in the gelation of the 30% colloidal silica solution, making it unsuitable for electrospinning. This gelation was probably due to the effect of the ethanol solvent had on the silica solution, which does not favour silica particle dispersion [14]. However, research by Liu *et al.* has demonstrated that it is possible to produce silica nanofibres by electrospinning an aqueous solution (sol-gel) made from an alkoxide precursor of TEOS, but with PVP in ethanol and PVP in *N,N*-dimethyl formamide as the carrier polymer [15].

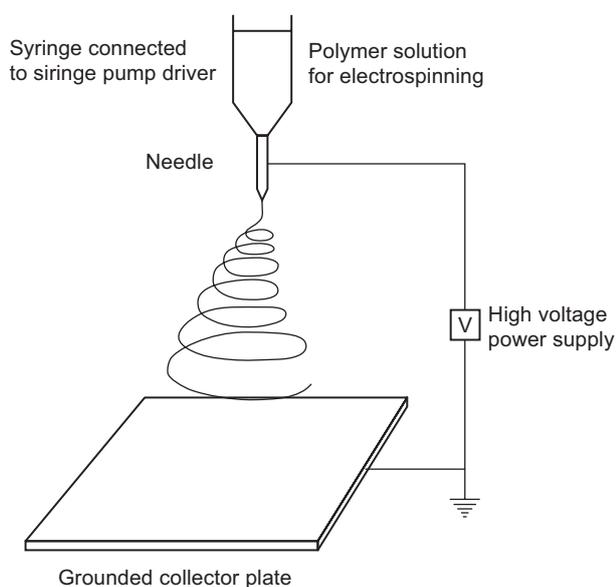


Figure 1. The setup for electrospinning.

The use of aqueous 10 wt.% PVA solution mixed with a 30 % colloidal silica solution also resulted in the production of an opaque gel. Research by Shao *et al.* has demonstrated that silica nanofibres can be made by electrospinning such a PVA/ silica composite [11, 12], but the method is time consuming. Prior to spinning, it is necessary to undertake hydrolysis and polycondensation of the TEOS using dropwise addition of phosphoric acid followed then by dropwise addition of aqueous 10 wt.% PVA solution to the silica gel over a further 12 hours at 60°C. Only then can electrospinning take place.

In the present study an aqueous 5 wt.% PEO solution was found to be compatible with the 30 % colloidal silica solution, resulting in the production of a solution that did not undergo gelation and was therefore suitable for electrospinning. Recent work by Liu *et al.* also utilised a 5 wt.% PEO solution, but in a solvent of ethanol, water and acetic acid to act as a carrier polymer solution for the electrospinning of a 5 wt.% TEOS in ethanol solution [15]. This approach differs in that TEOS was used, making it possible to use ethanol as a solvent. In the present investigation it was found that a 30 % colloidal

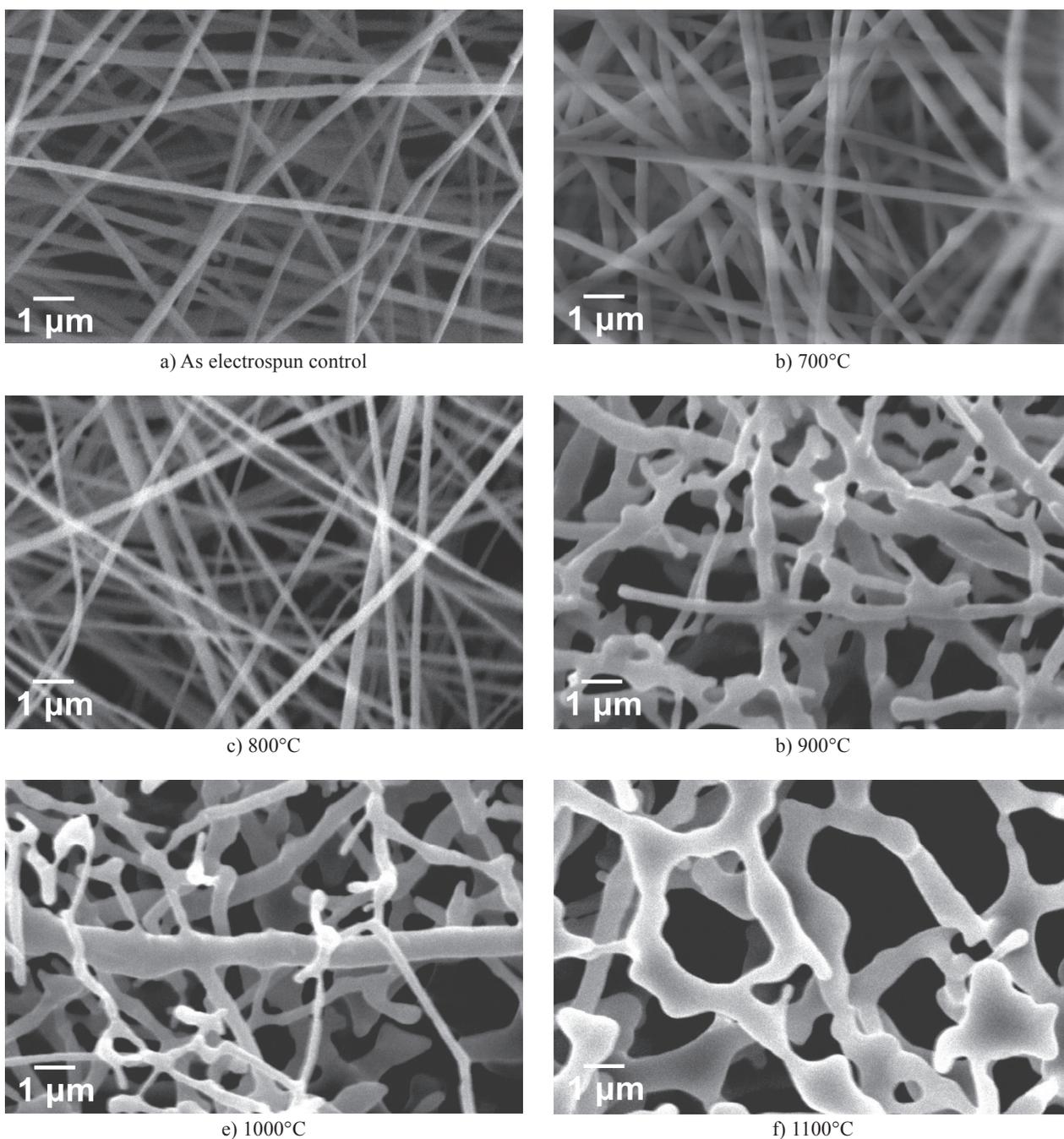


Figure 2. Scanning electron micrographs of PEO/ silica nanofibres a) as-electrospun and pyrolysed for 2 hours at b) 700°C, c) 800°C, d) 900°C, e) 1000°C and f) 1100°C.

silica solution would undergo gelation when combined with ethanol and so ethanol was not used. The use of the commercially produced 30 % colloidal silica requires an organic polymer carrier that produces a solution with the appropriate viscosity for electrospinning.

The scanning electron micrographs of the produced 80:20 PEO/silica electrospun 2D nanofibres membranes pyrolysed at 700°C and 800°C for 2 hours demonstrate nanofibre integrity (Figures 2b-c) similar to that seen with the as-spun composite PEO/ silica nanofibres (Figure 2a). At the higher temperatures of 900°C, 1000°C and 1100°C, nanofibre integrity was lost, resulting in the fusion of adjacent fibres (Figures 2d-f).

The PEO/silica composite nanofibres produced using this 80% [aqueous 5 wt.% PEO solution]: 20% [30% colloidal silica solution] solution demonstrated a mean fibre diameter of 291nm and were relatively uniform prior to pyrolysis (Figure 2a). These findings differ from those of Liu *et al.* whose method of producing PEO/TEOS nanofibres resulted in the production of nanofibres with diameters of approximately 800 nm. Following pyrolysis and removal of the PEO from the electrospun fibres the resultant silica fibres produced in

the current investigation had a mean diameter of 256 nm, which is much smaller than those previously reported when PVP was used as the polymer carrier solution [15]. The fibres produced in this study were similar in diameter to the nanofibres reportedly produced by electrospinning a silica gel without an organic carrier polymer (200-600 nm) [10] and also those produced by the sintering of PVA/silica nanofibres (200-300 nm) [11].

Figure 3 shows the XRD pattern for the as-electrospun control, and samples pyrolysed at 700 and 800°C. The sample pyrolysed at 800°C demonstrates an intense peak appears at 21.5°, which indicates that the silica nanofibres contain crystalline silica (Figure 3a). This intense peak is not seen when the sintering conditions were set at 700°C for 2 hours (figure 3b). Similar XRD patterns to this have been reported for silica nanofibres formed from silica gel without an organic polymer [10] and those formed from PVA/ silica composite nanofibres pyrolysed at 800°C for 10 hours [11]. Pyrolysis of PEO/ silica composite nanofibres at 700°C did not demonstrate the same sharp peak.

More interestingly, our results have also shown that, by alternating the ratio between PEO and silica colloidal solution, electrospinning of a 50:50 PEO/silica solution produced a 3D network of PEO/silica nanofibres with a wool-like appearance (Figure 4a). To electrospin this solution, the orientation of the needle tip and the grounded plate was changed to a horizontal position (figure 4a). The distance between the needle tip and the collecting plate was decreased to 17.5 cm and the potential difference reduced to 15 kV. When changing the ratio of PEO/silica solution from 80:20 to 50:50, the solid-loading of silica in the final electrospinning solution was increased and water content was substantially decreased. The PEO/silica nanofibres were thus easier to become solidified during the electrospinning process, and lead to wool-like structures. The produced wool-like PEO/silica nanofibres have larger pores compared to 2D membranes (Figure 4b). While previous studies showed that such 3D

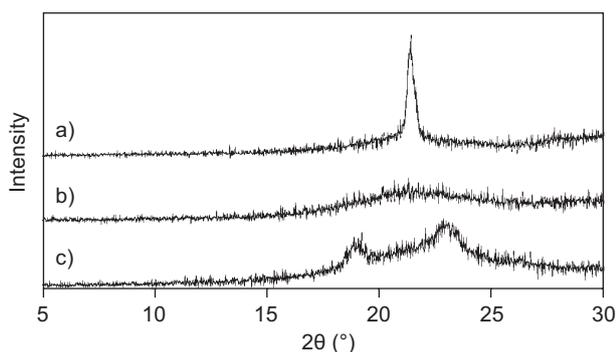


Figure 3. XRD pattern for various PEO/ silica nanofibre samples - a) 800°C for 2 hours, b) 700°C for 2 hours, c) as-electrospun control.

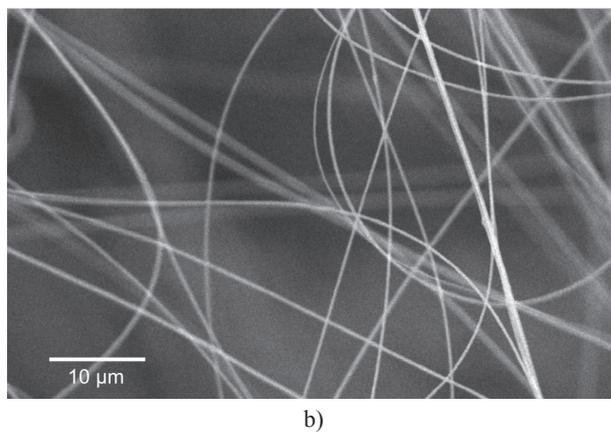
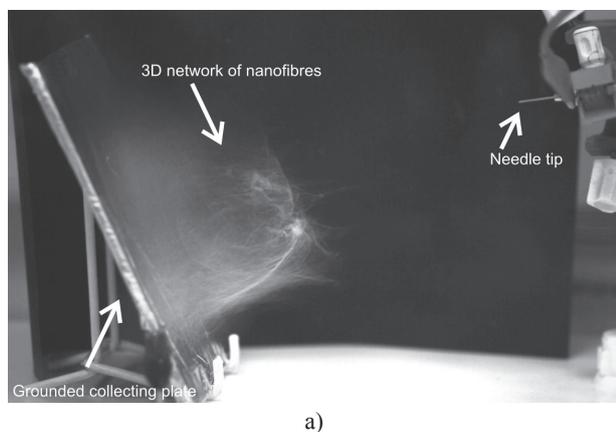


Figure 4. a) formation of a 3D network of nanofibres from a 50:50 PEO/silica solution. b) scanning electron micrograph of 50:50 PEO/silica fibres showing 3D network structures.

wool-like nanofibres could only be produce either by a cryogenic electrospinning method where nanofibres were deposited onto a frozen collector then freeze-drying [16-19] or by depositing nanofibres onto a special hemispherical collector with a metal pin array [20]. Our results demonstrate that such wool-like structures can be produced simply by changing the formulation of solution and using a standard electrospinning system with needle-plate configuration. This has not been reported before and has some advantages compared to the aforementioned methods.

CONCLUSIONS

In summary, we report a simple approach to the production of silica nanofibres by electrospinning a commercial colloidal silica solution. To produce the electrospinning solution the colloidal silica solution was combined with 5 wt.% aqueous PEO. The optimum conditions for pyrolysis were found to be 800°C for 2 hours at a heating rate of 5°C/ min. This produced silica nanofibres with a mean diameter of approximately 256 nm. By altering the ratio of aqueous PEO to silica solution it is possible to produce a 3D wool-like network of nanofibres.

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